INTERNATIONAL CONFERENCE OF LITHUANIAN SOCIETY OF CHEMISTRY

Theodor v. Grotthuſs

Dedicated to 210th anniversary of
publication of the first theory of electrolysis
proposed by

THEODOR GROTTHUSS
(1785 - 1822)

LITHUANIAN ACADEMY OF SCIENCE
Gedimino Str. 3, Vilnius, Lithuania
April 28-29, 2016

BOOK OF ABSTRACTS

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Thursday, April 28

08:00	**Registration**
09:00	**Opening**
09:15	Prof. J. Krikštopaitis (Lithuania)
09:30	Dr. F. Björefors (University of Uppsala, Sweden)
10:00	Prof. F. Scholz (Greifswald University, Germany)
10:30	Coffee break and poster session
11:15	Prof. E. Juzeliūnas (Klaipėda University, Lithuania)
11:45	Prof. A. Ramanavičius (Vilnius University, Lithuania)
12:05	Dr. E. Voitechovič (St. Petersburg State University, Russia)
12:20	Dr. M. Yıldırım (Canakkale Onsekiz Mart University, Turkey)
12:35	Prof. G. D. Sulka (Jagiellonian University Krakow, Poland)
12:50	P. M. Hannula (Aalto University, Finland)
13:05	Break
14:30	Prof. R Ramanauskas (FTMC, Lithuania)
15:00	Prof. E. Lust (Tartu University, Estonia)
15:30	Prof. M. Skompska (Warsaw University, Poland)
16:00	Coffee break and poster session
16:30	Prof. G. Valinčius (Vilnius University, Lithuania)
16:50	Prof. O. Forsen (Aalto University, Finland)
17:05	Dr. L. Niedzicki (Warsaw University of Technology, Poland)
17:20	H. Akbulut (Sakarya University, Turkey)
17:35	Prof. G. Lisak (Åbo Akademi University, Finland)
17:50	V. Čolić (Technische Universität München, Germany)

Friday, April 29

08:30	**Registration**
09:00	Dr. R. Skaudžius (Vilnius University, Lithuania)
09:20	Dr. E. Orentas (Vilnius University, Lithuania)
09:40	Dr. G. Juodeikienė (Kaunas University of Technology, Lithuania)
10:00	Dr. T. Malinauskas (Kaunas University of Technology, Lithuania)
10:20	Prof. H. Cesiulis (Vilnius University, Lithuania)
10:40	Coffee break
11:00	Dr. R. Valiokas (FTMC, Lithuania)
11:20	Dr. A. Sankauskaitė (FTMC, Lithuania)
11:40	Mr. J. Tunaitis (UAB "Achema", Lithuania)
12:00	M. Stankevičiūtė (Kaunas University of Technology, Lithuania)
12:15	A. Brangule (Riga Stradiņš University,Latvia)
12:30	M. Bakierska (Jagiellonian University, Poland)
12:45	Break
14:30	Poster Session
15:50	**Closing remarks**
16:00	Excursion
18:30	Gala dinner, "Taurakalnis", Universiteto Str. 7

DETAILED PROGRAM

Thursday, April 28

8:00-9:00 – Registration

Time	Type of presentation	Speaker, affiliation	Presentation title
9:00	Opening	*Conference Chair*: **Prof. Rimantas Ramanauskas** *Vice chancellor, Government of Lithuania*: **Prof. Rimantas Vaitkus** *President of LAS*: **Prof. Valdemaras Razumas** *FTMC Director*: **Prof. Gintaras Valušis** *ISE Regional Representative*: **Prof. Rasa Pauliukaitė**	
Session 1. Chairs: **Rimantas Ramanauskas, Enn Lust**			
9:15	Invited lecture I-1	**Juozas A. Krikštopaitis,** Lithuanian Association for the History and Philosophy of Science	Theodor von Grotthuss' contribution to the interpretation of electricity phenomenon in Volta's pile
9:30	Keynote lecture K-1	**Fredrik Björefors,** Dept. of Chemistry – Ångström Laboratory, Uppsala University, Uppsala, Sweden	*Electrolysis via Bipolar Electrochemistry*
10:00	Keynote lecture K-2	**Fritz Scholz,** Institute of Biochemistry, University of Greifswald, Greifswald, Germany	*The Thermodynamics of Insertion Electrochemical Systems*
10:30	Poster Session 1 and Coffee break		
Session 2. Chairs: **Fredrik Björefors, Eimutis Juzeliūnas**			
11:15	Keynote lecture K-3	**Eimutis Juzeliūnas,** Klaipėda University, Klaipėda, Lithuania	*Silicon Photoelectrochemistry for Solar Energy Applications*
11:45	Invited lecture I-2	**Arūnas Ramanavičius,** Department of Physical Chemistry, Vilnius University, Lithuania	*Conjugated Polymers in the Design of Sensors and Biosensors*
12:05	Oral presentation O-1	**Edita Voitechovič,** Institute of Chemistry, St. Petersburg State University, Russia	*Proteinase K Assisted E-Tongue for Protein Purity Evaluation*
12:20	Oral presentation O-2	**Mehmet Yıldırım,** Department of Materials Science & Engineering, Canakkale Onsekiz Mart University, Turkey	*Electrochromic Copolymers Synthesized from Aminothiazoles and Pyrrole*
12:35	Oral presentation O-3	**Grzegorz Sulka,** Department of Physical Chemistry and	*Metallic Nanowire, Nanotube and Nanocone Arrays Fabricated by Electrodeposition in Porous Anodic Alumina Templates*

		Electrochemistry, Jegelonian University, Poland	
12:50	Oral presentation O-4	**Pyry-Mikko Hannula,** Department of Materials Science and Engineering, Aalto University, Finland	*Electrochemical Behavior between Functionalized Carbon Nanotube Films and Copper*
13:05	*Lunch break*		
Session 3. Chairs: **Fritz Scholz, Gintaras Valinčius**			
14:30	Keynote lecture K-4	**Rimantas Ramanauskas,** Center for Physical Sciences and Technology, Vilnius, Lithuania	*The Development of Electrochemistry In Lithuania*
15:00	Keynote lecture K-5	**Enn Lust,** Institute of Chemistry, University of Tartu, Tartu, Estonia	*Novel Electrochemical Devices for Energy Recuperation Systems*
15:30	Keynote lecture K-6	**Magdalena Skompska,** Faculty of Chemistry, University of Warsaw, Warsaw, Poland	*Synthesis and Application of Nanostructured Metal Oxides: From Photovoltaics to Photocatalysis*
16:00	Poster Session 2 and Coffee break		
Session 4. Chairs: **Magdalena Skompska, Eugenijus Valatka**			
16:30	Invited lecture I-3	**Gintaras Valinčius,** Institute of Biochemistry, Life Science Center of Vilnius University, Vilnius, Lithuania	*Electrochemical Impedance of Tethered Bilayer Membranes*
16:50	Oral presentation O-5	**Olof Forsen,** Department of Materials Science, Aalto University, Finland	*The Effect of Electrolyte Composition on* RuO_2*-*IrO_2*-*TiO_2 *Anode Operation in Electrowinning of Metals*
17:05	Oral presentation O-6	**Leszek Niedzicki,** Polymer Ionics Research Group, Warsaw University of Technology, Poland	*Weakly Coordinating Anions for Electrolyte Applications: Salts, Functional Additives, Ionic Liquids*
17:20	Oral presentation O-7	**Hatem Akbulut,** Department of Metallurgical & Materials Engineering, Sakarya University, Turkey	*Enhanced Lithium Storage in Graphene/*$LiMnPO_4$*-C Nanocomposite Cathode Electrodes for High Performance Li-Ion Batteries*
17:35	Oral presentation O-8	**Grzegorz Lisak,** Laboratory of Analytical Chemistry, Åbo Akademi University, Finland	*Potentiometric Sensors with Bi-Layer Ion-Selective Membranes*
17:50	Oral presentation O-9	**Victor Čolić,** Physik-Department, Technische Universität München, Germany	*Structural Activity Descriptors for the Oxygen Reduction Reaction: A Step Towards The Rational Design of Catalysts*

Friday, April 29

8:30-9:00 – Registration

Time	Type of presentation	Speaker, affiliation	Presentation title
***Session 5*. Chairs: Arūnas Ramanavičius, Henrikas Cesiulis**			
9:00	Invited lecture I-4	**Ramūnas Skaudžius,** Department of Inorganic Chemistry, Vilnius University, Vilnius, Lithuania	*Luminescence Properties of Eu^{3+} Doped Garnets*
9:20	Invited lecture I-5	**Evaldas Orentas,** Vilnius University, Lithuania	*Towards General Strategy for Tubular Hydrogen-Bonded Polymers*
9:40	Invited lecture I-6	**Gražina Juodeikienė,** Kaunas University of Technology, Kaunas, Lithuania	*The Possibilities of Lactic Acid Bio-Production from Food Industry By-Products by Using Membrane Filtration Techniques*
10:00	Invited lecture I-7	**Tadas Malinauskas,** Department of Organic Chemistry, Kaunas University of Technology, Kaunas, Lithuania	*Solar Energy Harvesting: The Renaissance of Hybrid Solar Cells*
10:20	Invited lecture I-8	**Henrikas Cesiulis,** Department of Physical Chemistry, Vilnius University, Vilnius, Lithuania	*Electrodeposition of Co-W Alloys from Macro- to Nano- Scale*
10:40	Coffee break		
***Session 6.* Chairs: Gražina Juodeikienė, Dainius Martuzevičius**			
11:00	Invited lecture I-9	**Ramūnas Valiokas,** Center for Physical Sciences and Technology, Vilnius, Lithuania	*Molecular Nanolithorgaphy: A Tool to Study and Employ Chemical Reactions at Nanoscale*
11:20	Invited lecture I-10	**Audronė Sankauskaitė,** Textile Institute, Center for Physical Sciences and Technology, Kaunas, Lithuania	*Influence of Bio-Ceramic on Thermoregulation Effectiveness of Pet Knits*
11:40	Invited lecture I-11	**Juozas Tunaitis,** UAB "Achema"	*From Science to Industry*
12:00	Oral presentation O-10	**Monika Stankevičiūtė,** Kaunas University of Technology, Lithuania	*Formation of Intermediate Phases during the Synthesis of α-C_2SH*

12:15	Oral presentation O-11	**Agnese Brangule,** Riga Stradiņš University, Latvia	*How Statistical Methods Guide the Selection of The FTIR Method*
12:30	Oral presentation O-12	**Monika Bakierska,** Faculty of Chemistry, Jagiellonian University, Poland	*The Effect of Cation and Anion Doping on the Structure, Chemical Stability and Electrochemical Performance of* $LiMn_2O_4$ *Cathode Material for Li-Ion Batteries*
12:45	Lunch break		
14:30	Poster Session 3		
15:50	Closing remarks		
16:00	Excursion in the Vilnius Downtown		
18:30	Gala dinner at Vilnius university, Faculty of History, Restaurant “Taurakalnis”, Universiteto str. 7		

Posters

Thursday, April 28

Electrochemistry

Electrochemistry of Materials, Nanomaterials and Films

No.	Presenting author	Affiliation	Poster title
P-1	**Dovilė Sinkevičiūtė**	Kaunas University of Technology, Lithuania	*Characterization of Ultra Thin Mo-O-Se Films Electrodeposited on* SnO_2 *Surface*
P-2	**Karolina Syrek**	Jagiellonian University, Poland	*Photoelectrochemical Performance of Nanoporous Titanium Oxide Layers Formed by Multi-Step Anodization*
P-3	**Karolina Syrek**	Jagiellonian University, Poland	*Photoelectrochemical and Photocatalytic Properties of Nanostructured Tungsten Oxide*
P-4	**Aliona Nicolenco**	Faculty of Chemistry, Vilnius University, Lithuania	*New Electrolyte for Fe-W Electrodeposition*
P-5	**Anna Pawlik**	Jagiellonian University, Poland	*Heat Treatment Effect on Crystalline Structure of Oxide Layers Grown on Fe by Anodization*
P-6	**Anna Pawlik**	Jagiellonian University, Poland	*Nanoporous Titanium Dioxide Layers Modified with Sodium Hydroxide and (3-Aminopropyl)triethoxysilane (APTES)*

P-7	**Asta Ona Češūnienė**	Center for Physical Sciences and Technology, Lithuania	*Characterization of As-Deposited and Annealed Cr-Zn-P Coating Electrodeposited from a Trivalent Chromium Bath*
P-8	**Zita Sukackienė**	Center for Physical Sciences and Technology, Lithuania	*Electroless Deposition of CoBW Coatings Using Morpholine Borane as Reducing Agent*
P-9	**Antanas Nacys**	Center for Physical Sciences and Technology, Lithuania	*Microwave-Assisted Synthesis of Platinum-Cobalt-Molybdenum/Graphene*
P-10	**Joanna Kapusta-Kołodziej**	Jagiellonian University, Poland	*Formation of Ordered Anodic TiO_2 Nanopore Arrays in Glycerine Based Electrolyte under Various Anodizing Potentials and Temperatures*
P-11	**Ewa Wierzbicka**	Jagiellonian University, Poland	*The Effect of Foil Purity on Morphology of Nanoporous Anodic ZrO_2*
P-12	**Karolina Gawlak**	Jagiellonian University, Poland	*The Effect of Chemical and Electrochemical Polishing of Tin on Morphology of Anodic Tin Oxide*
P-13	**Anna Brudzisz**	Jagiellonian University, Poland	*Mechanism of Voltage Detachment of Porous Anodic Alumina Membranes*
P-14	**Anna Brudzisz**	Jagiellonian University, Poland	*AAO Membranes with Serrated Nanopores as Templates for Fabrication of Metallic Nanowires*
P-15	**Egidijus Griškonis**	Kaunas University of Technology, Lithuania	*Electrochemical Properties of Modified with Electroless Ag Graphite Felt Electrode in Aqueous Solution of $NaBr/Br_2$*
P-16	**Vitalija Jasulaitienė**	Center for Physical Sciences and Technology, Lithuania	*The Influence of Electrodeposition Conditions on Structure and Optical Properties of Transparent ZnO Films*
P-17	**Agnieszka Brzózka**	Poznan University of Technology, Poland	*A Comparative Study of Electrochemical Barrier Layer Thinning of Porous Anodic Oxide (AAO)*
P-18	**Alexey Dronov**	National Research University of Electronic Technology, Russia	*Relationship between Heat and Mass Transport Conditions and Anodic TNT Layer Growth Process*
P-19	**Mariusz Szkoda**	Gdansk University of Technology, Poland	*Electrosynthesis of Mo/Moo_3 and its Structural and Photocatalytic Properties*
P-20	**Natalia Tsyntsaru**	Institute of Applied Physics of ASM, Moldova	*Electrochemical Co-Deposition of Tungsten with Cobalt and Copper*
P-21	**Laurynas Staišiūnas**	Center for Physical Sciences and Technology, Lithuania	*Corrosion of Mg-xNb Coated by ALD Grown Nb_2O_5 in Hanks' Solution*

P-22	**Ramūnas Levinas**	Faculty of Chemistry. Vilnius University, Lithuania	*Study of Tungsten Anodization and Photoelectrochemical Behavior of Obtained Oxide Films*
P-23	**Virginija Kepenienė**	Center for Physical Sciences and Technology, Lithuania	*Synthesis and Characterization of* $AuCo_3O_4CD/C$ *Nanocomposites*
P-24	**Monika Bakierska**	Faculty of Chemistry, Jagiellonian University, Poland	*An Influence of Carbon Matrix Origin on Electrochemical Properties of Carbon-Tin Anode Nanocomposites*
P-25	**Joanna Świder**	Faculty of Chemistry, Jagiellonian University, Poland	*The Studies of Thermophysical and Electrochemical Properties of* $C/LiFePO_4$ *Nanocomposite Materials*
P-26	**Loreta Tamašauskaitė-Tamašiūnaitė**	Center for Physical Sciences and Technology, Lithuania	*Investigation of Electrodeposition of* MnO_2 *by EQCM*
P-27	**Anton M. Pastukhov**	Ural Federal University, Russia	*Electrochemical Reduction of Uranium in Strip Product Solutions on Carbon Electrode*
P-28	**Anton M. Pastukhov**	Ural Federal University, Russia	*Thermodynamic Studies of Geochemical Processes at Uranium In-Situ Leaching Mining*
P-29	**Olga Girčienė**	Center for Physical Sciences and Technology, Lithuania	*Active Corrosion Protection of Steel by Phosphate Conversion Coatings Dopped with Cerium*
P-30	**Yu. M. Baikov**	Ioffe Institute, RAS, Russia	*Solid Hydroxiode Eutectics as Self-Organized Nanostructured Electrolytes for Small-Sized and Low-Power Electrochemical Devices at 250-420 K*
P-31	**Yulia Nazarkina**	National Research University of Electronic Technology, Russia	*Features of Porous Anodic Alumina Galvanostatic Growth in Selenic Acid Electrolyte*
P-32	**Leszek Zaraska**	Jagiellonian University, Poland	*Formation of Crack-Free Nanoporous Tin Oxide Layers by Simple Anodization in Alkaline Electrolyte at Low Potentials*
P-33	**Leszek Zaraska**	Jagiellonian University, Poland	*Anodic Growth of* ZnO *Nanowires in Bicarbonate Electrolytes*
Electroanalysis			
P-34	**Karolina Syrek**	Jagiellonian University, Poland	*Photoelectrochemical Sensors for Glucose Based on Nanostructured Metal Oxides*
P-35	**Raimonda Celiešiūtė**	Center for Physical Sciences and Technology, Lithuania	*Electrochemical Glutamate Sensing Applying Poly(Riboflavin) and Graphene Oxide-Chitosan Film Modified Electrodes*

P-36	**Ewa Wierzbicka**	Jagiellonian University, Poland	*Epinephrine Sensing at Au Nanotube Array Electrode and Determination Its Oxidative Metabolism*
P-37	**Karolina Gawlak**	Jagiellonian University, Poland	*Synthesis of Nanoporous Silver Nanowires as Electrochemical* H_2O_2 *Sensor*
Electrocatalysis			
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P-40	**Jolita Jablonskienė**	Center for Physical Sciences and Technology, Lithuania	*Methanol and Ethanol Electro-Oxidation on Platinum-Cobalt/Graphene Catalysts Prepared by Microwave Synthesis*
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P-43	**Raminta Stagniūnaitė**	Center for Physical Sciences and Technology, Lithuania	*Cerium Oxide/Graphene Supported Pt and Pt-Co as Electrocatalysts for Methanol Oxidation and Oxygen Reduction Reaction*
P-44	**Irena Stalnionienė**	Center for Physical Sciences and Technology, Lithuania	*Anodic Oxidation of Formaldehyde on Electroless Copper Coatings Deposited from Cu(II)-EDTA Solutions*
P-45	**Virginija Kepenienė**	Center for Physical Sciences and Technology, Lithuania	*Comparison of Electrocatalytic Properties of* $PtCoCeO_2$*/Graphene and* $PtCoNb_2O_5$*/Graphene Catalysts Towards Methanol Oxidation*
P-46	**Aušrinė Zabielaitė**	Center for Physical Sciences and Technology, Lithuania	*Fiber Cobalt Decorated with Platinum Nanoparticles as Electrocatalysts for Hydrazine Oxidation*
P-47	**Ina Stankevičienė**	Center for Physical Sciences and Technology, Lithuania	*Autocatalytic Reduction of Platinum(IV) By Cobalt(II)-Diethylenetriamine Complex*
P-48	**Aldona Jagminienė**	Center for Physical Sciences and Technology, Lithuania	*Electroless Cobalt Deposition in Diethylenetriamine Solutions Using Morpholine Borane as a Reducing Agent*
P-49	**Dijana Šimkūnaitė**	Center for Physical Sciences and Technology, Lithuania	*Investigation of Borohydride Oxidation onto a Spontaneously Bi-Modified Polycrystalline Pt Electrode*

P-50	**Teofilius Kilmonis**	Center for Physical Sciences and Technology, Lithuania	*Graphene Supported PtM (Mo, W) Catalysts for Borohydride Oxidation*
P-51	**Anna Brudzisz**	Jagiellonian University, Poland	*Silver Nanowires and Nanocones Arrays as Electrocatalytic Electrodes*
P-52	**Žana Činčienė**	Department of Catalysis, Center for Physical Sciences and Technology, Lithuania	*Fabrication, Characterization and Properties of PtCoB/Cu Catalysts*
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Batteries and Energy Conversion			
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P-66	**Hatem Akbulut**	Sakarya University, Turkey	*Optimization SiO_2 and Al_2O_3 Nanoparticles on the Stability of TEGDME-$LiPF_6$/ PEO Electrolytes for Li-Air Batteries*
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P-71	**Jurga Juodkazytė**	Institute of Chemistry, Center for Physical Sciences and Technology, Lithuania	*Formation and Investigation of Fe_2O_3/Cu_xO Heterojunction for Possible Use in Solar Energy Conversion*
P-72	**Svetlana Lichušina**	Institute of Chemistry, Center for Physical Sciences and Technology, Lithuania	*Fabrication of Nanoporous Co by Dealloying Single-Phase γ-$Zn_{21}Co_5$ Alloy for Use in Electrochemical Supercapacitors*
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P-76	**Magdalena Z. Wiloch**	Faculty of Chemistry, Warsaw University of Technology, Poland	*Electrochemical Properties of Copper Complexes with β-Amyloid 4-16 and β-Amyloid 1-16*
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Analytical and Environmental Chemistry			
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P-86	**Laima Nedzveckienė**	Institute of Physics, Center for Physical Sciences and Technology, Lithuania	*Comparative Research of Vertical Migration of* ^{137}*Cs in the Soil of Flooded and Upland Banks of Lakes*
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Nanotechnology			
P-89	**Kristina Bliekaitė**	Vilnius University, Lithuania	*Study of Canvas Deacidification Process Using Magnesium Nanomaterials*
P-90	**Eva Raudonytė-Svirbutavičienė**	Faculty of Chemistry, Vilnius University, Lithuania	*Photochemical Approcah to the Inorganic Synthesis of Semiconductor Nanoparticles*
P-91	**Rūta Sidaravičiūtė**	Kaunas University of Technology, Lithuania	*PAN/TiO_2 Catalyst Formation by Electrospinning and its Structural Characterization*
P-92	**Olegas Eicher-Lorka**	Center for Physical Sciences and Technology, Lithuania	*Functionalization of Magnetic Nanoparticles with New Isocyanate Compound*
P-93	**Daina Upskuvienė**	Center for Physical Sciences and Technology, Lithuania	*Gold Nanoparticles: Synthesis, Characterazation and Application*
P-94	**Ieva Kulakauskaitė**	Center for Physical Sciences and Technology, Lithuania	*Nickel Sorption by Magnetic Nanocomposites*
P-95	**Aušra Baradokė**	Center for Physical Sciences and Technology, Lithuania	*Soft Lithographic Fabrication of Electrodes for Detection of Hydrogen Peroxide*
P-96	**Dovilė Baziulytė**	Faculty of Chemistry, Vilnius University, Lithuania	*Upconvertion Core-Shell Nanoparticles with Enhanced Photoluminescence for Application in Bioimaging and Cancer Therapy*
P-97	**Konrad Trzcinski**	Faculty of Chemistry, Gdańsk University of Technology, Poland	*The Influence of Gold Interlayer on Photoelectrochemical Properties of TiO_2 nanotubes/ $BiVO_4$ Junction*
P-98	**Konrad Trzcinski**	Faculty of Chemistry, Gdańsk University of Technology, Poland	*Micropatterned $BiVO_4$ Films as Templates for Photodeposition of Various Metallic Nanoparticles*
P-99	**Ieva Mikalauskaitė**	Faculty of Chemistry, Vilnius University, Lithuania	*Synthesis and Investigation of Upconverting $NaYF_4$ Nanoparticles Obtained in Oleylamine*
P-100	**Tomas Gadišauskas**	Kaunas University of Technology, Lithuania	*Electrochemically Etched Nano-Probes for Scanning Near-Field Optical Microscopy*
P-101	**Natalia Rezanova**	Kyiv National University of Technologies & Design, Ukraine	*Morphology and Rheological Properties of Incompatible Polymer Compositions with Nanoparticles TiO_2/SiO_2*
P-102	**Simona Streckaitė**	Center for Physical Sciences and Technology, Lithuania	*Formation of Silver Nanoparticles and their Influence on Fluorescence of Organic Materials*
P-103	**Rokas Žalnėravičius**	Center for Physical Sciences and Technology, Lithuania	*Nanoplatelet MoS_2 Films Decorated with Pt Quantum Dots for Effective Hydrogen Production*

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No.	Presenting author	Affiliation	Poster title
Chemistry and Chemical Technology of Organic Materials			
P-104	**Gintarė Kručaitė**	Kaunas University of Technology, Lithuania	*Wet- and Dry-Process Feasible Carbazole Type Hosts for Highly Efficient Phosphoresent OLEDs*
P-105	**Daiva Tavgenienė**	Kaunas University of Technology, Lithuania	*Phenylvinyl-Substituted Carbazole Twin Compounds as Hole Transporting Materials for Organic Light Emitting Diodes*
P-106	**Titas Deksnys**	Kaunas University of Technology, Lithuania	*Dimethoxydiphenylamino-Substitted 9-Naphthylcarbazole Derivative as Bipolar Emitter for Colour-Tunable OLEDs*
P-107	**Simona Streckaitė**	Center for Physical Sciences and Technology, Lithuania	*Fluorescence Quenching of Indolo[3,2-B]carbazole Compounds by Conformational Motions of Attached Substituents*
P-108	**Raminta Mazėtytė**	Center for Physical Sciences and Technology, Lithuania	*Fluorescence Quenching Of Glucose Oxidase Self-Encapsulated Within Polypyrrole*
P-109	**Ernestas Kasparavičius**	Kaunas University of Technology, Lithuania	*Dyes with 3-Pyrrolin-2-one Electron Accepting Moiety: Sintesis and Investigation in the Dye–Sensitized Solar Cells*
P-110	**Ingrida Tumosienė**	Kaunas University of Technology, Lithuania	*Synthesis and Antioxidant Activity of 1,3,4-Oxa(thia)diazole and 1,2,4-Triazole-5-(Thio)one Derivatives*
P-111	**Birutė Sapijanskaitė**	Kaunas University of Technology, Lithuania	*Transformation of Ethyl 1-Aryl-2-methyl-4-oxo-1,4,5,6-tetrahydropyridine-3-carboxylates under the Influence of Nitrogen Nucleophiles*
P-112	**Irena Ramanauskaitė**	Kaunas University of Technology, Lithuania	*Synthesis of 3-[4-(Aminosulfonyl)anilino]propanoic Acids with Azole Moieties*
P-113	**Birutė Grybaitė**	Kaunas University of Technology, Lithuania	*Synthesis of 5-Substituted N-(1-naphtyl)-N-(4-oxo-4,5-dihydro-1,3-thiazol-2-Yl)-β-alanines*
P-114	**Romualdas Striela**	Center for Physical Sciences and Technology, Lithuania	*An Efficient Conversion of 2-aminopyridines to 2-halogenpyridines*
P-115	**Artūras Peleckis**	Kaunas University of Technology, Lithuania	*Synthesis of 1-(5-Chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carbohydrazide Derivatives*
P-116	**Vaida Laukaitytė**	Kaunas University of Technology, Lithuania	*Synthesis of Novel Pyrazole Scaffold-Based Heterocyclic Systems*

P-117	**Monika Dargytė**	Kaunas University of Technology, Lithuania	*Synthesis of 5-Aryl-3,3-dimethyl-2,3-dihydro-1H-indole Carboxylic Acid Derivatives*
P-118	**Gabrielė Gudžinskaitė**	Kaunas University of Technology, Lithuania	*Synthesis of New 2-Aminothiazole Derivatives*
P-119	**Jurga Būdienė**	Center for Physical Sciences and Technology, Lithuania	*Eupatorium Cannabinum L. Essential Oils and their Bioactive Properties*
P-120	**Aušra Linkevičiūtė**	Center for Physical Sciences and Technology, Lithuania	*Lipid Liquid Crystalline Systems for the Protection of Flavonoids*
P-121	**Gita Matulevičiūtė**	Kaunas University of Technology, Lithuania	*Conversion of 2-Thioxo-2,3-dihydroquinazolin-4(1H)-ones to N(3)-Unsubstituted 2-(Het)arylquinazolin-4(3H)-ones*
P-122	**Vaida Milišiūnaitė**	Kaunas University of Technology, Lithuania	*A Straigtforward Approach to Novel Fused Pyrazole Systems*
P-123	**Ieva Matulaitienė**	Center for Physical Sciences and Technology, Lithuania	*Spectral Markers of N-(6-mercapto)hexylpyridinium (MHP) in Low and High Frequency Spectral Regions*
P-124	**Aistė Kveselytė**	Kaunas University of Technology, Lithuania	*Microwave-Assisted Synthesis of New Fluorescent Imidazo[1,2-a]indolone Derivatives by Suzuki-Miyaura Cross-Coupling Reaction in Aqueous Media*
P-125	**Matas Steponaitis**	Kaunas University of Technology, Lithuania	*Organic Quaternary Ammonium Compounds as Hole Transporting Materials for Optoelectronic Applications*
P-126	**Edvardas Golovinas**	Center for Physical Sciences and Technology, Lithuania	*Study of Temperature Influence on Molecular Interactions in Cholesterol Using Raman Spectroscopy*
P-127	**Sigita Kašėtaitė**	Kaunas University of Technology, Lithuania	*Photorheometrical Study of Compositions Based on Glycerol Diglycidyl Ether and Di- or Trihydroxylic Alcohols*
P-128	**Martynas Talaikis**	Institute of Biochemistry, Vilnius University, Lithuania	*FTIR Characterization of Amyloids*
P-129	**Elena Ščerbetkaitė**	Kaunas University of Technology, Lithuania	*Synthesis of 3’-Substituted 1,1,3-trimethyl-1,3-dihydro-4’H-spiro[benzo[e]indol-2,5’-[1,2]oxazole] Derivatives yy 1,3-Dipolar Cycloaddition*

P-130	**Jolita Kuginytė**	Institute of Synthetic Chemistry, Kaunas University of Technology, Lithuania	*Flow Synthesis of Cynnamic Acids Derivatives*
P-131	**Emilis Gudelis**	Institute of Synthetic Chemistry, Kaunas University of Technology, Lithuania	*Synthesis of Ionic Liquids from Natural Amino Acids*
P-132	**Linas Labanauskas**	Center for Physical Sciences and Technology, Lithuania	*Effects of Polyol Ester Structure on Their Visocsity and Solidification Trends*
P-133	**Karolis Petrauskas**	Center for Physical Sciences and Technology, Lithuania	*Utilization of Elastomer Swelling to Evaluate Rubber, De-Vulcanized by Environmentally Friendly Method*
P-134	**Svajus Asadauskas**	Center for Physical Sciences and Technology, Lithuania	*Improvement in Resistance to Wear and Corrosion of Anodized Alumina by Impregnation in Biobased Filler*
P-135	**Robertas Tiažkis**	Kaunas University of Technology, Lithuania	*Hole-Transporting Molecular Glasses Containing Fluorene/Triphenylamine Moieties*
P-136	**Aurimas Bieliauskas**	Kaunas University of Technology, Lithuania	*Synthesis of Highly Fluorescent 3-Substituted 4-styryl-1H-pyrazole Derivatives*
P-137	**Koleta Majewska**	Gdańsk University of Technology, Poland	*Solid-State Characterization of Tricyclic Pharmaceutical Compound and Cyclodextrin Inclusion Complex*
P-138	**Beata Kamińska**	Gdańsk University of Technology, Poland	*UV/$S_2O_8^{2-}$ Process for Degrading a Tricyclic Muscle Relaxant Pharmaceutical in Aqueous Solutions*
P-139	**Agnieszka Pazik**	Gdańsk University of Technology, Poland	*The Shiff Bases As Sensitive Analytical Reagents for F^- and Cu^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+} Ions*
P-140	**Gitarė Naujokaitytė**	Faculty of Natural Sciences, Vytautas Magnus University, Lithuania	*Phytochemical Analysis Diploid and Polyploid Forms of Ribes Using Spectrophotometric, Liquid and Gas Chromatographic Methods*
P-141	**Monika Kudžmaitė**	Kaunas University of Technology, Lithuania	*Products of Condensation Reactions of 5-Oxo-1-[4-(phenylamino)phenyl]pyrrolidine-3- carboxylic Acid and their Antioxidant Activity*
P-142	**Alisa Palavenienė**	Kaunas University of Technology, Lithuania	*Preparation and Characterisation of Ionically Cross-Linked Alginate/Cuttlebone Beads*
P-143	**Ilja Ignatjev**	Center for Physical Sciences and Technology, Lithuania	*Rapid Method to Determine Suitability of Acrylonitrile-Butadiene-Styrene Plastic for Metallization*

P-144	**Titas Braukyla**	Kaunas University of Technology, Lithuania	*Synthesis and Investigation of V-Shaped Hole-Transporting Materials Containing Tröger`s Base Core and Phenylethenyl Branches*
P-145	**Dalia Bražinskienė**	Center for Physical Sciences and Technology, Lithuania	*Influence of Oleate Oxidation on Metal Surface*
Chemistry and Chemical Technology of Inorganic Materials			
P-146	**Paulius Gibieža**	Institute of Cardiology, Lithuanian University of Health Sciences, Lithuania	*Preparation and Study of Antimicrobial Water-Soluble Cationic Starch Iodophors*
P-147	**Lina Pavasarytė**	Department of Inorganic Chemistry, Vilnius University, Lithuania	*Synthesis and Luminescence Properties of Eu*$^{3+}$*-Doped* $Y_{3-x}Nd_xAl_3O_{12}$
P-148	**Olga Opuchovič**	Department of Inorganic Chemistry, Vilnius University, Lithuania	*Mössbauer Spectroscopy for Mixed-Metal Yttrium Aluminium-Iron Garnets*
P-149	**Jurga Bagdzevičienė**	Lithuanian Art Museum, Pranas Gudynas Restoration Center, Lithuania	*Natural pieces of Baltic Amber: Investigation into the Reasons for their Disintegration and Preventive Conservation*
P-150	**Mantas Norkus**	Faculty of Chemistry, Vilnius University, Lithuania	*Synthesis of* MoS_2 *Thin Films from Ammonium Tetrathiomolybdate*
P-151	**Neringa Petrašauskienė**	Kaunas University of Technology, Lithuania	*Morphology of Cadmium Selenide Based Coatings Formed on Polyamide Substrate*
P-152	**Ingrida Ancutienė**	Kaunas University of Technology, Lithuania	*XPS Characterization of Mo-Cu-S Layer on Glass*
P-153	**Algimantas Ivanauskas**	Kaunas University of Technology, Lithuania	*XPS Studies of Cu-In-Se Layers on Glass*
P-154	**Kristina Jančaitienė**	Kaunas University of Technology, Lithuania	*Properties of Liquid – Multicomponent Systems*
P-155	**Giedrė Grincienė**	Center for Physical Sciences and Technology, Lithuania	*Properties and Characterization of CZTS Crystals Prepared by Microwave Heating Irradiation*
P-156	**Aurimas Urbutis**	Kaunas University of Technology, Lithuania	*Studies of Adsorbate Reactions on Single and Activated CuO Based Catalysts*
P-157	**Rasa Šlinkšienė**	Kaunas University of Technology, Lithuania	*Adsorption of Potassium, Zinc and Copper Ions on Clinoptilolte*
P-158	**Domantė Niūniavaitė**	Department of Silicate Technology, Kaunas University of Technology, Lithuania	*The Chemosorption Properties of Synthetic* α-C_2S *Hydrate*

P-159	**Gabrielė Sarapajevaitė**	Kaunas University of Technology, Lithuania	*C-S-H (I) Sample Stability under Different Partial Water Vapour Pressure Environment*
P-160	**Domas Stungys**	Kaunas University of Technology, Lithuania	*The Influence of Graphene Additive on The Hydration Properties of Binder Material Based on* α-C_2S *Hydrate*
P-161	**Kristina Ruginytė**	Kaunas University of Technology, Lithuania	*The Influence of Graphene Additive on the Hydration Properties of OPC*
P-162	**Laura Jefimovaitė**	Kaunas University of Technology, Lithuania	*The Simultaneous Adsorption Capacity of Hydrotalcite for* Co^{2+}, Cr^{3+}, Cu^{2+} *Ions*
P-163	**Viktorija Ringytė**	Kaunas University of Technology, Lithuania	*Effect of Partial Water Vapour on Hydrotalcite Sample Structure*
P-164	**Jolanta Donėlienė**	Kaunas University of Technology, Lithuania	*Surface Microstructure and Specific Surface Area of Synthetic Calcium Aluminium Hydrate*
P-165	**Aliona Iljina**	Kaunas University of Technology, Lithuania	*The Formation of Dibasic Calcium Silicate Hydrates*
P-166	**Agnė Šmigelskytė**	Kaunas University of Technology, Lithuania	*Influence of Forming Pressure on the Synthesis of Clinker Minerals*
P-167	**Pranas Ušinskas**	Faculty of Chemistry, Vilnius University, Lithuania	*Preparation of Calcium Titanate Powders and Thin Films by Sol- Gel Method*
P-168	**Birutė Šimkūnaitė-Stanynienė**	Center for Physical Sciences and Technology, Lithuania	*Formation of ZnO by the Silar Method for Thin Solar Cells*
P-169	**Giedrius Smalakys**	Kaunas University of Technology, Lithuania	*The Synthesis of 1.13 nm Tobermorite from Granite Polish Waste*
P-170	**Danas Sakalauskas**	Faculty of Chemistry, Vilnius University, Lithuania	*Synthesis of* $Sr_{1-x}Y_xF_2$+x *via Co–Precipitation Method*
P-171	**Monika Skruodienė**	Faculty of Chemistry, Vilnius University, Lithuania	*Doping Effect of* Tb^{3+} *Ions on Luminescence properties of* $Y_3Al_5O_{12}:Cr^{3+}$ *Phosphor*
P-172	**Tadas Matijošius**	Center for Physical Sciences and Technology, Lithuania	*Wear Behavior of Dry Sliding and Lubricated Titanium Alloys*
P-173	**Eglė Gražėnaitė**	Faculty of Chemistry, Vilnius University, Lithuania	*Commercial and Sol-Gel Derived Cobalt Chromites as Ceramic Pigments: a Comparative Study*
Polymer Chemistry			
P-174	**Rasa Keruckienė**	Kaunas University of Technology, Lithuania	*2-Phenylindolylcarbazole Derivatives with Reactive Functional Groups as Electroactive Materials*

P-175	**Ramunė Rutkaitė**	Kaunas University of Technology, Lithuania	*Immobilization of Rosemary Oil in Electrospun Cellulose Acetate Fibers*
P-176	**Vesta Navikaitė**	Kaunas University of Technology, Lithuania	*Electrospun Cellulose Acetate Fibers Containing Essential Oils for Active Food Packaging*
P-177	**Dalia Buivydienė**	Kaunas University of Technology, Lithuania	*Review: Biodegradable Polymers and Melt Electrospinning Method for Nanofiber Fabrication*
P-178	**Gintautas Šimkus**	Kaunas University of Technology, Lithuania	*Synthesis and Properties of Photocross-Linkable Carbazole-Based Monomers*
P-179	**Dainora Jankūnaitė**	Kaunas University of Technology, Lithuania	*Carbazole-Based Derivatives Having Donor and Acceptor Moeties*
P-180	**Karolis Norvaiša**	Kaunas University of Technology, Lithuania	*Derivatives of 9-Phenyl Carbazole with Indole Moieties for Electrophosphorecent Devices*
P-181	**Anton Magomedov**	Kaunas University of Technology, Lithuania	*Cheap and Efficient Carbazole-Based Hole Transporting Materials for Perovskite Solar Cells*
P-182	**Ieva Petrikytė**	Kaunas University of Technology, Lithuania	*Efficiency Enhancement of Perovskite Solar Cells via Incorporation of Phenylethenyl Side Arms into Indolocarbazole-Based Hole Transporting Materials*
P-183	**Deimantė Simanavičiūtė**	Kaunas University of Technology, Lithuania	*Adsorption of Chlorogenic Acid on Cationic Cross-Linked Starch with Quaternary Amino Groups*
P-184	**Dovilė Liudvinavičiūtė**	Kaunas University of Technology, Lithuania	*Starch Derivatives with Tertiary Amino Groups for Immobilization of Bioactive Phenolic Acids*
P-185	**Rasa Paleckienė**	Kaunas University of Technology, Lithuania	*Starch-Based Biodegradable Films for Coating Urea: Preparation and Properties*
P-186	**Rita Butkutė**	Kaunas University of Technology, Lithuania	*Vinyl-Functionalized Phenanthroimidazole: Synthesis, Properties and Self-Polymerization*
P-187	**Joana Bendoraitienė**	Kaunas University of Technology, Lithuania	*Cationic Starch Obtained by Reactive Extrusion*
P-188	**Edita Paluckienė**	Kaunas University of Technology, Lithuania	*SEM Investigation of Polyethylene, Polypropylene and Polyester with* Cu_xS *Layers*
P-189	**Joanna Świder**	Faculty of Chemistry, Jagiellonian University, Poland	*Copolymers of N-Vinylformamide as Support for Immobilization of Cellulolytic Enzymes*
Physical Chemistry			
P-190	**Linas Samardokas**	Kaunas University of Technology, Lithuania	*Optical Properties of Thallium Selenide Layers on the Polyamide Film Surface*

P-191	**Elena Binkauskienė**	Center for Physical Sciences and Technology, Lithuania	*Characterization of Long-Term Atmospheric Corrosion Products of Zinc*
P-192	**Skirma Žalenkienė**	Kaunas University of Technology, Lithuania	*Properties of CdSe Films Deposited by CBD-Silar Method on Polymer*
P-193	**Jonas Reklaitis**	Center for Physical Sciences and Technology, Lithuania	*Influence of Chloride Concentration in Thermofication Water on Formation of β-FeOOH on Carbon Steel*
P-194	**Agnė Mikalauskaite**	Center for Physical Sciences and Technology, Lithuania	*Synthesis, Characterization and Application of Red-Luminescent Gold Clusters*
P-195	**Austėja Bukauskytė**	Center for Physical Sciences and Technology, Lithuania	*Fluorescence Quantum Yield of Perylenediimide Derivatives*
P-196	**Renata Karpicz**	Center for Physical Sciences and Technology, Lithuania	*Structural and Fluorescence Studies of Polycrystalline A-Al_2O_3 Obtained on Anodic Alumina*
Chemical Engineering			
P-197	**Justė Kupčiūnaitė**	Faculty of Chemistry, Vilnius University, Lithuania	*Surface Active Materials for Paper Cleaning*
P-198	**Ieva Vilkaitė**	Kaunas University of Technology, Lithuania	*Hardening and Hydration Properties of Blended Cements*
P-199	**Marius Baltakys**	Kaunas University of Technology, Lithuania	*The Influence of Structure and Mineral Composition on Properties of Autoclaved Aerated Concrete*
P-200	**Jolita Rusinavičiūtė**	Kaunas University of Technology, Lithuania	*Analysis of Physical and Chemical Composition of Protein Fibres*
P-201	**Valentina Krylova**	Kaunas University of Technology, Lithuania	*Incorporation of Silver Selenide into Silk Matrice*
Biochemistry			
P-202	**Rasa Alaburdaitė**	Kaunas University of Technology, Lithuania	*Influence of Metal Ions Additives on Enzymatic Hide Unhairing in Oxidative Medium*
P-203	**Veslava Matikevičienė**	JSC “Biocentras”, Lithuania	*Characterization of Hydrogel with Antibacterial Activity*
P-204	**Iwona Ufnalska**	Warsaw University of Technology, Poland	*Yeast Pheromon as an Example of Biologically Active Oligopeptides Forming Ternary Complexes*
P-205	**Elena Binkauskienė**	Center for Physical Sciences and Technology, Lithuania	*The Influence of Mycobiota on the Interface of The Polyaniline Coatings*

P-206	**Maksym Koliada**	Kyiv National University of Technologies & Design, Ukraine	*Collagen Derivatives Application for Biodegradable Films Formation*
P-207	**Kristina Teišerskytė**	Kaunas University of Technology, Lithuania	*Impact of 4-[(9-Alkylcarbazol-3-yl)amino]-3-carboxybutyric Acid Disodium Salts on Rape (Brassica Napus L.) Germination In Vitro*

KEYNOTE LECTURES

ELECTROLYSIS VIA BIPOLAR ELECTROCHEMISTRY

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An alternative way to perform electrolysis is to establish an electric field in the electrolyte rather than connecting a working electrode to a potentiostat. The electric field can be controlled by forcing a current through the solution via two feeder electrodes, and if a conductor is present it can become a bipolar electrode provided that the field strength is sufficiently high to induce oxidations and reductions at each end, respectively. The conductor simply offers an alternative route for the total cell current as a result of the faradaic reactions.

This talk will present recent findings where different aspects of bipolar electrochemistry are used to perform electrolysis. A major advantage is the fact that the potential difference varies across the bipolar electrode, which in reality means that a wide range of potentials can be established on a single electrode (illustrated in Figure 1 below). This is, for example, useful in screening applications and to produce surfaces having a wide range of chemical properties. We have previously shown the possibility to produce biomimetic protein gradients [1,2], and more recently gradients in pitting corrosion on stainless steel [3]. Bipolar electrochemistry has also been used to modify or move small objects [4] and to improve detection capabilities in analytical applications [5]. In addition, we have also demonstrated the selective growth of surface immobilized gold nanoparticles, which also indicated the complex current- and potential distributions in bipolar experiments [6].

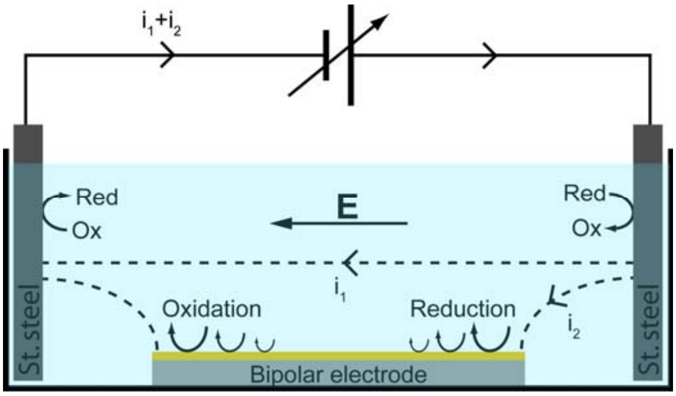

Figure 1. Schematic figure of a bipolar experiment where two feeder electrodes are used to create an electric field in the electrolyte, and hence induce redox reactions on a conductor (bipolar electrode). The potential difference hence varies in a wide range across the bipolar electrode.

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The thermodynamics of insertion electrochemical systems

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Insertion electrochemistry is the term for simultaneous electron and ion transfer between (a) an electroactive solid phase and (b) an electrolyte and (c) an electron conductor. The Gibbs energy of the overall reaction is the sum of the Gibbs energies of electron and ion transfer [1]. Systematic studies of the insertion electrochemistry of polycyanometalates has provided precious information on the effects of the structure, bonding, and composition of these compounds on their formal potentials [e.g.: 2, 3].
Previously it has been shown that instead of a solid phase, one can also use a droplet (organic liquid) of an immiscible solution immobilized on a solid electrode and immersed in an aqueous electrolyte solution [4, 5, 6]. In that case the Gibbs energy of ion transfer can be determined, as the Gibbs energy of electron transfer is known (although based on extra-thermodynamic assumptions) from measurements in the organic phase. This approach has been used to determine Gibbs energies of ion transfer also between miscible liquids, using in parallel experiments with one solid (or liquid) phase which is immiscible with the two miscible phases [7, 8, 9].
It seemed for a long time that a separation of the contributions from ion and electron transfer is impossible for electroactive solid phases. Recently systems where discovered where the ion transfer between a surface layer and a solution can be measured by potentiometry, and the ion + electron transfer by voltammetry [10, 11]. Provided that the surface layer is rather similar to the bulk of the solid phase, this gives access to both Gibbs energies, that of the electron and that of the ion transfer.
This talk emphasizes the importance of thermodynamic studies and demonstrates their value for the understanding of electrochemistry.

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Silicon photoelectrochemistry for solar energy applications

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ABSTRACT

Photoactivity of silicon is the main characteristic for its use as a solar material. Photoelectrochemical measurements with a liquid junction provide an opportunity to characterize the activity of silicon. The information correlates well with that obtained using the solid-state cells, so that there is no need to design a solar cell with p-n junction in order to characterize efficiency of solar energy harvesting.

To increase efficiency of silicon, its surface is textured by physical or chemical techniques such as reactive ion etching, laser scribing, photolithography and chemical etching. Most of these techniques, however, are costly and include hazardous reactants, such as hydrofluoric acid. We developed methods of silicon surface structuring, which are based on electrochemistry in molten calcium chloride. The approaches are relatively simple, not costly and friendly to the environment [1,2]. Of particular interest is formation of so-called black silicon - a material with nano-micro structured surface, which effectively absorbs visible light.

Activity of silicon surface architectures was studied by photoelectrochemical measurements such as photopotential variation, cathodic photocurrents and Mott-Schottky analysis. Experiments have been performed using white light illumination and the redox agents, which reduction potentials are within the band gap of silicon.

The proposed electrochemical methods in molten salt offer new opportunities for silicon surface technologies, for instance, preparation of efficient electrodes for batteries, photoelectrochemical hydrogen generation as well as the platforms for sensors and antireflection coatings for photodevices.

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THE DEVELOPMENT OF ELECTROCHEMISTRY IN LITHUANIA

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Lithuania may be reasonably proud that origin of electrochemistry science in the country is associated with Theodor Grotthuss, the world famous founder of the theory of electrolysis. Some think it could have been worthy of a Nobel Prize, if such had existed at that time. However, 100 years had to pass till next serious electrochemical investigations in Lithuania began and this gap of time inevitably is related to the historical turning points in the period of 19 – 20th centuries in the country [1].

Scientific research in electrochemistry in Lithuania started in the beginning of 20th century and is related to the name of professor V. Čepinskis. His creative pedagogical work and efforts to establish infrastructure for the research have formed the background for the developing of recognized Lithuanian electrochemist scientific school. J. Matulis and J. Janickis were the most talented and creative disciples of V. Čepinskis. They both had worked for several years in foreign scientific centers and had obtained academic degrees before 1940. To be fair, it should be acknowledged that before the World War II, only the foundations for development of electrochemical science were laid, while the most important accomplishments belong to the later times.

In the postwar period Lithuania began training its own qualified electrochemistry specialists having skills of scientific research. J. Matulis, who headed the Department of Physical Chemistry in Vilnius University in the period of 1945 – 1950 initiated research related with electrolytic deposition of metal coatings. The development of electrochemical science in Lithuania was greatly influenced by insightful decision of J. Matulis, made in the period of the profiling of the institutes of Lithuanian Academy of Sciences, to choose the area of metal electrodeposition, which was promising in all respects.The studies performed by the members of the scientific school of J. Matulis and R. Višomirskis advantageously combined scientific investigations with application of the obtained results in practice, therefore several dozens of metals and dielectrics surface treatment technologies were designed which were applied widely in industry.

After Lithuania had regained its independence new research directions were identified with a focus on an integration into global chemistry science. The qualitative changes took place in the field of research objects and scientific production during the last decade of the century. Fundamental and applied research initiated by J. Matulis spread out into such areas as autocatalytic metal reduction, bioelectrochemistry, spectro-electrochemistry and electrochemical materials science. The last decade of 20th century offered a lot of new opportunities in science and also new challenges, which the Lithuanian electrochemists had to face. The efforts to integrate into international research area and to search for new scientific contacts and possibilities of cooperation were productive. A qualitative change occurred in the field of scientific production as well, illustrating the fact that working in the open international scientific community is much more productive and more favorable for creation of research output of higher quality.

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Novel electrochemical devices for energy recuperation systems

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FIB-SEM, XPS, HRTEM, FIB-TOF-SIMS, neutron scattering and synchrotron radiation based XPS, and Brunauer-Emmett-Teller gas adsorption methods have been used for the characterisation of physical properties of microporous carbide derived carbon and carbon nano-spheres electrodes (prepared from different binary and ternary d-metal carbides, d-glucose and sugar) before and after electrochemical tests conducted within very wide two electrode cell potential region. Also the characteristics of the three-electrode cells will be analysed.

Cyclic voltammetry, constant current charge/discharge, constant power tests and electrochemical impedance method have been applied for electrochemical characterization of the hybrid devices consisting of the various aqueous and non aqueous electrolytes (1 M Na_2SO_4 and 1 M Rb_2SO_4 [1,2], $LiBF_4$, $NaBF_4$, $NaPF_6$ and Cs-carborane [3-7] and ionic liquids [6]) and different carbon electrodes within the very wide cell potential region ($\Delta E \leq$ 2.4 V for aqueous solutions and $\Delta E \leq$ 4.5 V for non-aqueous solutions and ionic liquids). Noticeable role of the activation reaction conditions of carbon materials in the electrochemical characteristics of the cells will be analysed.

Influence of the chemical composition of cations and anions and the properties of solvents and ionic liquids (dielectric constant, effective dipole moment and polarizability) on the electrochemical characteristics of hybrid supercapacitor / battery and polymer electrolyte fuel cell / supercapacitor combined type devices will be discussed. Complex kinetic behaviour of completed devices (adsorption, blocking adsorption and intercalation of Li^+, Na^+, Rb^+ and Cs^+ cations and I^- and Br^- anions, faradic charge transfer and mass transfer, gas formation and adsorption, etc.) has been established at $\Delta E \geq$ 1.5 V for aqueous solutions and $\Delta E \geq$ 3.6 V for non-aqueous and ionic liquid systems. At least three different characteristic time constants dependent on the electrolyte cation/anion composition and cell potential applied have been established. Non-linear square root fitting analysis has been made and the results obtained have been discussed. Influence of carbon support properties on the polymer electrolyte membrane fuel cell parameters will be discussed [8].

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SYNTHESIS AND APPLICATION OF NANOSTRUCTURED METAL OXIDES: FROM PHOTOVOLTAICS TO PHOTOCATALYSIS

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Zinc oxide in the form of nanorods (NRs) deposited on the solid substrates is attractive material for photoanodes in the solar cells sensitized with dye molecules or semiconductor nanoparticles [1] as well as for photocatalytic decomposition of organic dyes [2]. Due to a high length to diameter ratio, the real surface area of ZnO might be even 1000 times larger than the geometric surface area of the substrate. Extended surface area is essential for amount of light harvesting material responsible for the value of operating parameters of photovoltaic cell and amount of adsorbed pollutant involved in photocatalytic reaction.

In this work we discuss the mechanism of the growth of ZnO either in the form of highly aligned nanorod arrays (Fig. 1a) or urchin-like nanostructures (Fig. 1b) [3]. The influence of the pretreatment of the substrate, synthesis method (hydrothermal or electrochemical) and the growth conditions on morphology of ZnO nanostructures is considered.

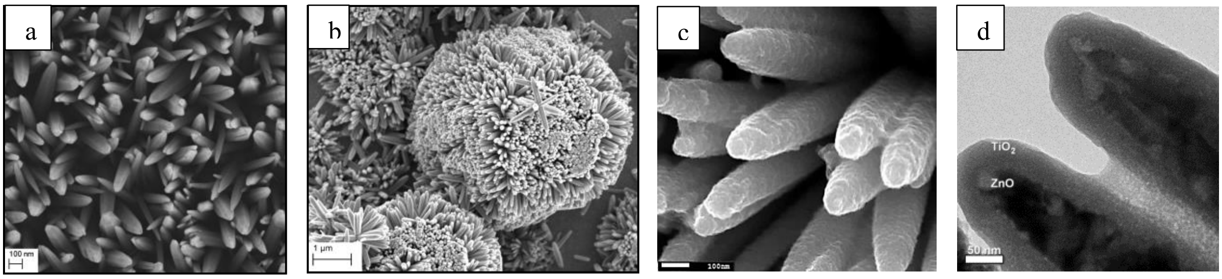

Fig. 1. SEM images of ZnO in the form of nanorod arrays (a) and urchin-like structures (b). Pictures (c) and (d) present SEM and TEM images of ZnO/TiO_2 core-shell structures

Application of ZnO nanorod arrays in semiconductor (SC)-sensitized solar cells is discussed taking into account the alignment of the edges of conduction and valence bands of the components (ZnO vs CdS, CdSe), semiconductor synthesis procedure and the type of redox electrolyte used as scavenger of photogenerated holes.

Application of urchin-like ZnO nanorods in photocatalytic decomposition of the model compounds (methylene blue and methyl orange) and real samples of wastewater is reported. The method of improvement of the photocatalytic properties of ZnO by formation of ZnO/TiO_2 core-shell material is presented [4] and the role of the metal oxides interface in separation of the photogenerated charge carriers and red-shift of the light absorption onset is discussed.

Acknowledgements

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INVITED LECTURES

Theodor Grotthuss contribution to the interpretation of electricity phenomenon in Volta‘s pile

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Alessandro Volta's invention of the electric battery (1799) became a major challenge to his contemporaries. This challenge can be best expressed in the form of a query: who shall be the first to explain the mysterious action of the voltaic pile? This challenge attracted the best men of science of the age, especially those already working in the field of electricity and chemistry, who tried to explain the nature and mechanism of the production of electric currents. One such person was Theodor Grotthuss (1785-1822); he was of German Baltic stock and spent most of his short life on his mother's estate in Lithuania. He became acquainted with Volta's pile while on a long visit to Paris (l803-1805) and did most of his research while in Naples and Rome (l805-1806).

In the interpretation of the electrolysis phenomenon, Theodor Grotthuss gave Volta's pile a particular importance. For him it was not just a generator of up till now not well understood galvanic phenomena but was also a model of a real "electropolar" system that existed in Nature and that manifested itself through this newly created artifact of Volta's invention. According to the explanation provided by Grotthuss, and today known as his first theory of electrolysis, Nature's foundation is based on electrical type polar opposites, what he called the elementary molecules （Grotthuss's "molecule" is closer to "ion", and that he was pioneering this concept). During electrolysis, water molecules will orient themselves into polar chains linking the electrodes into a unified system. The polarized molecules become the continuation of the copper-zinc couples that make up the pile. The Grotthuss interpretation is based on an experimental observation that crystal growth occurs always along the direction of the flow of current. Thus, in the interpretation provided by Grotthuss, the source of the electrical current is to be found in the copper-zinc stack of elements that make up the Volta pile and the aligned molecules in the solution between the electrodes, the two together constituting a united operating system.

It is worthwhile to emphasizing that by incorporating Volta's pile into this universal Nature's polarization system, Grotthuss creates the concept of influence between electrodes occurring along parallel lines. Some forty years later Michael Faraday developed his lines-of-force model from this concept. Faraday several times acknowledged in his papers (in his published work, the name of Grotthuss appears frequently, and therefore it would be impossible to cite all references to his name); that the starting point of his work was Grotthuss' 1805 electrolytic theory. This theory, the starting point of his reasoning and the concept of material lines, was a necessary but not sufficient condition for Faraday's development of the concept of electric field.

CONJUGATED POLYMERS IN THE DESIGN OF SENSORS AND BIOSENSORS

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The most of electrochemical sensors and biosensors are based on chemical or biochemical structures, which are selectively interacting with analyte. Dependently on the type of sensor the role of such structures could play molecularly imprinted polymers [1], enzymes [2], antibodies [3], receptors, single stranded DNA-oligomers, DNA-aptamers etc. However the incorporation of these structures in electrochemical systems is still challenging task, which could be solved by proper application of π -π conjugated polymers.

In this presentation methods, which could be used for the synthesis of conjugated polymers, will be addressed. These methods are ranging from basic chemical or electrochemical synthesis up to enzymatic or microorganisms based synthesis [4,5]. Monomers that could be polymerized by electrochemical methods will be overviewed. The advantages and problems related to the development of molecularly imprinted conjugated polymers, will be discussed [1]. During the presentation significant attention will be paid to electrochemical formation and deposition of conjugated polymers and incorporation of biological objects such as proteins or DNA within formed polymer layers. Advantages of some conducting polymers in the design of amperometric enzymatic biosensors will be outlined and significant attention of charge transfer from enzymes toward electrode *via* conjugated polymers will be presented. Special attention will be paid to discuss a good biocompatibility of conducting polymers and to the development of enzymatic biosensors suitable for the determination of glucose concentrations in biological samples. EQCM based evaluation of conducting polymer formation will be discussed [6]. Possibility to graft some conjugated polymers to carbon based surfaces will be addressed and future insights in development of conjugated polymer based sensors will be discussed.

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Electrochemical Impedance of Tethered Bilayer Membranes

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Tethered phospholipid bilayers are widely used models of the biological membranes. The electric properties of these models are accessible through the electrochemical impedance (EI) spectroscopy. Recently, an analytical solution for the spectral response of tBLMs containing natural or artificially introduced defects was derived [1]. The analysis shows that due to highly complex and asymmetric structure the tBLMs, impedance spectra of tethered bilayer membranes (tBLMs) cannot be modeled by the conventional electric elements such as resistors and capacitors. Local effects, including the impedance of the submembrane water reservoir separating solid support and phospholipid bilayer needs to be taken into account to reproduce features of EI spectra. There are, however, limiting cases, in which the complexity of the impedance of the tBLMs reduces. In the high frequency limit, the EIS response of the submembrane space that surrounds a defect transforms into a response of the constant phase element (CPE) with the exponent (α) value of 0.5. The onset of this transformation is, beside other parameters, dependent on the defect size. Large-sized defects push the frequency limit lower, therefore, the EIS spectra exhibiting CPE behavior with $\alpha \approx 0.5$, can serve as a diagnostic criterion for the presence of such defects. In the low frequency limit, the response is dependent on the density of the defects, and it transforms into the capacitive impedance if the area occupied by a defect is finite. The higher the defect density the higher the frequency edge at which the onset of the capacitive behavior in observed. Consequently, the presented analysis provides practical tools to evaluate the defect density in tBLMs, which could be utilized in tBLM-based biosensor applications [2]. Alternatively, if the parameters of the defects, e.g., ion channels, such as the diameter and the conductance are known, the EIS data analysis provides possibility to estimate other physical parameters of the system, such as thickness of the submembrane reservoir, and its conductance. In this talk we will illustrate theoretical analysis of EIS using as an example bacterial toxins capable of formation of well-defined water filled pores in phospholipid bilayer. We will address also the problem of the local heterogeneity on the major features of the EI spectra of tBLMs. Our theoretical approach demonstrates possibility to discriminate between the situations, in which the membrane defects are evenly distributed or clustered on the surface of tBLMs. Such sensitivity of EIS could be used for elucidation of the mechanisms of interaction between the proteins and membranes.

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Luminescence Properties of Eu^{3+} Doped Garnets

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Since 1926 when the preliminary structure of natural silicate minerals having cubic structure was determined the family of garnets became one of the most extensively studied group of compounds [1]. The most popular garnet is yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) which possesses good thermal and chemical stability and therefore it is an important composite for fluorescence. Europium doped phosphors are potential candidates for deep red light emitting diodes application, which could be used for plants and vegetables cultivation [2, 3]. The human eye sensitivity in the deep red range is very low, but radiation in this wavelength range has a rather high penetration depth into biological matter [4], therefore the europium or chromium doped garnets could be applied in the new field as optical imaging.

An overview in details of the luminescence of Eu^{3+} doped garnets are discussed in the present work. The series of powder samples were synthesized by citric acid sol-gel or combustion methods, while the crystals of garnets were grown by the traveling solvent floating zone method in order to investigate $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transitions of Eu^{3+} ions. The optical properties of Eu^{3+} are discussed with regard of dopant concentration, electronegativity and ionic radius In addition, luminous efficacies and percentage fraction of the $^5D_0 \rightarrow {}^7F_4$ transition were calculated and discussed.

It will be demonstrated that the transitions of $^5D_0 \rightarrow {}^7F_4$ are dominant in europium doped garnets independently on the crystallite size. The percentage fraction of Em_4 increases with the increasing average electronegativity in the compound indicating the polarization of the eight-coordinated site. This is in a good agreement with the neutron diffraction data refinement.

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Towards general strategy for tubular hydrogen-bonded polymers

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Tubular molecular structures are among the most versatile constructs that could be assembled in a predictable manner with the help of working principles of supramolecular chemistry. The unique properties of such assemblies are determined by the cylindrical dimensions in which information of directionality is encoded. Nanotubes can perform a variety of functions, such as transport of charged or neutral species, function as template for the synthesis of concave structures or nanowires and provide a nano-space with suitable dimensions for storage or catalytic purposes. We present several unique methods to obtain new types of supramolecular tubular aggregates and polymers, assembled from very small and thus, easily modifiable chiral hydrogen-bonding bicyclic building blocks. The full control of the nanotube structure is possible on the molecular level when careful consideration of tautomeric equilibrium and, thus hydrogen-bonding is implemented into monomer design. In this presentation, selected examples of tubular aggregates will be discussed highlighting their future application in material sciences.

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The possibilities of lactic acid bio-production from food industry by-products by using membrane filtration techniques

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The interest in the biotechnological production of lactic acid has increased due to the prospects of envi-ronmental friendliness and of using renewable resources instead of petrochemicals. Besides, this type oflactic acid is important for polylactic acid (PLA) production, as it is not toxic as packaging in food appli-cation while monomers of many fossil polymers are. However, there are still several issues that need to be addressed in order to produce LA biotechnologically within the targeted cost, such as the development of high-performance lactic acid-producing microorganisms and the lowering of the costs of raw materials, fermentation and biorefinery processes.

In the present study two membrane filtration techniques: nanofiltration (NO) and reverse osmosis (RO) were applied for the recovery of lactic acid (LA) from pretreated with β-galactosidase and fermented whey permeate (WP) using several lactic acid bacteria (LAB): (i) *Pediococcus acidilactici* KTU05-7 (Pa7), isolated from spontaneous Lithuanian rye sourdough and (ii) *Lactobacillus bulgaricus*, commonly used in dairies. The effect of each LAB strains on LA, its stereoisomers production and efficiency parameters has been examined. Obtained LA after RO was lyophilized and its solutions have been checked for antimicrobial activities.

Pa7 strain demonstrated more intensive lowering of pH in WP with the extension of fermentation time up till 24 h and increase in the lactose hydrolyses degree, compared with Lb. It has been noticed that after 24 h of fermentation, the intensity of pH declining and sugar conversion essentially changed: the lower values of pH and lactose content were obtained when WP was fermented with Lb. LAB strain Pa7 allows for the more rapid production of LA (4.55 g/L) during the first period of fermentation (24 h), while the application of Lb influenced the increase in higher concentration of LA by an average of 12 % as compared to Pa7 fermentation. After NF a 5.7-fold higher content of LA was obtained in whey permeate than in retentate and after RO LA mainly concentrated in retentate (Pa7 – 308,9 and Lb – 302,2 g/L). Both LAB strains produced racemic mixtures of both LA isomers in any time of fermentation with D/L ratios: 0.84 (Pa7) and 0.66 (Lb). The use of novel LAB strain with special properties for LA production simplified the filtration procedure of fermented WP, associated with protein aggregate formation in Lb fermented broth. A high antimicrobial effect was achieved, when higher concentrations of LA solution were used for pre-treatment of the dairy fermenter.

Keywords: whey permeate, lactic acid bacteria, fermentation, L(+)-lactic acid, D(-)-lactic acid, nanofiltration, reverse osmosis, detergents.

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SOLAR ENERGY HARVESTING: THE RENAISSANCE OF HYBRID SOLAR CELLS

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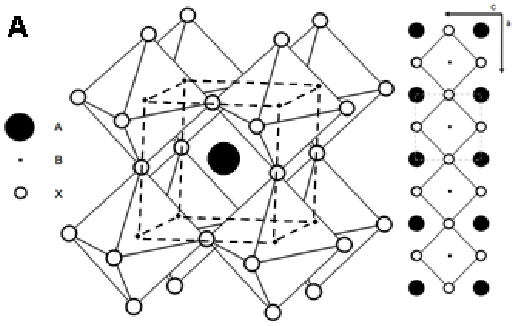
Efficient, energy-saving optoelectronic devices, such as solar cells, light emitting diodes and products containing these technologies are rapidly entering the market and are integrated into the future appliances and machines. One of the main sources of renewable energy is sunlight. Every hour Earth receives 1.78×10^{14}kWh of solar irradiation, while total annual energy consumption by the people of Earth is 1×10^{14}kWh. Perfecting the means of solar energy harvesting would allow us to substitute all other sources of energy used today.



During this decade a new and very promising type of hybrid solar cell technology has emerged from research laboratories worldwide. So called perovskite solar cells have demonstrated a meteoric rise of efficiency while retaining key advantages of construction simplicity and low-cost materials. Currently their efficiency has reached 21% [1], for comparison classic crystalline silicon solar cells are 21-25% efficient [2]. Characteristics of the perovskite solar cells are strongly influenced by type ligand and metals used for the formation of the perovskite structure as well as type of organic semiconductors used.

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ELECTRODEPOSITION OF Co-W ALLOYS FROM MACRO- TO NANO- SCALE

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Co-W alloys are often considered as high-performance alloys [1], and the attractiveness of these alloys is driven by their outstanding properties and multiple potential applications: the research is encouraged by the pronounced mechanical, tribological, and magnetic properties as well as the corrosion resistance of tungsten alloys. The magnetic properties of electrodeposited Co-W alloys are of interest in recording media and remotely-actuated micro-/nano-electromechanical systems. The given research presents an overview of versatility of Co-W alloys that can be used as flat coatings, and micro- or nanostructures. We electrodeposited them from citrate solutions at pH 5-8 and temperatures of 20÷60°C.

Morphology, chemical composition, and structure and its thermal stability of the deposits were characterized in deep. Higher deposition temperature enhances the deposition rate and leads to a higher W-content. Grain size of the deposits is affected by the polarization: normally a decrease in grain size is caused by increase in polarization. In order to have a uniform deposition in recesses, a nanocrystalline or amorphous structure should be obtained which is preferentially achieved at higher overpotentials. Both mechanical and tribological properties can be improved by increasing content of W in the alloys. Magnetic and tribological properties of the samples obtained under different electrodeposition conditions were also investigated to evaluate possible application of studied Co-W alloys.

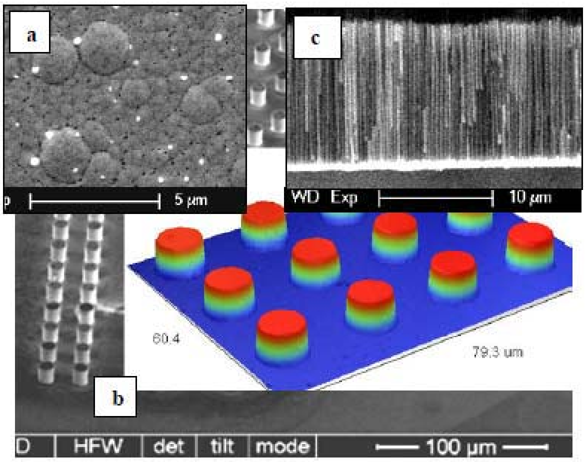

Fig.1. SEM images of the flat coatings (a), microbamps (b), and nanoarrays (c) of electrodeposited Co-W alloys.

The electrodeposition of Co-W alloys in the recesses having various aspect ratios has been investigated in order to demonstrate the possibilities of the multiscale engineering of Co-W alloys. Notably, the electrodeposition conditions used for the deposition on the flat surfaces are not applicable for Co-W deposition in the recesses on the patterned wafers or nanoporous membranes due to instable pH values inside recesses, and the photoresist compatibility limitations. Also, different methods were applied to improve the mass transport in the recesses, and the most optimal electrodeposition conditions for the industrial applications have been recommended.

The void free electrodeposition of Co-W alloys has been achieved under potentiostatic conditions at applied potential -0.87 V with high uniformity of micro-arrays (Fig.1). It has been proved that these optimum conditions can also be used successfully for the electrodeposition of Co-W alloys into AAO template.

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MOLECULAR NANOLITHORGAPHY: A TOOL TO STUDY AND EMPLOY CHEMICAL REACTIONS AT NANOSCALE

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The ever-growing field of nanochemistry relies on innovative experimental tools. During the past two decades, a powerful array of such tools has been developed, but their availability remains rather limited due to the still existing barriers between different scientific disciplines. In this presentation I will discuss the advantages of dip-pen nanolithography (DPN) and other directed self-assembly techniques in synthesis and analysis of nanoscopic molecular and hybrid entities on different supports. Recently, our group has shown that the performance of the DPN patterning can be very much improved by employing lipids as an ink, and also by controlling the dynamic interphase that consists of the scanning probe, surface and ink molecules and the ambient[1]. The fabricated lipid micro/nanodomains can be applied as tiny vessels for localized reactions and also for studies of pharmaceutical formulations. I will also describe fabrication of multivalent nanoarrays for controlled immobilization of proteins via chelation[2] or covalently. Finally, I will illustrate the potential of the directed self-assembly in developing metallic nanoreactors and localized surface plasmon devices.

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INFLUENCE OF BIO-CERAMIC ON THERMOREGULATION EFFECTIVENESS OF PET KNITS

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The purpose of this study is to investigate the thermoregulatory properties of poly(ethylene terephthalate) (PET) knitted materials with bio-ceramic additives which are highly sensible to far infrared radiation (FIR). In order to evaluate the most effective method for applying ceramic additives several types of ceramic compounds with heat-retaining function were selected: germanium (*Ge*), aluminium (*Al*) and silicium (*Si*) additives were applied by impregnation in squeezing padder and titanium (*Ti*) – by screen printing method. Quantitative and qualitative chemical compositions of untreated textiles and textiles with incorporated ceramic additives and also of ceramic additives themselves were performed using XRF and XRD spectroscopy. The main thermoregulatory properties (heat resistance, heat accumulation effectiveness, water vapor permeability and air permeability) of PET knits with bio-ceramic additives were estimated. The heat accumulation kinetic of ceramic containing knits was determined by using IR emitting source (250 W, λ=500-3000 nm) and FLIR SYSTEMS ThermaCAM (spectral range: 7.5 µm – 13 µm, temperature ranges from –10 ºC up to +350 ºC). The most significant values of temperature difference were found on *Ti* ceramic screen printed knits. Furthermore, better heat accumulation effectiveness of *Ti* ceramics containing knits was confirmed by FTIR analysis. SEM micrographs confirmed that the knits with incorporated *Ti* ceramic particles contain bigger quantities of bio-ceramic additives if compared with *Ge* or *Al-Si* ceramic containing textiles impregnated in squeezing padder.

ORAL PRESENTATIONS

PROTEINASE K ASSISTED E-TONGUE FOR PROTEIN PURITY EVALUATION

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Production of recombinant proteins for pharmaceutical use and scientific studies has become a highly developed technological discipline [1]. Purity control of such proteins is routine task, which usually requires a lot of time, expensive and toxic reagents, specialized equipment and highly educated personnel [2].

New concept for protein purity evaluation is proposed in this study. Method is based on potentiometric analysis of protein solutions with chemical sensor array known as electronic tongue (e-tongue), which is sensitive to certain ions. Proteinase K from *Tritirachium album* was used as medium bio-modulator to digest the protein (which is normally cannot be sensed with potentiometric sensors) into smaller molecules. The model object for analysis was recombinant protein A from *Staphylococcus aureus* (SpA). SpA is commonly used for monoclonal antibody purification [3]. Samples with different ratio between bacterial lysate (cell related impurities) and purified SpA (dialyzed against water), were incubated with proteinase and then were analyzed with e-tongue. Principal component analysis (PCA) and partial least square (PLS) regression modelling (Fig. 1A) were applied for processing of obtained sensor responses [4]. Size exclusion high-performance liquid chromatography (SE-HPLC) analysis of the modified samples was performed as well in order to validate the concept. It was shown that proteinase K is able to induce changes in pure and lysate-contaminated SpA samples (Fig. 1B, C) thus providing different mixtures of oligopeptides and aminoacids detectible by e-tongue. The proposed method allows for estimation of the impurity content with 12 % accuracy.

The suggested approach could be useful for early contamination warning at initial protein purification steps. The analysis requires no expensive materials and equipment, no enzyme immobilization, and its duration time is comparable with other commonly used methods like chromatography or electrophoresis though the main part of this time is related to the sample preparation.

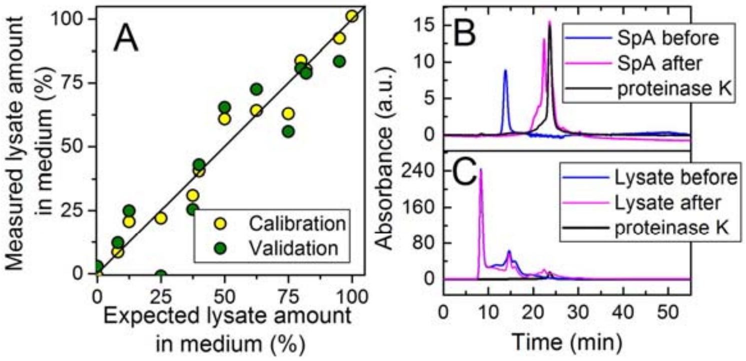

Fig. 1. PLS regression model for prediction of lysate amount in the medium (A). SE-HPLC chromatograms of SpA (B) and lysate (C) before and after incubation with proteinase K.

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ELECTROCHROMIC COPOLYMERS SYNTHESIZED FROM AMINOTHIAZOLES AND PYRROLE

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During the past few decades polymeric electrochromics have been good candidates of electrochromic devices (ECDs). Polymeric electrochromics could be used in smart windows, EC mirrors or flexible displays. EC homopolymers like PEDOT have been widely used with high optical contrast, low response time and color options in different redox states [1]. On the other hand, some EC copolymers can also be obtained to vary color options [2]. In these studies, two electroactive monomer kinds are used. Electropolymerization of aminothiazoles and aminobenzothiazoles were previously carried out, but their polymeric films were not EC [3]. But, their copolymers with pyrrole could form EC copolymer kinds having different colors.

For this aim, in the present study, new kinds of EC copolymers have been synthesized using pyrrole as the first monomer and aminothiazole/aminobenzothiazole monomers as the second (Fig.1). Electropolymerizations were carried out using cyclic voltammetry (CV) and bulk electrolysis techniques using ITO/glass as working electrode, Ag wire as reference electrode and a Pt wire as counter electrode. Structural characterizations were made by FT-IR and UV-vis analyses. EC properties of the obtained copolymer films were characterized by spectroelectrochemical analyses in which optical transmittance changes are measured simultaneously while a potential change applied in electrolysis cell. Response time determination and switching stabilities were clarified using the chronoamperometry technique.

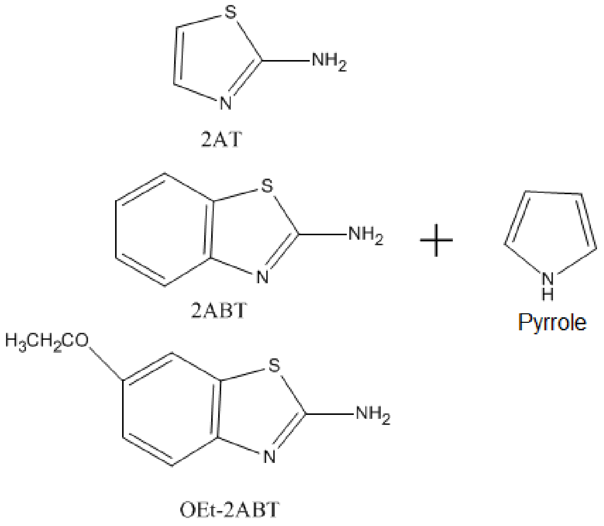

Figure 1. Electroactive monomers used in electrocopolymerization reactions

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METALLIC NANOWIRE, NANOTUBE AND NANOCONE ARRAYS FABRICATED BY ELECTRODEPOSITION IN POROUS ANODIC ALUMINA TEMPLATES

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Nanostructured materials, especially ordered arrays of metallic nanowires, nanotubes and nanocones have received considerable attention due to a successful combination of functional chemical/physical properties with a well controllable nanoarchitecture. Among different methods used for their fabrication, electrochemical deposition in porous anodic aluminum oxide (AAO) templates is one of the best, inexpensive and simple method.

Under specific electrochemical conditions used for the preparation of AAO templates, the oxide cells self-organize into hexagonal arrangement, forming a honeycomb-like structure which is characterized by structural parameters including pore diameter, interpore distance, porosity, and pore density. By controlling parameters of the electrochemical oxidation a variety of unique oxide structures with different morphologies and characteristic parameters can be obtained. Recently, AAO templates with more complex-shaped nanopores, including templates with conical, step-shaped, serrated, modulated and Y-branched nanopores were successfully synthesized by anodization [1,2].

Here, we present a template-assisted fabrication of various metal (e.g., Ag, Cu, Sn, Sb, Au-Ag), semiconductor (InSb) and polymer (e.g., polystyrene, polypyrrole) nanowire, nanotube and nanocone arrays [3,4]. Except linear nanowires with a uniform diameter along the nanowire length, the sophisticated arrays with hierarchically structured and hybrid nanowires were also fabricated. Examples cover such diverse nanowires as multilayered, Y-branched, two level branched, and ultrathin porous nanowires as well as nanowires with modulated pore diameter [1]. In addition, hybrid nanostructured materials such as multilayered CoPt nanowires, polymer nanowires with dispersed Ag and Bi nanoparticles (PPy-AgNPs and PPy-BiNPs) were synthesized as well [5]. There are several potential technological applications of these nanowires in as novel electrocatalysts, thermoelectric materials, chemical sensors for pH, H_2O_2 and adrenaline. Moreover, modern nanodevices with exceptional performance can be also fabricated on a basis of porous anodic alumina [6].

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Electrochemical Behavior between Functionalized Carbon Nanotube Films and Copper

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Carbon nanotubes (CNTs) used as reinforcements in composite materials have been the subject of significant research due to their various applications and electrochemical deposition is one of the commonly used methods for manufacturing CNT-Cu composites [1]. However, deposition of copper occurs preferentially at the CNT surface defects [2] leading to inhomogenous copper deposits. Theoretical calculations have predicted that oxygen containing functional groups promote adsorption and electron exchange between CNTs and Cu [3].

This research details the electrochemical testing of carbon nanotube films using a potentiostat controlling a three-electrode system (WE- CNT film; CE- copper sheet and RE- copper sulfate electrode) in a copper sulfate electrolyte. It was found that the chemical inertness of CNTs towards copper leads to difficulties in trying to achieve homogenous electrodeposition of copper on carbon nanotube films. Inhomogenous deposition is believed to occur on “as produced” CNT films due to differences in available active surface sites, figure 1a. In order to increase the amount of oxygen containing defects at the surface of CNT films, certain oxidative pre-treatments like heat treatment, acid treatment and anodization - were used.

Enhanced copper deposition on CNT films containing various degrees of functional groups was observed as shown in Figure 1b, and the results are similar to those previously observed on functionalized carbon fibre [4]. Results from the measured polarization curves indicate that functionalized CNT material shows an improved electrochemical response to copper after functional groups have been introduced at the CNT material surface by oxidative treatments.

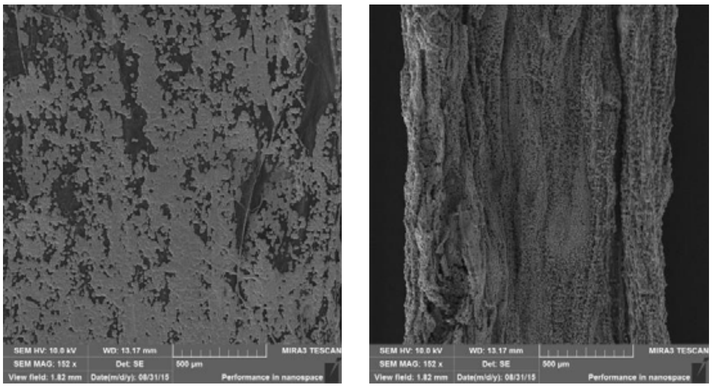

Figure 1 Galvanostatic Cu electrodeposition on (a) as produced CNT film (b) functionalized CNT film

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The effect of electrolyte composition on RuO_2-IrO_2-TiO_2 anode operation in electrowinning of metals

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Electrowinning is one of the main methods of electrometallurgy. In electrowinning, direct current is then used to deposit metal from the solution to the cathode. The anode material in electrowinning of metals from sulfuric acid solution has traditionally been lead because of their high corrosion resistance. On the other hand, oxide-coated anodes allow higher current densities, lower operating potential and do not generate sludge, which can contaminate the product and foul the system.

The anode material was RuO_2-IrO_2-TiO_2 coated titanium wire with 3 mm diameter having typical "cracked mud" structure. The anode was analysed to contain approximately 10 wt-% Ru and 16 wt-% Ir as the active materials and 43 wt-% Ti as the support material, the compounds being RuO_2, IrO_2 and TiO_2. The effect of electrolyte composition was measured with polarization curves in sulfuric acid solution without metal ions using H_2SO_4 concentration 50, 100, 150 and 200 g/l. With a constant acid concentration 100 g/l the effect of metal ions was tested using 20, 40 and 60 g/l of Cu, Zn or Ni. The anodic polarization curves were measured at 30, 40, 50 and 60 °C.

The purpose was to estimate the effect of electrolyte composition on anode overpotential. As the electrowinning cells operate at constant current density, an increase in anode operating potential will increase cell voltage and energy consumption. To model the effect of electrolyte composition and temperature Tafel slopes were determined from compensated polarization curves. The anodic polarization curves showed typically two Tafelian ranges. Example of the measured curve and Tafel slope fitting is shown in Figure 1. In sulfuric acid solution the Tafel slope changes at approximately 1.35 V vs. SCE and 100 A/m^2. The average Tafel slope at low current density range was 70 mV and at high current density range 113 mV. Tafel slope regression equation to calculate the overpotential [V] included logarithm of current density [A/m^2], inverse temperature [K] and logarithm of H^+ concentration [mol/dm^3], for example Table 1. Identical models were determined for electrolytes with dissolved metals. The addition of metals increased operating voltage by 1 to 20 mV per 10 g/l of dissolved metal. Based on the results the variations in the typical electrowinning electrolytes provide only a minor effect on anode operating voltage.

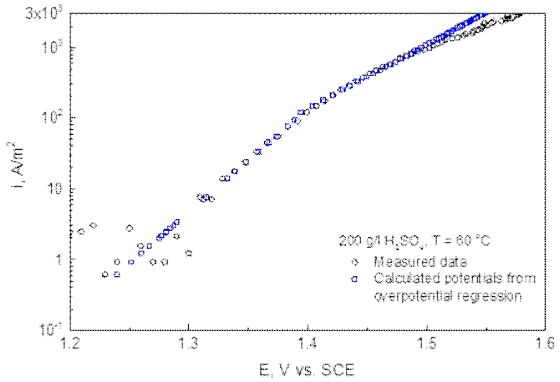

Figure 1. Measured and calculated oxygen evolution potentials in 200 g/l H_2SO_4 at 60 °C.

Table 1. Coefficients for the regression equation to calculate oxygen evolution overpotential for Ru-Ir-Ti oxide anode.

Factor	For i = 100-500 A/m^2
Constant	-0.39±0.05
log (i), A/m^2	$(110\pm6)\cdot10^{-3}$
1/T, K	169±15
log(c H^+), mol/dm^3	$(28.0\pm7.9)\cdot10^{-3}$

WEAKLY COORDINATING ANIONS FOR ELECTROLYTE APPLICATIONS: SALTS, FUNCTIONAL ADDITIVES, IONIC LIQUIDS

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Lithium-ion cells are the fastest developing energy storage technology. Most of the research effort concerns electrode materials due to their direct impact on cell capacity. However, it is electrolyte that causes main limitations of the cell. These are: cathode material choice limitation due to electrolyte stability window, cooling requirements due to thermal stability of electrolyte and maximum current of the cell that is limited by lithium cation conductivity of electrolyte. Similarly, electrolyte decomposition at the electrodes prohibits or limits use of new generations of anodes (silicon, for instance). As solvents and lithium cation are constant part of the electrolyte, the only variable is the anion. It affects all properties mentioned above, as well as plays the critical part in ionic liquids (ILs) synthesis.

Anions used in lithium salts or ionic liquids have to be weakly coordinating ones. However, almost all of the commercially available anions have big disadvantages: ClO_4^- is unstable (explodes) at higher temperatures (>110°C); PF_6^- is unstable both at higher temperatures (>70°C) and moisture presence (even at ppm level) producing toxic gases; $N(SO_2CF_3)_2^-$ corrodes aluminum. Thus, there is a need for new solutions in the field.

New organic weakly-coordinating anions are synthesized by us using stable carbon skeleton that could delocalize the negative charge with electron-withdrawing groups attached to it. All hydrogen atoms are substituted and no oxygen atoms are present to limit free electron pairs influence on cations. Few anions have been already synthesized and tested as salts using these principles. The most successful so far is LiTDI, but its analogues, LiPDI and LiHDI, have similar parameters [1,2]. Another two anions have been recently presented to public: LiTDPI [3] and LiTDBI [4]. All of them have very good thermal (at least up to 250°C) and electrochemical (at least up to 4.5 V vs Li) stability. Also lithium cation conductivity is comparable to that of commercial salts. Tests show good cycling properties, in new generation of electrodic materials as well [5,6]. They can be also applied to Na-ion cells [7].

In the presentation the most recent data on these salts will be shown. Two anions never shown before, LiPCP and LiHCAP will be also presented. They are very stable, have good conductivity and cycling parameters, like their predecessors. Their main advantage is that they are the first ever non-fluorine lithium salts for Li-ion cells electrolytes that are stable.

Additionally, presentation will cover recently discovered application of LiHDI as SEI-stabilizing additive and our weakly-coordinating anions' use in ionic liquids.

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ENHANCED LITHIUM STORAGE IN GRAPHENE/LiMnPO$_4$-C NANOCOMPOSITE CATHODE ELECTRODES FOR HIGH PERFORMANCE Li-ION BATTERIES

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To globally solve the problem of an environmentally clean and secure distribution of energy is a major task for scientist worldwide. The use of clean energy will have a direct positive influence on, for example, the emission of greenhouse gases and our future climate. Today the rechargeable battery with the highest energy density is the Li-ion or Li-polymer battery. Commercially this battery is used for mobile phones, laptops and camcorders. Both these routes will, however, require basic materials research within chemistry and physics; new materials must be synthesized (some materials used today are too expensive for up-scaling) and the complex chemistry occurring both in bulk electrode materials and at the interface between electrolyte and electrode most be better understood [1-3]. Among different electrode materials, layered transition metal oxides (LMO) are the most successful cathode material in application at present time, but its further development is severely hindered due to the intrinsic safety limitation and the cost. Seeking for some other cost-effective cathode materials with better performance is a significant task. And therefore, olivine-structured phosphate LiMnPO$_4$ materials have attracted great attention due to many advantages, such as lower toxicity, lower cost, better thermal, chemical stability and it's large availability in earth's crust. Unfortunately, phosphate based cathode material possesses low intrinsic electronic and ionic conductivity [4-7].

In this study, LiMnPO$_4$ nanostructured cathode electrodes were prepared via microwave hydrothermal synthesis methods using MnSO$_4$H$_2$O, citric acid (NH$_4$)2HPO$_4$ and LiOH.H$_2$O as the starting precursors. The obtained product was separated by centrifugation, washed by distilled water and ethanol several times, and finally dried under vacuum at 60 °C overnight. To improve the crystallinity of LiMnPO$_4$, the as-prepared samples were calcined at 700 °C for 12 h under a high-purity argon atmosphere. The obtained LiMnFePO$_4$ electrodes were also subjected to microwave hydrothermal carbonization process and the surfaces of the electrodes were coated with carbon. LiMnFePO$_4$-C hybrids with graphene were prepared as binder-free and free-standing hybrid electrodes. To the best of our knowledge, this is the first demonstration of a self-supporting binder-free anode prototype with a lamellar hierarchical structure and strong interfacial interaction, which is totally different from previously reported graphene-based hybrid films.

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POTENTIOMETRIC SENSORS WITH BI-LAYER ION-SELECTIVE MEMBRANES

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Poly(vinyl chloride) (PVC) based ion-selective membranes (ISMs) are commonly used in potentiometric ion-selective electrodes (ISEs) and selective optodes [1-3]. A drawback of PVC-based ISMs, however, is the leaching of the plasticizer [4, 5], ionophore [6] and other additives from the ISM to the solution phase [7]. This in turn influences the response and the lifetime of the sensor. Owning to the slower diffusion of ions a silicon rubber (SR), compared to plasticized PVC, an ISM based on SR may diminish the leaching of membrane components from the ion-selective membrane to the sample solution [8]. However, the utilization of SR alone as the matrix material for ISM fabrication is hampered by poor solubility of ionophores in the SR matrix [8].

In this work, bi-layer membranes of PVC and SR were developed and investigated in order to diminish ion diffusion in the ISM and at the same time to maintain all ISM components in the membrane phase. Bi-layer ion-selective membranes of the following compositions were studied: (i) PVC-based ISMs with a pure SR coating and (ii) PVC-based ISMs with a PVC-SR composite coating. ISEs based on these membrane materials were compared to traditional PVC-based ISEs. All electrode membranes and ISEs were potassium selective and were characterized by potentiometry, Fourier transform infrared spectroscopy (FTIR) and electrochemical impedance spectroscopy (EIS).

From the obtained results it can be concluded that all investigated ISEs exhibited Nernstian sensitivity to potassium. Moreover, all electrodes showed similar selectivity to potassium over interfering ions, which proves that modification of the outer layers of ISMs was successfully performed and did not interfere with the potentiometric performance of the sensors. Results obtained by FTIR confirmed the presence of plasticizer and ionophore even in the SR coating of the PVC-based ISMs with a pure SR coating. This suggests that a protective coating of SR may be applied for PVC-based ISMs in order to separate PVC-based ISMs from direct contact with the sample solution. Results obtained by EIS indicated deceleration of ion diffusion in SR modified ISMs, which in turn is directly proportional to the leachability of membrane components to the sample phase. This method opens the possibility to fabricate ISEs in order to diminish the leaching of ISM components and to extend the lifetime of the sensors.

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STRUCTURAL ACTIVITY DESCRIPTORS FOR THE OXYGEN REDUCTION REACTION: A STEP TOWARDS THE RATIONAL DESIGN OF CATALYSTS

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Finding more efficient and stable catalysts for the ORR is of paramount significance for the wider implementation of fuel cell technology, as well as some batteries and certain industrial processes. It is understood that an ideal catalyst for the ORR should bind the reaction intermediates ca 0.1eV weaker compared to a Pt(111) surface. However, in many cases it is challenging to assess energetic activity descriptors theoretically, and often even their experimental determination is not trivial. Therefore, it is an imperative to find suitable activity descriptors which can be more easily assessed, and particularly, to relate them to structural variables. A promising approach relies on the identification of active sites with an ideal coordination. We recently proposed the use of the so-called "generalized coordination number" (GCN) [1], as a more accurate descriptor of adsorption energy trends in comparison to the simple coordination number. DFT calculations have shown that the optimal GCN for the ORR on Pt should be ≈8.3. This coordination can be achieved by the removal of 5-6 adjacent Pt-atoms from a Pt(111) surface. To confirm this prediction, several techniques were implemented to introduce defects to the surface of these electrodes. Particularly, the de-alloying of Cu-Pt near-surface alloys, which in fact results in the formation of cavities, has led to exceptionally high activities towards the ORR (~3.5 times higher than Pt(111)). Alloys of Pt with late transition metals and lanthanides have been studied extensively and are known to be good ORR catalysts [2]. These alloys are not as stable as it was initially expected under PEMFC conditions as the less noble metal dissolves from the surface layers, which results in a structure in which several Pt-enriched layers cover the bulk alloy and protect it from further dissolution. Given that the Pt-overlayer is several atomic layers thick, we suggest that the strain effects dominate and are primarily determining the behavior of these alloys. The strain in the system is the result of the differences between the lattice parameters of the alloy and the Pt-overlayer. We propose that the atomic radius of the solute metal can be used as a simple "experimental" descriptor to explain and predict the lattice strain, and consequently, the catalytic activity of such alloys [3]. This can explain, e.g., the activity trends of nanoparticulate Pt-alloys, so far considered "anomalous".

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FORMATION OF INTERMEDIATE PHASES DURING THE SYNTHESIS OF α-C_2SH

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Ordinary Portland cement is the most popular hydraulic binder material worldwide [1], however, its industry is one of the most energy-consuming [2]. Another alarming issue in this field is an immense emission of the CO_2 gas [3]. One of the solutions of these problems is to produce alternative binder materials such as belite cement made from α-C_2SH [4].

In this work the materials used were: quartz sand (SiO_2 = 99.9 %), burnt limestone (CaO_{free} = 86.9 %) and reagent NaOH.

α-C_2SH was identified as the main compound in the XRD patterns of the 4 and 8 h synthesis products and confirmed by DSC and SEM analysis. In addition a small endothermic effect at 678 ºC was observed in the DSC curve of 8 h synthesis. The nature of this effect was determined when analysing the results of the 12 h synthesis product: killalaite ($Ca_3([HSi_2O_7](OH))$ was identified in the XRD pattern. This calcium silicate hydrate ($CaO/SiO_2 \sim 1.5$) was observed alongside portlandite, although the latter compound was not identified after 4 and 8 h of isothermal curing. According to the literature data, in the CaO-SiO_2-H_2O system α-C_2SH should transform into hillebrandite $Ca_2SiO_3(OH)_2$ at latter stages of the synthesis [5]. However, it is obvious that the reactions take another path in a presence of NaOH additive, because when the synthesis duration was extended the heat value of the α-C_2SH dehydration decreased while the one of killalaite dehydration increased. Presumably that latter compound forms during the decomposition of α-C_2SH when the duration of synthesis is prolonged. Furthermore, a nearly amorphous calcium silicate hydrate of C-S-H type was identified in the product of the 12 h synthesis.

By prolonging the duration of the synthesis to 16 h, the same products as after 12 h of synthesis were obtained: killalaite, a small amount of α-C_2SH, C-S-H and portlandite.

Obvious changes observed in the product of 20 h synthesis. In XRD pattern the peaks of α-C_2SH apparently increases and peaks of killalaite and portlandite – decreases. These results were also confirmed by DSC and SEM analysis. Thus, after 20 h of synthesis the reversible process begins: killalaite recrystallizes back to α-C_2SH. It is confirmed by further synthesis – when the duration was extended to 24 h, only α-C_2SH forms in the product. This mineral remains stable even after 72 h of synthesis and does not crystalize to hillebrandite.

These results were in a good agreement with the other author's observations: the formation of α-C_2SH is complicated and not always repetitive process. The crystallization of killalaite may be associated with the changes of Ca^{2+} ions concentration in the reaction media, because it is well-known, that α-C_2SH is stable only if an excess of Ca^{2+} ions is present.

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HOW STATISTICAL METHODS GUIDE THE SELECTION OF THE FTIR METHOD

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Fourier transform infrared (FTIR) spectroscopy is an important tool in the analysis of calcium phosphate. The most commonly used methods are Attenuated total reflectance spectroscopy (ATR) and Transmission FTIR spectroscopy with KBr pellet (FTIR KBr) less frequent - Diffuse reflectance FTIR spectroscopy (DRIFT) and Photoacoustic spectroscopy (PAS). FTIR methods are used for both qualitative analysis and quantitative analysis, for example, the crystallinity index (CI) and estimation of the relative CO_3^{2-}, OH^- and HPO_4^- content.

The main task of this study was to identify advantages and disadvantages of each method in the research of carbonate containing calcium phosphate (CP) powders with different degree of crystallinity.

All four FTIR methods are nondestructive and useful to analyze powders and raw solids, but the best analysis method is not determined by the equipment on the bench of the laboratory, but by the most information provided by the appropriate method.

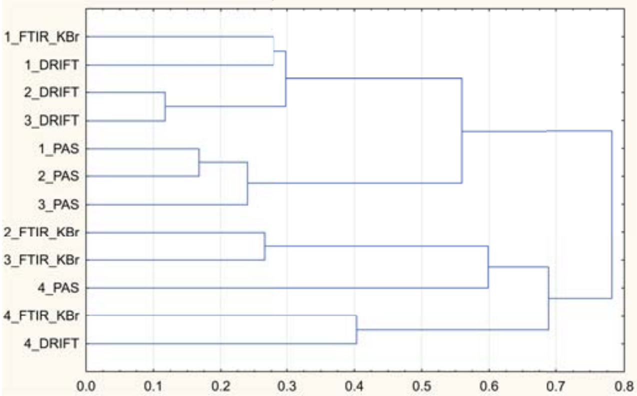

Figure 1. Chebyshev tree diagram

The statistical analyses of the spectra recorded from the CP powders involved 3 steps:

1. Preparation of carbonate containing CP powders with different level of crystallinity (crystallinity evaluated based on the XRD analysis and Rietveld method).
2. Parameterization of spectra: normalization and baseline correction; deconvolution of spectra in υ2, υ3 CO_3^{2-}, υ4 PO_4^{3-}, υL OH^- band region to enhance the resolution and selecting a spectral parts rather than using whole spectrum for analysis.
3. Statistical analysis, such as Principal component analysis (PCA), Factor analysis (FA), Pearson product-moment correlation coefficient (PPMCC) and Cluster analysis (CA). Cluster analysis uses Euclidean and Hierarchical methods.

Using statistical methods, we found that the parameters of all four methods are most consistent when we analyzed amorphous or microcrystalline samples. The biggest differences showed crystalline powder. This led to the conclusion that the analysis of such samples is essential both in the choice of methods and in information on the degree of crystallinity. By analyzing both the entire IR spectrum and specific parts of spectra, the greatest differences showed ATR method. This is explained by the low sensitivity of this method in CO_3^{2-} OH^- and H_2O.

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THE EFFECT OF CATION AND ANION DOPING ON THE STRUCTURE, CHEMICAL STABILITY AND ELECTROCHEMICAL PERFORMANCE OF $LiMn_2O_4$ CATHODE MATERIAL FOR Li-ION BATTERIES

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The most commonly used cathode materials in commercial, rechargeable lithium-ion batteries (LIBs) are layered lithium cobalt oxide ($LiCoO_2$, LCO) and its derivatives [1]. Nevertheless, the limited availability, high cost and safety hazards associated with cobalt have aroused a great interest in the development of new materials. Lithium manganese oxide spinel ($LiMn_2O_4$, LMO) is considered to be one of the most promising alternative cathode materials for LIBs owing to its high working voltage, relatively high energy density, good safety characteristic, low cost, environmental benignity and abundant resources [2]. Unfortunately, the practical application of the stoichiometric LMO is restricted by severe capacity fading during subsequent charge and discharge cycles [3]. This is mainly due to the unstable structure of the spinel near room temperature resulting from the Jahn-Teller distortion of high-spin Mn^{3+} ions. Another drawback is limited chemical stability towards liquid electrolytes that causes partial dissolution of the manganese according to the disproportionate reaction $2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$. To overcome the aforementioned obstacles, many efforts have been made so far and through the most widely adopted method is cation and anion doping [4-7].

This work is intended to examine the modification of LMO cathode material by ion-doping in order to improve its electrochemical performance. Therefore, cation (nickel) and anion (sulphur) doping were implemented. The effects of substitution for manganese and oxygen with Ni and S respectively on the crystal structure, chemical stability and electrochemical behaviour in the resulting nanostructured $LiMn_{2-x}Ni_xO_4$ (LMNO) and $LiMn_2O_{4-y}S_y$ (LMOS) spinel materials were studied.

Experimental results indicated that the applied method of the spinel modification significantly affect the structure, chemical stability as well as cycling performance of lithium manganese oxide spinel. It was demonstrated that Ni shifts the voltage profile of the LMO to a higher potentials by introducing new voltage plateaus corresponding to Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} redox couples. In terms of electrochemical performance, this substitution for Mn provides excellent rate capability, very good capacity retention and reversibility. On the other hand, partial substitution of O atoms with S appears to be more favourable as it not only suppresses the adverse phase transition near room temperature and consequently improves coulombic efficiency but also significantly increase the capacity of the material.

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POSTER PRESENTATIONS

CHARATERIZATION OF ULTRA THIN Mo-O-Se FILMS ELECTRODEPOSITED ON SnO_2 SURFACE

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Electrochemical deposition of thin and dense multicomponent Mo–O–Se films [1] has attracted interest due to their unique properties, which results from the rich chemistry caused by the multiple valence states of the metal. The application of these films depends on their properties, which can be talored by changing deposition conditions (bath composition, electrolysis temperature, applied voltage, current density and etc) [2].

The aim of present work is to characterize thin Mo-O-Se films electrodeposited under potentiostatic conditions on a polycrystalline tin oxide electrode. The working solution was an aqueous citrate solution containing Na_2MoO_4, H_2SeO_3 and $C_6H_5Na_3O_7 \cdot 2H_2O$.

A Perkin Elmer Analyst 400 Atomic Absorption spectrophotometer was used to determine molybdenum and selenium content in deposited films. The X-ray photoelectron spectroscopy employing Kratos Analytical XSAM800 XPS analyzer was used to determine the surface composition. The core level Mo 3d, Se 3d, O 1s and C 1s spectrum and valence band (VB) spectrum were measured. ATR−FTIR spectra were recorded using the compensation method with a Perkin Elmer FTIR Spectrum GX spectrophotometer. The UV–Vis absorbance spectra of the Mo-O-Se film layers were obtained using a UV–VISIBLE Spectronic Genesis spectrophotometer in the range 300–1100 nm.

Ultra - thin films layers with thickness from 33.6 to 71.0 nm were electrodeposited on SnO_2 surface. These films were analyzed without further treatment other than rising with distilled water and drying over the silica in desiccator. Visually, the as - deposited films are mirror-like and colored in a brown tint. The concentration of Mo and Se in film obtained varies from 38.58 to 69.85 at. % and 30.15 to 61.42 at. %, respectively.

The analysis of Mo 3d spectra allows to concluding that the molybdenum bounds to selenium and oxygen. The appearance of Mo 4d peak in the VB spectrum confirms that Mo(IV) is the predominant molybdenum oxidation state in all thin film layers.

In the ATR-FTIR spectra the most pronounced absorption peak at 740.98 cm^{-1} is related to Mo(IV) oxide. The symmetric stretching modes of the terminal Mo=O bond of MoO_2 and MoO_3 appears at 985 cm^{-1} and 990 cm^{-1} respectively. A broad bound, assignable to the stretching mode νOH of adsorbed water molecule and OH groups linked in the form of Mo–OH is seen at 3373.20 cm^{-1}.

Taken together the XPS and ATR-FTIR analysis results confirm $MoSe_2$, MoO_2, $Mo_x(OH)_y$ and MoO_3 on the surface and in the bulk of electrodeposits.

Optical studies revealed the ultra - thin Mo-O-Se films to be highly absorptive and direct band to band type optical transition. Depending on film thickness and composition the optical band gap (E_g) varies from 0.63 to 1.19 eV.

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PHOTOELECTROCHEMICAL PERFORMANCE OF NANOPOROUS TITANIUM OXIDE LAYERS FORMED BY MULTI-STEP ANODIZATION

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It is widely recognized that the morphology of semiconductor affects its photo activity. Studies have shown that when the top morphology changes, very often photochemical properties of TiO_2 changed as well. This aspect has great impact on its photoelectrochemical applications in dye sensitized solar cells (DSSCs), where the efficiency of the process depends on the top surface reflection [1]. The morphology of anodic titanium dioxide is also affected by: an electrolyte type and its composition (e.g., water content and the presence of fluoride anions), pH, previous usage of electrolyte, voltage, time of anodization, temperature, and hydrodynamic conditions [2].

In this study, the effect of short multi-step anodization on photoelectrochemical properties of formed nanoporous anodic titania was investigated. Nanoporous anodic titanium dioxide layers were synthesized at 20 ºC by a one- to six-step anodization carried out at the constant voltages of 40 V in electrolytes based on ethylene glycol containing NH_4F (0.38 wt.%) and water (1.79 wt.%).

Photoelectrochemical tests were performed using a three-electrode cell with a quartz window, where nanoporous TiO_2 was used as a working electrode (WE), a platinum foil as a counter electrode (CE), and a Luggin capillary with a saturated calomel electrode (SCE) as the reference electrode. The generated photocurrents were measured using a photoelectric spectrometer equipped with the 150 W xenon arc lamp and combined with the potentiostat. The photoelectrochemical characterization was performed in 0.1 M KNO_3 at the potential range of 0 - 1 V and wavelengths ranging from 300 to 400 nm.

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PHOTOELECTROCHEMICAL AND PHOTOCATALYTIC PROPERTIES OF NANOSTRUCTURED TUNGSTEN OXIDE

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The photoelectrochemical properties of semiconductors have been extensively studied for many years. Much of this interest has been driven by their photocatalytic properties and solar energy conversion applications [1]. Nanostructured tungsten oxide possess very useful properties, e.g., a strong photocorrosion stability in aqueous solutions and stable physicochemical properties [2]. WO_3 is an n-type semiconductor, in which the Fermi level (E_F) is approaching the conduction band. The crystal structure of WO_3 depends on the calcination temperature and vary from hexagonal, cubic, tetragonal, orthorhombic, monoclinic to triclinic. The band gap of the WO_3 depends on oxide structure and may be in the range of 2.6 - 3.5 eV [3]. What is more, the band gap of the tungsten oxide is lower (2.6 eV) than that of the commonly used titanium dioxide (3.2 eV), which leads to the fact that WO_3 can absorb 12 % of the visible light spectrum [4].

Nanostructured tungsten oxide was synthesized by a single-step anodization at constant voltages and 20 °C in an aqueous electrolyte containing fluoride anions. Afterwards, the anodized samples were annealed at 500 °C for 0.5, 1, 2 or 3 h in order to obtain photoactive WO_3 form. The structure and stoichiometry of the resulting oxide layers were examined using SEM and EDS, and after annealing by X-ray diffraction measurements.

Photoelectrochemical tests were performed using a three-electrode cell with a quartz window, where nanostructured WO_3 was used as a working electrode (WE), a platinum foil as a counter electrode (CE), and a Luggin capillary with a saturated calomel electrode (SCE) as the reference electrode. The generated photocurrents were measured using a photoelectric spectrometer equipped with the 150 W xenon arc lamp and combined with the potentiostat. The photoelectrochemical characterization was performed in 0.1 M KNO_3 at the potential range of 0 - 1 V and wavelengths ranging from 300 to 400 nm. The applicable potential range for photocurrent measurements was determined by cyclic voltammetery.

The photocatalytic degradations of methyl red were performed using a ultraviolet lamp with the excitation wavelength of 350 nm. During photodegradation tests, at given reaction intervals, the concentration of methyl red was determined by UV-Vis spectrophotometry.

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NEW ELECTROLYTE FOR Fe-W ALLOYS ELECTRODEPOSITION

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Various types of plating baths could be used for Fe-W alloys electrodeposition: containing Fe^{+2} or Fe^{+3} salts, acidic or alkaline, with inorganic or organic ligands [1]. Electrolytes with different organic complexing agents have been found as mostly useful for tungsten alloys electrodeposition, namely: malic, tarrtaric, gluconic, acetic, glycine, citric acid and etc. [2]. The citric acid as complexing agent is extensively explored by many researchers for tungsten alloys electrodeposition. However, it has been shown [3] that glycolic acid can be also a suitable candidate for Ni–W alloys electrodeposition and coatings produced from this bath demonstrated better overall performance in comparison with citric acid solutions. In this study Fe-W alloys have been obtained by the electrodeposition under direct current from citrate and glycolic-citrate bath (Table 1). Both electrolytes containing Fe(II) and Fe(III) salts (Table 1) were used to compare their behavior. Thermodynamic study of Fe^{+2} and Fe^{+3} containing electrolytes was performed and thermodynamical instability of solutions based on Fe(II) salts was revealed. In addition, the calculated distribution of species as a function of pH is provided for both citrate- and glycolate- based systems.

Table 1. Composition of the baths used for the Fe-W electrodeposition (composition is given in mol/l).

Chemicals	Cit-Fe(II)	Cit-Fe(III)	Glyco-Cit-Fe(II)	Glyco-Cit-Fe(III)
$Na_2WO_4 \cdot 2H_2O$	0.4	0.4	0.4	0.4
$FeSO_4 \cdot 7H_2O$	0.2	-	0.2	-
$Fe_2(SO_4)_3 \cdot H_2O$	-	0.1	-	0.1
$C_6H_8O_7 \cdot H_2O$ (citric acid)	0.2	0.2	*0.3*	*0.3*
$Na_3C_6H_5O_7 \cdot 2H_2O$ (tri-sodium citrate)	0.45	0.45	-	-
$C_2H_4O_3$ (glycolic acid)	-	-	1	1

The influence of electrodeposition temperature and current density on alloy composition and morphology was evaluated. The tungsten content in the deposits practically does not depend on temperature and is cca 20-23 at.% for alloys deposited from citric and glycolic-citric baths at 20 mA/cm^2. At high temperature the current density almost does not have influence on the tungsten content in the alloys obtained from citrate-based bath in contrary to glycolic-citric bath. The current efficiency of Fe-W coatings deposition from glycolic-citric bath can reach up to 80% that is much higher in comparison with pure citrate-based bath. Also, electrodeposition using pulse current mode and additives were carried out to overcome hydrogen embrittlement of the coatings.

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HEAT TREATMENT EFFECT ON MORPHOLOGY AND CRYSTALLINE STRUCTURE OF OXIDE LAYERS GROWN ON Fe BY ANODIZATION

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Nanomaterials have drawn scientists' attention because of their functional electronic, photocatalytic and magnetic properties. One of the methods used for the synthesis of nanostructured materials is anodization. It is a simple and low-cost electrochemical technique. It allows to obtain ordered oxide nanostructures on many metals, such as aluminum, titanium and zirconium. Recently, the formation of anodic films on iron has been reported as well [1]. Iron in oxides exists in a wide range of oxidation states. Among iron oxides, FeO, Fe_3O_4 and Fe_2O_3 are most often investigated. Fe_2O_3 possesses various polymorphs, such as hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) [2]. Iron oxide films can be used as photocatalysts (Fe_2O_3) or magnetic materials (Fe_3O_4). The formation of highly ordered oxide structure can further improve the properties of iron oxide nanostructures [1].

A Fe metal foil (99.5% purity, Advent) was pre-cut in coupons (1 cm × 2 cm). The samples were sonicated in acetone and ethanol for 20 min in each solution. The anodic films were prepared in an ethylene glycol- based electrolyte containing different amounts of fluoride ions (0.1 – 0.3 M) and water (0.1 – 1.5 M). The anodizing process was carried out using a two-electrode cell with iron foils as both the working and counter electrodes. The iron oxide layer was formed under a constant cell voltage ranging between 30 and 70 V at 20 ˚C. The duration of the anodization was: 15, 30 and 60 min. After anodizations, the samples were rinsed with ethanol and dried. In each anodizing process, a freshly prepared solution was used. A post-anodizing procedure included annealing of as-anodized samples in the air at different temperature for 1 h. The iron oxide layers were calcined at 200, 300, 400 and 500 ˚C. The heating rate was 2 ˚C min^{-1}. A field emission scanning electron microscope and EDX spectrometer were used for characterization of the morphology and composition of the obtained oxide films. The crystalline structure of oxide layers were examined using XRD spectrometer.

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NANOPOROUS TITANIUM DIOXIDE LAYERS MODIFIED WITH SODIUM HYDROXIDE AND (3-AMINOPROPYL)TRIETHOXYSILANE (APTES)

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Controlled anodization of titanium, which results in the formation of bioactive and nanoporous/nanotubular titanium dioxide films, is commonly used to modify the surface morphology of titanium-based implants. In order to further improve the bone cell attachment and growth TiO_2 nanopores/nanotubes can be modified in different ways. As a result of soaking TiO_2 layers in sodium hydroxide (NaOH), sodium titanate on the nanotubes walls grows [1]. In order to alter wettability of TiO_2 nanotubes self-assembled monolayers (SAMs) can be formed on their surface. Silane derivatives are commonly used to introduce functional groups, such as an amine group[2].

Nanoporous TiO_2 (ATO) layers were synthesized via a three-step anodization process in an ethylene glycol electrolyte containing 0.38 wt.% NH_4F and 1.79 wt.% H_2O under a constant voltage of 40 V. The first and second step of anodization lasted 3 h, while the duration of the third step was 10 min. The TiO_2 nanotubes were modified in two steps: by soaking in 0.5 M or 1 M NaOH for 15 min and in 10% 3-aminopropyltriethoxysilane (APTES) for 24 h. The crystalline structure of ATO layers was also changed. In order to obtain the anatase and a mixture of anatase and rutile phases the ATO samples were annealed in air for 2 h at 400 and 600 °C, respectively. The effect of crystalline structure of TiO_2 nanotubes on the modification of TiO_2 nanotubes with NaOH and APTES were examined. The modified nanoporous titanium dioxide layers were characterized by Scanning Electron Microscopy and EDX spectrometry. The contact angle tests were performed as well.

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Characterization of as-deposited and annealed Cr-Zn-P coating electrodeposited from a trivalent chromium bath

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Black chromium is widely used in solar collectors due its high absorptance, good stability and high thermal resistance. Traditionally, the solar selective coatings are deposited on metallic substrates. Effective selective coatings is characterized by high absorptivity in solar radiation range of $0.3\ \mu m < \lambda < 2.5\ \mu m$ and stability at high temperature. In order to improve of the deposits, more attempts have been made to obtained black alloy coatings as new materials for functional application. For the selective coatings, it is essential to clarify the relationship between the chemical composition of black chromium and its thermal degradation. It is known that codeposition of nickel and cobalt with chromium improves thermal resistance of black chromium [1]. Good optical properties were found to have Cr-Zn coating deposited from Cr(III)+ZnO bath [2]. However, absorptivity of such coatings decreases substantially after annealing of sample at 600^{0}C [3]. The black Cr-P coatings is characterized by the good optical properties with the high absorption ($\alpha \cong 0.90$) [4]. According to the XRD patterns as-prepared Cr-P deposit is of crystalline nature with uniform distribution of P and Cr in the alloy [5]. The occurrence of new phases at elevated temperature is related to a recrystallization of the coating as result of which the increase in grain sizes takes place. It is obvious, that optimized chemical composition of the bath and optimum plating conditions are responsible for the highest thermal resistance of black chromium.

Our interest in electrodeposition of the black Cr-Zn-P coating resides in search for a new material suitable for the use in solar thermal systems. With this purpose sodium dihydrophosphate was used as additive to Cr(III)+ZnO bath. According to scanning electron microscopy (SEM) data deposits were found to have nodular crystals of various sizes with microcracks undergoing changes by heat treated. X-ray diffractometry (XRD) patterns suggest that Cr-Zn-P alloy is a solid solution, which undergoes a series of transformations during annealing at 600^{0}C. The photoelectron spectroscopy (XPS) results suggest that near-surface layer is rich in hydroxides of both Cr and Zn, whereas, oxides become dominant towards the substrate/coatings interface. Besides, there are little amounts of phosphor and organic materials. The black Cr-Zn-P coatings has a good optical properties and these properties remain practically constant even when heat treated to a high temperature, 400^{0}C. However, after annealing of sample at 600^{0}C an increase in reflectance was found to be arising from the changes in the structure and chemical composition of the deposit and the diffusion of the substrate (Fe) into black chromium.

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ELECTROLESS DEPOSITION OF CoBW COATINGS USING MORPHOLINE BORANE AS REDUCING AGENT

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Cobalt coatings have recently attracted a lot of attention because of their unique magnetic and mechanical properties, as well as their potential applications in high wear-resistant coatings and electronic devices. Renewed interest to the cobalt electroless deposition process is due to the application of CoP or CoB films as barrier and cladding layers for protection of copper layer in microelectronic systems [1-2]. It is known that the inclusion of tungsten in the cobalt coatings can improve the barrier efficiency of the CoP or CoB coatings. An application of ternary Co-based films as diffusion barriers and capping layers for Cu improves interconnection performance and solves some problems preventing contamination by copper [3-4].

The main aim of our work was to investigate the peculiarities of electroless deposition of CoBW coatings in the glycine solutions using morpholine borane as a reducing agent.

Electroless deposition of the CoBW coatings was performed on a copper surface. The main composition of electroless plating solutions was (mol l^{-1}): $CoSO_4$ - 0.1, glycine - 0.2, morpholine borane 0.05 - 0.4, Na_2WO_4 - 0.003, citric acid - 0.175. The deposition of films was performed from a freshly prepared solution at 30 to 70 ºC. Solution pH in the range of 6-8 was adjusted with a solution of NaOH. The morphology and composition of the CoBW coatings was characterized using Field-Emission Scanning Electron Microscopy (FESEM) and X-ray Photoelectron Spectroscopy (XPS).

The deposition rate of CoBW coatings increases with increase in pH of the plating solution from 6 to 8 and reaches ca. 4.3 μg cm^{-2} h^{-1} at pH 8. A rise in concentration of morpholine borane in the range of 0.05-0.3 mol l^{-1} in a glycine solutions leads to an increase in cobalt deposition rate, whereas a subsequent increase in concentration of morpholine borane above 0.4 mol l^{-1} slightly diminishes the deposition rate of films.

The particles of the CoBW coating deposited from the solution containing 0.1 mol l^{-1} $CoSO_4$, 0.2 mol l^{-1} glycine, 0.2 mol l^{-1} morpholine borane, 0.003 mol l^{-1} Na_2WO_4, and 0.175 mol l^{-1} citric acid (pH 7) at a temperature of 60 ^{o}C for 30 min are in size of 110-750 nm and almost equilateral. According to the XPS spectral analysis of the CoBW coating obtained has the following composition at a depth of 20 nm: ca. 59.76 at. % of Co, 6 at. % of W and 4 at. % of B at a depth of 40 nm: 66.81 at. % of Co, 8.5 at. % of W and 4 at. % of B.

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MICROWAVE-ASSISTED SYNTHESIS OF PLATINUM-COBALT-MOLYBDENUM/GRAPHENE

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This work is focused on the synthesis of graphene supported platinum-cobalt-molybdenum catalysts (denoted as PtCoMo/GR) by means of microwave rapid heating as electrocatalysts for borohydride oxidation. The PtCoMo/GR catalysts were prepared by heating of the reaction mixture of different concentrations of H_2PtCl_6, $CoCl_2$, Na_2MoO_4 in ethylene glycol at a temperature of 150 ºC for 5 min. The catalysts were characterized by Transmission Electron Microscopy (TEM) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The electrocatalytic activity of the synthesized PtCoMo/GR catalysts towards the oxidation of borohydride was examined by means of cyclic voltammetry and compared with that of bare Mo/GR and CoMo/GR catalysts.

According to the data of TEM analysis, the spherical Pt nanoparticles with sizes of ca. 2-5 nm were dispersed uniformly on the surface of graphene. It was found that the catalysts having Pt:Co:Mo molar ratios equal to 143:1:3 and 6:2:1 were prepared. It has been determined that the PtCoMo/GR catalysts exhibit higher electrocatalytic activity and stability towards the oxidation of borohydride comparing with that of Mo/GR and CoMo/GR.

FORMATION OF ORDERED ANODIC TiO_2 NANOPORE ARRAYS IN GLYCERINE BASED ELECTROLYTE UNDER VARIOUS ANODIZING POTENTIALS AND TEMPERATURES

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Nanotechnology is an emerging interdisciplinary scientific field that has been booming in many areas during the last years, including materials science, electronics, optics, medicine and energy. Nanoscale control of the growth of inorganic metal oxides determines their structures and properties and leads to development of novel nanostructured materials with fundamental and practical importance in a point of view their further utilities. One dimensional (1-D) inorganic materials (such as nanorods, nanowires, nanowhiskers, nanobelts and nanotubes) have been a target for the vigil eyes of attraction for nanotechnologist, owing to the wide range of electrical and optical properties that depend on both size and shape. Among them, highly-ordered, self-organized TiO_2 nanotube/nanopore arrays formed via electrochemical anodization have attracted considerable interest due to their easy preparation method and anticipated high potential for technological applications. In this context, nanoporous/nanotubular anodic TiO_2 has been broadly investigated in photocatalysis, photovoltaics, sensors and used as templates for deposition of secondary nanomaterials. Other potential technological applications of anodic TiO_2 include dye-sensitized solar cells, energy storage systems, humidity sensors, gas sensors, biosensors and biocompatible material for synthetic bone graft substitutes [1-3].

Electrochemical anodization is one of the most promising and cost-effective method to synthesize TiO_2 nanostructures. Altough widespread research has been conducted, there is still much to be learned about the fabrication, morphological characterization and applications of anodic TiO_2 nanostructured materials. Our research interest is aroused by tailoring of the morphology of self-organized TiO_2 layers through precisely controlled adjustable experimental conditions. Thus, in our studies, we consider the effect of anodizing potentials and temperatures on the growth of ATO layers in a glycerine based electrolyte containing NH_4F (0.38 wt%) and H_2O (1.79 wt%). The structural and morphological characterizations of received anodic nanostructures were performed for all studied potentials and temperatures. Moreover, photoelectrochemical properties of formed TiO_2 were studied as well.

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THE EFFECT OF FOIL PURITY ON MORPHOLOGY OF NANOPOROUS ANODIC ZrO_2

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Nanostructured semiconducting oxides such as TiO_2, SnO_2, ZrO_2 in the form of nanowires, nanotubes and nanoporous layers, are widely investigated due to their extraordinary properties like an enormous surface-to-volume ratio and quantum confinement effect [1, 2]. Interesting physicochemical properties of ZrO_2 result in its broad applications, in many fields of engineering and industry including gas sensors, fuel cells, refractory materials, and catalysts. A relatively fast and easy way to obtain a high surface area of nanostructured ZrO_2 is electrochemical anodization. The use of metal substrates with a lower purity results in a further reduction of production costs.

In the process of two-step anodization of polished Zr substrates oxide layers with an unique morphology were obtained. These processes, carried out in selected conditions, ensure that nanoporous layers with a relatively good pore order are obtained. Anodic zirconium oxides were synthesized by using two kind of Zr substrates, namely Zr purity of 99,8% and 99,2%. The surface morphology of obtained oxides was studied by using scanning electron microscopy (SEM). The anodizations were performed in an aqueous environment, in the electrolyte containing 1 M NH_4SO_4 and 0.15 M NH_4F. The duration of the first and second anodizing step was short, respectively 30 min and 2 min. The applied voltage has a value of 20 V. These conditions were sufficient to obtain high ordered, bottom side closed ZrO_2 nanotubes with a length of about 4 μm. The structural parameters of anodic oxide such as a pore diameter, interpore distance, pore density, porosity, cell size, intercell distance, cell density, wall thickness and percentage of defective pores and cells were compared for both types of used Zr substrates [3]. In this way, the impact of starting material purity on structural parameters of anodic ZrO_2 were assessed.

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THE EFFECT OF CHEMICAL AND ELECTROCHEMICAL POLISHING OF TIN ON MORPHOLOGY OF ANODIC TIN OXIDE

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Recently, a simple procedure of electrochemical oxidation (anodization) of metals is widely used as an easy method for fabrication of nanoporous metal oxides, such as Al_2O_3, TiO_2, WO_3, ZrO_2 etc. Moreover, anodic oxidation of tin in acidic or alkaline electrolytes under appropriate conditions can also result in formation of nanoporous layer of tin oxide (SnO_x) [1]. It is widely recognized that that the homogeneity of metal surface can have a significant impact on the morphology of as grown anodic oxides [2,3]. Up to now, in most cases mechanical polishing of Sn substrate has been employed to improve the homogeneity of the metal surface before anodization. On the other hand, it is well known that chemical and electrochemical polishing can also cause the significant decrease in surface roughness, however, the optimization of the method for effective electropolishing of Sn is quite difficult.

Here we present some results on the effect of Sn polishing on the morphology of anodic tin oxide layers. The effect of polishing conditions such as composition of the electrolyte, temperature and duration of the process, applied voltage/current density on the morphology of the Sn surface was studied in detail. An example of SEM images of Sn surface before and after electrochemical polishing are shown in Figure 1A, and B, respectively. As obtained Sn substrates were anodized in alkaline electrolyte (1M NaOH) to obtain nanoporous tin oxide layers and the morphology of as synthesized oxides was investigated by FE-SEM.

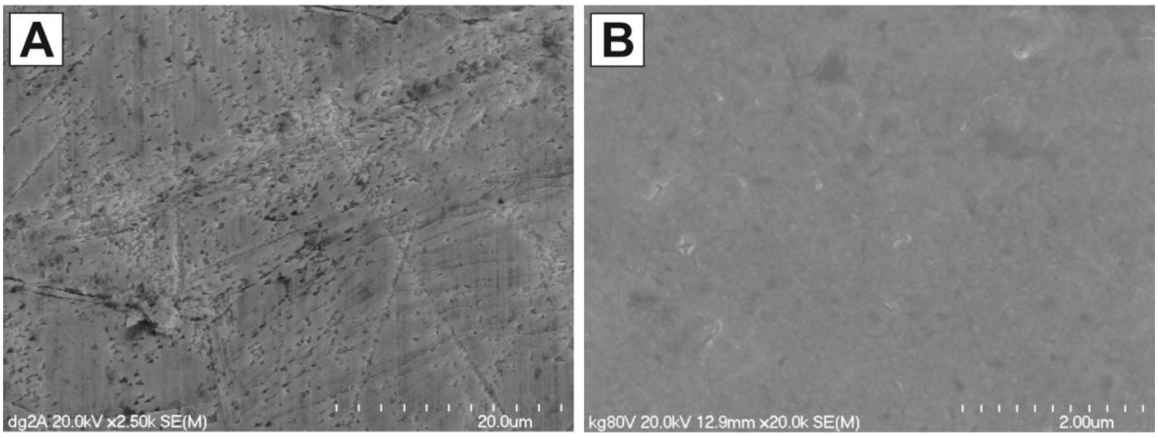

Figure 1. SEM images of Sn surface before (A) and after (B) electrochemical polishing carried out in 0.42 wt.% H_3PO_4 at 80V.

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Mechanism of voltage detachment of porous anodic alumina membranes

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The worldwide trend of device miniaturization has become an important reason for the development of inexpensive and efficient methods for synthesis of novel, nanostructured materials. In last few decades, porous anodic alumina membranes (PAMs) were widely investigated and frequently used as templates for the synthesis of functional 1D and 2D materials. A detachment of the porous alumina film from the Al substrate and removal of the barrier layer covering the pore bottoms are crucial steps in a preparation of the through-hole PAMs [1]. In typically used chemical methods, the remaining Al substrate is dissolved in a $CuCl_2$ or $HgCl_2$ solution and the barrier layer is removed by a wet chemical etching in phosphoric acid. As obtained PAM's are brittle, contaminated with heavy metal ions, pores are widen and the method is time-consuming. In 2002 Lira and Paterson presented a new electrochemical method for the PAM detachment from the Al substrate [2]. By applying a short voltage pulse, the membrane is detached and pore are opened.

Herein, we report a modified voltage detachment method that uses a mixture of $HClO_4$ and ethanol (1:1 vol.). In our research we applied different pulses for the detachment of porous alumina formed under selected experimental conditions. We also present a consistent mechanism of voltage pulse detachment.. The proposed method is better controllable, faster and more environmentally friendly as compared to the typically used chemical etching. As-obtained PAMs were successfully used for electrodeposition of metallic nanostructures.

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AAO membranes with serrated nanopores as templates for fabrication of metallic nanowires

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Self-assembled nanoporous anodic aluminum oxide (AAO) membrane with straight channels is now one of the most popular templates for synthesis of highly ordered and vertically aligned nanowires or nanotubes. In recent years, a new approach for shape-selective nanomaterials preparation in the AAO template was introduced. This is due the fact, that multibranched nanowires should possess more active functional sites than straight nanowires, and therefore their properties as sensor or catalyst should be improved. The shape of pores in the AAO can be controlled by the anodizing potential anodization. Branching of the AAO pores due to changes in anodization potential is quite well understood and was successfully used for branched nanowires preparation [1]. The AAO membranes with serrated pores can be also obtained when the electrolyte used for anodization was changed to diluted phosphoric acid solution (Fig.1). The formation of such kind of nanochannels can be attributed to the evolution of oxygen bubbles followed by the plastic deformation in the oxide film during anodization in H_3PO_4 electrolyte at potentials ranging from 10 to 80 V [2-4]. However, serrated pores were only observed when the Al samples were placed vertically to in the electrochemical cell, accompanied with a slight deformation of the direction of channel growth. Here, we present a detailed investigation on the direction of channel growth and serrated pore formation depending on the position of the Al substrate in the electrochemical cell.

Electropolished Al samples were pretextured during 1 h of anodization in 0.3 M oxalic acid at potential 40 V and at the temperature 20 °C. As prepared oxide was removed chemically and Al substrate was reanodized in 0.3 M phosphoric acid under the same conditions. The Al was placed in the cell vertically, horizontally or at selected angle. Moreover the position of the sample was changed during reanodization in order to achieve more complex structure of the AAO template.

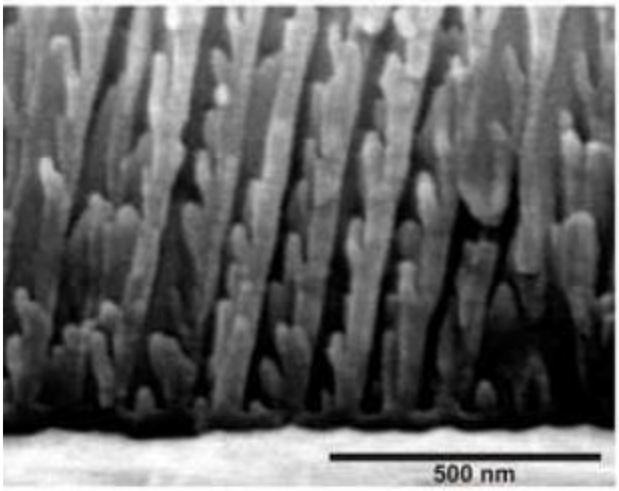

Figure 1. SEM image of the anodic alumina layer after the second anodization for 8 h in 0.3 M H_3PO_4 at 25 V and 1 °C.

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Electrochemical properties of modified with electroless Ag graphite felt electrode in aqueous solution of NaBr/Br_2

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The various carbon-based materials (activated carbon, carbon black, carbon paper and cloth, carbon and graphite felts etc.) are used as high surface area electrodes in fuel cells [1] and redox flow batteries [2]. The polyacrylonitrile-based carbon and graphite felts (GF) are the most common electrode materials in all-vanadium and polysulfide/bromine redox flow batteries [3-6]. In the positive half-cell of the last type redox flow batteries, the following electrode materials are usually utilized: activated carbon [4], carbon felt [5], and GF, Nafion® and carbon powder composite, loaded with Pt electrocatalyst [6]. It is known, that Pt has the positive effect on the electrochemical oxidation reaction of bromide Br^- ions to bromine Br_2 and the following formation of brombromide Br_3^- ions [7]. In this work, we introduce GF modified with electroless Ag as a new highly porous electrode material with the improved activity toward reversible redox reaction of bromide/brombromide (Br^-/Br_3^-) species in aqueous solution.

The modification of GF with electroless Ag was performed in Tollens' reagent by applying glucose as reducing agent and ultrasonication. All procedures for the preparation of the modified GF/Ag are described in detail in [8]. The cyclic voltammetry (CV) and chronotechnique were applied for the characterisation of GF/Ag activity toward electrochemical oxidation and reduction of Br^-/Br_3^- species in not stirred aqueous solution of 0.2 M NaBr and in equimolar (0.2 M) aqueous mixture of NaBr and Br_2. CV tests have shown that modified GF/Ag electrode is characterized by anodic depolarization effect during electrochemical oxidation of bromide ions to bromine and increased the cathodic current of bromine reduction to bromide, in comparison with the bare GF electrode. In addition, the enhancement of anodic and cathodic performance of the modified GF/Ag electrode toward electrochemical oxidation of bromide ions at 1.0 V (vs. Ag/AgCl sat.) and reduction of bromine at 0.4 V (vs. Ag/AgCl sat.), was determined by chronoamperometric measurements.

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THE INFLUENCE OF ELECTRODEPOSITION CONDITIONS ON STRUCTURE AND OPTICAL PROPERTIES OF TRANSPARENT ZnO FILMS

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ZnO is non-toxic, a naturally occurring as n-type wide and direct band gap semiconductor with a band gap of 3.37 eV (at 300 K), and a large free-exciton binding energy of 60 meV, which can be used for applications in sensors, solar cells, and optoelectronic devices . ZnO absorbs the UV part of the solar spectrum and allows lower energy photons to travel to the absorber layer [1]. In recent years, ZnO has attracted much attention as a key material for UV-light emitting diodes (LED) and UV-laser diodes [2]. Other advantages of ZnO include a high mechanical, chemical, and thermal stability [3], a high radiation hardness [4], and biosafety. Among the various growth methods of ZnO, the electrodeposition is widely used in order to obtain oxide materials with specific chemical and physical properties.

ZnO thin films were electrodeposited potentiostatically on the conductive indium tin oxide (ITO)-coated glass substrates at different cathodic potentials and various hydrogen peroxide concentrations from aqueous zinc chloride solution at 75 °C. It was shown that by increasing oxygen precursor concentration the highest deposition rate (3.8 $\mu m \cdot h^{-1}$) was achieved at 10 mM H_2O_2 and – 950 mV potential, which was *ca.* 16% higher than the calculated one. The electrochemical potential controls notably the current density and then the growth rate of the layer that influence the quality and surface morphology of ZnO films. The XRD reveals that ZnO films have polycrystalline structure with hexagonal wurtzite phase and [0001] preferential orientation. The lattice constants for as-grown ZnO films was determined as a = 3.258Å and c = 5.222Å ,which demonstrates an expansion of the lattice parameters. The optical properties of ZnO films have been characterized by the transmission spectra. The samples prepared at 2.5 mM H_2O_2 shows a very sharp absorption edge at 340 nm and were uniform and transparent (T >70%). Roughly linear relationship was found between E_g and the electrodeposition conditions.

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A COMPARATIVE STUDY OF ELECTROCHEMICAL BARRIER LAYER THINNING OF POROUS ANODIC OXIDE (AAO)

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Nanoporous Al_2O_3 can be prepared by the two-step anodization of aluminum in acidic electrolytes. During the anodization, Al foil [1] or Al film sputtered on conducting substrates [2] is subjected to anodic oxidation. The anodization of Al foil leads to the Al_2O_3/Al substrate, which is not suitable to carry out a direct electrodeposition into pores due to the presence of the non-conductive oxide barrier layer at the oxide/metal interfacial boundary. To enable the direct electrodeposition on Al_2O_3/Al substrate, the barrier layer at the bottom of the pores has to be removed. There are two basic methods used for the removal of the barrier layer: wet chemical etching [1] and electrochemical [3–5]. The first one, the wet chemical etching. Weaknesses of this method are: the use of harmful chemicals ($HgCl_2$, $CuCl_2$) [1] or concentrated acid solutions (H_3PO_4, HCl) [1] and multi-stage process (loss of the material at each stage). The alternative method to the potential step approach is a method based on the reduction of the barrier layer. Due to the fact that the thickness of the barrier layer depends on the anodizing potential, a gradual decrease in the applied potential leads to a significant reduction of the barrier layer thickness. As a result of this treatment we obtain AAO, with dendritic channels with a very thin barrier layer at the pore bottoms. An important advantage of this method is the fact that the potential reduction is carried out in the same electrolyte in which the anodization was carried out. Therefore, the potential reduction can be performed immediately after when the anodizing process is complete.

Highly ordered nanoporous anodic aluminum oxide (AAO) templates were fabricated by two-step self-organized anodization of aluminum carried out in 0.3 M oxalic acid at the temperature of 20 °C. In order to performed the electrochemical deposition of silver directly in the AAO template on Al substrate, the barrier layer was electrochemically thinned. The barrier layer thinning was done by applying an exponentially and linear decreasing voltage at the end of anodization process. This allows to achieve a high yield of nanopore filling during pulse deposition of Ag. The electrodeposition of Ag nanowires was performed in a tree-electrode cell with a Pt wire as a reference electrode and Pt plate as a counter electrode. The structural features of the barrier layer after thinning processes and deposited silver nanowires were investigated by means of FE-SEM. The chemical composition of Ag nanowires was performed by EDAX analyses.

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RELATIONSHIP BETWEEN HEAT AND MASS TRANSPORT CONDITIONS AND ANODIC TNT LAYER GROWTH PROCESS

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Currently, because of its formation methods simplicity and unique ordered structure with high aspect ratio, porous anodic valve metal oxides are increasingly attracting the attention of scientists and industry. The most actively studied of them at the moment, is the anodic titania nanotubular (TNT) layers. Due to its semiconductor and catalytic properties, this material has great potential for implementation in photovoltaic, sensory and energy storage devices and more [1-3].

At the same time, despite the huge number of works devoted to the study of properties, morphology and mechanisms of self-ordered TNT layers growth [4-6], at the moment practically no data can be found about the role of heat and mass transport conditions on TNT growth process.

In this work using RDE technique and chronoamperometry growth dependences analysis diffusion processes at the oxide/electrolyte interface during the growth of TNT layers at different formation stages in the fluorine-containing non-aqueous ethylene glycol based viscous solution (0.04 M NH_4F, 1M H_2O), in a potentiostatic mode from the temperature of electrochemical system and hydrodynamic conditions and in various combinations were studied. Also the morphology by SEM, crystallinity by XRD and composition by AES of obtained structures were studied and analyzed.

Analysis of current-time TNT layers formation dependences and SEM-images of the samples revealed that the process temperature increasing leads to TNT growth rate increasing due to increased convective mixing. However, on RDE high rotating speeds, the limiting diffusion current in the system restricts the metal anodic oxidation rate due to increased electrochemical etching rate. Also the temperature and intensive mixing at the porous oxide layer/electrolyte interface affects on final oxide layer thickness, due to increasing the chemical oxide dissolution rate on the top of the tubes. Thus, we can conclude that temperature of the electrochemical system and RDE rotation rate are effective process parameters which provide the control of nanostructures geometry during self-ordered porous oxides synthesis. Analysis of current-time dependencies allows counting relative rates of oxidation and etching processes at different TNT layer formation stages and their durations.

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ELECTROSYNTHESIS OF Mo/MoO_3 AND ITS STRUCTURAL AND PHOTOCATALYTIC PROPERTIES

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Molybdenum trioxide is one of the most important transitional metal oxides, which has gained increasing interest because of its outstanding properties like rich chemistry associated with multiple valence states, high thermal and chemical stability [1, 2]. It is frequently used in various applications: in photocatalysis, sensors, smart windows, batteries, supercapacitors [3] and photovoltaic cells [4].

In this work, we present procedure for the preparation of MoO_3 ordered crystalline nanostructured layers obtained using electrochemical anodization of Mo plate immersed in ethylene glycol–water mixed electrolyte with and without NH_4F. Ammonia fluoride was chosen to avoid intercalation of alkali cations into oxide structure. Morphology of deposited oxide was found to be strongly dependent on fluoride ions presence. Anions, as strongly adsorbed species take part in formation of soluble complexes with molybdenum. Simultaneously, other electrochemical reaction leads to formation of insoluble molybdenum oxide. Thus two, competitive, chemical steps resulted in non uniform growth of different crystallographic faces.

The morphology, composition and structure of obtained samples were investigated by SEM, EDX and Raman spectroscopy, respectively. The optical band gap energy was estimated using the Kubelka-Munk function and was equal to 2.85 eV. Electrochemical properties of obtained films were characterized both in dark and under simulated solar irradiation in aqueous electrolyte. Finally, the photocatalytic activity of MoO_3 samples were evaluated as a degradation efficiency of methylene blue as a model organic contamination. Additionally, the formation of hydroxyl ions was investigated by the photoluminescence spectra of terephthalic acid as a probe molecule.

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ELECTROCHEMICAL CO-DEPOSITION OF TUNGSTEN WITH COBALT AND COPPER

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Over the last years the electrodeposited tungsten alloys captured great attention, because of the increased requirements for coatings with versatile applications. Co-W alloy is characterized by high hardness and corrosion resistance, these alloys can to electroform structures with dimensions ranged from nano- to micro - size [1]. Meanwhile, the Cu-W deposits are interesting for their high electrical, thermal conductivity and non-welding properties [2]. The ternary Co-Cu-W alloys may possess superior properties which are resulted from Co, Cu and W properties combination. In this study the electrodeposition of Co-W, Cu-W and Co-Cu-W alloys has been performed on a stainless steel substrate from citrate baths under potentiostatic conditions at 20 and 60 °C. All deposited alloys were of uniform thickness, without any cracks and were well adhered to the substrate.

It was depicted that Co-W and Co-Cu-W alloys deposition starts at more positive potentials than it is expected from the calculated potentials of individual components of the alloys, whereas Cu-W electrodeposition is occurring at more negative potential compared to those of Co-W and Co-Cu-W. It was determined that highest amount of W that codeposits with Cu reach cca 6 at.%, and it strongly depends on deposition potential and temperature (see Fig. 1). The current efficiency of W alloys deposition varies from 28% for Cu-W to >65% for Co-Cu-W alloys.

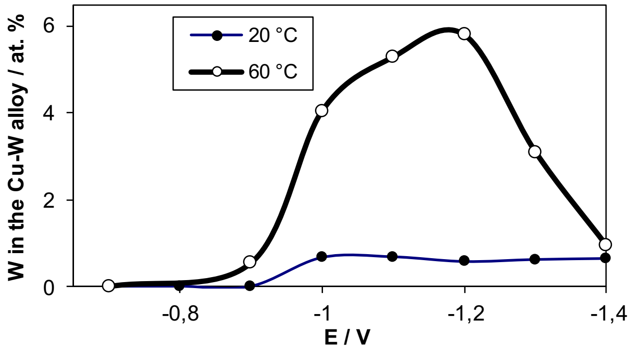

Fig. 1. *Tungsten content in the Cu-W alloys dependently on deposition potential and temperature.*

Morphology of the obtained Co-W, Cu-W and Co-Cu-W alloys having similar content of W (e.g. 6-10 at.%) is different. The Cu-W coatings were compact and formed of semi-spherical clusters. The incorporation of Co into the alloy eliminates the nodular structure, causing the formation of randomly orientated needle-like crystallites like in pure Co coating, while Co-W coatings consist of tri-pyramidal grains.

XRD analysis indicates that Cu-W alloy is a solid solution with typical Cu-type cubic lattice. Introduction of Co into this alloy resulted in the appearance of additional Co and W lines in XRD patterns, that can be identified as W solid solution in Co taking into account the solubility limit of tungsten that is equal to 17.5 at.% [3].

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Corrosion of Mg-*x*Nb coated by ALD grown Nb_2O_5 in Hanks' solution

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Mg alloys are promising materials for in-vivo applications due to their excellent biocompatibility and superior mechanical properties. A high corrosion activity of Mg is regarded as a valuable property for construction of self-degradable temporary bone implants and stents [1, 2]. However, due to inhomogeneous character of Mg corrosion, rapid rate of the process and poor wear properties of many Mg-based compounds, commercial products aren't yet available. An alloying of Mg with other metals, miscellaneous surface modifications and protective coatings are studied to achieve the effective control of Mg corrosion. The corrosion behavior of magnetron sputtered binary Mg-Nb alloys in Hanks' balanced salt solution (HBSS) was studied in our previous works [3, 4]. It was determined that corrosion resistance of these systems in great extent depends on composition and microstructure of developed Mg and Nb mixed oxide/hydroxide surface layers. The ~1 μm thick Mg-xNb compositions with different Nb content were formed on the substrates of AZ31 (Mg-3Al-Zn) alloy by magnetron sputtering method. A layer of Nb_2O_5 about ~25 nm in thickness was formed on top of each sample by Atomic Layer Deposition (ALD) method to mitigate a porosity of sputtered Mg-*x*Nb coatings. The ALD technology is the most suitable for formation of especially conformal, pinhole-sealing coatings on precision parts. Niobium (V) ethoxide ($C_{10}H_{25}NbO_5$) was the metal precursor and deionised water was used as the oxygen precursor. The temperature of Nb_2O_5 formation was 300°C. The deposition rate of Nb_2O_5 was ~0.025 nm per cycle. Nb_2O_5 formed at these conditions was the most dense: ~(3.89-3.97) g/cm^3. Corrosion behavior of the Mg-*x*Nb coated by Nb_2O_5 layers was evaluated in a HBSS. The measurements have been performed by dc-voltammetry and electrochemical impedance spectroscopy (EIS) methods, using coated samples as working electrodes. The positive shift of the open circuit potentials (E_{ocp}) of oxide coated AZ31/Mg-55Nb in comparison with uncoated one indicates a decrease of corrosion activity. For Mg-26Nb and Mg-9Nb alloys the influence of Nb_2O_5 on E_{ocp} was considerably smaller. The measurements of corrosion kinetics by dc-voltammetry and EIS showed a decrease of corrosion current density and an increase of anodic passive region (i.e., an increase of corrosion resistance) of Nb_2O_5-coated systems. The Nyquist diagrams of AZ31/Mg-xNb/Nb2O5 electrodes are characterized by significant inductive loops at low frequencies. The influence of Nb_2O_5 layers on the corrosion of the underlying alloy was explained in terms of permeability (porosity) of magnetron sputtered Mg-Nb and catalytic activity of Nb_2O_5 on the cathodic process of hydrogen evolution.

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STUDY OF TUNGSTEN ANODIZATION AND PHOTOELECTROCHEMICAL BEHAVIOR OF OBTAINED OXIDE FILMS

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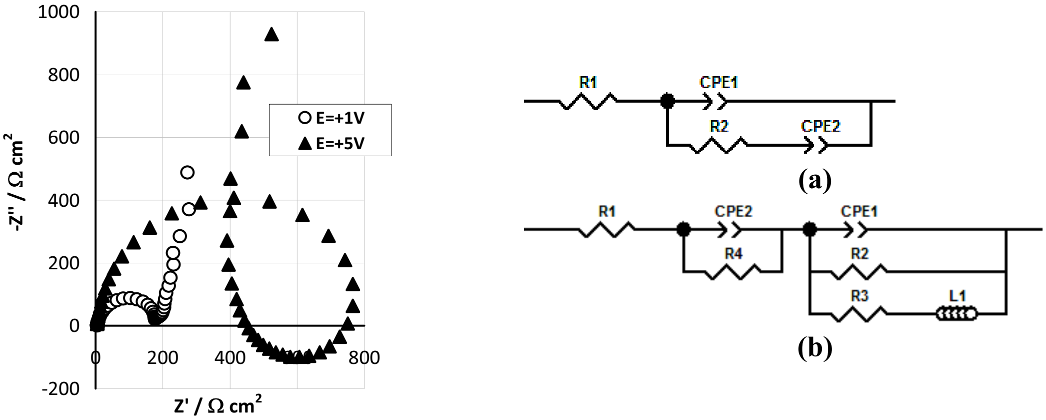
It has been recently shown that anodization of tungsten substrates in certain (corrosive) media form oxide semiconductor surfaces with various morphologies on the nanometer size scale [1]. The photoelectrochemical aspects of these materials, however, have not been extensively studied like TiO_2, and this is especially true for WO_3, and recently the growing interest for this system is evident [2]. This then constitutes the focus of the present study: the growth kinetics and mechanism of amorphous tungsten oxide layers, and photoelectrochemical properties were investigated. An oxalic acid was chosen as media for anodization. The tests were carried out on a tungsten electrode, and passivation curve with a peak at 1.2 V was obtained. Chronoamperometry showed a steep decrease in anodic current; then the current density would reach a stable value at the level of several $\mu A/cm^2$. Thus, an anodization time of 10-30 minutes has been chosen for further study. The sufficient growth of WO_3 film is obtained at higher anodization potential, and thickness of resulted film linearly increases with anodization potential and may range from 40 to 120 nm when potential is changing from 5 to 70 V. SEM examination reveals that those layers were also thicker and of entirely different surface morphology. The growing film mechanism was studied by means of electrochemical impedance spectroscopy. The Nyquist plots similar to shown in Fig. 1 were obtained and described based on equivalent electrical circuits. The physical meaning of discrete elements is discussed. In addition, the films were tested for their capability to generate photoelectochemical current under UV illumination. In general, WO_3 films obtained at higher anodization voltages (e.g. at >60V) show the higher values of photocurrent.



(a)

(b)

Fig. 1. *Nyquist plots of EIS spectra of WO_3 obtained at anodic potentials 1V and 5 V on the metallic tungsten and equivalent circuits fit to the experimental spectra obtained: (a) at 1V; (b) at 5V.*

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SYNTHESIS AND CHARACTERIZATION OF $AuCo_3O_4CD/C$ NANOCOMPOSITES

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Carcbon-supported noble metal composites have attracted a growing interest in industrial communities in the last decades due to their unique physical properties and their applications in catalysis, electrochemical energy storage, electrochemical sensor and other industries. Recently, investigation of various surfaces carbon, graphene, graphene oxide, modified graphene with gold decorated nanoparticles is still in progress. It is known, that β-cyclodextrins CD have emerged as potential tools for the preparation of metal or metal oxide materials [1, 2].

In this study $AuCo_3O_4CD/C$ nanocomposites were prepared using aqueous impregnation of cobalt oxide and gold on carbon. The composition of $AuCo_3O_4CD/C$ was detected by Inductively Coupled Plasma Optical Emission Spectroscopy ICP-OES, Field Emission Scanning Electron Microscopy FESEM), Transmission Electron Microscopy TEM) and X-ray diffraction XRD. The electrocatalytical properties of $AuCo_3O_4CD/C$ towards the oxidation of methanol are compared and discussed on the basis of electrochemical data.

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AN INFLUENCE OF CARBON MATRIX ORIGIN ON ELECTROCHEMICAL PROPERTIES OF CARBON-TIN ANODE NANOCOMPOSITES

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Tin seems to be a promising anode material due to its lithium uptake at low potential and high theoretical capacity (994 mAh/g for $Li_{4.4}Sn$ alloy phase). However, the major problem during formation of Li_xSn_y alloys are cyclic changes of elementary cell volume, reaching up to 300%, which lead to loss of electrical contact between active material and current collector as well as physical damage of the cell caused by high strains. Over the last decade most of the studies related to anode materials based on tin were focused on designing composites containing Sn and carbon-based buffer matrix [1-4]. Such nanocomposites are able to provide appropriate electrochemical properties, only if the formed carbon layer is flexible, has appropriate porosity which feature local free space that compensate volume changes.

Presented studies examine the effects of a carbon matrix origin on the electrochemical performance of carbon-tin nanocomposites. Electrochemical impedance spectroscopy (EIS) analysis in different states of charge (SOC) at initial cycle together with a long term galvanostatic charge-discharge cycling tests allowed determining the influence of carbon coating origin on electrochemical properties of C/Sn nanocomposites.

SnO_2 nanopowder, as a tin precursor, was coated by various sources of carbon (potato starch or modified poly(N-vinylformamide)) [5,6]. Afterwards the carbon-tin precursors were pyrolysed at 800 °C allowing encapsulation of tin nanograins in carbon buffer matrix. The optimal condition for preparation process was studied using thermal analysis methods (EGA-TGA/DTG/SDTA). The structure and the morphology of the samples were characterized by X-Ray diffraction analysis (XRD) and transmission electron microscopy (TEM). Obtained working electrodes combined with Li metal discs were used to assembly R-2032 coin type cells. The galvanostatic charge-discharge cycling tests (CELL TEST) were conducted at different current rates within a voltage range from 0.01 to 1.5 V using ATLAS 0961 MBI multichannel battery testing system. The electrochemical impedance spectroscopy measurements were performed using a potentiostat/galvanostat AUTOLAB PGSTAT204/FRA32. The impedance data were fitted using Autolab software (Nova 1.11 program). X-ray photoelectron spectroscopy (XPS) measurements of C/Sn materials before cycling and after first cycle were performed to observe changes in surface of the material which occur during electrochemical reaction.

The results of electrochemical studies of C/Sn nanocomposites indicated that the origin of carbon precursor has major impact on morphology and electrochemical properties. The C/Sn material in which carbon matrix was fabricated from modified polymer determined higher gravimetric capacity and better cell performance.

Acknowledgment

The authors acknowledge a financial support from the National Science Centre of Poland under research grant No. 2012/07/N/ST8/03725.

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THE STUDIES OF THERMOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF C/$LiFePO_4$ NANOCOMPOSITE MATERIALS

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Nowadays, most lithium-ion batteries (LIB) are used in portable electronic devices (such as cell phones and laptops). The fast growing of global LIB market is due to increasing demand across various energy storage sectors like automotive, military and industrial [1]. The market is currently driven by usage of LIB in electric vehicles and hybrid electric vehicles (xEV) and energy storage systems (ESS). Nevertheless, there are still needed improvements in safety, durability, energy and power density together with cost reductions [2]. Among the various materials under development for use as cathodes in lithium-ion batteries, lithium iron phosphate ($LiFePO_4$, LFP) has additional advantages such as good cycle performance, wide raw material sources, environmental benignity, high thermal and chemical stability. However, low electronic conductivity and low Li^+ diffusion rate limits the application of this material for high-power battery[3]. The methods of minimizing the particles size and surface coating overcome these limitations[4].

CCL/$LiFePO_4$ composites were prepared by using different types of carbon source. The process of preparation conductive carbon layers (CCL) on $LiFePO_4$ material [5,6] consists two main stages. In first step carbon precursors were prepared from hydrophilic polymers based on modified poly-*N*-vinylformamide (PNVF). In second step grains of LFP undergo a process of wet impregnation in water solution of PNVF with addition of pyromellitic acid (PMA), subsequently composite precursors were pyrolysed under controlled conditions. The effects of the carbon sources on the structure, morphology and electrochemical properties of obtained cathode materials were investigated. The structure of the samples were characterized by powder X-ray diffraction (XRD), low-temperature nitrogen adsorption method (N_2-BET) and transmission electron microscopy (TEM). The electrical properties of CCL/$LiFePO_4$ composites were determined by an ac 4-probe method. Change of thermal diffusivity with temperature of CCL/$LiFePO_4$ with different coatings were measured using a Netzsch 457 MicroFlashTM apparatus (LFA). The electrochemical performance was carried out in galvanostatic mode with stable charge-discharge current and performed in Li/Li^+/(CCL/$LiFePO_4$) type cells. The process of formation CCL/$LiFePO_4$ nanocomposite significantly enhances the electrical conductivity of the material and improves its capacity retention, thermal and electrochemical performance.

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INVESTIGATION OF ELECTRODEPOSITION OF MnO_2 BY EQCM

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In the present study formation of MnO_2 was studied by means of cyclic voltammetry and electrochemical quartz crystal microgravimetry (EQCM). MnO_2 was grown by electrodeposition from aqueous solutions. Influence of anions on the mechanism of electrodeposition of MnO_2 from an acetate-based neutral and acidic solutions as well as on structural, morphological and electrochemical properties has been investigated. The capacitance properties of electrodeposited MnO_2 were studied by cyclic voltammetry and galvanostatic charge-discharge cycling in 1 M Na_2SO_4 solution at a scan rate of 10 mV s^{-1}.

The data obtained are discussed in terms of properties of MnO_2 deposited.

ELECTROCHEMICAL REDUCTION OF URANIUM IN STRIP PRODUCT SOLUTIONS ON CARBON ELECTRODE

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The aim of any uranium refining method is to obtain nuclear grade material, which could be used as a reactor fuel. The uranium purification is achieved by combining several refining methods. Mainly, the flowsheets use a combination of solvent extraction and preparation of uranium tetrafluoride. The main disadvantage of this approach is the multi-step process of producing uranium tetrafluoride and the use of complicated, expensive and highly energy-consuming operations, such as evaporation, denitration, and the reduction of UO_3 to UO_2. The number of operations could be significantly decreased by obtaining uranium tetrafluoride directly from strip product solutions in two steps, reduction and precipitation.

This work describes the electrochemical reduction of U(VI) to U(IV) in strip product solutions on carbon electrode. The strip product solutions containing 0.08-0.42 M U(VI) and 0.3-0.4 M HNO_3 were prepared through the stripping of uranium from tri-*n*-butyl phosphate using dilute nitric acid (0.05 M HNO_3). The electrochemical reduction procedures were performed in a cell with polyethylene membrane separating cathode and anode compartments at 20-25 °C. Nitric acid medium is a favorable condition for tetravalent uranium oxidation. Therefore, the fluoride ions and hydrazine were used for stabilization of U(IV) in solution during the electrochemical reduction.

According to the study, a high U(IV) yield as well as a high current efficiency could be achieved during the electrochemical reduction of U(VI) in strip product solutions at applied potentials between -400 to -500 mV. However, the current efficiency is only 30-35% for the electrochemical reduction of U(VI) to U(IV) in strip product solutions without the addition of stabilizing agents. The use of solutions with fluoride ions addition for electrolysis results in increased process efficiency due to formation of fluoride complexes. The current efficiency is approximately 90% at F/U molar ratio of 0.8-1.0. The U(IV) is partially precipitated as fluoride compounds during the electrochemical reduction at F/U molar ratio greater than 1.

The addition of hydrazine hydrate in strip product solution ($N_2H_4/HNO_3 > 0.02$) results in complete suppression of HNO_3 reduction at the cathode. Furthermore, the hydrazine addition is very effective for preventing the oxidation of U(IV) and destruction of the anode.

The efficiency of electrochemical reduction of U(VI) to U(IV) in solutions depends on the medium acidity. It limits the use of hydrazine. Hydrazine has basic chemical properties. Therefore, the addition of hydrazine hydrate in the strip product solution results in the neutralization of acid. The U(IV) yield as well as a current efficiency decreased with increasing pH due to changes in the reduction process. Furthermore, the U(VI) is partially precipitated at pH greater than 3. It was found that the molar ratio of N_2H_4/HNO_3 in the fluoride-containing solutions ($F/U > 0.5$) should be less than 0.16 to achieve efficient electrochemical reduction of U(VI) to U(IV).

The uranium tetrafluoride was prepared from obtained solutions of U(IV) by precipitation using hydrofluoric acid. According to the studies, this uranium tetrafluoride is a product, which meets conversion plants requirements.

The results of this work clearly indicate that the electrolysis can be used for the efficient reduction of U(VI) to U(IV) in strip product solutions with addition of fluoride ions and hydrazine. This method can lead to the elimination of some processing steps of uranium refining.

THERMODYNAMIC STUDIES OF GEOCHEMICAL PROCESSES AT URANIUM IN-SITU LEACHING MINING

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In-situ leaching uranium consists of two stages: acidification and active leaching. Acidification is carried out before a favorable geochemical environment in the ore body for the full extraction of uranium, after which an active leaching is conducted in the same hydrodynamic conditions.

At the acidification stage of new cells in the frontal zone of weakly acid solutions ($pH \geq 4$) creates favorable conditions for reduction of U(VI) by ions of Fe(II) and their subsequent precipitation. In the course of investigation of thermodynamic model of uranium in situ leaching at acidification stage of productive stratum the calculation of free energy change and oxidation-reduction potential values were performed for the system $U–Fe–H_2O$ including the following reactions:

$$UO_2SO_4 + 2\ FeSO_4 + 8\ H_2O \rightarrow U(OH)_4 + 2\ Fe(OH)_3 + 3\ H_2SO_4 \ (1)$$

$$UO_2(OH)_2 + 2\ FeSO_4 + 6\ H_2O \rightarrow 2\ Fe(OH)_3 + U(OH)_4 + 2\ H_2SO_4 \ (2)$$

$$UO_2^{2+} + 2\ H_2O + 2e \rightarrow U(OH)_4\downarrow \ (3)$$

$$UO_2(OH)_2 + 2\ H^+ + 2e \rightarrow U(OH)_4\downarrow \ (4)$$

$$Fe^{2+} + 3\ H_2O - e \rightarrow Fe(OH)_3 + 3\ H^+ \ (5)$$

Criterion of behavior spontaneity of every reaction was studied separately considering that on the whole the entire system was nonequilibrium. Standard values of free energy of initial substances and reaction products were taken from the reference literature. Calculation of the reaction free energy change was performed for real leaching solutions containing 10^{-5}-10^{-2} M Fe(II), 10^{-6}-10^{-3} M U(VI).

The calculation results of free energy change for reactions Eqs. (1) and (2) depending on the salt composition of leaching solution show that in terms of thermodynamics behavior of these reactions is possible at pH = 4.0-5.5 and pH = 5.5-7.0 correspondingly. It should be noted that the condition of complete precipitation of $UO_2(OH)_2$ is a pH of 5.5.

The calculation of values of oxidation-reduction potential was conducted also for real conditions of uranium in situ leaching of the reactions Eqs. (3)-(5) of the system $U–Fe–H_2O$. If to compare the values of reaction potentials it can be concluded that at specified conditions ions of Fe(II) are the reductant for oxidated forms of uranium. It confirms the conclusions made from calculations of free energy change of the reactions proceeding in the system $U–Fe–H_2O$.

In order to confirm the possibility of uranium reduction process behavior by ferrous ions at acidification stage of new cells in the frontal zone of weakly acid solutions laboratory investigations were carried out to define the main parameters of the reaction behavior Eq. (1). Experiments for uranium reduction by ions of Fe(II) were carried out in laboratory conditions in test sulfate solutions containing $4.2 \cdot 10^{-4}$ M U(VI). It is determined that uranium reduction degree is more than 90 % of the total content at just threefold excess of Fe(II).

The thermodynamic model of uranium in situ leaching was investigated. It was demonstrated that at the stage of acidification of new cells in the frontal zone of weakly acid solutions (at $pH > 4$) reduction of uranium by ions of Fe(II) and its precipitation in the form of $U(OH)_4$ are possible. Addition in the leaching solutions of artificial oxidizers at the stage of acidification enables to decrease the degree of uranium reduction due to ions of Fe(II).

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ACTIVE CORROSION PROTECTION OF STEEL BY PHOSPHATE CONVERSION COATINGS DOPPED WITH CERIUM

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Active corrosion protection of metals implies not only mechanical covering of the protected surface with a dense barrier coating, but also provides self-healing properties, which allow durable protection even after its partial damage. The phosphate film on a steel surface was chosen as the base for the active corrosion protection coating. It is expected that an appropriate addition of another agent to the phosphate treatment solution may result in the synergetic effect on the protective properties of the resulting film. The protective abilities of phosphate coatings could be enhanced by the passive layer modification with Mo and Mn compounds. The self-healing ability can be achieved by introduction of specific corrosion inhibitors into the coating system. Rare earth metal ions, such as cerium, lanthanum, and yttrium, have been recognized as effective corrosion inhibitors for different metals and alloys. The aim of the present study was to develop the deposition processes of Ce doped phosphate, phosphate/permanganate and phosphate/molibdate conversion coating on a carbon steel surface and to evaluate its protective and self-healing capacities.

The SEM, TEM, XRD and XPS techniques were applied for the structural, phase and composition characterization of the investigated coatings, voltammetric measurements were carried out to determine the passive layer protective ability, while EIS studies yielded information on the self-healing properties of different protective systems affected by introduced artificial defects.

The attempts to modify phosphate and phosphate/permanganate films with Ce compounds revealed the fact that the highest protective ability and the highest amount of Ce in the conversion film was obtained when Ce was introduced from a solution containing sulphate ions. However, the "self- healing" effect for this type of coatings was not significant, most probably, because of the low amount of Ce(IV) in the top layer of the coating and the presence of structural defects at the base metal/conversion film interface. Both the highest protective and self-healing abilities were exhibited by Ce modified molybdenum/phosphate films, which were produced in the $Ce(NO_3)_3$ solution containing sulphate ions. The active corrosion protection ability of the latter conversion film secured a larger amount of Ce in general and a large amount of Ce(IV) in the top layer of the film. EIS measurements, performed with these samples, the surface of which was intentionally damaged, confirmed the fact that Ce modified molybdenum/phosphate coatings exhibit a self-healing effect. The TEM and EDS techniques were applied to prove the presence of the active corrosion protection of these coatings. The presence of a newly formed passive film on the steel surface in the intentionally damaged area was evidenced, which implies that the remaining undamaged conversion film healed the naked area of the steel.

Acknowledgments

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SOLID HYDROXIODE EUTECTICS AS SELF-ORGANIZED NANOSTRUCTURED ELECTROLYTES FOR SMALL-SIZED AND LOW-POWER ELECTROCHEMICAL DEVICES AT 250-420 K

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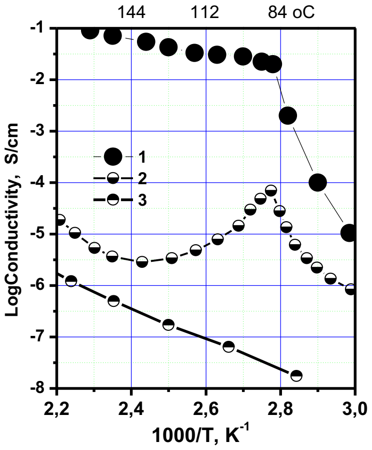
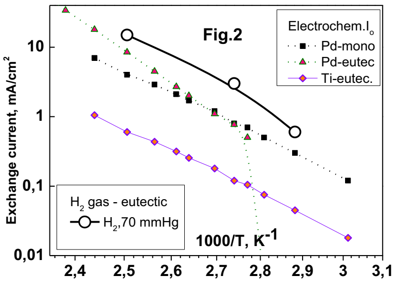
A particular phenomenon was recently discovered, whereby self-organized microheterogeneity of a NaOH+KOH solid eutectic modifies the properties of this proton conductor and thus changes the characteristics of a related “M1|NaOH+KOH|M2” heterostructure. (M1 and M2 are different combinations of electrodes (Pd, Ti, TiFe, Sn, Ge) and C as graphite textile) [1-4]. The basic and applied interest in this phenomenon has related to a high proton conductivity of the NaOH+KOH solid (!!!) eutectic (10–30 mS/cm, 400 – 500 K) . It was several orders of magnitude higher than the conductivity of individual compounds at 360–450K.Fig.1: 1- eutectic NaOH+KOH (1:1), 2- KOH, 3- NaOH. The much greater conductivity and specific features of the low-frequency impedance spectrum are related to the formation of a microheterogeneous mixture of NaOH and KOH crystals in the course of self-organization accompanying solidification of the eutectic. An information on the physical nature of structural characteristics of the phase transition was obtained from an analysis of the shapes of peaks in the temperature dependence of the heat capacity of the eutectic samples measured near the phase transition (357 K, Fig.1). Sizes of species forming eutectic composite were evaluated ~35–80 nm. The electrochemical activity of such heterostructures was revealed in study [1-5].On Fig.2 the data on exchange current measured electro-chemically (*Electrochem.*I_O) and by *H/D* exchange gas –eutectic are presented. *Electrochemical* I_O for Pd | KOH.H_2O (Pd-mono) are shown. Investigations described directed to the search for nano-heterogeneous ionic conductors .





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FEATURES OF POROUS ANODIC ALUMINA GALVANOSTATIC GROWTH IN SELENIC ACID ELECTROLYTE

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The increasing interest in nanoscale materials and the simplicity of porous anodic alumina (AAO) fabrication and application as a matrix for different nanostructures formation has promoted porous alumina to become one of the most popular materials. Nowadays, the electrolytes for AAO preparation are developed extensively. The electrolytes and the regimes for ordered AAO fabrication are of special interest.

Selenic acid solution is one of such novel self-ordering electrolytes. In this paper, we investigate the features of porous alumina formation in selenic acid in galvanostatic regime. Aluminum sheets (99.99%) were cleaned in ultrasonic bath with acetone for 10 min and electropolished in a 1:6 perchloric acid-ethanol solution at 50 mA/cm^2 current density. Series of experiments of anodization were performed in selenic acid solutions with concentrations ranging from 0.4 wt% to 10 wt % at constant current densities of 2-20 mA/cm^2. During the processes, selenic acid solutions were vigorously stirred with a magnetic stirrer (500 r.p.m) at constant temperature of 6◦C.

First, the effect of selenic acid concentration on the process of anodic oxidation was investigated. The voltage-time curves were analyzed and the morphology of the samples obtained was examined by field-emission scanning electron microscopy. At the fixed current density, porous alumina growth rate and pore ordering have a maximum at the certain concentration. In particular, it was found that in selenic acid solutions with concentrations higher 3wt% at 5 mA/cm^2 normal AAO growth was observed, at concentrations lower 3wt% – abnormal growth with “burning” effects was detected. The samples with the highest pore ordering were obtained in 3-5 wt% selenic acid electrolytes, that is, in the conditions closed to the border between abnormal and normal growth.

Secondary, dependence of AAO growth behavior and morphology on current density at fixed electrolyte concentrations was analyzed. During the first stage of AAO formation, with the current density increasing the slope of v-t curves rise linearly (for example, proportionality constant for 5 wt% solutions is 0.34). Nevertheless, it was found that with the current density increasing the border between normal and abnormal alumina growth leading to the inhomogeneous porous structure formation and “reduced” apparent thickness shifts to the higher selenic acid concentrations.

Composition analysis was carried out by Auger electron spectroscopy. It was found that quantity of Se species increase with the selenic acid concentration from 0.5 to 2%.

Finally, some promising properties of AAO formed in selenic acid were found. Photoluminescence properties were investigated by multichannel spectrometer S2000 (Ocean Optics). The samples exhibit the smallest luminescence intensity compared to the oxide films obtained in standard electrolytes. Therefore, AAO formed in selenic acid can be applied as a transparent matrix for functional nanostructures for optoelectronics synthesis and investigation.

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FORMATION OF CRACK-FREE NANOPOROUS TIN OXIDE LAYERS BY SIMPLE ANODIZATION IN ALKALINE ELECTROLYTE AT LOW POTENTIALS

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During the recent years, nanostructured tin dioxide (SnO_2) has become a subject of great scientific interest due to its many promising electronic, optical and photoelectrochemical properties, and a wide variety of potential applications including solid-state gas sensors, catalysis, or even Li-ion batteries. Among many methods used for fabrication of nanostructured SnO_2, a simple anodic oxidation (anodization), proposed originally by Shin et al. in 2004, seems to be a very interesting and cost-effective strategy for the synthesis of nanoporous tin oxide-based layers on the surface of metallic tin. In most cases the typical anodic tin oxide exhibits a layered structure with a lot of internal gaps and transversal pores. Such kinds of discontinuities, being a result of vigorous oxygen evolution can strongly affect the properties of as grown oxide layers, e.g. their mechanical strength, resistivity and optical properties [1]. Despite the fact that some attempts to the formation of crack-free nanoporous tin oxide layers via anodizing in electrolytes containing fluoride and sulfide ions have been already reported [2], this issue is still a challenge for the scientific community.

Here we propose some novel strategy for fabrication of crack-free porous anodic tin oxide layers by simple anodic oxidation of metallic tin in sodium hydroxide solution at relatively low potentials (2–4 V). A low-purity Sn foil (98.8%) was used as a starting material. A series of anodizations were performed in 1 M NaOH at different conditions such as anodizing potential, and duration of the process. The morphology of as synthesized materials was characterized using a field-emission scanning electron microscope (FE-SEM). An example of as obtained porous anodic tin oxide is shown in figure 1.

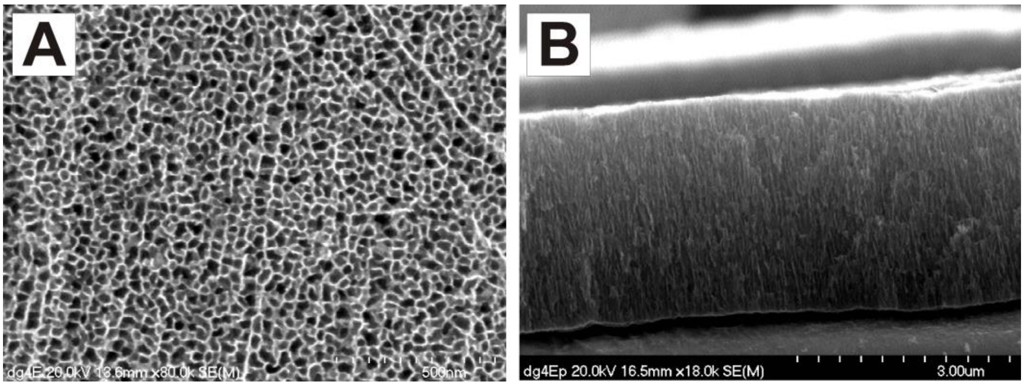

Figure 1. SEM images of anodic tin oxide layer formed by 30 min of anodization in 1M NaOH at 4 V and room temperature. A – top-view, B – cross-sectional view.

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ANODIC GROWTH OF ZnO NANOWIRES IN BICARBONATE ELECTROLYTES

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During the recent years, zinc oxide (ZnO) has become a main competitor to photoelectrochemical applications of titanium dioxide due to its similar wide bandgap (~3.4 eV), comparable band edge positions and considerably higher electron mobility. Moreover, ZnO has proven to be a versatile material for various modern applications such as gas sensing, piezoelectrics, optoelectronics etc. Among various nanostructures of ZnO, ordered arrays of one dimensional structures such as nanowires or nanotubes seem to be the most promising morphology. Therefore, a variety of methods have been already employed for fabrication of ZnO nanowires such as chemical vapor deposition, hydrothermal growth, sol-gel methods, etc. On the other hand, very recently it was found that it is possible to synthesize an arrays of ultralong ZnO nanowires via simple anodic oxidation of metallic zinc in bicarbonate electrolytes [1-3].

Here, we present some initial results on the fabrication of ZnO nanowires by the controlled anodization of metallic Zn in various bicarbonate electrolytes ($NaHCO_3$, NH_4HCO_3). A series of anodizations were performed at different conditions such as anodizing potential, composition and concentration of the electrolyte and duration of the process. After anodization a thermal annealing was carried out to obtain crystalline product. The morphology of as synthesized materials was characterized using a field-emission scanning electron microscope (FE-SEM) and the composition and structure of as obtained oxides were examined by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The mechanism of nanowires growth has been also proposed. An example of ZnO nanowire arrays grown on the Zn surface is shown in figure 1.

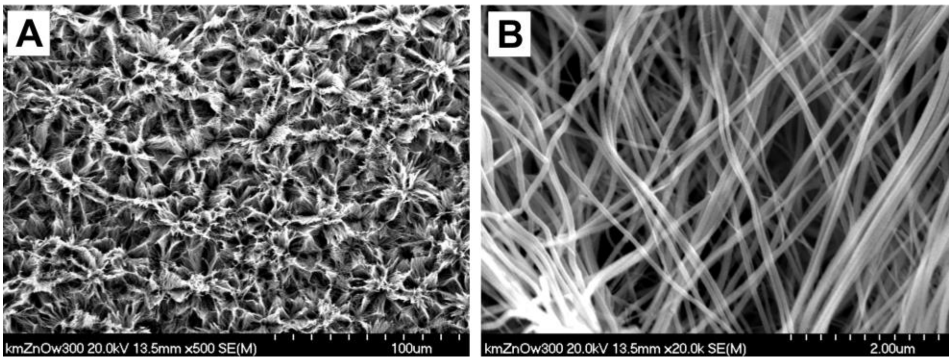

Figure 1. SEM images of ZnO nanowires formed by 20 min of anodization in 5 mM $NaHCO_3$ at 10 V and room temperature followed by 2 h of annealing in air at 300 °C.

Acknowledgement
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PHOTOELECTROCHEMICAL SENSORS FOR GLUCOSE BASED ON NANOSTRUCTURED METAL OXIDES

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Photoelectrochemical sensors become a very popular research topic due to its sensitivity, inherent miniaturization, portability and easy integration. They are used in the field of biology, medicine, and environment monitoring [1]. The most commonly determined compound is glucose. Its level in blood is a crucial indicator for the diagnosis and treatment of diabetes mellitus, one of the leading illness causing human death [2]. Intensive development of nanomaterial science, allows today for the synthesis of nanostructured transition metal oxides such as TiO_2, WO_3, and ZnO. Their excellent optical, electrical and chemical properties may be improved by decreasing the size of material and tailoring its structure [3].

Nanostructured tungsten oxide was synthesized by a one-step anodization at 40 V and 20 °C in an aqueous electrolyte containing fluoride anions. Afterwards, the samples were annealed at 500 °C for 1 h in order to obtain a photoactive WO_3 form. On the other hand, anodic titanium oxide (ATO) layers were obtained by a three-step anodization of titanium carried out at 40 V and 20 °C in the electrolyte based on an ethylene glycol solution containing NH_4F (0.38 wt.%) and water (1.79 wt.%). After anodization, resulting amorphous TiO_2 was annealed at 400 °C for 2 h in order to obtain the anatase structure.

Photoelectrochemical tests were performed using a three-electrode cell with a quartz window, where nanostructured TiO_2 or WO_3 was used as a working electrode (WE), a platinum foil as a counter electrode (CE), and a Luggin capillary with a saturated calomel electrode (SCE) as the reference electrode. The generated photocurrents were measured using a photoelectric spectrometer equipped with the 150 W xenon arc lamp and combined with the potentiostat. The photoelectrochemical characterization was performed in 0.1 M KNO_3 using cyclic voltammetery in the potential range of 0 - 1 V vs. SCE and the light wavelength of 350 nm. Chronoamperograms were taken to determinate the influence of glucose additions on generated photocurrents.

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ELECTROCHEMICAL GLUTAMATE SENSING APPLYING POLY(RIBOFLAVIN) AND GRAPHENE OXIDE-CHITOSAN FILM MODIFIED ELECTRODES

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Glutamic acid is a nonessential amino acid playing different roles in many biological functions; a monosodium salt of glutamic acid is widely used in food industry as a food additive, responsible for the fifth taste – umami. The determination of this compound is important in clinics as well as in food industry. Different methods are applied for the detection of this compound, one of them being electrochemical, which is fast, low cost, besides, sample preparation is relatively simple. The architecture of electrochemical biosensors must be carefully elaborated, in order to develop a biosensor of good properties, e.g. the mediator of natural origin can be applied [1,2]. Besides, in order to improve biosensors properties, they are miniaturised. In our work, electrochemical glutamate biosensor was developed electrochemically synthesizing poly(ribloflavin) film (PRf, vit. B_2) on the glassy carbon electrode (GCE) surface in order to get a redox mediator of natural origin, which was used to improve biosensor performance. The PRf/GCE was additionally modified with chitosan-graphene oxide film [3]. Moreover, the microchip biosensor was developed on chitosan-graphene oxide film covered glass by laser patterning three electrodes, where working electrode had combe-like shape consisting of parallel strings, which was modified with PRf film the same way as for GCE based electrode [3]. The reference electrode was modified with silver paste. Glutamate oxidase was immobilized applying cross-linking in both cases [3].

Electrochemical response to glutamate was recorded applying cyclic voltammetry and fixed potential amperometry for GCE based biosensor; however, the microchip electrode worked in CV mode only. The sensitivity and limit of detection of the developed biosensor based on GCE was 71.1 ± 1.0 μA cm^{-2} mmol L^{-1}and 2.64 ± 0.04 μmol L^{-1}, respectively; the microchip biosensor had the sensitivity of 27.5 mA cm^{-2} mmol L^{-1} [3]. The results of the analysis will be presented and discussed.

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EPINEPHRINE SENSING AT Au NANOTUBE ARRY ELECTRODE AND DETERMINATION ITS OXIDATIVE METABOLISM

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Epinephrine (EP) is a neurotransmitter and hormone involved in an enormous number of processes in living organisms, however its highly active oxidation metabolites can cause hard damages and lead to serious health consequences. This work described a relatively simple method of fabrication of Au nanotube array electrodes for electrochemical determination of EP [1,2], which could be easily transfer to non-laboratory conditions. Using electrochemical techniques like cyclic voltammetry (CV) and chronoamperometry, some physicochemical parameters of EP oxidation process were determined. The linear sweep voltammetry (LSV) and differential pulse voltammetry (DPV) revealed a good linear response for determination of EP in the range of 60 – 1000 μM EP and 10 – 150 μM, respectively. The proposed DPV method was successfully applied to the determination of EP in a pure, ascorbic acid containing, and real samples. The DPV results were evaluated and compared with those obtained by the high-performance liquid chromatography (HPLC) method.

Combining the ROXY™ EC System with mass spectrometry creates an analytical tool for studying oxidative products of EP and conjugation of EP reactive potential metabolites characterized for I and II stage of biotransformation. The presence of leucoadrenochrome-o-semiquinone radicals confirmed by mass spectrometry implies that the ECE (electron transfer-chemical reaction-electron transfer) mechanism of EP oxidation at the nanostructured Au electrode is more feasible.

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SYNTHESIS OF NANOPOROUS SILVER NANOWIRES AS ELECTROCHEMICAL H_2O_2 SENSOR

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Precise determination of small amounts of hydrogen peroxide is a very important issue in the field of many sciences. The most promising strategies for determination of hydrogen peroxide are based on electrochemical methods that offer high accuracy, reliability and can give results quickly and at relatively low cost. Up to now, the most common electrodes used for determination of hydrogen peroxide are enzymatic electrodes [1]. Unfortunately the major drawbacks of this systems are low chemical stability, especially against pH changes and loss of sensing properties with time. An extensive research is performed to overcome these problems. One of the most promising strategies is to replace “standard” electrodes with nanostructured materials [2]. We present some initial results on fabrication of nanoporous Ag nanowires (Ag-NWs) via template assisted electrochemical deposition of AgZn alloy followed by Zn dealloying in 5 % sulfuric acid solution. Such parameters as: type of template (anodic aluminum oxide – AAO and polycarbonate membranes - PC were used), composition of the electrolyte, electrodeposition conditions (potential or current density) and dealloying time were optimized. The morphology of nanoporous Ag nanowires and their composition were characterized using Field-Emission Scanning Electron Microscope (FE-SEM) and the energy dispersive X-ray spectroscopy (EDS), respectively.

As obtained porous silver nanowires were investigated as amperometric sensors for the detection and determination of hydrogen peroxide. Typical chronoamperometric curve is shown in Fig. 1b.

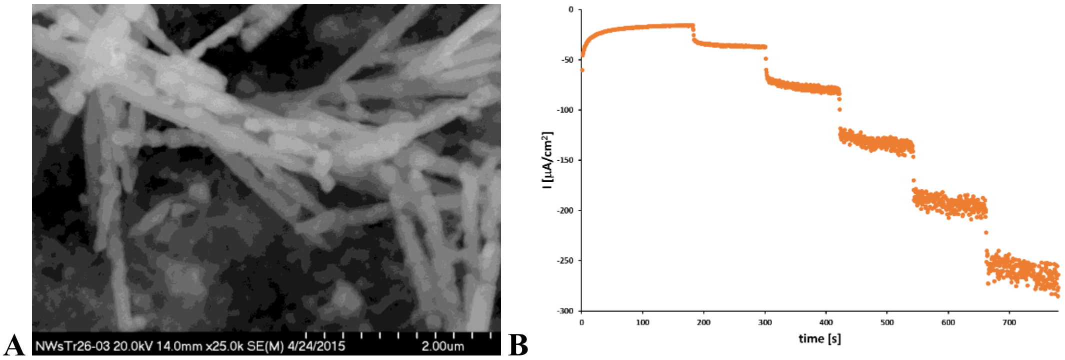

Fig. 1. A) SEM image of nanoporous silver nanowires obtained by electrochemical deposition of the Ag-Zn nanowires at a potential of –1,7 V for 5 min in polyvcarbonate mebrane, followed by its etching in a 5% solution of sulfuric acid for 6 h. B) Typical chronoamperometric curve for obtained nanoporous silver nanowires after adding five portion of 0.5 mM H_2O_2 at -0.2 V vs. SCE in stirred 0.01 M PBS (pH 7.4).

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SYHNTHESIS AND CHARACTERIZATION OF Ag PROMOTED Pd NANOPARTICLES AND THEIR ENHANCED ETHANOL ELECTROOXIDATION ACTIVITY

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Direct alkaline alcohol fuel cells (DAAFCs) could offer an excellent alternative solution to the current energy generation problems. Palladium is recognized as the most efficient material for the ethanol electrooxidation (EOR) in alkaline media. Palladium is recognized as the most efficient material for the ethanol electrooxidation (EOR) in alkaline media. Nevertheless, both the catalytic activity and stability of Pd for the EOR in alkaline media need to be further enhanced. In order to improve the electrocatalytic activity and stability of Pd for EOR, some binary electrocatalysts such as PdAu/C, PdSn/C, PdRu/C, PdIr/C, and others have been proposed [1, 2]. The objective of the current study is to improve the activity direct ethanol fuel cells in alkaline media using PdAg/C electrocatalysts prepared in different atomic ratios. The PdAg/C materials were prepared by the borohydride reduction process and supported on carbon at different Pd:Ag ratios. These catalysts were characterized by BET, XRD, XPS, SAXS, SEM-EDX. Characterization results indicate that Ag doping to Pd change the electronic structure of Pd. The details of the characterization results will be presented furtherCyclic voltammetry (CV), chronoamperometry (CA), electrochemical impedance spectroscopy techniques were performed on Pd/C and PdAg/C catalysts. The electrocatalytic performance of carbon supported PdAg and Pd electrodes toward EOR in alkaline was examined by CV in the potential range from -0.25 to 1.0 V. Figure 1 shows the CV of these catalysts in the presence of 1 M KOH + 1M C_2H_5OH. PdAg/C (70:30) showed a better onset potential of −0.76 V than the other PdAg catalaysts, showing that the introduction of Ag leads to an increase in the electroactivity of the binary electrocatalysts (PdAg). CA and EIS results will be presented in further.

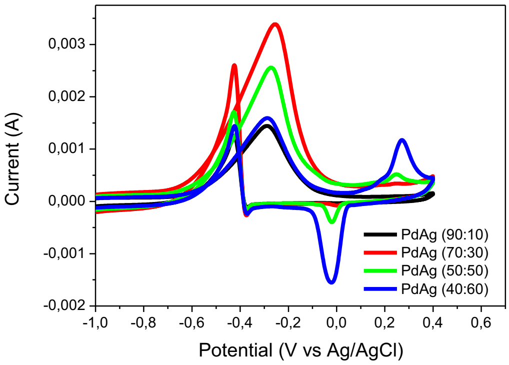

Figure 1: CVs of PdAg/C in 1 M KOH + 1M C_2H_5OH. Scan rate: 50 mV s^{-1}.

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Ni PROMOTED Pd ETHANOL ELECTROOXIDATION CATALYSTS

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Fuel cells are electrochemical devices that could generate electrical energy by oxidation and reduction of the externally supplied fuel and oxidant respectively [1]. One recent system of fuel cells is the direct ethanol fuel cell (DEFCs) in which the liquid ethanol is supplied into the anode. There are two DEFC systems according to the used solution; alkaline and acidic. The acidic ones have been applied extensively between the fuel cell anode and cathode, but the alkaline-electrolyte DEFC has proved intrinsic advantages as compared to the acidic counterparts: faster reaction kinetics, the non-Pt metal catalyst possibility, better water management, higher degree of freedom in selecting fuels, and no need for fluorinated polymers are some of them. Pd-catalysts are currently the best metal alternative to Pt-ones for alcohol oxidation in alkaline solution. In this work, carbon supported Pd-Ni bimetallic catalysts were synthesized and their electrocatalytic activity for ethanol oxidation reaction (EOR) in alkaline medium was investigated [1, 2]. The PdNi/C (10 wt% Pd loading) nanocatalysts were prepared by the borohydride reduction at varying Pd:Ni atomic ratios. Cyclic voltammetry (CV), chronoamperometry (CA), and Electrochemical impedance (EIS) measurements were performed on Pd/C and PdNi/C catalysts. Cyclic voltammograms and chronoamperomograms were recorded in 1 M KOH + 1M C_2H_5OH solution on these catalysts. Figure 1 shows the CV performance for the prepared PdNi catalysts supported on carbon. The CV voltammograms show that alloying Pd with other elements can enhance the electrochemical activity for ethanol oxidation in alkaline medium clearly. The details will be further presented in detail.

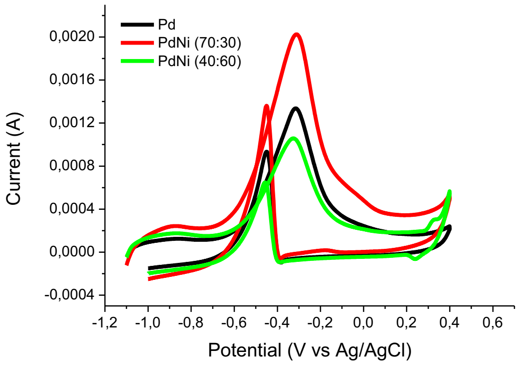

Figure 1: CVs of PdNi/C in 1 M KOH + 1M C_2H_5OH. Scan rate: 50 mV s^{-1}.

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METHANOL AND ETHANOL ELECTRO-OXIDATION ON PLATINUM-COBALT/GRAPHENE CATALYSTS PREPARED BY MICROWAVE SYNTHESIS

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The graphene (GR) supported PtCo catalysts with different Pt:Co molar ratios equal to 1:3, 1:6, 1:20, 1:50 and 1:60 were fabricated by means of the rapid microwave heating method [1]. The size and shape of catalyst nanoparticles were determined by means of Transmission Electron Microscopy. Electrochemical properties of the PtCo/GR catalysts were investigated towards the electro-oxidation of methanol and ethanol in acidic medium by means of cyclic voltammetry and chronoamperometry and compared to those of pure Pt/GR catalyst.

The PtCo/GR catalysts with an average Pt particle size of ca. 1-3 nm were synthesized from the reaction mixture containing H_2PtCl_6, $CoCl_2$ and ethylene glycol. The electrocatalytic activity of PtCo/GR catalysts depends on the molar ratio of Pt:Co in the catalysts. It was found that the synthesized PtCo/GR catalysts with the Pt:Co molar ratios equal to 1:3 and 1:6 exhibit the highest electrocatalytic activity for methanol and ethanol electro-oxidation as compared with that of catalysts with the Pt:Co molar ratios equal to 1:20, 1:50 and 1:60 and 1:0.

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STRUCTURE AND PROPERTIES OF ELECTRODEPOSITED COBALT SULFIDE CATALYST

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The increased demand of effective solar energy conversion technologies leads to the development of efficient, stable and solar light sensitive catalysts for water splitting into hydrogen and oxygen. It has been found that the transition metal sulfides, including sulfides of cobalt, nickel or copper can demonstrate improved electrochemical performances with a combination of low cost precursors and simple fabrication techniques. Cobalt sulfide (CoS) is identified as a promising material for dye-sensitized solar cells (DSSC) and active electrocatalyst for photoelectrochemical hydrogen generation in aqueous solutions [1-3].

The aim of this work was to form cobalt sulfide films on conductive glass substrates and to study their structure and electrochemical behavior in aqueous solutions.

The thin films of cobalt sulfide on FTO substrate were prepared by potentiodynamic deposition. The synthesis was carried out using a deposition bath containing 0.5 M thiourea and 0.005 M $CoCl_2$ in a three-compartment cell. The neutral pH value of the deposition bath was maintained by adding a small amount of ammonia. The electrodeposition potential was cycled from -1.2 V to 0.2 V vs. Ag/AgCl at a scan rate of 5 mV/s. 0.1 M potassium phosphate buffer solution (pH 7) was used as a supporting electrolyte for the electrochemical measurements.

Understanding of cobalt sulfide formation by cyclic voltammetry was the first step of this study. The experimental results revealed the possibility to form thin films by varying the number of sweep cycles. Various electrochemical methods were used to characterize the performance of cobalt sulfide (CoS) films in aqueous solutions. Structural and chemical characterization of the prepared films was carried out by means of XRD, FTIR, SEM and DR-UV-vis spectroscopy.

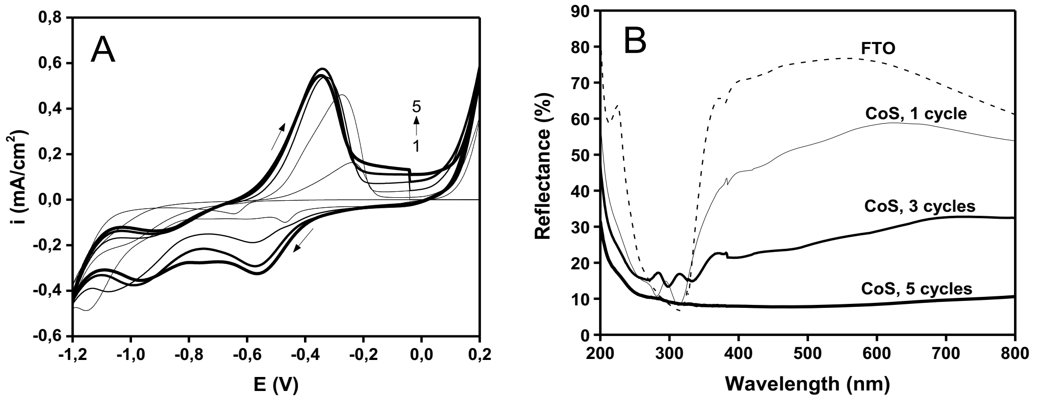

Figure. Characteristic cyclic voltamperograms of FTO substrate in electrolysis bath (a) and UV–vis diffuse reflectance spectra of prepared CoS/FTO films (b)

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EVALUATION OF Au/Co AND Au/CoB ELECTROCATALYSTS IN BOROHYDRIDE FUEL CELL ANODES

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Direct borohydride fuel cells (DBFCs) are among the latest fuel cell types under considerable research and development. DBFCs with sodium borohydride ($NaBH_4$) as fuel and hydrogen peroxide (H_2O_2) as oxidant, known as direct borohydride/peroxide fuel cells (DBPFCs), have been proposed and nowadays find various potential applications.

A simple approach for preparing effective anode catalysts with low gold (Au) loadings for DBPFC is presented herein. The cobalt (Co) or cobalt boride (CoB) thin layers were deposited on the copper (Cu) surface using borane morpholine complex as reducing agent [1]. Then, the surface of obtained Co or CoB was modified with Au nanoparticles (denoted as Au/Co/Cu and Au/CoB/Cu) via the galvanic displacement technique [1-3]. Au nanoparticles were deposited on the Co and CoB surfaces using different gold-containing solutions. The Co/Cu and CoB/Cu electrodes were immersed in acidic 1 mM $HAuCl_4$ (pH 1.8) and neutral 1 g l^{-1} $KAu(CN)_2$ + 0.4 M $(NH_4)_2C_6H_6O_7$ complex solutions at a temperature of 25 ºC for 0.5, 1 and 5 min. It was found that the Au loadings were in the range of 3-44 µg cm^{-2}.

Performance of $NaBH_4/H_2O_2$ fuel cell using an Au/Co/Cu or Au/CoB/Cu as the anode and Pt as the cathode was studied at room temperature. 5 M H_2O_2 + 1.5 M HCl solution was used as catholyte and 1 M $NaBH_4$ + 4 M NaOH as anolyte, separated by a Nafion 117 membrane.

Peak power densities of 105 and 95 mW cm^{-2} were attained using the Au/CoB/Cu anode with Au loading of 44.2 µg cm^{-2} and using Au/Co/Cu anode with Au loading of 36.1 µg cm^{-2}, respectively, prepared by immersion of the CoB/Cu and Co/Cu electrodes in the acidic Au-containing solution for 5 min. As for the electrocatalysts prepared by immersion of the CoB/Cu and Co/Cu electrodes in the neutral Au-containing solution for 5 min, peak power densities up to 79 and 96 mW cm^{-2} were attained using the Au/CoB/Cu anode with Au loading of 14.0 µg cm^{-2} and using the Au/Co/Cu anode with Au loading of 15.3 µg cm^{-2}, respectively.

The highest mass-specific power density of 18.1 kW g_{Au}^{-1} was obtained at 0.9 V and 62.5 mA cm^{-2} using the Au/CoB/Cu electrode with Au loading of 3.1 µg cm^{-2} and prepared by immersion of CoB/Cu in the neutral Au-containing solution for 0.5 min.

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CERIUM OXIDE/GRAPHENE SUPPORTED Pt AND Pt-Co AS ELECTROCATALYSTS FOR METHANOL OXIDATION AND OXYGEN REDUCTION REACTION

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In the present work, cerium oxide/graphene supported the Pt and PtCo catalysts denoted as $PtCeO_2$/GR and $PtCoCeO_2$/GR w ere fabricated by means of the rapid microwave heating method. The synthesized catalysts were examined by Field Emission Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy and Inductively Coupled Plasma Optical Emission Spectroscopy. The electrocatalytic activity of the $PtCeO_2$/GR and $PtCoCeO_2$/GR catalyst towards the oxidation of methanol and reduction of oxygen was investigated by means of cyclic voltammetry and chrono-techniques.

It was found that Pt nanoparticles of ca. 1-6 nm in size were successively deposited onto the surface. Pt nanoparticles were uniform and well dispersed on the surface of graphene.

The $PtCeO_2$/GR, $PtCoCeO_2$/GR and Pt/C catalysts with the Pt loadings of 0.134, 0.178 and 0.128 mg Pt cm^{-2}, respectively, were synthesized. Methanol oxidation current densities were found to be ca. 8 times higher at the $PtCeO_2$/GR and $PtCoCeO_2$/GR catalysts in comparison with those at the Pt/C catalyst. In the case of oxygen reduction, the $PtCoCeO_2$/GR catalyst outperforms the $PtCeO_2$/GR and Pt/C catalysts towards oxygen reduction and shows higher onset potential, as well as higher current density towards the oxygen reduction reaction as compared with those at the aforementioned catalysts.

ANODIC OXIDATION OF FORMALDEHYDE ON ELECTROLESS COPPER COATINGS DEPOSITED FROM CuII) -EDTA SOLUTIONS

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Electroless copper plating solutions are widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics silicon wafers, resins etc.). The industrial electroless copper plating solution containing formaldehyde as reducing agent are known from the middle of the last century and are widespread in the practice up to now. Electroless copper deposition process is recognized now as being electrochemical by nature and consisting of two reactions, anodic formaldehyde oxidation and cathodic Cu(II reduction, occurring simultaneously on the same surface. The anodic formaldehyde oxidation on Cu in a negative potential region is described by the stoichiometry (1:

$$HCHO + 2OH^- \rightarrow HCOO^- + H_2O + \frac{1}{2} H_2 + e^- \qquad 1)$$

Ethylenediaminetetraacetic acid EDTA is one of the most widely used ligand in alkaline electroless copper plating baths due to its perfect chelating properties. The data on use of EDTA in electroless copper plating as a Cu(II ligand are enough wide -ranging, but, it is worth noting that practically all data are obtained at room or higher temperature. Therefore in this work copper coatings were deposited from alkaline formaldehyde-containing solutions, using EDTA as Cu(II ligand at temperatures, mainly lower than room temperature.

Our studies were carried out in electroless plating solutions at pH 12.0 - 13.0 and 5 - 30 °C temperature during 0.5 and 1h. The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h can reach ca. 4 µm, depending on the pH and temperature. The maximum values of plating rate are reaching at pH 12.5 at all investigated temperatures. The real surface areas R_f of deposited copper coatings vary widely, i. e. from ca. 3.1 up to 39.3. The maximum R_f values were obtained at pH 12.0 for investigated temperatures.

Anodic formaldehyde oxidation measurements were carried out in formaldehyde solution at pH 12.5. It was found, that the rate of formaldehyde anodic oxidation depends on conditions of the formation of copper coatings – the highest rate of HCHO oxidation was determined on the surface’s electrolessly obtained at 5 ºC and pH 13.0.

Results were compared with those for systems operating with other copperII ligands .

COMPARISON OF ELECTROCATALYTIC PROPERTIES OF PtCoCeO$_2$/GRAPHENE AND PtCoNb$_2$O$_5$/GRAPHENE CATALYSTS TOWARDS METHANOL OXIDATION

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In this study the PtCoCeO$_2$/graphene and PtCoNb$_2$O$_5$/graphene catalysts were prepared by polyol method using the simple and rapid microwave heating method. To obtain the catalysts, required amounts of CeO$_2$/graphene or Nb$_2$O$_5$/graphene, H_2PtCl_6 and $CoCl_2$ were heated in ethylene glycol at 170 ^{o}C for 30 min in the microwave reactor. It was found that Pt nanoparticles were successively deposited onto the surfaces of CeO$_2$/graphene and Nb$_2$O$_5$/graphene. For comparison the Pt/carbon catalyst was prepared in the same manner. The composition of catalysts was detected by Inductively Coupled Plasma Optical Emission Spectroscopy ICP-OES, Field Emission Scanning Electron Microscopy FESEM), and Transmission Electron Microscopy TEM . The synthesized PtCoCeO$_2$/graphene, PtCoNb$_2$O$_5$/graphene and Pt/carbon catalysts were examined as electrocatalysts towards the electro-oxidation of methanol. The main data are given in Table 1.

Table 1. Data of electrocatalytic parameters of the investigated catalysts.

Catalyst	ESA, cm^2	Pt loading, mg cm^{-2}	Peak current density, mA cm^{-2}	Peak potential, V
PtCoCeO$_2$/GR	2.5	0.178	41.4	0.03
PtCoNb$_2$O$_5$/GR	4.3	0.285	21.7	0.00
Pt/C	1.3	0.128	8.5	-0.03

It has been found that CeO$_2$/graphene or Nb$_2$O$_5$/graphene supported PtCo catalysts show an enhanced electrocatalytic activity towards the oxidation of methanol in an alkaline medium as compared with that of Pt/carbon catalyst. Methanol oxidation current densities were found to be ca. 3 – 5 times higher at the PtCoCeO$_2$/graphene and PtCoNb$_2$O$_5$/graphene catalysts, respectively, in comparison with those at the Pt/carbon catalyst. The prepared catalysts seem to be a promising anodic material for direct methanol fuel cells.

FIBER COBALT DECORATED WITH PLATINUM NANOPARTICLES AS ELECTROCATALYSTS FOR HYDRAZINE OXIDATION

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In the present study simple and cost-effective electrochemical and chemical methods were used for preparation of PtCo catalysts. The Co coating with a fiber structure was used as a sublayer for deposition of Pt nanoparticles. The fiber Co coating with the thickness of ~3 µm was electroplated onto the Cu surface (denoted as Co_{fiber}/Cu). Then, the Pt nanoparticles were deposited on the prepared Co_{fiber}/Cu by its immersion into the 1 mM H_2PtCl_6 + 0.1 M HCl solution at the temperature of 25 ^{o}C for 10, 20 and 60 s, respectively. The morphology, structure and composition of the prepared catalysts were characterized by means of Field Emission Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy and Inductively Coupled Plasma Optical Emission Spectroscopy. The electrochemical behaviour of catalysts was evaluated with respect to the oxidation of hydrazine in an alkaline medium by means of cyclic voltammetry and chrono-techniques.

It was found that the Pt loadings were 5.4, 15.4 and 28.7 $\mu g\ cm^{-2}$ in the prepared $Pt(Co_{fiber})/Cu$ catalysts after the immersion of Co_{fiber}/Cu into the platinum(IV)-containing solution for 10, 30 and 60 s, respectively. The cobalt with a fiber structure decorated with the platinum nanoparticles show enhanced electrocatalytic activity towards the oxidation of hydrazine in an alkaline medium as compared to that of bare Pt and Co deposited on the Cu surface.

AUTOCATALYTIC REDUCTION OF PLATINUM(IV) BY COBALT(II)-DIETHYLENETRIAMINE COMPLEX

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Interest in the deposition of platinum group metals and alloys arises often in connection with applications to the fabrication of electronic devices. Electroless platinum has been plated using hydrazine, borohydride [1] and $TiCl_3$ [2] as the reducing agents in previous investigations.

The cobalt(II) complex with diethylenetriamine (dien) was found to be an effective reducing agent in the autocatalytic reduction of platinum(IV) to metal (electroless platinum plating). Kinetic investigations of platinum deposition were carried out in this system and rather high rate of reduction process on glass surface substrate without appreciable bulk reduction was observed at certain reactants concentration and solution pH.

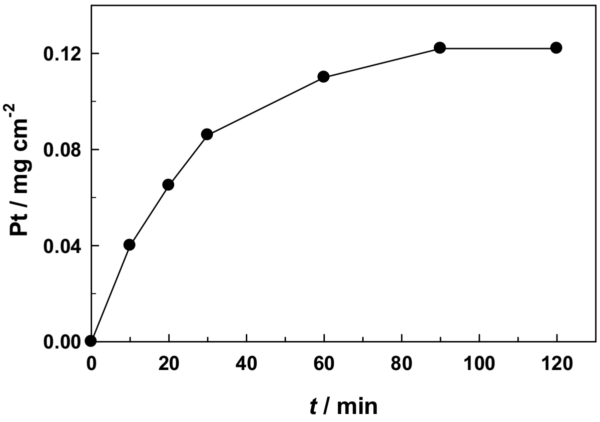

Fig. 1. Kinetic of electroless platinum deposition. Solution composition (M): H_2PtCl_6 – 0.004; dien – 0.2; NH_4OH – 0.4; $CoCl_2$ – 0.2; pH 7.5; 20 °C.

Acknowledgment

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ELECTROLESS COBALT DEPOSITION IN DIETHYLENETRIAMINE SOLUTIONS USING MORPHOLINE BORANE AS A REDUCING AGENT

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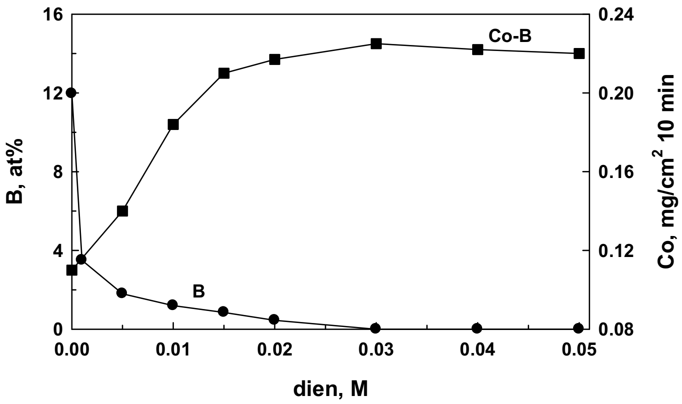
Electroless cobalt films were deposited in a neutral pH solution using morpholine borane (MB) as a reducing agent without additional activation. The suitability of MB for cobalt and nickel deposition is mentioned in some patents [1-2].

It is determined, that the rate of deposition Co and B increases with increase in concentrations of solution components, pH and temperature. The efficiency of cobalt reduction rises when the deposition is performed from the Co(II) complex with diethylenetriamine (dien). XPS data indicate that boron is incorporated into the cobalt films.



Data on electroless Co deposition using morpholine borane as reducing agent. Solution composition (M): $CoSO_4$ – 0.05; MB-0.05; pH 7.3; 30 °C.

The rate of electroless cobalt deposition increased with increase in amine concentration up to 0.03 M. Further increase dien concentration does not effect the plating rate.

Increase in dien concentration is accompanied with decrease in boron content in cobalt coatings, when dien concentration reaches and exceeds 0.03 M, the coating obtained do not contain boron.

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INVESTIGATION OF BOROHYDRIDE OXIDATION ONTO A SPONTANEOUSLY Bi-MODIFIED POLYCRYSTALLINE Pt ELECTRODE

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Sodium borohydride oxidation has been intensively studied as an electrocatalytic reaction related to fuel cell (direct borohydride fuel cells (DBFCs)) applications, in particular for further development of mobile and portable electronic devices [1-4]. The principal drawback in the performance of DBFCs is unfavoured hydrolysis reaction of sodium borohydride. Therefore, the search for efficient anode catalysts being able to suppress the hydrolysis reaction and exhibit high catalytic activity towards sodium borohydride oxidation is of fundamental importance.

In this study a polycrystalline Pt electrode modified with irreversible adsorbed Bi species has been fabricated. Spontaneous modification of the catalyst was performed by immersion of the Pt electrode into the $BiCl_3$/HCl solution under open-circuit conditions at ambient temperature. The morphology and surface composition of the prepared catalysts were examined by means of X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM), whereas electrocatalytic activity towards the oxidation of borohydride was investigated by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

It has been determined that spontaneously Bi-modified Pt catalysts contain metallic Bi and Bi-oxychloride/hydroxide/oxide and exhibit an outstanding electrocatalytic activity towards direct borohydride oxidation at fuel cell anode relevant potentials. Meanwhile hydrogen oxidation remains highly suppressed implying the inhibition of borohydride hydrolysis reaction. A considerable gain of current on the Bi-modified polycrystalline Pt electrode is supposed to be due a gradual conversion of Bi-oxychloride and Bi-hydroxy/oxy surface species into higher valent Bi-oxygenated surface species along with borohydride oxidation. Borohydride oxidation current density changes determined by CV technique were investigated in combination with EIS measurements and considered regarding the different potential regions applied. The zones of the negative resistances were identified.

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GRAPHENE SUPPORTED PtM (Mo, W) CATALYSTS FOR BOROHYDRIDE OXIDATION

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In the study presented herein a rapid microwave heating method was used to prepare the graphene supported PtM (tungsten, molybdenum) catalysts (denoted as PtW/GR or PtMo/GR) with the different Pt:M molar ratios. The graphene supported platinum-tungsten catalysts were prepared by microwave-assisted heating of Pt(IV) and W(VI) or Mo(VI) salts in ethylene glycol solutions. The prepared catalysts were characterized by means of Transmission Electron Microscopy and Inductively Coupled Plasma Optical Emission Spectroscopy. The electrocatalytic properties of the PtW/GR and PtMo/GR catalysts towards the oxidation of borohydride in an alkaline medium were investigated by means of cyclic voltammetry and chrono-techniques.

It was found that the following graphene supported platinum-tungsten catalysts with the Pt:W molar ratios equal to 1.6:1, 2.4:7 and 7.1:1 were prepared, whereas the graphene supported platinum-molybdenum catalysts with the following Pt:Mo molar ratios equal to 3:1, 7:1 and 43:1 were prepared. The synthesized PtW/GR and PtMo/GR catalysts with the different Pt:W and Pt:Mo molar ratios show an enhanced electrocatalytic activity towards the oxidation of H_2 generated by catalytic hydrolysis of BH_4^- and direct oxidation of BH_4^- comparing with the Pt/GR, W/GR or Mo/GR catalysts.

Silver nanowires and nanocones arrays as electrocatalytic electrodes

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Halogenated volatile compounds (HOCs) have recently been the object of intensive investigation, mainly due to their toxicity and mutagenicity. A broad spectrum of methods to eliminate those hazardous compounds from the natural environment has been developed. However, most of them do not guarantee a complete removal of HOCs or results in secondary contamination. Electrochemical methods seem to completely remove these compound without producing toxic by-products, though they require high energy usage. To reduce the cost and improve the efficiency of removal, cathodic materials with electrocatalytic properties are being employed.

The electrocatalytic reduction of halogenated volatile compounds is already well established in organic solutions, hence the scope of this study is the reduction of HOCs in water environment/aqueous solutions. Silver is known to possess extraordinary electrocatalytic properties towards dehalogenation of HOCs [1]. The use of silver electrode as a catalyst, results in a significant positive shift of the reduction potential peak for the electrochemical conversion of chloroform compared to the glassy carbon electrode. It was suggested by Xu et al. [2] that the electrocatalytic activity of Ag electrode can be improved by rise of its surface roughness. Therefore the aim of this research was also to investigate electrocatalytic behavior of nanostructured Ag electrodes with different morphologies and compare the obtain results with a silver disk.

The two-step anodization process in oxalic acid ($H_2C_2O_4$) was used in order to obtain highly ordered anodic aluminum oxide (AAO) membranes that served as templates to synthesize silver nanowires. The electrochemical anodization of aluminum is a cost-effective method that results in hexagonally arranged nanopores. The barrier layer at the pore bottom was removed by using a potential-shock method that results in AAO membranes with through-hole pores [3]. In order to obtain silver nanocone array electrodes, alternating multistep processes of anodization in $H_2C_2O_4$ and pore widening of Al_2O_3 in H_3PO_4 were performed. Then, a thin layer of Ag was sputter deposited, and finally, the electrodeposition of Ag nanostructures was carried out in a commercially available silver plating solution by applying a constant current density. The electrocatalytic properties of synthesized nanostructured Ag electrodes were investigated by various voltammetric techniques. All experiments were carried out in an Ar-saturated 0.1 M NaOH solution. The voltammetric experiments allow to determine kinetic parameters of the reduction process as well as values of LOD (limit of detection) and LOQ (limit of quantification).

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FABRICATION, CHARACTERIZATION AND PROPERTIES OF PtCoB/Cu CATALYSTS

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At present one of renewable energy sources is fuel cells, where chemical energy is directly converted to electrical energy. The development of cost-effective, active, and stable catalysts, able to substitute Pt or allow reducing the amount of it in low temperature fuel cell anodes is still in progress.

In this study fabrication of the PtCoB/Cu catalysts using the electroless and galvanic exchange methods is presented. A CoB adlayer, deposited on the Cu surface, was used as an underlayer for deposition of Pt nanoparticles. Electroless CoB layer was deposited on the Cu surface using borane morpholine complex as a reducing agent as described in details in Refs. [1, 2]. Then, Pt particles were deposited on the CoB/Cu electrodes by their immersion into a 1 mM H_2PtCl_6 solution at 25 ºC for 10, 30 and 60 s. Field emission scanning electron microscopy and energy dispersive X-ray spectroscopy were used to characterize the surface morphology and composition of the samples. Activity of the PtCoB/Cu catalysts towards borohydride oxidation was investigated by cyclic voltammetry.

It was found that Pt particles in size of 15-290 nm were deposited on the CoB/Cu electrodes after their immersion into the 1 mM H_2PtCl_6 solution for 10-60 s. The Pt loadings in the prepared PtCoB/Cu catalysts were in the range from 5-10 µg cm^{-2}. It has been determined that the PtCoB/Cu catalysts exhibited an enhanced electrocatalytic activity towards the oxidation of borohydride as compared to that of pure Pt and CoB/Cu.

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SYNTHESIS AND ELECTROCATALYTIC PROPERTIES OF Au-Pt CATALYST ELECTRODEPOSITED ON POLY(1,8-DIAMINOCARBAZOLE) FOR FORMIC ACID OXIDATION

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Metal nanoparticles have attracted great interest because of their unique physical and chemical properties. The surface area and the reactivity of nanostructured metal materials are much higher than those of the corresponding bulk metals, due to the high proportion of surface to bulk atoms in nanoscale particles. Therefore, metal nanoparticles are widely used as efficient catalysts for various chemical and electrochemical reactions [1]. One important area, where the development of highly effective catalyst is crucial, is fuel cell technology, and aqueous solution of formic acid (FA) is a potentially attractive fuel for fuel cells.

Among noble metal catalysts, platinum shows the highest catalytic activity for electrooxidation of formic acid. In order to achieved enhancement of catalytic efficiency, bimetallic Pt@Me systems may be formed, in which Me is Ru, Pd or Au [2]. Such an enhanced of catalytic activity is mainly attributed to the decreased number of adsorption sites for poisoning species, CO, as a result of so called "third body effect" [3].

In this work we present the results on synthesis and electrocatalytic properties of organic-inorganic hybrid systems composed of conducting polymer film and monometallic (Au, Pt) and bimetallic (Au@Pt) nanoparticles. In such composite systems, the polymer plays the role of solid support for nanostructures and also their stabilizer preventing from aggregation.

Monometallic and bimetallic nanoparticles of Au, Pt and Au@Pt were electrodeposited potentiostatistically on poly(1,8-diaminocarbazole) (PDACz)-modified glassy carbon (GC) electrode in an acidic ($HClO_4$) electrolyte. The electrocatalytic properties of these systems towards electrooxidation of formic acid are discussed in terms of electrodeposition potential, molar ratios of the two metal precursors, $AuCl_4^-$ and $PtCl_6^{2-}$, and are related to the properties of the systems prepared by electroless synthesis of Au@Pt nanoparticles inside the poly(1,8-diaminocarbazole) film. The role of the polymer matrix in this process is also discussed.

The form and composition of bimetallic alloys prepared at different molar ratios of the two metal precursors were studied by means of SEM and HRTEM.

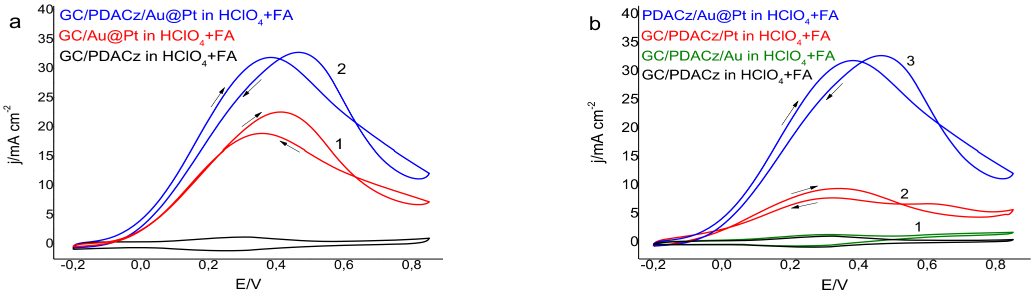

Fig. 1. Comparison of cyclic voltammograms obtained on GC electrode covered with (a): Au@Pt (curve 1) and PDACz/Au@Pt (2) and (b): PDACz/Au (1), PDACz/Pt (2) and PDACz/Au@Pt (3) in aqueous solution of 0.1 M $HClO_4$ + 0.2 M HCOOH.

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ELECTROCATALYTIC PROPERTIES OF ELECTRODEPOSITED MOLYBDENUM ALLOYS FOR HYDROGEN EVOLUTION REACTION

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The technological potential of hydrogen leads to the sustainable grow of the world economy and reducing the emissions of carbon dioxide [1]. Usually expensive noble metals are typically applied in electrocatalytic systems for hydrogen evolution and replacement of ones is attractive from the various points of view. The electroplated metallic molybdenum or alloys with a high content of Mo can be used as electrodes for hydrogen evolution. Moreover, in [2] authors declared the fact of metallic molybdenum electrodeposition from aqueous solutions, and we further discuss on this findings. The electrochemical hydrogen evolution reaction can be effectively catalyzed also by binary Mo alloys containing transition metals, such as Ni, Co and Fe [3, 4].

Molybdenum alloys containing up to 54 at.% of Mo were electrodeposited under galvanostatic mode at 30 °C. The selection of ammonia-acetate electrolyte was inspired by the assumption that the deposits with a high Mo content can be deposited. The scanning electron microscopy observations showed the compact fine-grained structure of the coatings (Fig. 1).

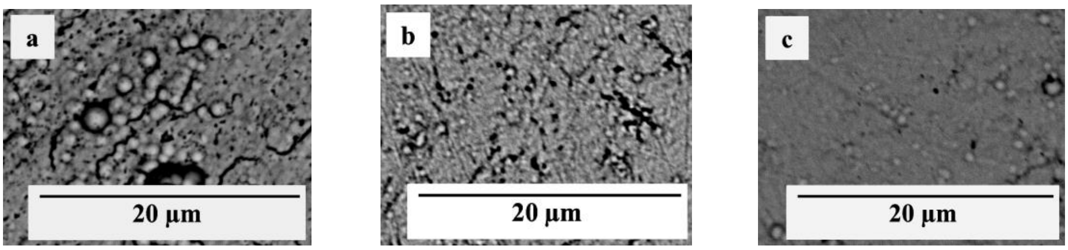

***Fig. 1.** SEM micrographs of (a) Fe-54 Mo; (b) Co-52 Mo; (c) Ni-54 Mo alloy coatings (in at.%).*

Electrocatalytic activity of electrodeposited Co-Mo, Fe-Mo and Ni-Mo alloy coatings was studied for hydrogen evolution reaction in alkaline solution by cathodic polarization curves recorded in 30 % NaOH solution in the temperature range of 25-65 °C. The exchange current density of hydrogen for the Co-Mo and Fe-Mo deposits were considerably higher than of those for Ni-Mo alloy coatings in the whole range of the temperature. It was found that the exchange current densities hydrogen reaction grow with the increasing the temperature. The Co-Mo and Fe-Mo alloy coatings demonstrated the highest catalytic effect for hydrogen evolution reaction at 65 °C (0.45 A/cm^2).

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ELECTROCOPOLYMERIZATION OF B-GROUP VITAMINS

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As known, riboflavin (RF, Vit. B_2) and folic acid (FA, Vit. B_9) belong to B-group vitamins. Their determination in human body and food is essential. Both vitamins are important to organism in flavoprotein enzymatic reactions, producing new cells, preventing changes to DNA, etc. Also they can prevent from several diseases such as: stomatitis, child birth defects, anemia and even cancer. Morever, it has been demonstrated that RF and FA due to their electron delocalization are electrochemically active and can be polymerized to form conducting polymers [1,2].

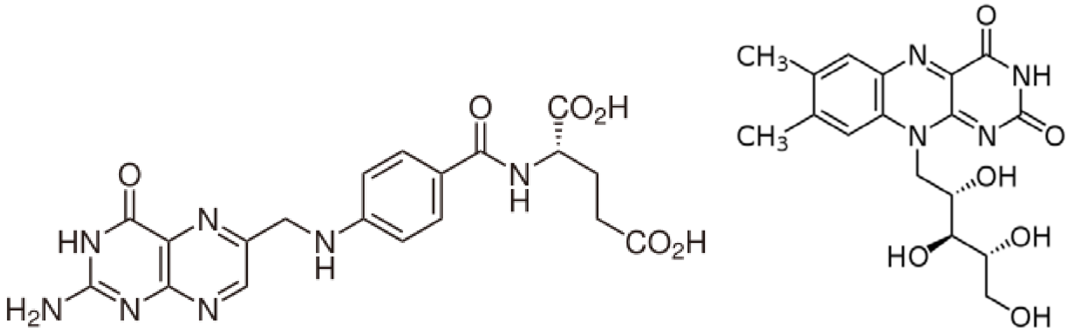

Figure 1. Riboflavin (right) and folic acid (left) chemical structures [1,2].

In the previous work [1], the conditions of the electrochemical polymerization of folic acid have been optimized. It includes the solution pH, supporting electrolyte, potential window and number of polymerization cycles of cyclic voltammetry. However, electrochemical investigations (square wave voltammetry and cyclic voltammetry) show that polyfolic acid (PFA) is washed out of the electrode surface, and polymer needs stabilizing composite layer, for example: modified graphene in aqueous chitosan solution (G_m-Chit) composite [3]. In order to improve PFA stability without extra modification layer, folic acid is copolymerized with another electroactive vitamin - riboflavin. The same polymerization conditions (solution pH, supporting electrolyte, potential window and number of polymerization cycles of cyclic voltammetry) are being optimized to form the most stable copolymer on carbon electrode.

Further, PFA-PRF is used as mediator for ascorbate sensing. In previous work [4] G_m-Chit composite (containing 10 pg mL^{-1} of modified graphene) modified glassy carbon electrode (GCE) showed the best sensitivity (247 ± 8 µA mM^{-1} cm^{-2}) for ascorbate. In this work, two sensors (PFA-PRF/GCE and G_m-Chit/PFA-PRF/GCE) were constructed in order to study the influence of the additional layer to the sensor sensitivity and to compare the analytical parameters with previous sensors. The mentioned results will be presented.

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Investigation of conductive polymers influence on ion-selective electrodes based on derivatives of benzo-15-crown-5

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The ability of precise determination of potassium ions activity is one of the most important part of a diagnostics of many diseases as well as in routine health screening which is conducted in large number of laboratories for medical analysis. The atomic absorption spectrometry (AAS), flame emission spectrophotometry and ion selective electrodes (ISE) are currently leading methods of a determination of K^+ concentration in human blood. The potentiometric method with the use of the ISE is one of the cheapest and fastest. Synthesized by our group, commercially unavailable, highly lipophilic derivatives of benzo-15-crown-5 especially bis(benzo-15-crown-5) ethers were tested for selective complexation of potassium ions in the structure of *solid-contact* miniature ion-selective electrodes based on glassy carbon. Results which were obtained previously for classic electrodes [1,2] exhibited significantly lower properties than ion selective electrodes electrochemically modified by conductive polymers.

Conductive polymers were electrodeposited directly on glassy carbon surface from electrolyte containing monomer and source of various counter ions, *e.g.* Cl^-, ClO_4^-, PSS. Three types of polymers were tested: polyindole (PIN), polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT). The most promising results were obtained for PEDOT:PSS modified electrodes. The optimization of electrodeposition consists of selection of: *i*) monomer electrooxidation method (potentiostatic, potentiodynamic and galvanostatic) and *ii*) charge consumed for polymerization. Membrane, which is the main element of the properly functioning potentiometric sensor was constructed with typical membranes composition that contains macrocyclic ionophore, plasticizer, PVC and salt with lipophilic anion. The best selectivity coefficient $\log_{K/Na}$ for electrodes with derivatives of benzo-15-crown-5 was equal to about $\log_{K/Na} = -5$ and was obtained for a potentiostaticly electrodeposited PEDOT:PSS. Next studies will be focus on further optimization of the electropolymerization conditions and membrane composition. The comparison between the best of obtained ion-selective electrode and ion-selective electrode with commercially available valinomycin will be performed for a sample of human blood plasma.

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ELECTROCHEMICAL STUDIES OF PURE MAGNESIUM SURFACE COATED WITH ELECTROSPUN CELLULOSE ACETATE (CA) NANOFIBERS

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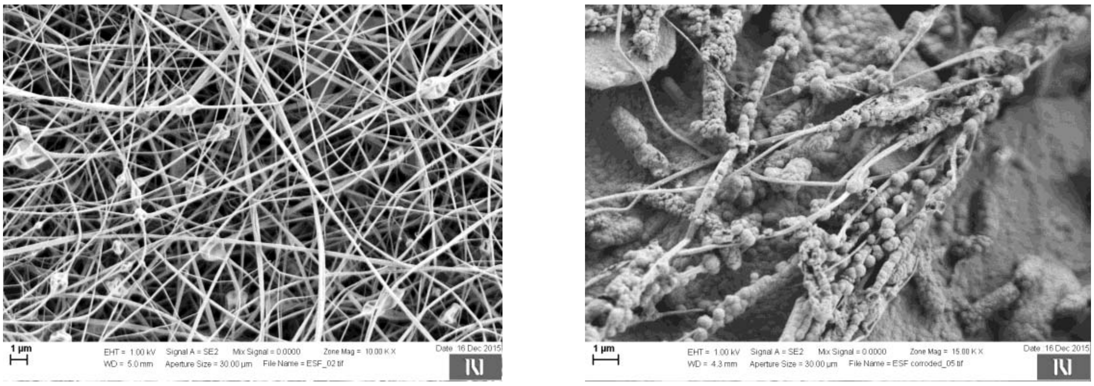
Magnesium and Mg alloys have gained great interest in the orthopaedics and tissue engineering applications because of their mechanical properties being close to the natural bone [1,2]. However, the rapid corrosion rate represents the main drawback of the magnesium. To overcome this problem, electrospun cellulose acetate (CA) nanofibrous membranes were coated on the magnesium surface and its efficiency on corrosion behaviour was examined.

Electrospinning is relatively simple technique for production of nano-scale fibers, which possess unique properties (high (active) surface area to volume ratio and a tuneable porous structure) useful in the field of implants and tissue engineering [3]. Electrospun cellulose acetate (CA) nanofibers have shown great potential in different biomedical applications [4].

In our study the electrochemical behaviour of CA coated Mg was investigated in simulated body fluid (SBF) at 37°C for 24 h. The corrosion performance was evaluated through the analysis of corrosion resistance with time by using electrochemical impedance spectroscopy (EIS) and corrosion current density by potentiodynamic polarization measurements. The CA electrospun nanofibrous coating stability was confirmed by SEM images and FTIR spectroscopy analysis.



(a) (b)

Figure: SEM images of Mg alloy surface coated with CA nanofibers
a) before and b) after the electrochemical testing in SBF at 37°C for 24 h.

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THE IMPACT OF POLYMERISATION CONDITIONS ONTO THE MORPHOLOGY AND PROPERTIES OF ORDERED INORGANIC-ORGANIC HETEROJUNCTION

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Composite materials based on conducting polymer and inorganic semiconductor undoubtedly is regarded as one of the most promising classes of prospective photoactive materials. The combination of metal oxide characterized with highly ordered nano-architecture (e.g. titania nanotubes) and an electroactive polymer creates opportunities to construct a high quality p-n junction with expected synergistic effects in electronic and ionic properties between its counterparts [1,2]. The key role in the uniform distribution of organic material over inorganic one is played by the type and conditions of preparation method. According to many reports, the electrochemical approach allows direct growth of polymer on metal oxide layer and the morphology of the whole heterojunction could be easily controlled *via* variation of electrochemical procedure [3].

Here, we show the formation of inorganic-organic composite material where as inorganic part highly ordered titania and as organic element conducting polymer: poly(3,4-ethylenedioxythiophene) was used. Titania nanotubes were formed carrying out two-steps anodization and then were subjected to calcination procedure [4]. Finally, TiO_2 sample underwent hydrogenation in order to decrease its resistance and to activate its surface.

The polymer deposition was carried out under different polymerization protocols: potentiostatically at selected oxidation potentials and potentiodynamically. Both approaches were realized when electrode covered by TiO_2 nanotubes was immersed in the solution containing monomer and counter ion. It will be shown that both composition and nanoscale architecture of the hybrid can be precisely controlled by employing carefully designed electrochemical method. Furthermore, the photoactivity of obtained p-n junction depending on the deposition conditions will be demonstrated.

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GRAPHENE SUPPORTED TIN-BASED NANOCOMPOSITE ANODES AS FLEXIBLE AND FREE–STANDING FOR HIGH PERFORMANCE LI–ION BATTERIES

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Because of having four times the theoretical capacity of the general anode material (graphite), tin dioxide (SnO_2) is an attractive material for anodes in lithium ion batteries. On the other hand the poor cycling stability of the Tin based anode materials because of the severe volume expansion during the intercalation/deintercalation process inhibits its application. Many attractive solutions have been developed to overcome these problems. Fabricating nanostructured tin oxide which includes nanotubes/nanofibres/nanowires, nanosheets and porous structure is the first approach [1]. The second approach is to form a dispersed tin oxide nanostructures in a buffering matrix that could support the mechanical effects of the volume changes of SnO_2 during the charge-discharge process [2]. Graphene supported structures can provide good electrical conductivity and a buffer layer to compensate the volume change of anode material [3,4].

Herein a facile and novel method for preparation of graphene supported tin-based nanocomposites was reported. Tinoxide was synthesized via a microwave-assisted method using $SnCl_2 \cdot 2H_2O$ as raw material. Graphene oxide was produced by Hummer [5] method and reduced to graphene with hydrazine hydrate solution. A trace amount multi-wall carbon nano tube (MWCNT) was added between graphene layers to preventing aggregation and increasing to surface area and pore volume [6]. Tinoxide that synthesized via a microwave-assisted method was introduced to the produced Graphene/MWCNT frame structure which is attributed to buffer effect for the volume change of SnO_2 during the charge-discharge process. Graphene supported tin-based nanocomposite anodes were prepared with with vacuum filtration technique as flexible and free-standing. The structure and morphology of the nanocomposite electrodes were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy. The electrochemical characterization tests including galvanostatic charge/discharge, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurement of the electrodes were carried out by using an CR2016 test cell. These high performance graphene supported composite electrodes provide competitive properties relative to other electrode materials for Li-ion batteries.

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α–MnO_2/MWCNT/GRAPHENE NANOCOMPOSITE ELECTRODES AND THEIR ELECTROCHEMICAL BEHAVIOURS FOR Li–O_2 BATTERIES

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Li-O_2 batteries have attracted academic and technological interest for the development of energy storage systems and vehicle energy. The Li-O_2 batteries have a theoretical energy density high up to $5200 WhKg^{-1}$ (including the mass of O_2), close to the energy density of fossil energy sources [1]. Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) which take place in the discharge/charge process at the air-cathode of Li–O_2 batteries are important processes which control the overall cell performance [2]. α–MnO_2 has received attention as catalyst because of its advantages, as abundance, low cost, environmental friendliness and favourable ORR and OER activity [3]. Since α–MnO_2 has low electrical conductivity, it needs to be combine with highly conductive supports like MWCNT and Graphene [4].

In this study, α–MnO_2/MWCNT/Graphene nanocomposite electrodes were produced by a facile method as flexible and free–standing. Graphene oxide was produced by Hummer method [5] and reduced to graphene with hydrazine hydrate solution. Multi-wall carbon nano tubes were added at 1:1 (w_{GO}/w_{MWCNT}) ratio between graphene layers to prevent from aggregation of graphene layers and increase interlayer distance, surface area and pore volume. α–MnO_2 was synthesized as nanorods by using $KMnO_4$ and $MnSO_4$. A series of α–MnO_2/MWCNT/Graphene nanocomposite containing different values of α–MnO_2 were produced and used as electrode for Li–O_2 batteries. The structure and morphology of the nanocomposite electrodes were characterized by X-ray diffraction, scanning electron microscopy and N_2 adsorption/desorption. The electrochemical characterization tests including galvanostatic charge/discharge, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurement of the electrodes were carried out by using an ECC-Air test cell.

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INVESTIGATION OF GRAPHENE/$LiNiPO_4$-C NANOCOMPOSITE CATHODE ELECTRODES FOR ENHANCED LITHIUM STORAGE BATTERY APPLICATIONS

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In recent years, rechargeable lithium-ion batteries with high energy density, long cycle life and environmental benign have been considered as potential power sources for portable electronic devices and hybrid electric vehicles. However, cost, lifetime and safety prohibit its extensive application. Among the various cathode materials for lithium-ion batteries, olivine-type structured $LiFePO_4$ has been extensively studied as the most promising cathode material, owing to its high theoretical specific capacity (170 mAh g^{-1}), low cost, good safety and acceptable environmental characteristics. $LiMnPO_4$ has been widely investigated so far, and the latest progress on $LiMnPO_4$ has attracted the intensive attention of lithium ion battery industry.[1] In contrast to $LiFePO_4$ and $LiMnPO_4$, the reports[2,3] on $LiNiPO_4$ are very limited due to its high redox potential, which exceeds the stable limitation of current electrolytes based on carbonate solvents. In recent years, lithium metal phosphate ($LiMPO_4$) with the olivine structure has received a lot of attention to be a potential candidate for cathode materials in lithium ion batteries [4-6]. Unlike lithium transition metal oxides (LMO), $LiMPO_4$ does not liberate oxygen on decomposition. In addition, $LiMPO_4$ is cheaper, benign, and environmentally friendly and has greater stability than LMO.

In this study, $LiNiPO_4$ was prepared by the sol-gel method with tartaric acid and calcined in air. Sol-gel has considerable advantages of good mixing of the starting materials and good chemical homogeneity of the product. The as-synthesized pristine $LiNiPO_4$ powders were then subjected to microwave hydrothermal carburization process in order to obtain $LiNiPO_4$-C composite cathode electrodes. $LiNiPO_4$-C composite cathode electrodes were dispersed in bidistilled water and the as-prepared suspension was poured into the funnel and filtered through a porous polyvinylidene fluoride (PVDF) membrane (Millipore, 0.22 μm pore size, 47 mm in diameter) by positive pressure from a vacuum pump. Since the solvent passed through the pores of the membrane, the $LiNiPO_4$-C/graphene material was trapped on the membrane surface, forming a mat. The resultant mat, together with the PVDF membrane, was then dried in an oven for 2h, and the mat could finally be peeled off from the membrane. The resulting LiNiPO4 powders obtained were then characterized by thermogravimetric analysis (TGA),) and X-ray diffraction (XRD). The formation mechanism for the synthesis of $LiNiPO_4$ is also discussed in this paper. To the best of our knowledge, reports on $LiNiPO_4$ nanocrystalline structured powders prepared by tartaric acid and calcined in air are rare.

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HIGH-CAPACITY GRAPEHEN/Cu_6Sn_5-C COMPOSITE THIN FILM ANODES FOR LITHIUM ION BATTERIES

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Tin anodes have attracted much attention because it delivers a capacity up to three times higher than that of graphite. Theoretically, one tin atom can maximally react with 4.4 lithium atoms to form $Li_{4.4}Sn$ alloy, reaching a capacity of 993 mAh g^{-1} [1]. However, the large amount of lithium insertion/extraction into/from Sn causes a large volume change (about 300%), which causes pulverization of tin particles and loss of contact with current collector, resulting in poor electrochemical performance [2]. Various approaches have been carried out to overcome this issue, including the use of nanosized active materials, active/inactive composite materials, and tin-copper intermetallic alloys. These studies have resulted in improvements of the electrochemical performance of Sn-based anodes, but only to a limited extent. In commercial Li-ion batteries, the metal current collector on the anode side is usually a 10 μm thick copper sheet with an areal density $\approx$10 mg/cm^2. This copper sheet is a relatively heavy component in a lithium ion cell, which is comparable in weight to the anode active material and accounts for $\approx$10% of the total weight of the cell [3-6].

In this study, firstly Cu_6Sn_5 nanoparticles were synthesized by chemical reduction method. This method is more suitable for the Cu_6Sn_5 nanoparticle synthesis because the chemical reduction can use a low temperature, resulting in a better control of thermal oxidation of Cu_6Sn_5 nanoparticles. During the synthesis process, surfactants were used to protect the Sn nanoparticle from oxidation. Multilayer graphene was obtained from graphite flakes using the method described by Hummers. Free-standing and flexible Cu_6Sn_5/Graphene nanocomposite paper produced by a vacuum filtration technique for use as an anode electrode without using any binder or additives. The unique feature of the sheet-to-sheet assembly (2D–2D) is that each tin and graphene nanosheet will have maximum electrical contact with graphene, which could result in high conductivity of the hybrids. Moreover, strong interfacial interactions between tin and graphene contribute to a robust linking between the two components, which further promoted interfacial electron and lithium ion transport. Benefitting from the morphological compatibility and intimate integration between tin and graphene, the binder-free and free-standing hybrid electrode exhibited significantly enhanced lithium storage properties in terms of higher specific capacities, better cyclic stability and rate capability compared to traditional binder-containing electrodes and pure tin electrodes.

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AMORPHOUS MIXTURES OF SOLVENTS AND LITHIUM ELECTROLYTES

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The lithium-ion technology is developing very fast in the past few years. Most of portable electronic devices are in need of lithium-ion batteries and we almost cannot imagine the future world without this type of cells. But still there are problems with battery performance at extremely low temperatures. It is mostly due to crystallization of the electrolyte while freezing. This behavior of electrolyte we find very hazardous because of possible electrode damage and battery destruction. Avoidance of this problem is crucial for applications at very low temperatures or possibility of battery cooling below -70°C.

Some of the ionic liquids (ILs) or electrolytes based on IL show only amorphous state without any other phase transitions. However, their conductivity performance is still very poor. That is why we may gain an electrolyte that possibly would not damage the electrodes, but also would not be able to conduct. Our goal was to obtain the electrolyte without ILs use, which would have very low glass transition temperature T_g and would exhibit relatively good conductivity.

The new type of solvent mixtures will be presented. Results of DSC (differential scanning calorimetry) measurements of both new mixtures and electrolytes will be shown. The measurements of viscosity, conductivity and cyclic voltammetry would be the topic of this presentation as well.

Two lithium salts were used in this work. $LiPF_6$ (lithium hexafluorophosphate), the most popular one in commercial lithium-ion batteries and LiTDI (lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide), the new salt synthesized at Faculty of Chemistry, Warsaw University of Technology. Both salts were fully investigated. $LiPF_6$ is the most popular salt, but decomposes when only traces of water are present. LiTDI can be dissolved in water and it does not show any signs of decomposition after drying.

We found that mixing two crystalizing solvents results in the systems that do not possess any phase transitions except for glass transition. We have chosen the solvents that have negligible vapor pressure, because of the safety issues. The liquid solvent in electrolyte would not evaporate inside the battery cell at the room temperature, so it would decrease the risk of fire outbreak.

HIGH REVERSIBLE MnO_2/GRAPHENE CATHODES FOR IMPROVED Li-ION BATTERIES

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Up-to-date electronic devices such as mobile phones, laptop computers, and electric vehicles require high-performance batteries to power them. So far, lithium-ion batteries are the most developed energy storage technology to satisfy the requirement because of their high energy density, high voltage, and light weight. It is generally recognized that the selection of electrode materials (e.g., anode and cathode materials) is a crucial factor in determining the performance of lithium batteries [1]. Unfortunately, the initial commercial introduction of Li-ion batteries composed of $LiCoO_2$ (cathode) and graphite (anode) exhibit the cell performance, which has fallen behind the rise in demand for higher energy and power density, longer cycling life, and safer batteries [2]. Recent studies have shown that transition metal oxides have significant advantages in lithium ion batteries due to their high theoretical capacity, high intrinsic specific density, low cost, low toxicity and natural abundance [3]. Among these transition metal oxide compounds, Manganese dioxide (MnO_2) can exist as α, β, γ, λ, δ and ε polymorphs which are considered as promising cathode materials for primary lithium batteries [4-6]. However, low reversible capacity and poor cycle stability of MnO_2 compound limits their usage in Li-ion batteries. The electrochemical properties of MnO_2 are highly influenced by structure, morphology and synthetic method.

Until recently, in most reports on MnO_2-based cathodes they are cycled less than 50 times and always suffer from declining capacity fading at high current densities. Thus, excellent cycle stabilities and intercalation capacities for MnO_2 cathodes need to be achieved, especially at high rates. Graphene nanosheets are more promising supporting materials because of their favorable electrical conductivity, high specific surface area and excellent structural flexibility. In this paper, we prepared α, β, γ polymorphs of MnO_2 structures via facile microwave hydrothermal method. Then, graphene/MnO_2 flexible freestanding cathode electrodes were produced through a facile vacuum filtration technique. The structural and electrochemical properties of obtained freestanding electrodes were evaluated. To the best of our knowledge, it is the first investigation of graphene/MnO_2 freestanding electrodes with so much high specific capacity and excellent cycle performance, and it is firstly reported.

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IMPROVED ELECTROCHEMICAL PERFORMANCE OF GRAPHENE/$LiMn_2O_4$ NANOCOMPOSITES FOR Li-ION BATTERIES

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Due to the technological improvements, portable consumer electronics, such as mobile phones and notebook computers require more energy that makes lithium-ion batteries are the dominant power source. In addition, to meet the environmental concern for global issue, lithium-ion batteries are also in the focus for electric vehicle and hybrid electric vehicle to save oil and to decrease exhaust emissions. The increasing demands for high-energy density and high-power density of batteries have attracted investigators to develop new materials for lithium-ion batteries. It is well known that, when spinel $LiMn_2O_4$ cathode electrode for Li-ion batteries overdischarged at the 3 V level, a structural transformation from cubic spinel phase to tetragonal rock-salt phase will happen, i.e., the so called Jahn–Teller distortion, and results in a fast fading of capacity [1, 2]. The capacity fading of pristine lithium manganese oxide is strongly influenced from Jahn–Teller distortion occurring on the surface of the particles and manganese dissolution into the electrolyte, especially at elevated temperatures. To overcome these drawbacks, two strategies were mainly pursued: elements substitution or oxygen excess to increase the oxidation state of Mn for suppressing the Jahn–Teller effect and surface modification or coating for suppressing the dissolution of Mn into the electrolyte [3]. The first strategy of doping is known to be an effective route. It is reported that substitution of Mn ions with other metals such as Mg, Al, Cr, Co, Ni, Zn, Mg, Ga slows dissolution of Mn from the cathode into the electrolyte [4]. Partial replacing Mn, could increase the average valence of Mn in $LiMn_2O_4$, and could depress the Jahn–Teller effect [5].

In this study, it is aimed to produce a cathode electrode based hybrid Graphene/$LiMn_2O_4$ structure which will overcome the intrinsic safety limitations and the cost. Lithium manganese oxide $LiMn_2O_4$ has been produced by a microwave assistant hydrothermal synthesis. Spinel $LiMn_2O_4$ particle surfaces were coated graphene nanosheets by controlling the thickness of the graphene layers. Graphene/$LiMn_2O_4$ cathode electrode exhibited higher rate capability, specific capacity and cycle performance when compared with pristine $LiMn_2O_4$ electrode. This is due high surface area of $LiMn_2O_4$ nanoparticles and good electronic conductivity of graphene. The improved electrochemical performance of the graphene coated $LiMn_2O_4$ electrode was attributed to decreasing Mn dissolution into electrolyte. The improved electrochemical performance of the $LiMn_2O_4$/graphene nanocomposite makes it the promising cathode material for high-performance lithium-ion batteries.

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OPTIMIZATION SiO_2 AND Al_2O_3 NANOPARTICLES ON THE STABILITY OF TEGDME-$LiPF_6$/ PEO ELECTROLYTES FOR LI-AIR BATTERIES

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Energy and the environment are among the most important issues of the twenty-first century.. In response, energy conversion from renewable sources has been considered as a promising solution to decrease CO_2 emissions that has paved the way for governmental incentives toward both the implementation of electric vehicles and hybrid electric vehicles [1, 2]. The worldwide energy shortage has driven people to replace the fossil fuels by green energy sources, such as solar, wind, tide and biomass and, energy storage devices are essential components of any renewable energy source [3]. Rechargeable lithium-air (Li-air) batteries have the potential to provide gravimetric energy three to five times greater than that of conventional Li-ion batteries. Identifying the appropriate electrolyte is one prerequisite for the application of Li-air batteries [4]. In this work, an ether-based electrolyte containing TEGDME/$LiPF_6$ was optimized. In order to prevent air breathing cathode clogging by lithium oxide and provide stability of Li metal anode, an extensive work was carried out to provide most functional polymeric additives and Poly(ethylene oxide) (PEO) was found one of the most effective polymers as recently stated by different a work [5]. PEO inorganic filler was chosen to add into the electrolyte to prevent conductivity decrease and provide stability of the air cell. Nano Al_2O_3 and SiO_2 were incorporated into TEGDME- $LiPF_6$/PEO composite homogenously. Graphene/α-MnO_2 nanocomposite air breathing structure was used as cathode. In the carbon cathode materials, Graphene nanosheets (GNS) have been reported as ideal cathode materials for Li-O_2 batteries because of their unique morphology and structure that provide both diffusion channels for O_2 and active sites for cathode reactions. On the other hand, α-MnO_2 catalysts is helpful to increase the reversibility of the lithium-oxygen interactions due to hollandite type crystal structure of MnO_2 consists 2x2 tunnels. A lithium disk was used as anode while glass fiber was used as the separator in ECC-Air test cell. The cells were cyclically tested using 0.1 mA/cm^2 current density over a voltage range of 2.15-4.25 V. Electrochemical impedance spectroscopy (EIS) measurements was applied to investigate the effect of the polymeric and inorganic additives on the resistivity of the electrolyte. Results revealed that nanocomposite electrolyte structures provided not only good discharge capacity but also excellent stability of the Li-air cells. Excellent cycleability was obtained by using the nanocomposite electrolytes with both organic (PEO) and inorganic (Al_2O_3, SiO_2) additions. After the electrochemical cycling tests, no significant capacity fade was detected and studies show the air cell shows excellent stability with increasing cycle number.

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Synthesis and Characterization of Graphene/MWCNT/Silicon Free-Standing Electrodes for Lithium-Ion Batteries

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Lithium-Ion batteries are the most commonly used batteries in the electronic market and the energy storage systems of electrical vehicles [1]. However enhancing life span and energy density is still one of the most important deals of these systems. Commercial graphite anodes with their theoretical capacity of 372 $mAhg^{-1}$ are not enough for further development and silicon with 4200$mAhg^{-1}$capacity is the greatest candidate for future lithium ion battery anodes [2]. Despite of highest theoretical capacity, volume variations during lithiation, causes pulverization and failure of electrode due to high mechanical stress [3]. There are many researches in order to solve this problem and yet there is not any study which will make silicon available practically.

We report a work which was conducted to be able to increase the cycle life of silicon anodes by utilizing novel composite structure. In this work conventional Si powder and Graphene/MWCNT/Si free standing composite anodes were produced in order to emphasize the effect of Graphene/MWCNT/Si composite anode structure. Si powder anodes were produced from Si powder slurry on copper current collectors with conventional route. Free – standing composite anodes (binder-free) were produced via vacuum filtration from well dispersion of Graphene, MWCNT and Nano sized (100 nm) silicon powders. Graphene which was used in this study was synthesized from well-known Hummers method and hydrazine reduction of graphene oxide. The morphological and phase characterization of either type of electrodes were performed via X-Ray Diffraction analysis, RAMAN spectroscopy and scanning electron microscopy techniques. In order to reveal the role of surface area on the electrochemical performance of anodes BET surface test were used for both anode types. In the stage of electrochemical performance analysis galvanostatic charge/discharge, cyclic voltammetry and electrochemical impedance spectroscopy analyses were carried out.

Keywords: Silicon, Graphene, Li-Ion, MWCNT.

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NEW TRIVALENT IMIDAZOLE-DERIVED SALT FOR LITHIUM-ION CELL ELECTROLYTE

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Lithium-ion cells are still the fastest developing energy storage technology. Most of the research is directed towards electrode materials evolution due to their main influence on cell capacity. Electrolyte, central component connecting the electrodes, needs bigger focus because of its limitations, which also define the limitations of the whole cell. The most important of them are: electrochemical stability (cathode material choice limitation), thermal stability (limiting applications of the cell or enforcing use of cooling devices) and conductivity/lithium cation transference number (limiting maximum current of the cell). As solvents and lithium cation are constant parts of the electrolyte, the only variable that affects all properties mentioned above is the anion.

Apart from scarce works on sulfonyl imide derivatives, even in terms of basic parameters, little is known about multivalent lithium salts' behavior in electrolytes [1-3]. Here we present the new trivalent lithium salt dedicated to electrolytes for lithium-ion cells. Trilithium 2,2',2''-tris(trifluoromethyl)benzotris(imidazolate) (Li_3BTI) have been synthesized and its performance in PC and EC:DMC solutions have been examined. The structure and stability of this new lithium salt was fully characterized by NMR and Raman techniques as well as thermal methods. Basic electrochemical parameters of electrolytes based on this salt were investigated by linear sweep voltammetry, lithium cation transference number and conductivity measurements. The salt was designed specifically to manifest extraordinarily high lithium cation transference number (0.73 in EC:DMC 1:1 ratio mixture). However this new salt exhibits also thermal stability of 160 °C and electrochemical stability up to 4.5 V vs Li, as well as conductivities of the 1 mS cm^{-1} order of magnitude in liquid electrolytes. Promising compatibility results of the obtained electrolyte against Si/C composite anodes [4] will also be presented.

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TERNARY MIXTURES OF IONIC LIQUIDS AND LITHIUM SALT WITH SOLVATED CATION AS Li-CONDUCING ELECTROLYTE

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The steadily increasing demand for energy in the modern world requires more intense research in the field of development and improvement of energy storage systems. The most common cells in portable electronics are Lithium-Ion Batteries (LIBs), which have favorable properties, such as low weight, high energy density and small self-discharge effects. That is the reason why they are in constant development and steadily improving. While most of the scientific interest is focused on electrode materials, it is the electrolyte requiring more consideration due to its important role and several limitations.

Electrolytes used in LIBs nowadays mostly consist of $LiPF_6$ salt and mixture of organic solvents, which components can be dangerous. Ionic liquids (ILs), salts in the liquid state below 100°C, can be helpful in removing these unsafe substances. The properties of ILs, i.e. low volatility, high thermal stability, high ionic conductivity, wide electrochemical windows and wide operating temperature range make a huge potential of application for this class of compounds. These advantageous properties suggest ILs as excellent solvents in electrolytes for electrochemical devices [1-3]. Obviously, ILs have also disadvantages when compared with organic solvents: higher melting point (sometimes higher than room temperature), high viscosity, low transference numbers of lithium cation, decrease of ionic conductivity for higher concentration of lithium salt in ILs and worse compatibility with electrodes.

In order to reduce these disadvantages we have decided to create more mobile solvated lithium cation after analysis of crystallographic investigation. In these molecules ligand – short chain oligomer molecules strongly coordinate Li^+ ions and form a solvated cation. Such solvate of Li^+ and properly chosen oligomer allows to create single cationic species and receive higher lithium cation conductivity and transference numbers.

We would like to present these newest result of measurements on ternary system containing LiTDI (lithium 4,5-dicyano-2-(trifluoromethane)imidazole, proprietary of WUT) that shows many advantages over commercially available salts. It has better electrochemical and thermal stability (and no aluminum corrosion), stability in case of a moisture presence, good conductivity, non-toxicity and low-cost production [4,5]. Sodium salt NaTDI was also investigated with a great success [6]. Ionic liquids used in our measurements were also based on TDI anion.

It will be confirmed that our method improve the electrochemical properties of the previously investigated binary system containing LiTDI salt dissolved in the XMImTDI ionic liquid [7].Improvements include the conductivity, lithium cation transference numbers, viscosity and electrochemical stability measurements.

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STRUCTURAL AND ELECTROCHEMICAL CHARACTERIZATION OF $Li_3Fe_2(PO_4)_3$ AS A CATHODE ELECTRODE FOR ENERGY STORAGE APPLICATIONS

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Lithium secondary batteries have been considered as an attractive power source for a wide variety of applications, such as cellular phones, notebook computers, camcorders, electric vehicles, etc. Recently, $LiFePO_4$ has been extensively studied for use as cathode in rechargeable lithium ion batteries due to its low cost, high reversibility and safety [1]. This material has a relatively larger theoretical capacity of 170 mAh g^{-1} compared with other iron-based compounds [2]. Olivines have been the subject of intensive study due to their redox behavior. Complete solid solution on the iron site has been found for most divalent cations of comparable size, and such behavior is found. Trivalent cations could be incorporated onto the iron site, then that might lead to vacancies on the lithium site because of the need for charge balance [3]. Those vacancies might be expected to lead to enhanced lithium-ion conductivity, and therefore higher power capabilities, a key requirement for batteries to be used for electric vehicle propulsion, whether in hybrid electric vehicles, plug-in hybrid electric vehicles, or all electric configurations. Among the iron compounds, $Li_3Fe_2(PO_4)_3$ can be used as positive poles vs. lithium anode [4]. Comparing $LiFePO_4$ and $Li_3Fe_2(PO_4)_3$ as positive materials shows that all of them have been used successfully as cathode of Li-ion batteries commercially. These materials demonstrated good reversibility for the Fe^{3+}/Fe^{2+} couple redox [5]. Iron compounds have the advantages of low cost, excellent thermal stability, satisfactory safety, low toxicity and natural abundance. Meanwhile lithium iron phosphates have received much attention as an interesting cathode material for Li-ion batteries [6].

In this work, a new synthesis method, using an alcoholic colloidal suspension, was developed by a sequence of systematic chemical reactions. Our attention on the synthesis of $Li_3Fe_2(PO_4)_3$ by a new sol–gel c method based on citric acid as gel making agent to synthesis uniform nanostructures. The advantages of the synthesis method has been used in this work are low cost of raw material, simple process, short synthesis time. The presented method can be used to produce the nanomaterials in small and large amounts. The synthesized compound was used as working electrode material in cyclic voltammetry (CV) and cathode material in lithium-ion batteries. The obtained results by CV and battery tests showed that the sample has good reversibility, excellent discharge capacity and long cycle life.

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FORMATION AND INVESTIGATION OF Fe_2O_3/Cu_xO HETEROJUNCTION FOR POSSIBLE USE IN SOLAR ENERGY CONVERSION

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Ever increasing importance of renewable energy resources promotes active search for semiconductor materials and their composites, which could be used for efficient solar-to-electric or solar-to-chemical energy conversion. Main requirements that should be met by these materials are low cost, stability and efficiency. Various photovoltaic and photoelectrochemical systems as well as their combinations are being investigated with the purpose of achieving higher values of energy conversion efficiency. Application of metal oxides for both photovoltaic and photoelectrochemical conversion has been attracting more and more attention recently [1], because these materials are chemically stable, environmentally friendly, not-expensive and less prone to photocorrosion in aqueous solutions compared to sulfides, selenides, phosphides or nitrides. Heterojunction composed of iron (III) oxide and copper oxide has not been explored much so far [2, 3].

In the present study various methods, including spray-pyrolysis, spin-coating, atomic layer deposition and electrodeposition techniques were applied in an attempt to form thin-layered heterostructure, composed of iron (III) oxide and copper oxide on glass substrate with transparent conductive layer of fluoride-doped tin oxide (FTO). The composition, structure and surface morphology of the layers formed was investigated using X-ray photoelectron spectroscopy, X-ray diffraction and scanning electron microscopy techniques (Fig 1). UV-Vis spectrophotometry was applied to measure the absorption spectra of individual layers and heterostructure. Photoelectrochemical measurements were performed to investigate the possibilities of the application of Fe_2O_3/Cu_xO heterojunction for solar energy conversion.

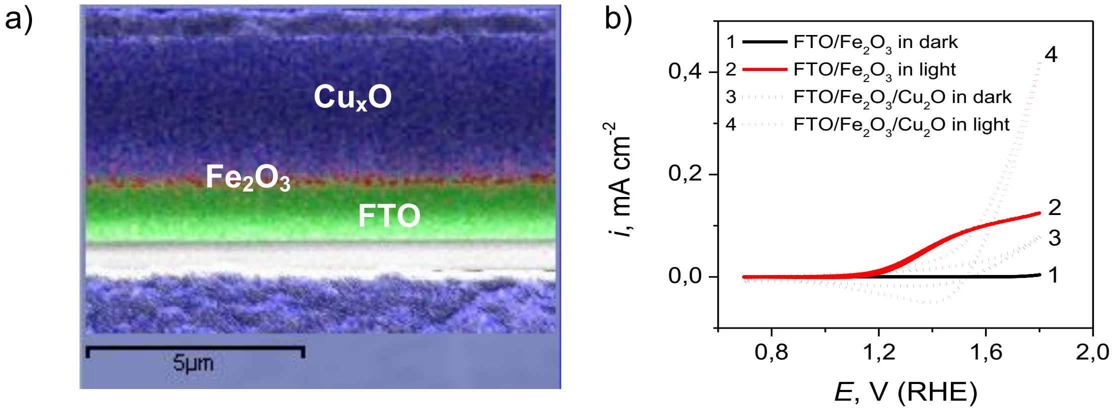

Fig.1. a) X-ray mapping image of Sn, Fe and Cu elements in heterostructure formed on glass/FTO substrate; b) cyclic voltammograms of FTO/Fe_2O_3 and $FTO/Fe_2O_3/Cu_xO$ heterostructures in 0.1 M KOH, showing performance of the electrodes in oxygen evolution reaction region in dark and under illumination, potential scan rate 50 mV s^{-1}

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FABRICATION OF NANOPOROUS Co. BY DEALLOYING SINGLE-PHASE γ-$Zn_{21}Co_5$ ALLOY FOR USE IN ELECTROCHEMICAL SUPERCAPACITORS

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Dealloying is an effective and controllable method to prepare nanoporous metals and alloys, which involves the selective dissolution of active elements and the rearrangement of inert elements. This process results in the formation of a nanoporous sponge composed almost entirely of the more noble alloy constituents. To prepare uniform nanoporous metals by dealloying, it is essential to design suitable precursors, which satisfy two basic requirements: homogeneous single phases and a large electrochemical potential difference between the alloy components. This concept holds true for many noble metals [1, 2]. More and more works have been carried out on non-precious nanoporous metals because of the need for practical applications [3]. Our approach mainly involves the alloying of the Co with more active metal Zn, and a subsequent selective leaching of Zn. During this etching process, Co atoms will undergo spontaneous oxidation at the metal/electrolyte interface to form metal oxides.

Single-phase γ-$Zn_{21}Co_5$ alloy was electrodeposited on Cu plate from electrolyte as noticed in [4] and Zn was etched from the alloy in 30 wt.% NaOH solution at room temperature. The microstructures of the dealloyed samples were characterized by scanning electron microscopy, chemical analysis was performed by an energy-dispersive X-ray spectrometer. Electrochemical tests were carried out in 1 M NaOH solution at room temperature using an a Parstat 2273 potentiostat in a three-electrode cell with a Pt foil as counter electrode and Ag/AgCl,KCl_{sat} as the reference electrode.

Table 1. Dependence of the composition of $Zn_{21}Co_5$ alloy on dealloying time

Element at. %	Dealloying time, h			
	0	0.5	1	4
Co	18.25	52.27	82.3	81.13
Zn	81.75	47.73	17.7	18.87

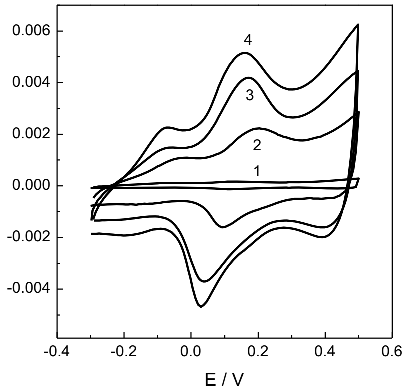

Fig.1.Cyclic voltammograms measured at 20 mV s^{-1} in 1 M NaOH: (1) bulk Co; dealloying time, h: (2) 0.5; (3) 1; (4) 4.

In comparison to the bulk Co, dealloyed Co shows substantially larger capacitive current densities, suggesting its higher electrochemical activity. This indicates the good capacitive behavior of dealloyed structure.

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NANOPOROUS TITANIUM DIOXIDE FOR SIMULTANEOUS DELIVERY OF IBUPROFEN AND GENTAMICIN

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Nowadays titanium and its alloys are widely used as implantable materials in the dentistry and orthopedics due to their desired properties, such as good biocompatibility and moderate elasticity. One of their disadvantages is their disability to firmly attach to bones. In order to decrease the risk of the implant failure the surface of titanium can be coated with a thin bioactive film. One of the method to modify titanium surface is its anodization. The formed nanoporous anodic titanium dioxide (ATO) layer not only improves the osteoblast cell adhesion, but also can be used as a drug delivery system [1]. Gentamicin, a representative of aminoglycoside antibiotics, is usually administered after orthopaedic operations in order to treat bacterial infections because of its activity against Gram-negative bacteria [2]. Ibuprofen, a representative of a nonsteroidal anti-inflammatory drug, is used to treat or reduce the symptoms of pain [3]. A simultaneous delivery of gentamicin and ibuprofen is desirable due to their different medical properties.

Nanoporous TiO_2 layers were prepared via a three-step anodization process in an ethylene glycol electrolyte containing NH_4F (0.38 wt.%) and H_2O (1.79 wt.%). The first and second step of anodization lasted 3 h, while the duration of the third step was: 10, 5 and 2 min in order to obtain the different length of nanotubes. The as-prepared TiO_2 layers have an amorphous structure. ATO layers were annealed in air at 400 and 600 °C for 2 h using a muffle furnace in order to obtain the anatase and a mixture of anatase and rutile phases, respectively. Ibuprofen and gentamicin were used in the research. Three different loading procedures were applied: (1) first ibuprofen, then gentamicin, (2) first gentamicin, then ibuprofen and (3) simultaneously both drugs. They were loaded inside nanopores by pipetting 1 ml of the drug solution (10 wt.%) onto the ATO surface, and then dried in the air. This step was repeated five times for each loading case. The loaded samples were immersed in a phosphate buffer solution (PBS, pH = 7.2) at 37 °C for appropriate time intervals and replaced with the fresh portion of PBS. The drug content was determined by spectrophotometry. The absorbance of ibuprofen was measured directly at 222 nm, while gentamicin was determined as a complex with silver nanoparticles (AgNPs) at 394 nm. The drug release profiles were compiled based on calculated concentrations of ibuprofen and gentamicin. The proposed function, being a combination of desorption and diffusion processes, was fitted to the resulting profiles. The effects of the crystalline structure and length of TiO_2 nanotubes on the drug release profiles were analyzed.

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SCANNING ELECTROCHEMICAL MICROSCOPY FOR THE DETERMINATION OF ENZYMATIC KINETICS

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Biosensors are based on immobilized biological objects (e.g. enzymes, antibodies, DNA, etc.) and they are powerful analytical tools, which could be used for selective determination of analyte concentration. Enzymatic biosensors are the most popular among many different types of biosensors. In enzymatic biosensors the measurement of analytical signal is based on the chemical reaction catalyzed by enzyme. In some particular cases the response of biosensor could be related to the rate of reaction product formation. Therefore investigations, which are related to the evaluation of enzymatic rate, are very important in biosensorics. Recent developments in scanning electrochemical microscopy (SECM) illustrate that this method could be successfully applied for the evaluation and mapping of electrochemical activity of modified electrodes used in electrochemical sensor design [1, 2]. The SECM is based on electrochemical measurements performed by ultramicroelectrode (UME) or microelectrode (UME), which is scanning 3D space close to surface of the interest, which could contain catalytic, redox or other electrochemically active sites. In such experiments the UME in electrochemical setup is mostly connected as a working electrode, and the current, which is measured by the UME, depends on the local concentration of electroactive species. Thus, the concentrations of chemicals produced and/or consumed by immobilized enzyme at different position can be determined by SECM. For the first time electron transfer kinetics of non-conducting surfaces modified by enzymes was investigated by Bard's group using feedback (FB) mode of FB-SECM [3]. Since then, the investigation of heterogeneous reactions catalyzed by immobilized enzymes using the SECM has been applied in many biosensorics-related researches [4].

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Improvement of bisphenol A biodegradability by electro-Fenton process in a plug-flow electrochemical reactor with fixed bed three-dimensional cathode

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Unlike a few years ago, bisphenol A is now classified as an endocrine disruptor compound that can be detected in the wastewater treatment plant indicating that the classical biological treatment of bisphenol A (BPA) wasn't effectively adequate for such type of pollutant. However, to avoid BPA entrance in wastewater, a pre-treatment process is needed in order to eliminate the BPA (mineralization) or to transform it in biodegradable substances [1-2].

In this paper, bisphenol A biodegradability was improved by electro-Fenton process using a plug-flow electrochemical reactor with fixed bed three-dimensional cathode. The pre-treatment process was firstly developed at lab scale before to be scaled-up at semi-pilot plant. A fixed bed of glassy carbon pellets was used as cathodic material. The performance of BPA elimination by the electro-fenton process at lab and semi-pilot scale has been studied. The biodegradability of BPA was also investigated by the electro-Fenton process for different treatment times at different initial pollutant concentrations (1-150 mg.L^{-1}).

This study was carried out following (BOD_5/COD) ratio, COD and TOC abatement (%). The results show a noteworthy biodegradability enhancement after 90 minutes of treatment (BOD_5/COD > 0.6) with 33 % of TOC abatement at 50 mg/L of BPA initial concentration (Fig. 1). However, for lower initial concentrations of BPA only few minutes of treatment was effectively needed to improve the biodegradability and make the charge biodegradable.

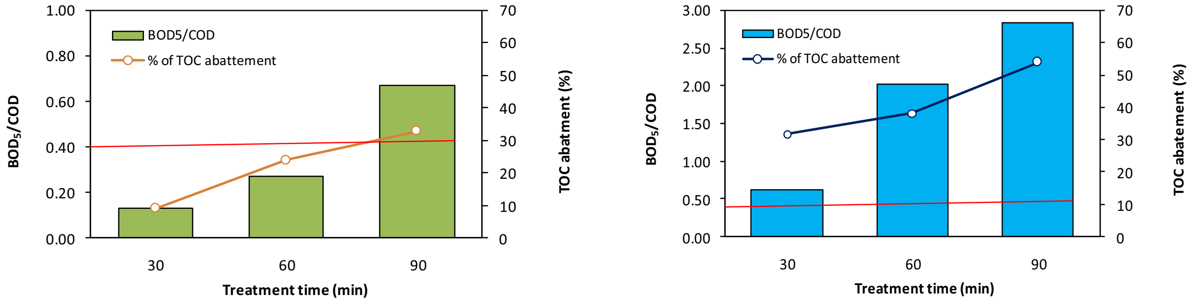

Fig. 1: Variation of (BOD_5/COD) ratio and TOC abatement (%) after 30, 60 and 90 minutes of treatment by the electro-Fenton process. 🟩 : $[BPA]_i$= 50 mg/L and 🟦 : $[BPA]_i$= 10 mg/L

In conclusion, the electro-Fenton process has demonstrate his capability to reduce the charge of non-biodegradable pollutant which make it an appropriate solution to be used as pre-treatment process upstream the biological treatment of wastewater.

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ELECTROCHEMICAL PROPERTIES OF COPPER COMPLEXES WITH β-AMYLOID 4-16 AND β-AMYLOID 1-16

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Alzheimer's disease (AD), characterized by progressive cognitive and memory impairment, is one of the most common progressive neurodegenerative disorder in the elderly. A proposed key event in the pathogenesis of AD is the formation of neurotoxic β-amyloid (Aβ) oligomers and amyloids plaques in specific brain regions. Until know it was believed that the main plaques components were β-amyloid 1-42 and 1-40, which aggregated upon exposure to copper ions. The copper binding properties of Aβ 1-x (where x is 16/28/40/40) have been studied since these peptide-copper complexes are involved in extensive redox chemical reactions generating reactive redox species, resulting in oxidative stress. Recent studies revealed that the prevailing isoform detected in healthy and diseased brains is N-truncated Aβ 4-42 containing novel N-terminal FRH sequence [1,2]. Therefore, unexpected function of Aβ in metal homeostasis in the central nervous system is postulated.

The main goal of this work was to investigate the interactions between copper(II) ions and two β-amyloids which have different N-terminal tail. Voltammetric studies were performed to compare the redox behavior of Cu(II)-Aβ 1-16 and Cu(II)-Aβ 4-16 complexes. The influence of peptide sequence on their redox properties was studied. Due to the fact that these both peptides contains two Cu(II) binding sites the measurement were carried out in two Cu(II)-peptide ratios: 1:1 and 1:2. The proposed approach could provide better description of the Aβ-Cu(II) complex formation and thus could be helpful to understand the pathogenesis of AD. Presented results are promising for the elucidation of the relationship between structural and redox properties of active copper centers not only in Aβ-Cu(II) complexes, but also in different copper dependent proteins.

Acknowledgments
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FLAVOENZYME-CATALYZED REDUCTION REACTIONS AND CYTOTOXIC ACTIONS OF SUBSTITUTED PYRIDINE N-OXIDES

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Heterocyclic N-oxides received considerable attention due to their usefulness as synthetic intermediates and biological importance. Pyridine N-oxides (PyNOs) were applied in drug discovery programs. They were shown to possess antivirus activity being dependent upon the nature and location of substituent(s) in PyNO molecule. Due to electrophilic character of N-oxides, they acted as bio-reductive drugs, causing DNA damage and cell death. Some of the natural N-oxide compounds were shown to act as efficient antibacterial agents.

Herein we briefly report the study of flavoenzyme-catalyzed conversion and cytotoxic activity of a number of substituted PyNOs. The compounds used in the study have been synthesized through oxidation reactions of pyridine by CH_3CO_3H or 3-Cl-Ph-CO_3H followed by the nucleophilic substitution reactions.

Enzymatic reactivity. The reactivity of PyNOs was examined towards NAD(P)H-dependent flavoenzymes. i.e., single- and two-electron transferring cytochrome P-450 reductase (P-450R, EC 1.6.2.4) and quinone oxidoreductase 1 (NQO1, EC 1.6.99.2), respectively, which are known to be the key enzymes responsible for the bioreductive activation of various redox-active xenobiotics/drug agents. The reduction of PyNOs by P-450R was accompanied by their redox-cycling (i.e., the excess oxidation of NADPH over NPDOs, followed by concomitant O_2 uptake, being sensitive to superoxide dismutase (SOD)), that implies the production of reactive oxygen species (ROS). The P-450R-catalyzed rates, in terms of second-order rate constant values ($k_{cat}/K_{m(PyNO)}$), varied in the range of ≈ 10^2-10^7 M^{-1} s^{-1} and linearly increased with an increase in the electrophilic potency of PyNOs ($R = 0.880$; $F = 30.00$; $P < 0.0004$), expressed in terms of absolute LUMO energy values ($|LUMO|$). This may be consistent with an 'outer-sphere' electron transfer (ET) model. In contrast to P-450R, NQO1 showed no substantial activity towards PyNOs, except the nitro-PyNOs whose reactivity is most likely to be caused by two(four)-electron reduction of their nitro-group(s). The DFT calculation of the local electrophilic sites of the nitro-PyNOs, in terms of their *LUMO* coefficients (C^2) or electrophilic Fukui function (f^+_k) values, showed that the electron-accepting potency, condensed upon the nitro-group(s), is higher than that of N-oxide moiety. The nitro-substituted NPDOs showed inhibiting potency towards NQO1 in its quinone reductase reactions, competing with NADPH substrate for the same or over-lapped binding site within the active center of the oxidized enzyme form.

Cytotoxic/antibacterial activity. The cytotoxic activity of PyNOs, examined against primary mice splenocytes (in terms of CL_{50} values, reflecting 50 % cell death), varied in the range of 1.9 - 280 µM; halide-substituted PyNOs showed the highest cytotoxic potency. Among PyNOs tested as antibacterial agents, methoxy-substituted PyNOs containing nitro- and halide-group(s) (Cl or Br) in 2 and 6 positions of pyridine nucleus exhibited the highest potency, with minimal inhibitory concentration (MIC) values of 5-10 µM defined against *Entherococcus faecalis*, *Klebsiella pneumoniae* and *Bacillus subtilis* strains.

NITRO-DERIVATIVES OF N-HETEROCYCLIC *ORTHO*-QUINONES: SYNTHESIS, X-RAY STRUCTURE, QUANTUM MECHANICAL, ELECTROCHEMICAL, ENZYMATIC AND CYTOTOXIC STUDIES

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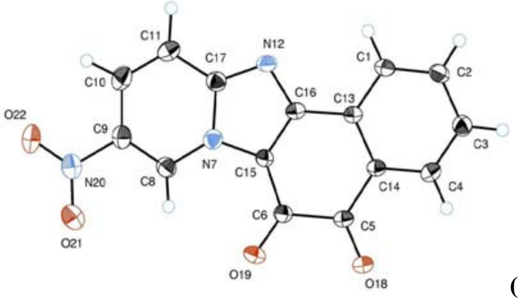
N-Heterocyclic quinones are known to possess a broad spectrum of their biological activity [1, and references therein]. Herein we report the synthesis and elucidation of the detailed structure, electrophilic potency, flavoenzyme-catalyzed reduction reactions, antitumor/antibacterial activity of naphtho[1',2':4,5]imidazo[1,2-a]pyridin-5,6-dione (NPDO) (**I**) and two of its NO$_2$-substituted derivatives 3-NO$_2$- (**II**) and 9-NO$_2$-NPDO (**III**). They were synthesized by condensation reactions starting from 6-R-2,3-dichloro-naphtho-1,4-quinone (R=NO$_2$ or H) with 2-amino-5-X-pyridines (X=H or NO$_2$). The high purity well-shaped crystal of (**III**) was grown by slow evaporation of solution in 1-propanol. The X-ray analysis followed by the quantum mechanical calculation (QMC) showed that tetracyclic molecule of III is almost planar, crystal symmetry system - monoclinic, P 21:



(III)

Their spectral properties are given in [1]. The QMC showed that nitro group introduced into NPDO markedly increased its electrophilic potency. The assessment of the local electrophilic sites of NO$_2$-NPDOs (in terms of Fukui function (f^{+}_{k}) values) revealed that quinone moiety is the most probable site of their reductive activation. The study of electrochemical reduction of NPDO by means of cyclic voltammetry (CV) showed that in aqueous media (pH 7.0) the compound is reduced by single two-e$^-$ reduction step followed by protonation. In non-aqueous media (AcN), the reduction took place by two successive one-e$^-$ reduction steps, producing two separate cathodic waves corresponding to quinone radical and dianion states. The compounds were efficient substrates in reactions with 1-/2-e$^-$ transferring flavoenzymes, producing reactive oxygen species [1]. Among NPDOs tested, 3-NO$_2$- (II) showed the highest antitumor activity against A-549 and MCF-7 cell lines, with CL$_{50}$ values of 0.12 μM and 0.28 μM, respectively. The defined MIC values of antibacterial activity of NPDOs against *S. aureus* strain varied in the range of ~ 14-16 μM. The X-ray analysis and QMC revealed the planar structure of NPDO molecules implying for their potential ability to act as DNA-intercalators.

We are grateful for the financial support of the Scientific Council of Lithuania (the project **No. MIP-032/2014**).

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DETERMINATION OF COUMESTROL IN PERENNIAL LEGUMES BY ULTRA-HIGH PRESSURE LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY

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Phytoestrogens are a group of nonsteroidal polyphenolic compounds that occur naturally in a wide range of plants and induce biological responses based on their ability to bind to estrogen receptors. They are generally either isoflavones (e.g., biochanin A, daidzein, genistein, formononetin) or coumestans such as coumestrol, trifoliol or repensol. Although phytoestrogens are widespread throughout the plant kingdom, they are most common in legumes such as clover, lucerne and some others.

In the present study, ultra-high pressure liquid chromatography coupled with mass spectrometry was employed for the determination of coumestrol in perennial legumes growing in Lithuania.

All separations were carried out on a 1290 Infinity UHPLC system equipped with a diode array detector (DAD) and 6410 triple quadrupole mass spectrometer (Agilent Technologies, USA). The Acquity UPLC BEH C18 (2.1×100 mm, 1.7 µm) column (Waters, Milford USA) was employed for the separations. The mobile phase was composed of (A) water and (B) methanol/water (80:20 *v/v*) both containing 0.25% (*v/v*) acetic acid. The gradient elution program was as follows: 0-15 min, 2-100% B linear; 15-17 min, 100-2% B linear; 17-22 min, 2% B isocratic. The column temperature was maintained at 30 °C, the mobile phase flow rate was 0.25 mL/min, and the injection volume was 5 µL.

The electrospray ionization (ESI) source operated in the selected ion monitoring (SIM) mode. The nebulizer pressure, capillary voltage and drying gas flow rate were 60 psi, 4000 V and 10 L/min, respectively. The drying gas temperature was set at 280°C. Data were acquired and processed using the MassHunter software (Agilent).

Coumestrol was extracted with acidified (2 mol/L HCl) methanol/water (8:2, *v/v*) solution by sonication for 30 min at room temperature and then incubated in a water bath at 80–85°C for 1.5 h with magnetic stirring. The calibration curve was linear over the concentrations range 0.05-5.00 mg/L. The limit of detection and limit of quantification were 0.015 and 0.05 mg/L, respectively. Measured recoveries of coumestrol were in the range 88.5-96.1% with RSD values ranged from 4.5 to 7.2%. Finally, coumestrol was quantified in leaves, stems, flowers, and entire aerial parts of the legume species. The species chosen for the study were *T. pratense, T. medium*, *M. sativa, M. lupulina, O. viciifolia, A. glycyphyllos* and *A. cicer*. Only in lucerne species (*M. sativa* and *M. lupulina*) detectable amounts (0.003-0.034 mg/g of dry matter) of coumestrol were found. Different plant parts showed significantly different concentrations of coumestrol: the leaves contained the highest overall concentration, followed by the stems and flowers.

Acknowledgements

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HYDROPHILIC INTERACTION CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY FOR THE DETERMINATION OF SWAINSONINE IN PLANTS

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Swainsonine, an indolizidine alkaloid, is found in some *Astragalus*, *Oxytropis*, and *Swainsona* species of the Leguminosae family growing throughout the world [1]. Consumption of swainsonine containing plants by grazing animals leads to a chronic neurologic disease characterized by weight loss, depression, altered behavior, decreased libido, infertility, abortion, birth defects, and death [2, 3]. Rapid, sensitive and accurate analytical methods are therefore needed to detect and to determine swainsonine in plants.

In the present study, hydrophilic interaction chromatography (HILIC) combined with tandem mass spectrometry (MS/MS) was developed and validated for the rapid and sensitive quantification of swainsonine.

HILIC separations were carried out on a 1290 Infinity UHPLC system connected to 6410 triple quadrupole mass spectrometer, equipped with electrospray ionization (ESI) source operated in the positive ion mode (Agilent Technologies, USA). The Acquity UPLC BEH HILIC (2.1×100 mm, 1.7 µm) column (Waters, Milford USA) was employed for the separations. The mobile phase was a mixture of acetonitrile and water (90:10, v/v) containing 10 mmol/L formic acid and set at a flow rate of 0.5 mL/min. The column temperature was 25 ºC and the injection volume was 5 µL. MS data acquisition was performed in selected reaction monitoring mode.

Swainsonine was extracted with 5 mL of 2% acetic acid for 16 h with agitation. The matrix-matched calibration curve was linear over the concentrations range 0.005-0.5 mg/L. The limit of detection and limit of quantification were 0.002 and 0.005 mg/L, respectively. Measured recoveries of coumestrol were in the range 81.2-95.4% with RSD values ranged from 6.4 to 14.8%.

The optimized HILIC-MS/MS method was applied to determine swainsonine in two milkvetch species (*Astragalus cicer* and *Astragalus glycyphyllos*) growing in Lithuania. Aerial part of each plant sampled in 2014 at flowering stage was divided into two subsamples. One of them was investigated as a sample of whole aerial plant part and the other subsample was fractionated into morphological plant parts: stems, leaves and flowers. None of the samples contained detectable amounts of swainsonine.

Acknowledgements

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Limit of detection improvement in gas chromatography system equipped with programmable temperature vaporization (PTV) injector.

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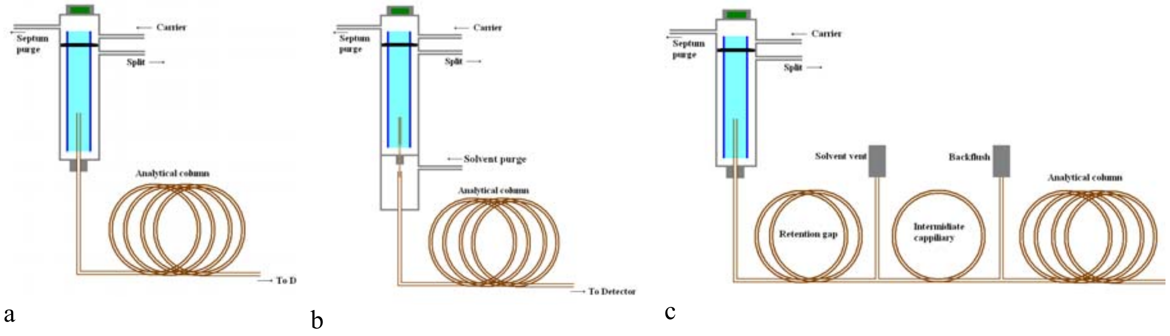
Programmable temperature vaporization (PTV) injector is most common injector in gas chromatography. Worldwide analysis methods using gas chromatography is increasing rapidly and penetrate to variety branches of industry, subsequently requirements for detection limits are tighten too. PTV allows to use solvent purge or large volume injection (LVI) technique [1]. We checked PTV injector capabilities using n-alkanes mixture (from C8 to C40) which cover whole temperature range used in gas chromatography and compared it with advance LVI technics such as Prevent (trade mark of PerkinElmer company) and retention gap with integrated solvent flush option.
Basic scheme of injection systems are shown in 1 picture.



a b c

Picture 1. Injection system scheme: a) standard PTV, b) PTV with Prevent; c) PTV with retention gap and solvent flush

Standard PTV research data shows poor recovery of components with boiling point close to solvent when: a) initial injector temperature hold time have been increased; b) increase solvent purge time; c) increase solvent purge flow.
Components with high boiling point shows poor recovery when initial oven temperatures hold time were short
All components shows better recovery when a) carrier flow were elevated up to 4 ml/min; b) pressure pulse injection technique were applied; c) injector cleanup (split open) time were extended.

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NEW SENSITIVE, SELECTIVE AND STABLE CHEMOSENSORS BASED ON 5-TRIFLUORMETHYL-2,3,3-TRIMETHYL-3*H*-INDOLE

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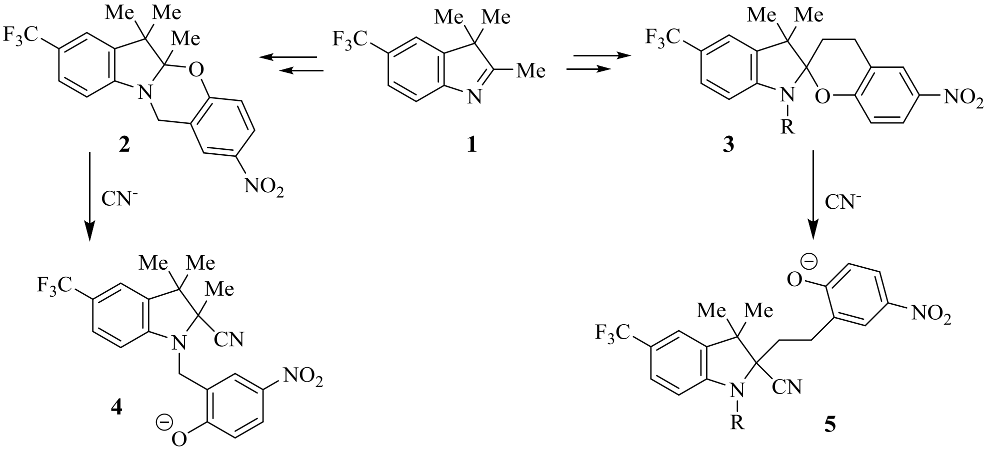
The electron-withdrawing trifluoromethyl group (CF_3) is considered to be an important structural motif in synthetic organic chemistry with applications in pharmaceuticals, agrochemicals and materials [1, 2]. Recent examples on the beneficial effects of trifluoromethyl groups on target properties of functional materials include dyes for dye-sensitized solar cells [3, 4], chelating agents [5], overcharge protection agents in lithium-ion batteries [6] and liquid crystals [7]. This work aims to synthesize trifluoromethyl group bearing indoline adducts with 2-chloromethyl-4-nitrophenol and to investigate their potential as molecular chemosensors for cyanide detection.

The treatment of **1** with 2-chloromethyl-4-nitrophenol afforded 8-(trifluoromethyl)-5a,6-dihydro-12*H*-indolo[2,1-*b*][1,3]benzoxazine **2**. The alkylation of **1** alkyl halides and following work-up of the intermediate 5-trifluoromethyl-3*H*-indolium salts with base gave the corresponding 5-trifluoromethyl-2-methylidene derivatives. The reaction of the latter enamines with 2-chloromethyl-4-nitrophenol yielded 5'-trifluoromethyl-1',3,3',4-tetrahydrospiro[chromene-2,2'-indoles] **3**.



Compounds **2** and **3** exhibited significant colour changes when treated with cyanide in acetonitrile solutions buffered with sodium phosphate, which was measured colourimetrically or observed by the naked eye. Additionally, they exhibited high selectivity toward cyanide, and were not significantly affected by halides or other common anions.

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ELECTRODEPOSITION APPLICATION TO THE SAMPLE PREPARATION FOR PLUTONIUM DETERMINATION

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Plutonium is a transuranic radioactive element with symbol Pu and atomic number 94. In the environment trace amounts of at least four plutonium isotopes (^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{244}Pu) can be found. Small traces of ^{239}Pu, a few parts per trillion and its decay products are naturally found in some concentrated ores of uranium [1]. Currently 20 radioactive isotopes of plutonium, of which the most important isotopes (alpha emitters) are ^{238}Pu, ^{239}Pu, ^{240}Pu, are known. They are important because of their long half-life, respectively 87.74; 24100; 6537 years [2], and the possible long-term impact on the environment and living organisms. Plutonium isotopes in nature mainly occur from nuclear weapons testing, nuclear fuel reprocessing, nuclear power plant accidents (Chernobyl and Fukushima power plant accidents) [3]. Plutonium behavior in the environment is controlled by its multi-valence (III, IV, V, VI) forms, which can exist simultaneously.

Evaluation of the activity concentration of alpha particle emitting radionuclides in environmental, biological and technical samples requires a multi-stage sample preparation for the spectrometric detection.

Determination of the plutonium activity concentration includes the following main stages: the sample pre-concentration, radiochemical analysis - separation, purification by anion chromatography and extraction chromatography procedures, electrodeposition and the spectrometric measurement. The separated and purified plutonium analytes using radiochemical analysis for alpha spectrometric determination might be prepared applying two techniques: electrodeposition or co-precipitation with a non-isotopic carrier. Electrochemical deposition allows us to achieve a very thin layer on a highly polished metal disc. Commonly, plutonium is electrodeposited on a polished stainless steel or platinum disk.

Plutonium detection is always a multi-step analysis and it is a highly indirect process because of which some part plutonium in one or another step of analysis might be lost. To prevent this a well known amount of ^{242}Pu or ^{236}Pu is added into the sample at the beginning of analysis so that the percentage of plutonium recovered might be determined, i.e. the chemical yield. The added plutonium must be in the same chemical form as the plutonium in the sample or the yield estimates will not reflect the percentage of plutonium recovered from the sample. According to the scientific literature, the chemical yield of plutonium commonly varies from 20 to 80 %. Our obtained results showed the mean plutonium yield values to be in a range of 50 – 60 % in different types of environmental samples studied for the Pu alpha-spectrometric determination. This analytical technique based on chemical separation of plutonium isotopes by ion exchange followed by alpha spectrometry allows the determination of the plutonium isotopes ^{238}Pu, ^{239,240}Pu with the detection limit of 1×10^{-3} - 1×10^{-4} Bq/kg.

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TREATMENT OF FLUORIDE-CONTAINING SOLUTIONS FROM A CHEMICAL ETCHING OF SILICON

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The chemical etching of silicon using HF–HNO_3 mixture is a widely used process in the manufacturing of silicon wafers for microelectronic or photovoltaic applications. During the etching process HF and HNO_3 concentrations decrease gradually, whereas H_2SiF_6 becomes enriched in the solution. That diminishes etching solution performance, consequently, the spent etching solution has to be utilized or replaced by a new one or the already used etching solution has to be replenished by the addition of concentrated acids.

The utilization of spent etching solution of silicon has been investigated by precipitation tests using solution obtained from BOD Group plant in Lithuania. Solution concentration was: HF – 65 g/l, HNO_3 – 450 g/l, CH_3COOH – 10 g/l, Si – 40 g/l and pH<1.

Concentration of HF and H_2SiF_6 were measured using potentiometric titration with KOH [1.2]; the total fluoride - with a fluoride ion-selective electrode (F-ISE) (HI4110 (Hanna Instruments USA) and by colorimetry with zirconium alizarin reagent; silicon - using ICP optical emission spectrometry (Optima 7000DV, Perkins Elmer). The X-ray powder diffraction (XRD) data were obtained with X-ray diffractometer SmartLab (Rigaku, Japan).

It was determined that the simultaneous precipitation of fluoride and silicon using various precipitants with Ca^{2+}: such as slaked lime, CaO, $CaCO_3$, $Ca(NO_3)_2$, not satisfied economically allowable level of concentrations for utilization. For example: using widely available slaked lime for the precipitation of fluoride the amount of reagent higher 9-10 times than stoichiometric ratio (0.5:1) of calcium to fluoride and pH ≥11.2 is always needed. Moreover, CaF_2 and $Si(OH)_4$ precipitates are very difficult to separate from water.

The investigation suggests that the separate precipitation of fluoride and fluorosilicate should be economically more favourable. In the first step, the insoluble fluorosilicate can be separated with KOH at pH 5. The diffraction pattern of precipitate identified peaks typical of hierite K_2SiF_6 and fluoride nitrate $K_3Si(NO_3)F_6$. In the second step, supernatant from the first step with a small amount of Si was treated using $Ca(NO_3)_2$. The formed precipitate was separated by centrifugation. The diffraction pattern of precipitate identified peaks typical of fluorite CaF_2, villiaumite NaF and sodium nitrate $NaNO_3$. Supernatant becomes pH 6.7 and concentrations of F and Si are undetectable.

Precipitates can be more easily integrated in industrial application, for example: K_2SiF_6 for wood preservation; CaF_2 (>97% CaF_2) as acid-grade in aluminium industry or as metallurgical-grade (60-72.5%) in steel industry [3]. While supernatant with calcium and potassium nitrate - as a material for agricultural application.

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THE INFLUENCE OF ZEOLITE CATALYST ON KINETICS AND THERMODYNAMICS OF VARIOUS PLASTIC WASTE THERMOLYSIS

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Nowadays polyolefins are widely used as industrial and household thermoplastics, and they are the main components of plastic wastes. These plastics, however, are not biodegradable, and their wastes cause many environmental problems related with disposal in landfill or incineration. The amount of plastic waste in European Union as well as in Lithuania is still increasing [1], and for this reason the physical and chemical recycling of polyolefin waste is crucial.

Thermolysis (catalytic and thermal) is one of the major chemical recycling way of plastic waste. The catalytic activity of additives (catalysts) can be proved using kinetic parameters. The main parameter for catalysis is considered to be the activation energy which is higher for the non-catalytic process.

In this work the FCC catalyst was used as an additive for the thermolysis of various different plastic materials (wastes): polypropylene (PP), polyethylene (PE), polystyrene (PS), ethylene-propylene co-polymer (E/P), thermoplastic elastomer based on the ethylene–propylene–diene terpolymer and polypropylene (PP/EPDM). The FCCC amounts in the mixtures were 0, 5, 10, 25 mass%. The estimation of kinetic parameters was performed using thermogravimetric analysis data according to standard method ASTM E 1641-99 [2] and Flynn-Wall method [3]. The thermodynamic parameters were estimated only at the maximum degradation rate temperature (T_m) using the transition state theory and Eyring equation. The calculation results show that the activation energy for all raw materials in the beginning of the reactions are in the range of 125.3-192.7 kJ/mol. Mixing plastic wastes with 25 % FCC catalyst leads to the reduction of activation energy by ~25-84 kJ/mol depending on the raw material used. Generally, kinetic and thermodynamic parameters for all mixtures at the beginning of the reaction and at the T_m temperatures also show tendency to decrease with increasing FCCC amount in the mixtures.

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Comparative research of vertical migration of ^{137}Cs in the soil of flooded and upland banks of lakes

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In the environment, ^{137}Cs is exclusively of anthropogenic origin. Among different released fission radionuclides, ^{137}Cs is the most significant as it contributes to the long-term dosage to human population. It belongs to a group of radionuclides which, under accidental situations, can be dispersed worldwide due to the air mass transport. ^{137}Cs deposition in Lithuanian terrestrial and aquatic ecosystems is basically related to the global fallout and contaminated air masses from the Chernobyl NPP accident [1-3].

The aim of the present study was to investigate the vertical profiles of ^{137}Cs in the flooded soil and the upland forest soil, collected from the lake banks, and, based on experimental results, to compare the vertical distribution of this radionuclide activity concentration in tested profiles.

The flooded soil sample was taken at the bank of Lake Lydekinis (54°46“13‘N, 25°27′22″ E). The upland forest soil was sampled at the bank of Lake Juodis ((54°4649″ N, 25°26′29″ E). Soil samples were collected with a special metal cylinder (diameter 12.5 cm; height 30 cm). The soil sample was split into every 1 cm layer down to the 30 cm depth.

Gamma-spectrometric measurements were carried out using a CANBERRA GC 2520 gamma-spectometer with the HPGe detector (relative efficiency 26.2 %, resolution—1.76 keV/1.33 MeV) according to the gamma line at 661.62 keV of 137mBa (a daughter product of ^{137}Cs). Measurement errors of radiocesium activity concentrations in samples were evaluated by the GENIE software program.

Analysis of experimental results showed a different vertical distribution of the ^{137}Cs activity concentration in the tested soil of flooded and upland banks of lakes. The maximum activity concentration peaks of ^{137}Cs in the flooded soil were found at the 2-3 cm depth (54.1 – 49.0 Bq/kg) and the second one was found at the 8-10 cm depth (51.5 - 56.5 Bq/kg). A gradual decrease of this radionuclide activity concentration was observed (to 5.4 Bq/kg at the 30 cm depth). The vertical distribution of the ^{137}Cs activity concentration in the soil of the upland bank showed one peak on the profile surface, at the 1-3 cm depth with values of 42.5 - 56.0 Bq/kg. Significantly lower values of the ^{137}Cs activity concentration were determined beginning from the 10 cm depth (4.0 Bq/kg) and at the 30 cm depth the activity concentration was only 0.20 Bq/kg. Different ^{137}Cs migration could be explained so that ^{137}Cs in the flooded soil can be dissolved and its solubilized form can migrate into the deeper layers of soil. In the upland forest soil, ^{137}Cs is apparently accumulated in the soil mineral lattice and therefore its migration into deeper layers is restricted.

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Prussian blue based nano-composites for radiocesium removal

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Long-lived anthropogenic radionuclides were introduced into the environment after nuclear tests in the atmosphere as a result of the global fallout, discharges from nuclear industry and nuclear accidents , e.g. at the Chernobyl nuclear power as well as the Fukushima nuclear power plant in March 2011. Radioactive caesium is one of the toxic radionuclides which was released in the environment and is present in the radioactive waste. In order to protect the environment from radioactive Cs isotopes modern, efficient and cost-effective technologies are required. One of the possible ways of removing radioactive Cs from contaminated liquid media is based on the application of Prussian blue (PB) nano-composites.

This study was carried out to develop the graphene oxide (GO) and PB based nano-sorbents for the effective removal of radioactive caesium from contaminated solutions and nuclear waste capable of reducing discharges to low-levels as well as suitable for environmental application, e.g. for pre-concentration of Cs ions from seawater. The aim of this work was to synthesize and characterize adsorbents as well as investigate sorption of Cs^+ to Magnetic Prussian blue (MPB) and Prussian blue magnetic graphene oxide (PBMGO).

GO synthesis was performed from the graphite powder (<20μm synthetic, Sigma-Aldrich, Switzerland) using the modified Hummer's method. PBMGO sorbent was synthesized by mixing together aqueous solutions of GO and magnetite. Then aqueous solution of $FeCl_3$ and $K_4[Fe(CN)_6]$ was slowly introduced into the mixture. The obtained precipitate was washed with water and dried at 50^o C. MPB and MPBGO were characterized by Mössbauer spectroscopy, X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The batch technique was used to study the adsorption of elements and three sets were conducted for each experiment. In experiments with Cs, in addition to CsCl solutions, 100 mg L^{-1} of CsCl in seawater (35‰) and natural seawater from the Baltic Sea were used.

The adsorption of Cs(I) to nano-composites was studied in a wide range of initial concentrations and analyzed by the Langmuir model. In addition, the effects of pH and coexisting ions on the adsorption of Cs to Prussian blue based composites were investigated. The maximum adsorption capacities of studied elements varied from 333 to 362 mg g^{-1}. The efficiency of studied sorbent in natural sea water was about 100%.

STUDY OF RADIONUCLIDES AND HEAVY METALS SORPTION ON GO

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Recently, great attention has been paid to environmental protection, thus there is a need for new low-cost and effective technologies based on progressive materials. Various materials such as activated carbon, iron oxide nano-particles of titanium silicates, nano-graphene and graphene oxide (GO) have been used for removal of radionuclides and heavy metals from liquid media. However, those materials are not always appropriate for specific conditions which are required for a certain technology. Graphene oxide is an oxidized graphene form obtained by oxidation of graphite. GO has a large surface area and a variety of groups such as epoxy (COC), hydroxyl (-OH), carboxyl (-COOH) and carbonyl (-C = O), which can efficiently bind metal ions and radionuclides. In addition, recent studies have shown that graphene oxide is a precursor and a substrate for various chemical modifications. GO and its composites have been adapted for the waste water treatment and clean-up of contaminated areas from pollution [1]. It is believed that GO is also suitable for the radioactive waste management.

However, sorption mechanism and effect of pH on it are not they are poorly understood. GO features to absorb metal ions are not sufficiently explored. The aim of this work was to synthesize and characterize adsorbents as well as to study the pH effect on sorption of Cu(II), Co(II), Ni(II), Pb(II), Am(III), Pu(IV) and Cs to GO.

GO was synthesized using a modified Hummer's method, by oxidation of graphite powder [2]. Synthesized materials were characterized by XRD, SEM and FTIR.

Sorption experiments were carried out with Cu, Co, Pb and Ni, Pu, Am and Cs. The effect of pH and contaminant concentration on the sorption efficiency has been studied. The results showed a fast Co2+, Cu2+, Pb2+ and Ni2+ adsorption. Sorption equilibrium was reached after 10-60 minutes. The maximum Pu and Am sorption on GO was observed at the initial pH values from 3 to 5. It has been found that GO can effectively absorb up to 88% of Co, 100% of Ni, 100% of Pb and 100% of Cu when their concentrations in the solution range from 50 to 1,000 µmol/L. The maximum sorption of Co up to 90% is achieved at pH 5, that of Ni - 88% at pH 8, Cu - 85% at pH 5, Pb - 95% at pH 5.

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Study of Canvas Deacidification Process Using Magnesium Nanomaterials

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Nanotechnology has found practical applications in the conservation and restoration of the world's cultural heritage. Acid catalyzed depolymerization of cellulose is one of the major problems in canvas conservation, because it causes cellulose degradation processes, which lead to a catastrophic loss of canvas strength. These processes can be stopped or consistently slowed by a deacidification treatment (introduction of alkaline reservoir) [1, 2].

The object of study was to synthesize the nanoparticles of magnesium compounds and to study its application for canvas deacidification process. Nanoparticles, because of its' dimensions, excellently penetrate into the cellulose fibers and fate better introduction of alkaline substances. Nanoparticles of MgO were prepared by sol–gel process [3] using magnesium nitrate hexahydrate and oxalic acid dehydrate as precursors. Magnesium hydroxide nanoparticles were obtained via hydrolysis under nitrogen for 48 hours at room temperature. Suspension of $Mg(OH)_2$ nanoparticles has been prepared using 90% isopropanol, 10% water, 2% MgO. Different molecular mass and concentration polymer additives hydroxypropyl cellulose (Klucel) have been added in accordance with the required amount. The smallest particles of $Mg(OH)_2$ (DLS analysis) were obtained via MgO hydrolysis in isopropanol with 2% hydroxypropyl cellulose (Klucel E) additive.

The suspensions of 2 % $Mg(OH)_2$ with hydroxypropyl cellulose (Klucel) additive of different molecular mass in isopropanol were prepared and tested for paper deacidification process efficiency. Absorption, pH, alkaline reserve of samples, distribution of particles on the surface of the canvas in differently alkalinized canvas samples were identified and compared. The suspension of 2 % $Mg(OH)_2$ with 1-2 % Klucel E additive could be used for canvas deacidification process. This suspension created the largest alkaline reserve (1.76–1.50 mol/kg) and optimal pH values (9.63 – 9.57). $Mg(OH)_2$ nanoparticles distributed evenly over the surface of the canvas (SEM/EDS analysis). The results of IR spectroscopic analysis showed successful introduction of an alkaline material which neutralize acidic compounds. These compounds are being formed on oxidation and acid hydrolysis during aging processes of the canvas. So far, the problem of painting canvas acidification has not been resolved yet in Lithuania. However, this work has managed to find an effective method of painting canvas alkalizing.

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PHOTOCHEMICAL APPROCAH TO THE INORGANIC SYNTHESIS OF SEMICONDUCTOR NANOPARTICLES

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Photochemical route is a promising way to produce nanoparticles as it possesses the spatial and temporal control of the process. Whereas organic compounds, decomposing into reducing radicals when affected with radiation, are usually chosen as photoactive materials, the photochemical synthesis is usually carried out in organic solvents [1].

In this research, CeO_2 nanoparticles have been prepared in aqueous solution via photochemical route using sodium azide (NaN_3) as a photo-active compound. Synthesis was carried out without any surfactants or using different amounts of polyvinylpyrrolidone (PVP) as a stabilizing agent.

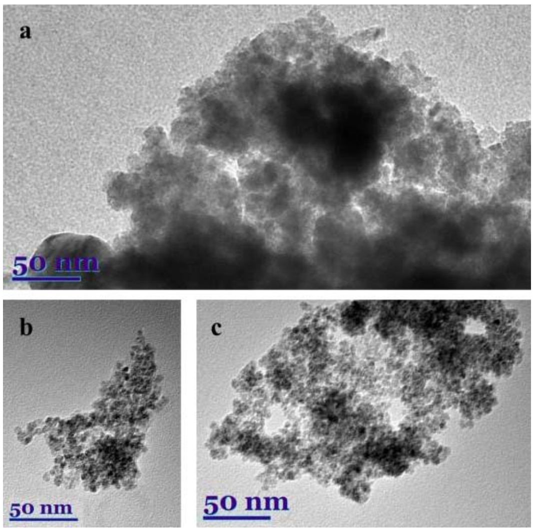

Figure 1. TEM images of synthesized CeO_2 nanoparticles: (a) without surfactant, irradiated for 90 min; (b) 2.5 mmol/L PVP, irradiated for 90 min; (c) 5 mmol/L PVP, irradiated for 90 min.

TEM bright field images reveal that synthesis without surfactants resulted in the formation of highly agglomerated particles while adding PVP to a primary solution resulted in decreased agglomeration and slightly smaller particles, uniform in shape and with a narrow size distribution. It is also clear that higher PVP concentration in the primary solution is responsible for the reduced particle size. TEM results are in good agreement with the powder X-ray diffraction analysis and Raman spectroscopy data.

PVP is reported to act both as molecule capping agent and as a sensitizer for photochemical processes [2]. A strong interaction between CeO_2 nanoparticles and PVP was revealed by TG analysis.

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PAN/TiO_2 CATALYST FORMATION BY ELECTROSPINNING AND ITS STRUCTURAL CHARACTERIZATION

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Introduction

Photocatalysis is a decomposing process under UV radiation with the presence of catalyst. It is considered as clean process, which can decompose all kind of organic materials and can be used for many applications including water and air purification. TiO_2 is the most popular metal oxide for photocatalysis due to its chemical stability and availability [1]. For practical application TiO_2 has often been proposed to immobilize on a solid support. However, most reported supports may have a low specific surface area, which leads to the decrease in TiO_2 activity. Therefore, seeking continuous media with high surface area is still a practical task [2]. Electrospinning is a method to produce fiber by the use of electric force to draw charged threads of a polymer solution. It is possible to get down to fiber diameters in the order of hundreds to tens of nanometers. The synthesis of TiO_2 nano-catalyst by electrospinning technique is presented in this paper.

Experimental

Materials: PAN (M_{w}.=1.5x10^5g/mol), titanium isopropoxide, acetic acid, DMF. All materials were used as received. Preparation of fibers: 10 wt% PAN/DMF solution containing 2 wt% of TTIP was prepared. The prepared solution was loaded into syringe equipped with 23G needle. The voltage source of 27 kV was used. The rotating collector was covered with stainless steel plate. The tip-to-collector distance (TTCD) was 21 cm, flow rate was 0.75 ml/min. As spun fibers were calcined at 450-750°C for 2 h in air, in order to eliminate the organic components and to activate the crystallization of titania. Characterization: images of morphology of the samples were obtained by SEM, TEM. The crystallinity was determined by XRD. BET surface area was characterized by a N_2 adsorption–desorption isotherm.

Results

Significant efforts were paid in adjusting electrospinning conditions which allowed forming PAN fibres containing the TiO_2 precursor, including adjustments of polymer concentration and composition as well as needle diameter, voltage and TTCD. The formed fibres were mainly composited of TiO_2, with additions of carbon as a product of the calcination of PAN. The fiber layer was characterized as smooth and uniformly deposited. The diameters of fibers were in range of 250-500 nm. TiO_2 particles were also uniformly distributed, as revealed by TEM analysis. Relatively high surface area was determined, as compared to single layer catalysts. The photocatalyst properties of TiO_2 are known to be dependent on crystallinity. Titanium alkoxides at room temperature are amorphous, the phase transformation occurs at a temperature higher than 700°C in this experiment. Anatase and rutile mass fractions were calculated from the intensities of XRD diffraction peaks [3] (28% and 72% respectively), which is comparable to the commercially available TiO_2 powder.

Conclusions

TiO_2 nanofibers were successfully synthesized by electrospinning method using PAN/DMF/TTIP solution. Electrospun TiO_2 shown properties have great potential for applications in photo catalysts, which will further be determined.

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FUNCTIONALIZATION OF MAGNETIC NANOPARTICLES WITH NEW ISOCYANATE COMPOUND

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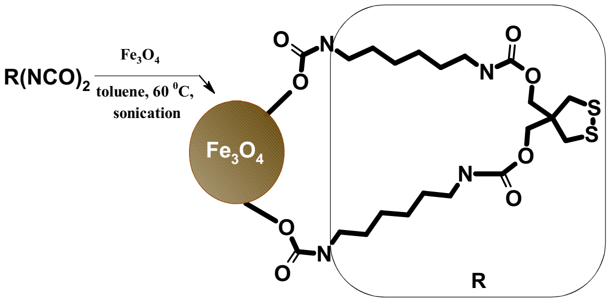
Biocompatible functionalized magnetic nanoparticles (Nps) attract great interest in recent years due to their prospective applications in nanomedicine. In this study, a new recently discovered strategy for anchoring organic molecules onto magnetic iron oxide Nps using isocyanate functional group was realized [1]. For the synthesis of magnetite, Fe_3O_4, Nps in average size of 15 nm, the hydrothermal synthesis from the alkaline solutions of Fe(II) and Fe(III) precursors and diglycolic acid, as reported in [2] was applied.

We report that the isocyanate moiety of newly synthesized cyclic disulfide easily and efficiently reacts with the hydroxyl residues of the Fe_3O_4 nanoparticles surface under sonication, leading to the formation of a stable covalent carbamate bond (Fig. 1). Concerning IR, for nanoconjugate, the strong absorption bands of organic part are clearly visible, while the typical strong band of isocyanate group stretching at 2256 cm^{-1} is absent (Fig.2). This coating of magnetite Nps can provide a flexible surface chemistry for further disulfide functionalization with noble metals colloids and biomolecules with free thiol group for specific biological interactions and a wide range of biomedical applications [3].



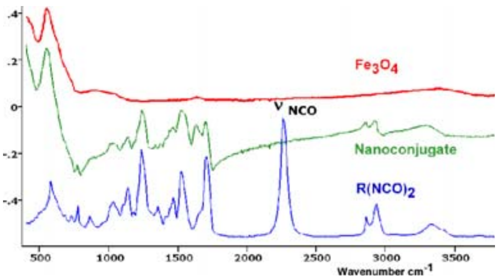


Fig. 1. Chemical functionalization of magnetite nanoparticle.

Fig. 2. IR spectroscopy data.

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GOLD NANOPARTICLES: SYNTHESIS, CHARACTERIZATION AND APPLICATION

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The nano-sized gold nanoparticles GNPs' have been known from the very beginning of human civilization, but systematic scientific investigations were performed much later [1]. One of the most popular and thoroughly studied methods for GNPs' synthesis developed by Turkevich is the citrate method [2]. Recently, formation of new composites by adsorption of gold nanoparticles on carbon has attracted interest due to their physical properties and applications in catalysis, electrochemical energy storage or electrochemical sensor [3-5].

In this work, the synthesis of gold nanoparticles, based on classical Turkevich method, was performed. Gold nanoparticles were obtained by reducing of Au^{3+} $HAuCl_4$ to Au^0 with trisodium citrate $Na_3C_6H_5O_7 \cdot 2H_2O$ in an aqueous solution. Different parameters of synthesis were changed and their effects on particles size were observed. Further GNPs'were deposited on carbon by adsorption using stirring.

The morphology, size and shape of gold nanoparticles were characterized by using UV-Vis spectrophotometry and Field Emission Scanning Electron Microscopy. The electrocatalytical properties of gold nanoparticles, prepared under various conditions, towards the oxidation of methanol are compared and discussed on the basis of electrochemical data.

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Nickel sorption by magnetic nanocomposites

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Heavy metals are persistent environmental contaminants since they cannot be degraded or destroyed. Nickel (Ni (II)) has become hazardous because of its tendency to accumulate in living species. Nickel exists in the effluent of industries such as plating, the removal of which regarding environmental standards is not avoidable. Various treatment techniques and processes have been used to remove the metallic ions from the wastewater. Magnetic nanomaterials apart from having the high surface area to volume ratio, have so many unique properties which make the remediation process economical, efficient and environmentally friendly, such as least toxic, biodegradable, and magnetically removal of pollutants. [1] In this work we synthesized different magnetic nanocomposites and applied them to the nickel removal.

Magnetite nanoparticles are synthesized by the co precipitation method, using ferric and ferrous salts in basic medium. Magnetic graphene oxide was synthesized via a chemical deposition of Fe3O4 NPs onto GO, followed by reduction of GO to graphene in a hydrazine hydrate solution. [2] Magnetic Prussian blue (PB) and magnetic Prussian blue-graphene oxide composites were prepared anchoring Fe3O4 magnetic nanoparticles (MNPs) onto a large surface area of GO and in situ coating Fe3O4 MNPs with PB. [3] All nanocomposites were used for batch adsorption of Ni (II) aqueous solution. Adsorption data are well fitted with the Langmuir and Freudlich adsorption model. Data are represented in Table 1.

Table 1. Langmuir and Freudlich adsorption coefficients.

Langmuir				**Freudlich**			
Composite	**Cation**	**R^2**	**b**	**Q (max)**	**K**	**n**	**R^2**
M	Ni^{2+}	0.96625	0.017	212.31	14.93	2.173	0.92111
MGO	Ni^{2+}	0.99472	0.0254	156.25	16.598	2.551	0.9207
MPB	Ni^{2+}	0.97715	0.0162	350.87	6.008	1.234	0.94297
MPBGO	Ni^{2+}	0.94981	0.007	526.31	6.0844	1.242	0.97013

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SOFT LITHOGRAPHIC FABRICATION OF ELECTRODES FOR DETECTION OF HYDROGEN PEROXIDE

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Electrochemical detection of single cell metabolites is a very promising strategy for the next generation of diagnostic methods. ROS (reactive oxygen species) are the major group of metabolites of cancer cells and their detection by electrochemical methods is attractive for biochip applications [1]. Platinum is highly sensitive to hydrogen peroxide and is used for low concentration of hydrogen peroxide detection [2]. Nevertheless, preparation of nanoelectrodes for single/cell analytics is a challenging task, not only due to the required precision of the layout but also due to high sensitivity and biocompatibility. In this work, we have demonstrated feasibility of alternative fabrication techniques for developing hydrogen peroxide sensor chips for analysis in cell culture. We have obtained platinum microelectrodes (e.g. 40 µm-wide) by fabricating gold templates by the microcontact printing technique, followed by electrochemical deposition of platinum. We could modify the electrode to form single cell adhesion zones consisting of fibronectin. Further on, we have miniaturized the size of the individual electrodes in the array by dip-pen nanolithography [3]. We have characterized the fabricated micro/nano electrodes by scanning electron microscopy and atomic force microscopy, as well as we have evaluated their functional characteristics by means of electrochemical measurements, including cyclic voltammetry and chronoamperometry.

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UPCONVERTION CORE-SHELL NANOPARTICLES WITH ENHANCED PHOTOLUMINESCENCE FOR APPLICATION IN BIOIMAGING AND CANCER THERAPY

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Lanthanide-doped upconversion nanoparticles (UCNPs) have been extensively investigated due to the advantages associated with their unique optical properties [1]. UCNPs are becoming a new class of powerful tools in broad range of applications, mainly including bioimaging, biosensors, drug delivery, and photodynamic therapy [2]. These applications require nanoparticles to be hydrophilic, biocompatible and have intense upconversion luminescence.

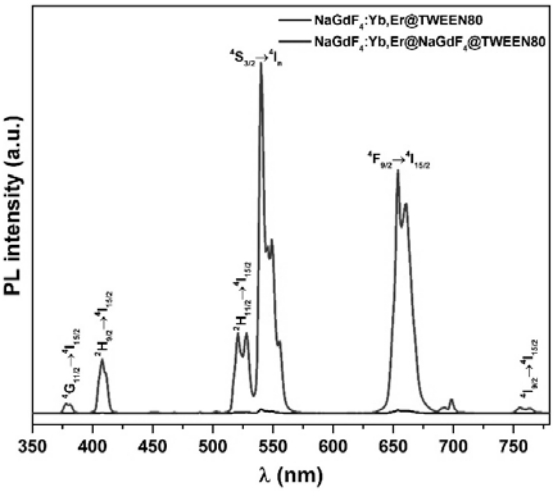

Fig. 1. Upconversion luminescence spectra of Tween 80 coated core and core-shell nanoparticles upon 980 nm excitation.

In this study, hydrophobic UCNPs was converted into hydrophilic ones using a commercially available surfactant Tween 80. Furthermore, it is shown that the epitaxial growth of an optically inert $NaGdF_4$ layer around $NaGdF_4$:Yb,Er core nanoparticle effectively prevents surface quenching of excitation energy. Scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and photoluminescence (PL) spectra have been used to characterize the size, crystal structure and emission color of the samples, respectively. In comparison with the core-only nanoparticles (Fig. 1), an obvious UCL enhancement can be observed after the $NaGdF_4$ shell growth, suggesting that coating a shell with a similar crystal lattice structure around the $NaGdF_4:Yb^{3+}$, Er^{3+} core can effectively minimize the luminescence quenching from surface defects and ligands. Due to the good water-solubility and strong UC luminescence, these hydrophilic nanocrystals may be used for imaging and detection applications in biological assays.

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The influence of gold interlayer on photoelectrochemical properties of TiO_2 nanotubes/ $BiVO_4$ junction

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TiO_2 in a form of nanotubes is one of the most promising n-type semiconductor that finds applications in photocatalysis, photoelectrochemical cells and photovoltaics [1]. However, wide energy band gap does not allow to direct use of solar light [2]. On the other hand, bismuth vanadate with an energy band gap 2.5 eV [3] is a promising photoanode for water oxidation, but the low mobility of charge carriers lead to the low efficiency of electron/hole separation [4]. The combination of TiO_2 and $BiVO_4$ leads to the formation of photocatalyst characterized by high photoactvity in photodecomposition of organic contaminations [5] and improved efficiency of water photooxidation in comparison with its counterparts [6].

In this work, TiO_2 nanotubes/$BiVO_4$ composite material is tested as a photoanode for water splitting. Such inorganic/inorganic junction allows to enhance charge carrier separation and inhibits adverse recombination process. Additionally, presence of $BiVO_4$ makes photoanode active in visible range of electromagnetic radiation. Furthermore, the influence of gold discontinuous layer (sputtered between two materials) on photoelectrochemical and electrical properties will be investigated.

Titania nanotubes were prepared via a two-step electrochemical anodization of titanium foil immersed in fluoride ions containing electrolyte. Gold layer was deposited onto titania nanotubes using magnetron sputtering. Afterwards, TiO_2/Au samples were modified by bismuth vanadate thin layer deposited using pulsed laser deposition technique. The morphology and composition of obtained materials on each step of photoanode preparation was tested using SEM and EDX. The crystalline phase of materials was determined by Raman spectroscopy. Electrical properties of electrodes with and without gold interlayer were investigated using electrochemical techniques. Anodic photocurrent of water oxidation in potentiostatic and potentiodynamic conditions was estimated under simulated solar light irradiation in aqueous K_2SO_4 electrolyte.

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Micropatterned $BiVO_4$ films as templates for photodeposition of various metallic nanoparticles

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Following the impressive success of development of artificial light harvesting photocatalysts *e.g.* TiO_2, $BiVO_4$, ZnO, a strong research focus is being put to improve energy storage and conversion techniques. Up to date, the most promising technology of photoconversion is based on the work of Fujishima and Honda who used TiO_2 as a photoanode for water splitting and hydrogen generation [1]. However, there is a special interest also in *e.g.* CO_2 photoreduction [2] and photodecomposition of hazardous chemical compounds [3].

This work is focused on the possibility of photodeposition of various metallic nanoparticles used as photocatalysts on micropatterned $BiVO_4$ thin films. Amorphous layers of $BiVO_4$ were prepared using pulsed laser deposition technique on glass substrates. Then, light induced crystallization using focused 514.7 nm laser illumination was utilized to obtain well-defined crystallized regions [4]. The micropatterns are characterized by higher conductivity and much better photoactivity than the amorphous surroundings. Since the band gap of crystallized $BiVO_4$ equals to ~2.5 eV and amorphous bismuth vanadate does not absorb in visible range, using the UV cut off filter should allow the selective photodeposition on crystallized regions. The crystallization process was tracked with Raman spectroscopy.

Two ways of photodeposition will be applied (*i*) reduction of cations and metals deposition and (*ii*) oxidation of cations and formation of oxides [5]. The deposition of metals *e.g.* silver, gold, copper will allow to prepare conductive patterns or $BiVO_4$/metal junctions with enhanced catalytic and plasmonic activity. On the other hand, the phenomenon of photo-oxidation of *e.g.* Mn^{2+} or Pb^{2+} and deposition of oxides directly on patterned catalyst will be utilized in water purification process. The photodeposition will be carried out from aqueous solutions of precursors (*e.g.* $AgNO_3$, H_2PtCl_6, $Mn(NO_3)_2$) with addition of electron or hole scavenger to enhance process by inhibiting adverse e^-/h^+ recombination. Glass/$BiVO_4$ micropatterned layers will be immersed in precursor solution and illuminated with visible electromagnetic radiation (>420 nm). The photodeposition processes will be investigate by scanning electron microscopy coupled with electron dispersive X-ray spectroscopy (EDX), and micro-Raman spectroscopy.

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SYNTHESIS AND INVESTIGATION OF UPCONVERTING $NaYF_4$ NANOPARTICLES OBTAINED IN OLEYLAMINE

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An emerging class of lanthanide-doped nanomaterials have attracted a huge amount of interest due to the potential to be used as catalysts, biosensors but most importantly for applications in biomedicine [1]. Since various studies of organic dyes and quantum dots for cancer diagnostics and therapy revealed several drawbacks, nontoxic lanthanide-doped upconverting nanoparticles (UCNP) are expected to overcome surpass certain limitations. UCNP's with deeper NIR light penetration into tissue, high signal to noise ratio, photostability [2] and low photodamage to biological samples more superior to conventional fluorophores.

Thermal decomposition synthesis in organic solvent (oleylamine, OM) by varying ratio of precursors was investigated. Examination of $NaYF_4$ nanoparticles doped with Yb^{3+} and Er^{3+} with XRD revealed that two different phase crystallites (cubic and hexagonal) were formed when using $(CF_3COO)_3RE{:}CF_3COONa$ concentrations 0.5:1 and 0.75;1. Furthermore, additional NaF peaks occurred because of rare earth deficiency in initial composition. Only when $(CF_3COO)_3RE{:}CF_3COONa$ ratio is 1:0,5 pure cubic phase was obtained. From morphological investigation of nanoparticles (SEM) it was determined that ultra-small spherical shape 5-10 nm particles were synthesized. In order to investigate unique upconverting properties of Yb^{3+}, Er^{3+} doping pair emission spectra were recorded (λ_{exc}=980 nm). From integrated red and green (R/G) spectral range a slight shift to overall yellow colour output is seen when nanoparticles were synthesized with 1:0.5 ratio. Thus, varying ratio of precursors in thermal decomposition synthesis procedure pure phase ultra-small nanoparticles can be obtained. This feature is beneficial working in biomedical field, although it can become a drawback considering weaker overall luminescence due to ultra-small nanoparticles.

Acknowledgements

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Electrochemically etched nano-probes for scanning near-field optical microscopy

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Atomic force microscopy (AFM) technique, combined with scanning near-field optical microscopy (SNOM) is a powerful tool for research of single nano-objects, biological macro-molecules, etc. [1]. The aperture-less silicone probes, coated with optically active nano-structured metallic coatings and illuminated with the laser beam, demonstrate the excitation of localised surface plasmon resonance [2]. The very sharp metal probe, localized in the evanescent electromagnetic field, has long-term optical activity in the near-field interaction "probe-surface" until there is no mechanical deformation of the probe tip due to direct contact with the surface. Therefore, preparation of metallic probes is an important issue. However, there are major challenges related to the reproducibility of nano-probe geometry, i.e. taper shape, apex angle and radius of curvature (ROC) of the tip.

In this work, electrochemical etching technique was applied in order to obtain Ag nano-probes with wide apex angle and minimum radius of curvature of the tip. The fabrication of Ag nano-probes was carried out by anodic etching of annealed Ag wire (purity 99.99%, 125 μm diameter) in the mixture of 2 M nitric acid HNO_3 and 96 % ethanol C_2H_5OH (volume ratio 1:2) [3]. The ring of 20 mm diameter, made from Pt wire (99.95 %, 500 μm diameter), was used as the cathode. DC voltage (in the range from 0.8 to 3 V) and pulsing voltage (in the range from 2 to 50 V, frequency 8Hz, impulse duration from 100 to 400 ns) were applied during electrochemical etching of Ag wire. The taper shape, apex angle and tip ROC of obtained Ag nano-probes were observed by scanning electron microscopy. The dependence of above-mentioned parameters of Ag nano-probes on voltage nature, nominal and "cut off" currents, immersion depth of Ag wire into electrolyte were determined. It was found that current "cut off" synchronization with "drop off" of the lower part of etched Ag wire is very important for the quality of Ag nano-probes. The optical activity and light scattering from the tip of obtained Ag nano-probes was investigated by dark field spectroscopy. The sharpest and wide angle nano-probes were also tested in constructed experimental platform. Here, in the phase boundary evanescent electromagnetic field and the tip of nano-probe were excited by totally reflected laser beam (λ=532 nm). The light, scattered from the tip of Ag nano-probe was collected by the inverted optical microscope, equipped with high refractive index objective, and routed through the system of the optical lens into photosensitive device for the further readout. The optical activity of Ag nano-probes was evaluated by the spectral response and Rayleigh scattering was determined from the spectra.

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MORPHOLOGY AND RHEOLOGICAL PROPERTIES OF INCOMPATIBLE POLYMER COMPOSITIONS WITH NANOPARTICLES TiO_2/SiO_2

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Development of nanomaterials and its production technologies is a promising scientific trend in polymer and chemical fiber modification. Introducing nanoadditives to polymer compositions allows to regulate material properties both by nanoadditive properties and by its effect on structure formation during multicomponent composition transformation [1].

Objective of this study was to explore the effect of titanium oxide/silica (TiO_2/SiO_2) composite nanoadditive on polypropylene/copolyamide (PP/CPA) morphology and its melt flow regularity.

Object of this study was 30/70 wt.-% PP/CPA composition filled with (0.1 to 3.0 wt.-%) TiO_2/SiO_2 additive with 62 m^2/g specific surface and 7.0 wt.-% of titanium dioxide. First the additive was introduced to a fiber-forming polymer (PP) and then mixed with matrix (CPA). Compositions were prepared using worm-disc extruder. Morphology of extrudate was evaluated by determining quantity and size of all polymer structure types after the matrix polymer extraction. Method of capillary viscosimetry was used to study rheological properties of extrudate.

Microscopy showed that during the flow of PP/CPA nanocompositions, phase distribution effect took place where fine jets (microfibers) were created by disperse phase component (PP) and then elongated by the flow of second component (matrix). Introduction of nanocomponents TiO_2/SiO_2 improved PP fiber-forming process in CPA matrix: average diameter of microfibers decreased from 4.0 μm in initial composition down to (1,8÷2,5) μm. Herewith concentration of nanoparticles significantly affected the level of component dispersing during phase distribution: minimal diameter (1.8 μm) was obtained with 1.0 mass concentration of nanoparticles.

Evidently, nanoadditive lowered interfacial tension by creating developed transitional layer at mixture components interface. A significant effect was achieved by prevalent localization of nanoparticles. During preliminary mixing, particles of nanofiller dispersed mainly at polymer composition interface due to different polymerophilic qualities of components towards the surface of nanoparticles [1,2]. Hydrophilic nanoparticles TiO2/SiO2 were poorly moistened by non-polar PP melt and were extruded to PP/CPA interface.

Viscosity (η) of nanofilled composition melts decreased sharply (2.0÷6.5 times) comparing to η of initial PP and CPA. Viscosity decrease is distinctive for composition melts where disperse phase component creates fluid jets during conversion, since compositions with deformable drops need smaller pressure drop than individual polymers to ensure flow of melt [3]. Viscosity decrease in $PP/CPA/TiO_2/SiO_2$ composition melts is fundamental since it reflects the change in flow mechanism, specifically transition from segmented relocation of polymer macromolecules in the flow to stratificated flow regime. Thereby studied approach allows to regulate micro- and macrorheological processes in thermodynamically incompatible polymer composition melts.

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FORMATION OF SILVER NANOPARTICLES AND THEIR INFLUENCE ON FLUORESCENCE OF ORGANIC MATERIALS

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Metal nanoparticles and nanostructured metal films excited by electromagnetic radiation exhibit collective oscillations of their conduction electrons, known as localized surface plasmon resonance (LSPR), that give these materials a number of interesting and useful optical properties. Possible manipulations of these properties lead to various applications of silver nanoparticles (AgNPs) in optoelectronics [1], biosensing [2], catalysis, metal enhanced optical spectroscopies (metal enhanced fluorescence (MEF) [3], surface enhanced Raman scattering (SERS) [4]), as antimicrobials [5] and other. For optimized applications of these metal nanostructures and their unique features, it is important to understand the dependence of spectral properties of metal-fluorophore complex on their individual optical behavior.

In this work, layers of AgNPs of different sizes were formed and their influence on optical properties of low fluorescent conjugated polymer RZ11 and highly fluorescent organic dye Uranin was investigated. Spherical AgNPs were formed by thermal evaporation and annealing: Ag layer was deposited on glass and heated until AgNPs were formed (Fig. 1, A-C). Organic materials (Fig. 1, D and E) on layers of AgNPs were spin-coated of few hundred nanometers thickness. Samples were studied by using steady-state and time-resolved absorption and fluorescence spectroscopy.

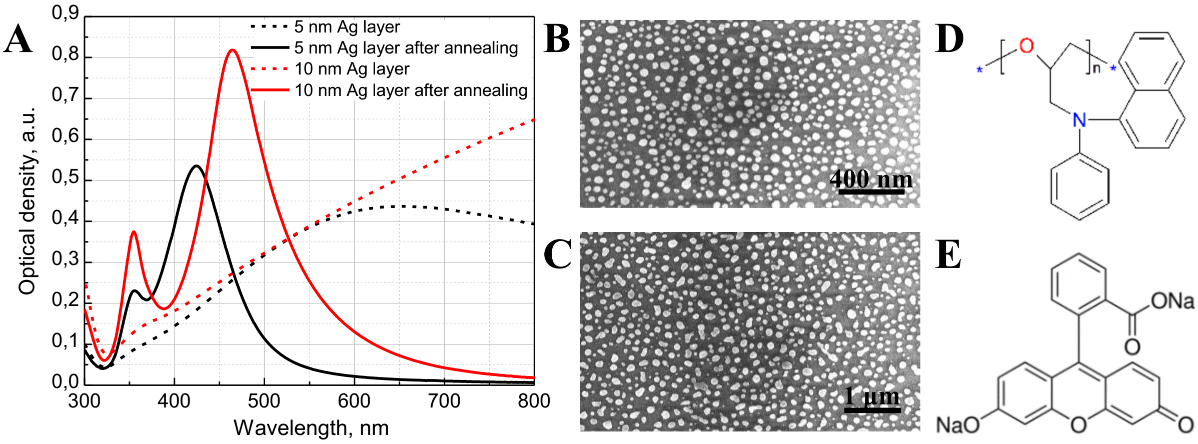

Fig. 1. Absorption spectra (A) and SEM images of 5 nm (B) and 10 nm (C) deposited Ag layers after annealing, and chemical structures of investigated compounds: polymer RZ11 (D) and dye Uranin (E)

We conclude that for achieving fluorescence changes or enhancement, absorption and fluorescence spectra of fluorophores and plasmon resonance overlap must be ensured and wavelength of the excitation light is of great importance too.

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NANOPLATELET MoS_2 FILMS DECORATED WITH Pt QUANTUM DOTS FOR EFFECTIVE HYDROGEN PRODUCTION

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The precious metals of Pt group (Pt, Pd, Rh) are ascribed to most effective electrocatalyst for hydrogen evolution reaction (HER) from acidic solutions. Note that the HER at these electrodes starts in a vicinity of zero volt *vs* RHE attaining roughly 200 mA cm^{-2} current density at -200 mV. Recently, nanostructured MoS_2 architectures have been also reported as prospective HER electrocatalysts [1,2]. However the HER at MoS_2 nanoplatelet edges starts just at about -200 mV vs RHE. Besides, the efficiency of HER at MoS_2 depends significantly on the thickness of nanoplatelets [3]. In this study, we preset the formation of the novel MoS_2-based nanoplatelet electrodes (Fig. 1a) decorated with numerous Pt quantum dots (Fig. 1b) for HER efficiency enhance, attaining quite similar efficiency, ca 200-250 mA cm^{-2} at -300 mV *vs* RHE with the onset of reaction at 0 V.

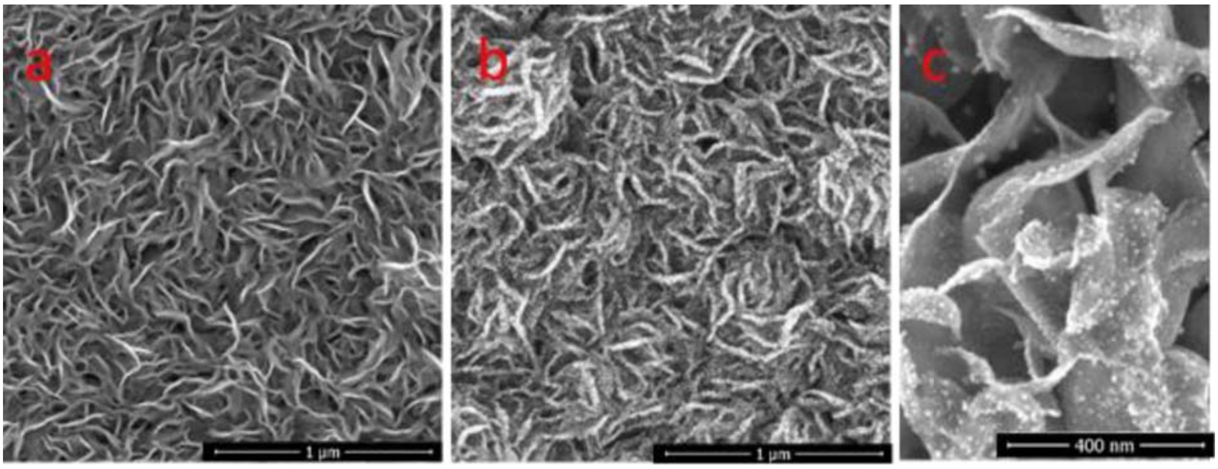

Figure 1. Top-side SEM views of the MoS_2 film fabricated onto the Ti surface by hydrothermal treatment in the solution containing 5.0 amonium heptamolybdate and 90 mmol L^{-1} thiourea at 220 ^{0}C for 5 h before (a) and after 250 (b, c) potential cycling in 0.5 mol L^{-1} H_2SO_4 within [-0.3 to 0.04] V range *vs* RHE. The Ag/AgCl,KCl_{sat} was used as a reference.

Notably that these HER parameters was obtained just with $\leq$ 5 mg m^{-2} Pt quantum dots loading. This effect was linked with the synergetic catalytic behavior of MoS_2 edges and Pt quantum dots as well as with the formation of new active areas for hydrogen evolution reaction onto the nanoplatelet surface.

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WET- AND DRY-PROCESS FEASIBLE CARBAZOLE TYPE HOSTS FOR HIGHLY EFFICIENT PHOSPHORESENT OLEDs

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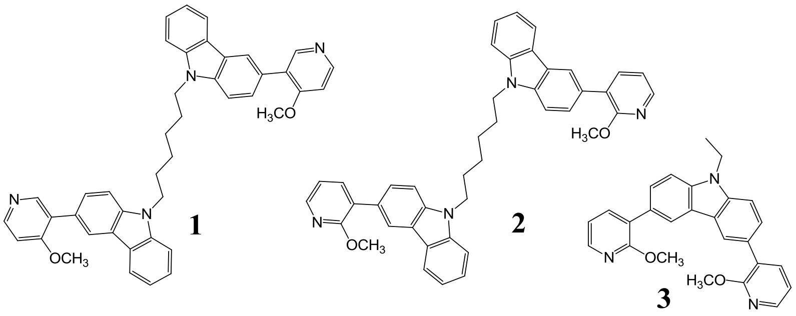
Organic light-emitting diodes (OLEDs) have drawn enormous attention due to their increasing applications in flat-panel displays and solid state lightings[1]. Nowadays, phosphorescent materials become ideal for fabricating high-efficiency OLEDs, because they can theoretically approach a nearly 100% internal quantum efficiency by harvesting singlet and triplet excitons simultaneously through intersystem crossing[2-5].

A wet- and dry-process feasible host material is crucial to realize, respectively, low cost roll-to-roll fabrication of large area and high performance organic light-emitting diodes with precise deposition of organic layers. We demonstrate high efficiency phosphorescent OLED devices by employing a newly synthesized carbazole- based hosts materials: 1,6-bis[3-(2-methoxy-3-pyridinyl)carbazol-9-yl]hexane (**1**), 1,6-bis[3-(6-methoxy-3- pyridinyl)carbazol-9-yl]hexane (**2**) and 3,6-di(2-methoxy-3-pyridinyl)-9- ethylcarbazole (**3**). By doping a typical green emitter *fac* tris(2-phenylpyridine)iridium (Ir(ppy)3) in the compound **1**, for example, the resultant wet-processed device exhibits at 100 cd m-2 a current efficiency of 27 cd A-1 and a power efficiency of 16.1 lm W-1. The dry-processed device shows a current efficiency of 61 cd A-1 and a power efficiency of 62.8 lm W-1. The high efficiency may be attributed to the host possessing an effective host-to-guest energy transfer, effective carrier injection balance, and the device architecture enabling excitons to generate on both host and guest.



1

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Acknowledgements

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PHENYLVINYL - SUBSTITUTED CARBAZOLE TWIN COMPOUNDS AS HOLE TRANSPORTING MATERIALS FOR ORGANIC LIGHT EMITTING DIODES

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Carbazole-based polymers and low-molecular-weight derivatives are among the most studied materials for electronic applications due to their good electron donating properties and high hole mobility in their layers [1, 2]. Derivatives containing electronically isolated carbazole rings have also high triplet energies and are widely used as host materials for phosphorescent OLEDs [3, 4]. We synthesized twin derivatives containing two phenylvinyl substituted carbazole fragments, which were expected to show enhanced hole injection and transport properties and to be suitable as hole transporting materials for multilayer OLEDs.

The twin compounds 1,6-Di(3-(2-phenylvinyl)carbazol-9-yl)hexane (1), 1,6-Di{3-[2-(4-methoxyphenyl)vinyl]carbazol-9-yl} hexane (2) and 1,6-Di{3-[2-(4-methylphenyl)vinyl]carbazol-9yl}hexane (3) were prepared by reaction of the formylcarbazol-9-yl-containing dimer 1,6-Di-(3-formylcarbazol-9-yl)hexane with excess of diethyl benzylphosphonate, diethyl 4-methoxybenzylphosphonate, or diethyl 4-methylbenzylphosphonate, respectively. The synthesized compounds were identified by mass spectrometry and ^{1}H NMR spectroscopy. The results were found to be in good agreement with the proposed structures. All the materials are soluble in common organic solvents. Transparent thin films of compounds (1–3) can be prepared from their solutions by spin coating. The derivatives form homogeneous amorphous layers with glass-transition temperatures in the range 74–119 ºC. The electron photoemission spectra of the layers showed their ionization potentials were in the range 5.05–5.45 eV.

Twin compounds containing two phenylvinyl substituted carbazole rings were characterized as hole-transporting layer materials for organic light-emitting devices. The compounds were tested as HTL in organic light-emitting diodes with Alq_3 as green emitter and electrontransporting layer. The best overall performance was observed for the device based on the twin compound containing 3-[2-(4-methylphenyl)vinyl]carbazolyl groups—maximum photometric efficiency was 2.34 cd/A and maximum brightness was approximately 7380 cd/m^2. Photometric efficiency at 1000 cd/m^2 was substantially higher than that of a PEDOT:PSS-based device.

Acknowledgements

The OLED materials were prepared in the frame of the project TAP LLT 01/2014.

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DIMETHOXYDIPHENYLAMINO-SUBSTITTED 9-NAPHTHYLCARBAZOLE DERIVATIVE AS BIPOLAR EMITTER FOR COLOUR-TUNABLE OLEDS

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The molecular structure of the organic semiconductors determine the properties of their functional films. Combining of donor and acceptor moieties within a single molecule provides the background for the good balance between the electron and hole mobilities that constitutes one of the mandatory conditions for the fabrication of the single-layer high-efficiency organic light-emitting diodes (OLEDs) [1]. The choice of the bipolar semiconductors with the high electron and hole mobilities and high luminescence quantum yields is rather limited [2]. One way to improve the efficiency of OLEDs and to extend the EL spectra is an exciplex-type emission that can be induced at the interface between the functional organic layers [3].

In the present work we present the synthesis and the results of spectroscopic, thermal and electrochemical characterization of bipolar semiconductor 3,6-di(4,4'-dimethoxydiphenylaminyl)-9-(1-naphthyl)carbazole (DPNC) which demonstrates the voltage-dependent green-blue electrofluorescence (Fig. 1). We also successfully fabricated the bilayer OLED which demonstrate the exciplex emission from the interface between the DPNC layer and adjacent electron-transporting layer of bathophenanthroline. We have clearly observed that the DPNC demonstrates the voltage-dependent electroluminescence both in the short-wavelength region as well as in the long-wavelength region due to the electroplex emission. These observations open up the new possibilities for the fabrication of color-tunable OLEDs with the minimal number of functional layers.

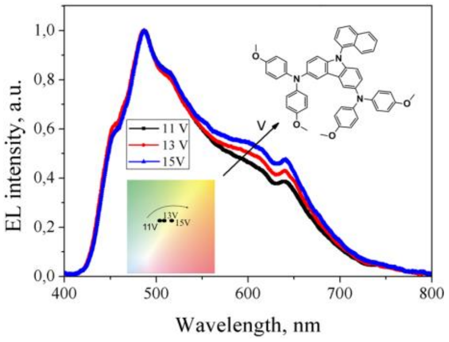

Figure 1. Electroluminescence spectrum

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FLUORESCENCE QUENCHING OF INDOLO[3,2-*b*]CARBAZOLE COMPOUNDS BY CONFORMATIONAL MOTIONS OF ATTACHED SUBSTITUENTS

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Indolo[3,2-b]carbazoles (ICZ) is a popular class of organic materials for various electronic applications. They have been used in a number of devices such as organic light-emitting diodes (OLEDs) [1], organic field-effect transistors (OFETs) [2], solar cells [3], etc.. ICZ is an important unit to synthesize various oligomers and polymers with interesting electrical, optical, magnetic and other features. ICZ molecules have ladder-type planar structure, similar as the pentacene, and two nitrogen atoms in the carbazole fragments, which provide electron-donating ability [4]. For excellent performance and practical applications it is essential to understand the influence of different substituents to the behavior of ICZ compounds.

In this work, six new ICZ derivatives with different connected substituents were investigated. Steady-state and time-resolved absorption and fluorescence spectroscopy methods were used to study their spectroscopic properties in solutions and in solid films, and to reveal differences among molecules caused by different substituents. Quantum chemical calculations were also performed to support the experimental data.

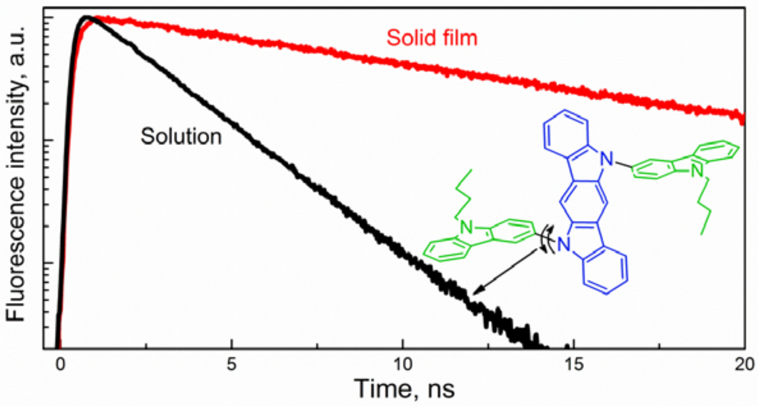

Fig. 1. Fluorescence decay kinetics of one of the investigated ICZ molecules in solution and in thin film. Conformational motions of substituents lead to increased non-radiative relaxation

We conclude that spectroscopic properties of ICZ compounds may be significantly altered by attaching substituents at different positions of ICZ molecules, however, in order to maintain their high fluorescence yield, conformational motions of the substituents shall be restricted.

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FLUORESCENCE QUENCHING OF GLUCOSE OXIDASE SELF-ENCAPSULATED WITHIN POLYPYRROLE

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The usage of biosensing systems is promising - rapid and accurate method for the detection and analysis of various compounds. Nowadays one of the best-known and the most common biosensors are the glucose biosensors [1]. The active part of the biosensor is glucose oxidase (GOx) enzyme immobilized on the surface of the electrode. Usually free enzymes are not stable, but different immobilization procedures have confirmed that immobilized enzymes exhibit better stability, sensibility, specificity and durability compared to the free enzymes in a solution. Using the conducting polymers as a matrix for immobilization that facilitates electrons transfer, it is possible to design sensitive and biologically compatible biosensors [2].

Spectroscopic properties of GOx, flavin adenine dinucleotide (FAD) and compounds immobilized in polypyrrole polymer matrix were investigated. The purposes of this research were to evaluate absorption and fluorescence spectra changes and to determine polypyrrole shell influence to fluorescence quenching of the glucose oxidase self-encapsulated within polypyrrole. Fig.1. shows the fluorescence decay times changes in 29-day period.

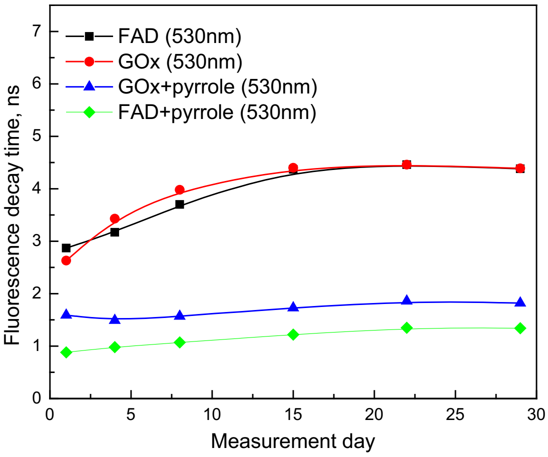

Fig.1. Fluorescence decay average time dependence of measurement days.

During this study we found that GOx enzyme fluorescence band at 530 nm belongs to coenzyme FAD fluorescence [4]. The increase of GOx fluorescence, which is due to the fact that the enzyme has changed its structure and denatured, was visible in 29 day measurement period. To stabilize GOx and reduce FAD's release, the enzyme was immobilized in the polypyrrole matrix.

The exploration of GOx and pyrrole solution confirms that the encapsulated GOx enzyme has become more stable. It was found that polypyrrole shell reduces the fluorescence quenching twice. Changes of FAD and pyrrole average fluorescence relaxation times showed that FAD was also encapsulated within polypyrrole. FAD quenching time decreased and their changes in 29 day period have become more even.

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DYES WITH 3-PYRROLIN-2-ONE ELECTRON ACCEPTING MOIETY: SINTESIS AND INVESTIGATION IN THE DYE–SENSITIZED SOLAR CELLS

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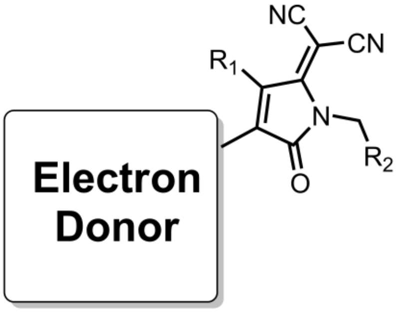
Accelerated development of technologies and their influence on people's lives is increasingly associated with energy demand. In order to meet this growing energy demand and minimize related costs new and effective energy generation methods are indispensable. Among several alternative sources, photovoltaics are among the most promising, as solar energy is free and unlimited energy source. Solar cell performance depends on the dye compatibility with other solar cell components, its energy level, light absorption spectrum and intensity. Organic dyes offer a lot of possibilities for improving a wide range of properties such as molecular structure, efficient light-harvesting ability in different parts of the solar spectrum, control over the molecular energy levels, molecule-to-molecule interactions and charge generation and separation [1, 2].



In this work new dyes with 3-pyrrolin-2-one electron accepting moiety have been synthesized and their thermal, optical and photovoltaic properties investigated. It has been observed that the introduction of the long aliphatic chain into the dye molecule reduces intermolecular interactions and affect the ionization potential of the materials.

UV-VIS-NIR measurement of the investigated dyes revealed that they absorb light in the 450-950 nm range. Dye-sensitized solar cells, containing investigated materials, were constructed and preliminary measurements have been performed.

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SYNTHESIS AND ANTIOXIDANT ACTIVITY OF 1,3,4-OXA(THIA)DIAZOLE AND 1,2,4-TRIAZOLE-5-(THIO)ONE DERIVATIVES

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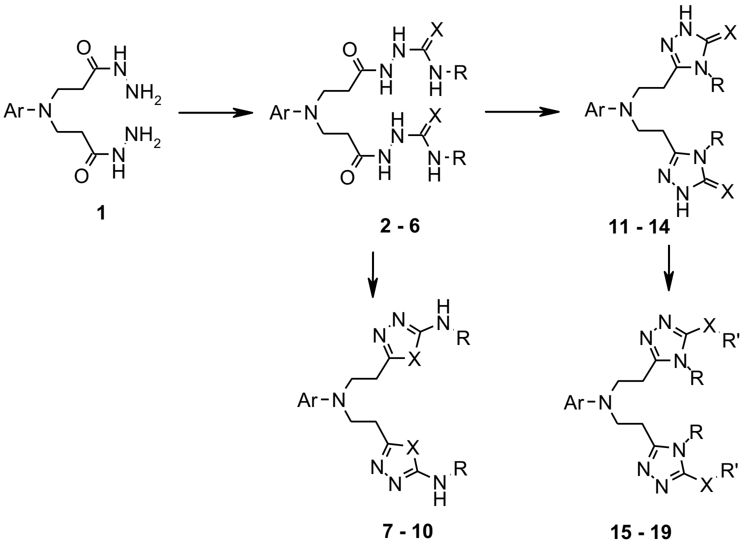
A series of novel derivatives of 3-((2-carboxyethyl)phenylamino)propanoic acid bearing two identical heterocyclic moieties were synthesized. Reaction of bispropanehydrazide **1** with phenyl- or 4-chlorophenyl isocyanates, or methyl, phenyl or 2,6-dimethylphenyl isothiocyanate in methanol gave bishydrazinecarboxamides **2** and **3**, and bishydrazinecarbothiamide derivatives **4**–**6**.

Bisoxadiazoleamine **7**, and its chloro analogue **8** were synthesized by heating bisphenylsemicarbazides **2** and **3** under reflux in phosphoryl chloride. Thiadiazole derivatives **9** and **10** were synthesized from bisthiosemicarbazides **4** and **5** by stirring their mixture in concentrated sulfuric acid at room temperature for 15 min. Cyclization of bissemicarbazides **3**–**6** in basic medium resulted in formation of bistriazolone **11**, and thio derivatives **12**–**14**. Alkylation reactions of bistriazolethione **13** with haloalkanes, in DMF in the presence of NaH at room temperature, furnished compounds **15**–**20**.



Ar = C_6H_5; R: **2**, **5**, **7**, **10**, **13**, **15**–**19** C_6H_5; **3**, **8**, **11** 4-Cl-C_6H_4; **4**, **9**, **12** CH_3; **6**, **14** 2,6-$(CH_3)_2$-C_6H_3. R′: **15** $CH_3CH_2CH_2CH_2CH_2$; **16** NH_2COCH_2; **17** $C_6H_5COCH_2$; **18** 4-$ClC_6H_4COCH_2$; **19** 4-$NO_2C_6H_4COCH_2$.

5,5'-((Phenylazanediyl)bis(ethane-2,1-diyl))bis(4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione) (**18**) showed excellent antioxidant activity, 3 times higher than that of the antibiotic control (cefazolin).

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TRANSFORMATION OF ETHYL 1-ARYL-2-METHYL-4-OXO-1,4,5,6-TETRAHYDROPYRIDINE-3-CARBOXYLATES UNDER THE INFLUENCE OF NITROGEN NUCLEOPHILES

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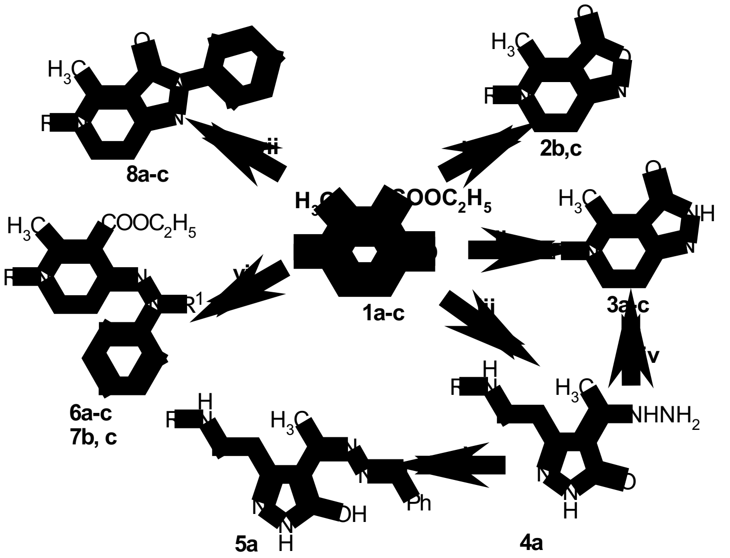
Compounds containing hydropyridone moiety are important intermediates in the synthesis of other biologically active heterocyclic compounds [1–4].

In this work, condensation reactions of tetrahydropyridones with hydroxylamine, hydrazine, phenylhydrazine and *N*,*N*-disubstituted hydrazines were investigated.



R = **a)** 4-CH_3CH_2-C_6H_4;
b) 2-CH_3-5-Cl-C_6H_3;
c) 3-Cl-4-CH_3-C_6H_3.

Reagents and conditions:
(**i**) $NH_2OH{\cdot}HCl$, iPrOH, pyridine, reflux, 3 h;
(**ii**) $N_2H_4{\cdot}H_2O$, AcOH, reflux, 3 h;
(**iii**) $N_2H_4{\cdot}H_2O$, MeOH, reflux, 7.5 h;
(**iv**) AcOH, reflux, 8 h;
(**v**) C_6H_5CHO, iPrOH, 1,4-dioxane, rt, 4 h;
(**vi**) *N*-methyl-*N*-phenylhydrazine (**6a-c**) or *N*,*N*-diphenylhydrazine (**7b, c**), iPrOH, HCl, reflux, 3 h;
(**vii**) $C_6H_5NHNH_2$, AcOH, reflux, 3 h.

Condensation of pyridones **1b, c** with hydroxylamine hydrochloride in 2-propanol in the presence of pyridine as a catalyst afforded bicyclic compounds **2b, c**. Reaction of pyridones **1a-c** with hydrazine in acetic acid gave bicyclic compounds **3a-c**. Under treatment of **1a** with hydrazine monohydrate in methanol at reflux pyrazolone derivative **4a** was formed. Condensation of compounds containing hydrazide moiety with carbonyl compounds is rather facile. However, reaction of pyrazolone **4a** with benzaldehyde in 2-propanol in the presence of concentrated hydrochloric acid at reflux did not provide the expected hydrazone derivative **5a**; instead the bicyclic compound **3a** was obtained. When analogous reaction of **4a** was carried out in the presence of acetic acid, bicyclic compound **3a** was isolated again. Therefore, it can be assumed that cyclization of pyrazolone **4a** is facile under the influence of acids. The target hydrazone-type product **5a** was synthesized by condensation reaction of **4a** with benzaldehyde in the mixture of 2-propanol and 1,4-dioxane (1:1) at room temperature.

When *N*,*N*-disubstituted hydrazines were employed in the reactions with pyridones **1a-c**, only the pyridone 4-CO group participated in the condensation reaction providing the corresponding hydrazones **6 a-c** and **7b, c**, meanwhile interaction of **1** with phenylhydrazine afforded cyclic compounds **8a-c**.

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SYNTHESIS OF 3-[4-(AMINOSULFONYL)ANILINO]PROPANOIC ACIDS WITH AZOLE MOIETIES

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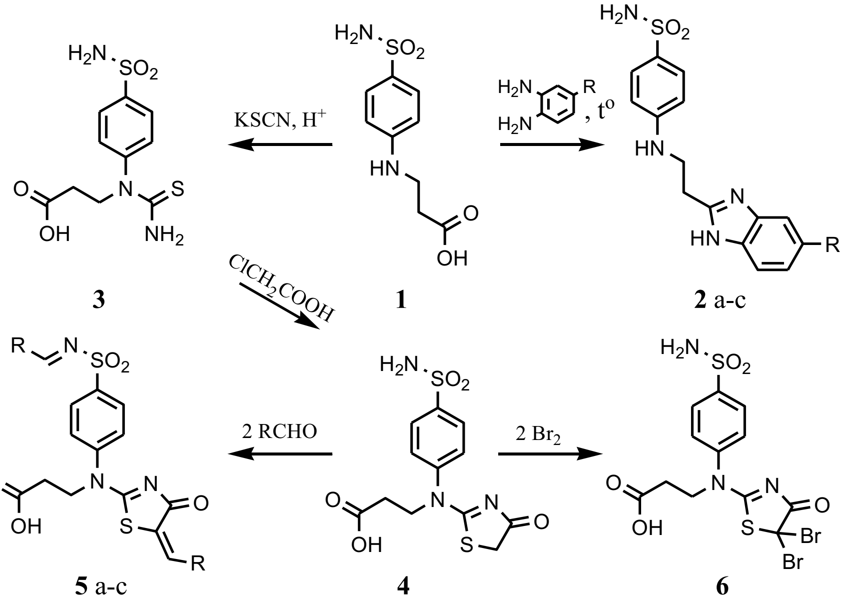
Heterocycles are present in a wide variety of drugs, most vitamins, many natural products, biomolecules, and biologically active compounds, including antibiotic, anti-HIV, antimicrobial, antibacterial, antifungal, antiviral, fungicidal, and insecticidal agents [1-4].

New 3-[4-(aminosulfonyl)anilino]propanoic acid derivatives **2a-c** with benzimidazole moiety in this work were synthesized from β-alanine **1** and 1,2-diaminobenzenes by Philips condensation reaction. The condensation of β-alanine **1** with potassium thiocyanate in acetic acid was formed 3-[(aminocarbothioyl)-4-(aminosulfonyl)anilino]propanoic acid (**3**). 3-[4-(Aminosulfonyl)(4-oxo-4,5-dihydro-1,3-thiazol-2-yl)anilino]propanoic acid (**4**) was synthesized from compound **3** and monochloroacetic acid.



2 a) R = H, b) R = CH_3, c) R = Cl; **5** a) R = C_6H_5, b) R = 4-Cl-C_6H_4; c) R = 4-Br-C_6H_4.

The condensation of thiazolone **4** with excess of aromatic aldehydes afforded of thiazolone derivatives **5 a-c**. The reactions were performed in water in the presence of sodium carbonate. Bromination of compound **4** was performed in acetic acid at 60 °C, which resulted in the 5,5-dibromothiazolone **6**. The structure of the synthesized compounds was confirmed by elemental analysis, ^{1}H, ^{13}C NMR and IR spectral data.

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SYNTHESIS OF 5-SUBSTITUTED *N*-(1-NAPHTYL)-*N*-(4-OXO-4,5-DIHYDRO-1,3-THIAZOL-2-YL)-β-ALANINES

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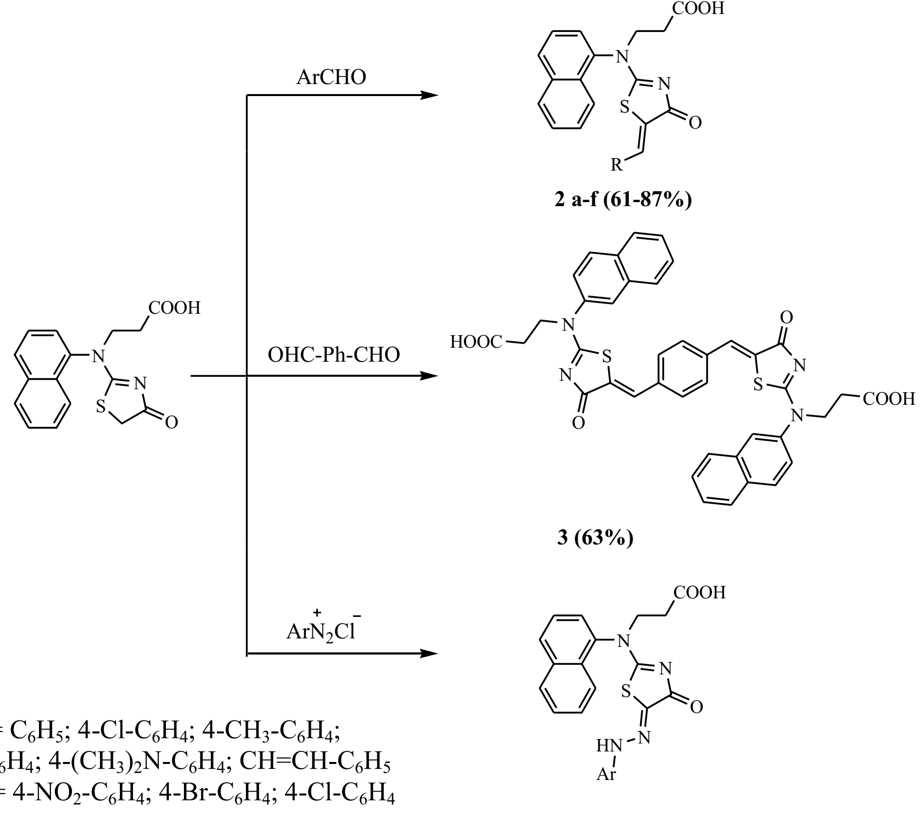
The thiazolidinone scaffold have found in a number of drugs, which characterictic antimicrobial, antitubercular, anti-inflamantory, antiviral and etc. biological activity [1]. Hydrazones have interesting biological properties, such as anti-inflammatory, analgesic, anticonvulsant, antituberculous, antitumor, anti-HIV and antimicrobial activity [2]. The coupling of diazonium compounds with active methylene compounds is one of the oldest methods for the synthesis of arylhydrazones.

The reactions of of *N*-(1-naphthyl)-*N*-(4-oxo-4,5-dihydro-1,3-thiazol-2-yl)-β-alanine (**1**) with aromatic aldehydes in water in the presence of sodium carbonate at 90-100 °C provided compounds **2 a-f, 3.** The products **2 a-f, 3** were obtained after 4 h and were isolated from the reaction mixtures by acidifying them with acetic acid.



2 a-f (61-87%)

3 (63%)

2 a-f Ar = C_6H_5; 4-Cl-C_6H_4; 4-CH_3-C_6H_4;
4-NO_2-C_6H_4; 4-$(CH_3)_2N$-C_6H_4; CH=CH-C_6H_5
4 a-c Ar = 4-NO_2-C_6H_4; 4-Br-C_6H_4; 4-Cl-C_6H_4

4 a-c (46-66%)

Hydrazones **4 a-c** were synthesized by coupling of coresponding diazonium compounds with *N*-(1-naphthyl)-*N*-(4-oxo-4,5-dihydro-1,3-thiazol-2-yl)-β-alanine (**1**) at 0-5 °C temperature. The structures of the synthesized compounds have been established mainly on the basis of ^{1}H and ^{13}C NMR spectra.

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AN EFFICIENT CONVERSION OF 2-AMINOPYRIDINES TO 2-HALOGENPYRIDINES

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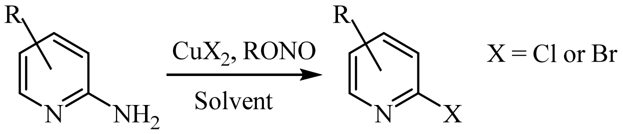
The Sandmeyer reaction is a widely used method for the preparation of aryl halides from aryl amines. Aryl diazonium halides, obtained from aryl amines by diazotization using sodium nitrite/hydrohalic acid in water [1] or alkyl nitrites [2] react with copper halides to form corresponding halides in average to good yields. However, this reaction in case of substituted 2-aminopyridines gives only small yields or even no 2-halopyridines under usual conditions [3].



In this paper we present a direct and efficient conversion of some 2-aminopyridines to 2-halogenpyridines in non-aqueous media.

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SYNTHESIS OF 1-(5-CHLORO-2-HYDROXYPHENYL)-5-OXOPYRROLIDINE-3-CARBOHYDRAZIDE DERIVATIVES

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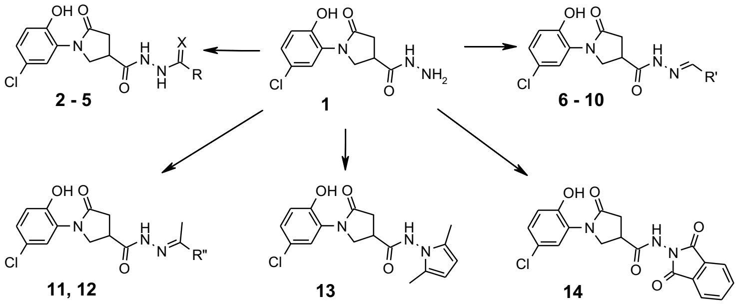
N-Substituted *β*-amino acids and their derivatives exhibit a variety of biological activities including antibacterial, antiviral, fungicidal, antihelminthic, anticancer, antiinflammatory etc [1-5]. New potentially biologically active 1-(5-chloro-2-hydroxyphenyl)-5-oxopyrrolidine-3-carboxylic acid derivatives were designed and synthesized.



2 R = C_6H_5, X = O; **3** R = 4-Cl-C_6H_4, X = O; **4** R = CH_3, X = S; **5** R = C_6H_5, X = S; **6** R' = C_6H_5; **7** R' = 4-Br-C_6H_4; **8** R' = 4-Cl-C_6H_4; **9** R' = thiophen-2-yl; **10** R' = pyridin-4-yl; **13** R" = CH_3; **14** R" = C_6H_5.

Reaction of 5-oxopyrrolidine-3-carbohydrazide **1** with phenyl- or 4-chlorophenyl isocyanates, or methyl, phenyl isothiocyanates in methanol gave hydrazinecarboxamides **2** and **3**, or hydrazinecarbothiamide derivatives **4** and **5** respectively. The corresponding hydrazones **6–10** were synthesized in good yields by the reaction of acid hydrazides **1** with aromatic aldehydes in methanol at reflux. The structures of **6–10** have been established on the basis of ^{1}H and ^{13}C NMR spectra.

Pyrrolidine-3-carbohydrazides **11** and **12** were synthesized from hydrazide **1** by treating it with acetone and acetophenone. The reaction of carbohydrazide **1** with 2,5-hexanedione in the presence of acetic acid was facile and resulted in formation of 1-(5-chloro-2-hydroxyphenyl)-*N*-(2,5-dimethyl-1*H*-pyrrol-1-yl)-5-oxopyrrolidine-3-carboxamide (**13**).

Oxopyrrolidine-3-carboxamide (**14**) was synthesized from hydrazide **1** and phthalic anhydride.

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SYNTHESIS OF NOVEL PYRAZOLE SCAFFOLD-BASED HETEROCYCLIC SYSTEMS

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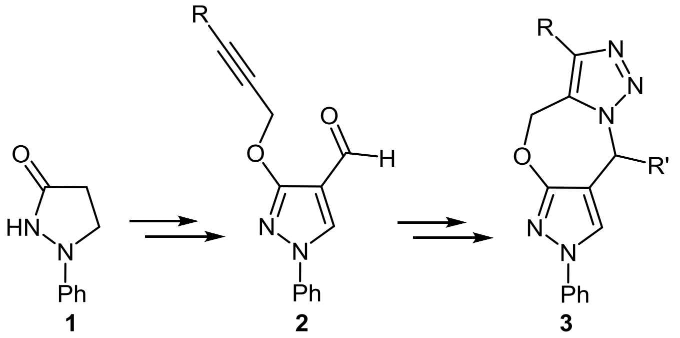
Condensed and substituted pyrazole derivatives are mostly applied in pharmacy because they possess a broad spectrum of biological activities [1-4]. Pyrazole compounds continue to attract significant interest due to their applicability in dye and agriculture industries [5,6].

The aim of this work was to synthesize pyrazolo[4,3-*f*][1,2,3]triazolo[5,1-*c*][1,4]oxazepines using intramolecular 1,3-dipolar cycloaddition of azide-alkynes. The starting material was first converted into 1-phenyl-3-(prop-2-yn-1-yloxy)-1*H*-pyrazole-4-carbaldehyde following oxidation, alkylation and Vilsmeier-Haack reaction, respectively. The obtained product was then treated with various Grignard reagents to afford secondary alcohols which were transformed into azide-alkynes by reaction with trimethylsilyl azide and boron trifluoride diethyl etherate. The formation of desired condensed heterocyclic systems **3** was obtained *via* intramolecular 1,3-dipolar cycloaddition employing various azide-alkynes.

Pd-catalyzed Sonogashira cross-coupling reaction was a useful tool to afford more various condensed derivatives possessing aryl moiety in triazole ring.

The structures of the products were confirmed by data of NMR and IR spectroscopy, mass spectrometry and elemental analysis.



Scheme 1

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SYNTHESIS OF 5-ARYL-3,3-DIMETHYL-2,3-DIHYDRO-1*H*-INDOLE CARBOXYLIC ACID DERIVATIVES

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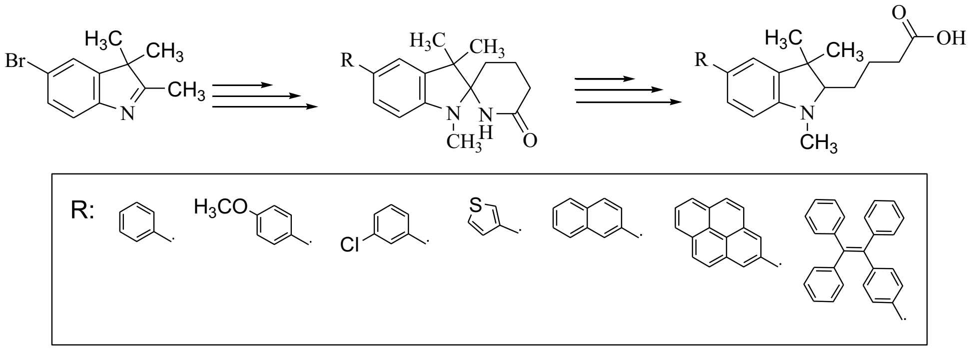
The halogenated 2,3-substituted indole derivatives can be obtained by Fischer indole synthesis [1]. They can be used for synthesis of different dyes: cyanine, squaraine, implantable fluorescent dyes and spiroxazine. One of the most attractive research topics are fluorescent dyes which are widely used as sensitizers for color photography [2], medical diagnostics [3], DNA or RNA molecules labeling or as molecular sensors [4].

In the present work synthesis of 5-arylspiro[indole-2,2'-piperidin]-6'-ones starting from 5-bromoindole *(Scheme 1)* will be presented. The obtained spiro compounds were transformed to indole carboxylic acid derivatives, which can be suggested as a potential agent of quorum sensing research.



Scheme 1

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SYNTHESIS OF NEW 2-AMINOTHIAZOLE DERIVATIVES

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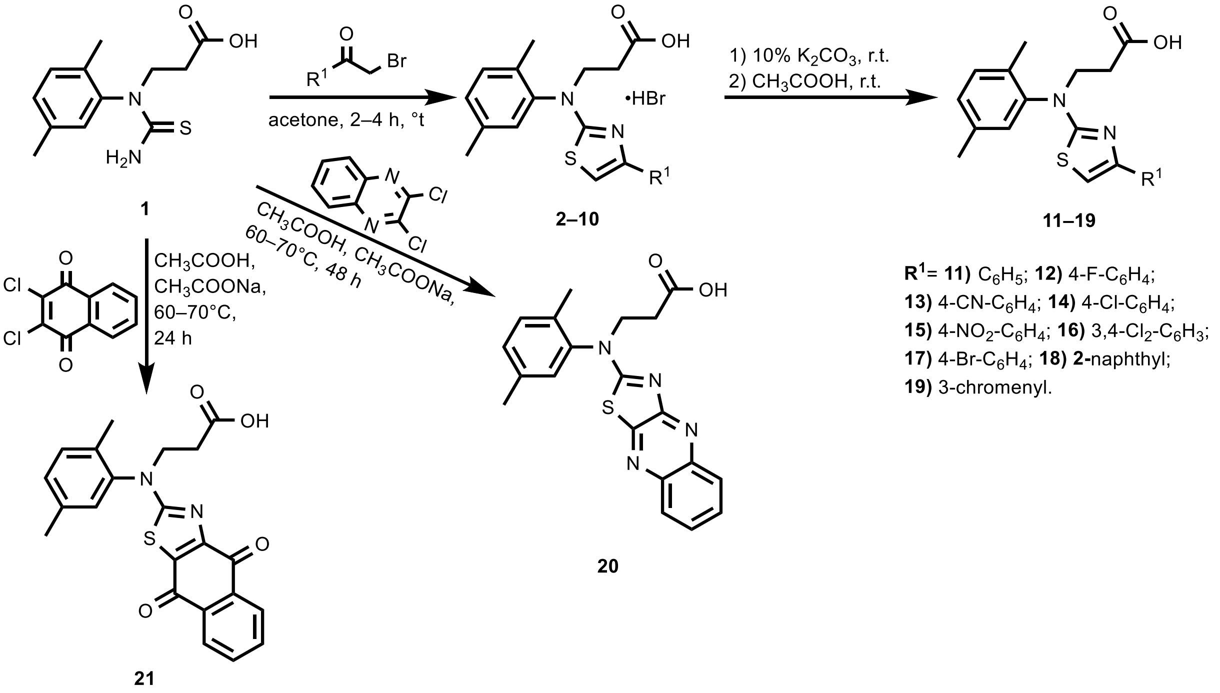
Thiazole derivatives are widely known for their extensive pharmacological activities, such as antiallergic [1], anti-inflammatory [2], antihypertensive [3], antibacterial and antifungal [4], and they are frequently applied in medicine. Therefore, synthesis of thiazole fragment containing compounds is a perspective field for a further research.

In order to obtain compounds **11–19**, first, their hydrobromides **2–10** were synthesized by interaction of 3-(1-(2,5-dimethylphenyl)tioureido)propanoic acid (**1**) and various *α*-bromoacetophenones in acetone. After that, salts **2–10** were dissolved in aqueous 10% K_2CO_3 solution and compounds **11–19** were isolated after treating the solution with acetic acid to pH~6.



R^1= 11) C_6H_5; **12)** 4-F-C_6H_4; **13)** 4-CN-C_6H_4; **14)** 4-Cl-C_6H_4; **15)** 4-NO_2-C_6H_4; **16)** 3,4-Cl_2-C_6H_3; **17)** 4-Br-C_6H_4; **18) 2-**naphthyl; **19)** 3-chromenyl.

Fig. 1. Synthesis of *N,N*-disubstituted *β*-alanines with 2,5-dimethylphenyl and thiazole fragments

Thiazole derivatives **20**, **21** were synthesized from compound **1** and 2,3-dichloroquinoxaline or 2,3-dichloro-1,4-naphthoquinone. Both reactions were carried out in acetic acid in the presence of sodium acetate.

The structure of newly synthesized compounds were characterized by ^1H, ^{13}C NMR, IR spectra and elemental analysis.

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EUPATORIUM CANNABINUM L. ESSENTIAL OILS AND THEIR BIOACTIVE PROPERTIES

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Eupatorium cannabinum L., commonly known as hemp agrimony is a medical and aromatical plant with antibacterial, anti-inflammatory, fungicidal properties. It was widely used in folk medicine to treat liver diseases and diarrhea [1]. Extracts of hemp agrimony aerial parts and its essential oils contain many biological active constituents such as sesquiterpene lactones, flavonoids, pyrrolizidine alkaloids and terpenoids.

The aim of this study was to investigate in detail the variability of essential oils of *E. cannabinum* growing wild in various localities in Lithuania and to evaluate their toxicity and antioxidant properties.

Plant material was collected from 11 wild populations in Lithuania at flowering stage and dried at room temperature. Leaves and inflorescences were separated before drying. Essential oils of hemp agrimony were obtained by hydrodistillation in the Clevenger type apparatus according to the European pharmacopeia. GC (FID) and GC-MS chromatography were used for quantitative and qualitative analyses of the essential oils. *In vivo* toxicity tests were done using brine shrimp *Artemia* sp. (larvae) and the lethality (LC_{50}) of nauplii was calculated [2]. Instead of usual spectrophotometric methods, cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques were applied to determine antioxidant activity of hemp agrimony essential oils [3].

The major components indicating individual chemotypes of studied *E. cannabinum* oils were Germacrene D, neryl acetate, spathulenol, α-terpinene, δ-2-carene, methyl thymol, α-zingiberene, β-bisabolene, neryl isobutanoate, (E)-nerolidol, geranyl tiglate, and isoborbyl-2-methyl butanoate. Data of toxicity and antioxidant activity of the oils provided an evident support for the potential uses of hemp agrimony in pharmacology.

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LIPID LIQUID CRYSTALLINE SYSTEMS FOR THE PROTECTION OF FLAVONOIDS

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Cranberry flavonoids have been associated with many possible beneficial effects for human health. Cranberry antioxidant quality and quantity rank highly among fruits. However, it is evident that flavonoids are sensitive to the environmental effects: oxygen, UV-light, temperature, water, etc. Thus, it is very important to create new stable delivery vehicles for such compounds.

The natural cranberry flavonoids were successfully extracted by matrix solid-phase dispersion (MSPD) method and loaded into different lipids of soya phosphatidylcholine (SPC) and glycerol dioleate (GDO) based delivery systems. The results indicated that solubility limit of differencefractions of flavonoids in non-aqueous SPC/GDO formulations with 10% of ethanol were in the range of 1% – 3%. Upon hydration these formulations can easily self-assemble into non-lamellar bulk liquid crystal (LC) matrices with different nanostructures. When the SPC/GDO ratio is 60/40 the entrapped flavonoids do not affect the structure of reverse cubic (H_2) LC phase. However, when lipid weight ratio is 35/65, the cubic $Fd\overline{3}m$ phase is sensitive to the concentration of entrapped flavonoids. The results have shown that loaded flavonoids retain antioxidant properties even after 30 days of storage, whereas the antioxidant properties of natural cranberries extracts are decreasing over time.

CONVERSION OF 2-THIOXO-2,3-DIHYDROQUINAZOLIN-4(1*H*)-ONES TO *N*(3)-UNSUBSTITUTED 2-(HET)ARYLQUINAZOLIN-4(3*H*)-ONES

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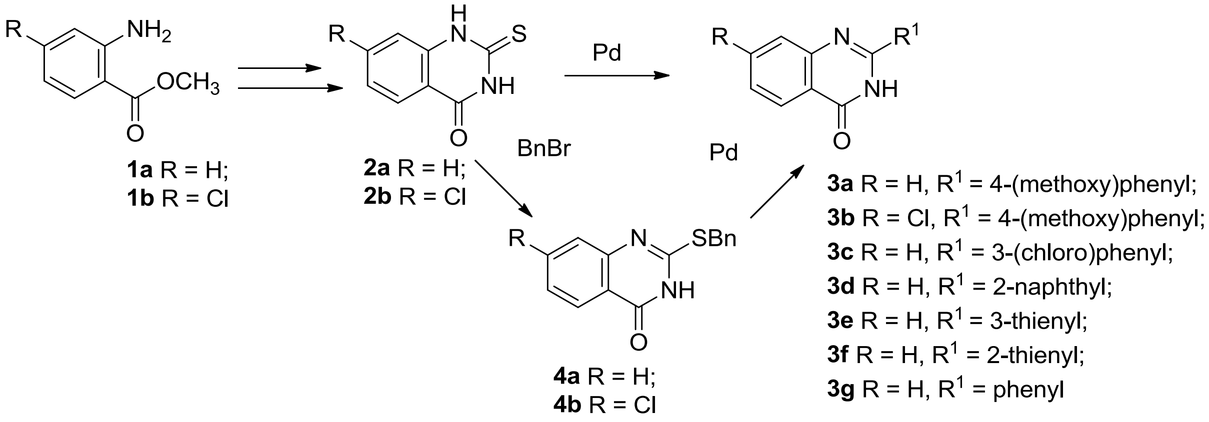
Derivatives of 2-thioxo-2,3-dihydroquinazolin-4(1*H*)-one exhibit interesting biological activities and have found practical applications as diacylglycerol kinases inhibitors[1] and serotonin antagonists.[2]

The required for the synthesis 2-thioxo-2,3-dihydroquinazolin-4(1*H*)-one **2a**,**b** were obtained from the corresponding methyl anthranilates **1a**,**b** using several synthesis steps.[3]

2-(Het)arylquinazolin-4(3*H*)-ones **3a-g** can be directly obtained from 2-thioxo-2,3-dihydroquinazolin-4(1*H*)ones in good to excellent yields by Pd-catalysed Stille-type CuBr·Me$_2$S promoted Liebeskind-Srogl reactions with (het)arylstannanes or by a two-step procedure *via* their *S*-benzylated derivatives **4a,b** applying CuMeSal promoted Suzuki-type Liebeskind-Srogl reactions with arylboronic acids.



1a R = H;
1b R = Cl

2a R = H;
2b R = Cl

4a R = H;
4b R = Cl

3a R = H, R^1 = 4-(methoxy)phenyl;
3b R = Cl, R^1 = 4-(methoxy)phenyl;
3c R = H, R^1 = 3-(chloro)phenyl;
3d R = H, R^1 = 2-naphthyl;
3e R = H, R^1 = 3-thienyl;
3f R = H, R^1 = 2-thienyl;
3g R = H, R^1 = phenyl

Selective *S*-benzylation of 2-thioxo-2,3-dihydroquinazolin-4(1*H*)-ones **4a,b** can be performed with excellent yields by their reaction with benzyl bromide in dioxane.

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A STRAIGTFORWARD APPROACH TO NOVEL FUSED PYRAZOLE SYSTEMS

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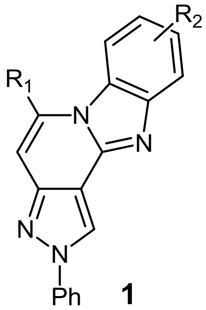
Organic compounds possessing the pyrazole unit are of interest to medicinal chemists and their synthesis is a worthwhile task. This is particularly true for condensed pyrazoles, of which Sildenafil, Zaleplon and Allopurinol are well-known drug examples [1]. In addition, fused heterocyclic systems such as dipyrazolo[3,4-*b*:3',4'-*d*]pyridines exhibit strong fluorescence and have been applied in the preparation of blue light-emitting diodes [2].

In continuation of our works on the synthesis of condensed heterocyclic systems possessing the pyrazole nucleus, we present here the efficient methods for the preparation of derivatives of pyrazolo[4',3':3,4]pyrido[1,2-*a*]benzimidazole and relative new condensed ring systems. The synthesis of 3*H*-pyrazolo[4',3':3,4]pyrido[1,2-*a*]benzimidazole derivatives **1** from 3-alkynylpyrazole-4-carbaldehydes and benzene-1,2-diamine was carried out using copper-free tandem cyclization. When 2,3-diaminopyridine was applied as the diamine component in this type of tandem cyclisation, 3*H*-pyrazolo[4,3-*c*]imidazo[1,2-*a*:5,4-*b*']dipyridine derivatives **2** were obtained as the main products. Copper catalysis and microwave activation were required for the reaction of 5-alkynylpyrazole-4-carbaldehydes and 1,8-naphthalenediamine, affording the corresponding 13,13a-dihydro-3*H*-pyrazolo[4',3':3,4]pyri-do[1,2-*a*]perimidines **3** (Scheme 3). The reaction of 5-alkynyl-4-carbaldehyde with benzene-1,2-diamine resulted in formation of 2*H*-pyrazolo[4',3':3,4]pyrido[1,2-*a*]benzimidazole derivatives **4**. The pyrazolo [4',3':3,4]pyrido[1,2-*a*]benzimidazole fluorophores were characterized by their good quantum yields and large Stokes shifts [3].



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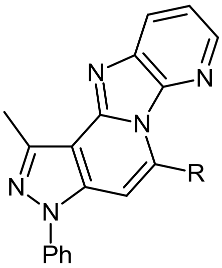

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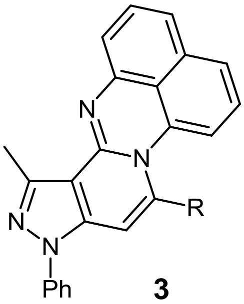

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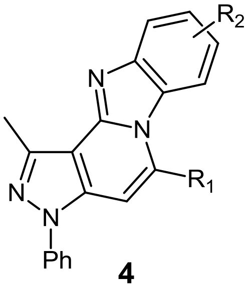

4

The structure assignments were based on data from ^{1}H, ^{13}C and ^{15}N spectroscopy and single-crystal X-ray diffraction analyses.

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Spectral markers of N-(6-mercapto)hexylpyridinium (MHP) in low and high frequency spectral regions

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Bifunctional self-assembled monolayers (SAMs) from organethiol molecules adsorbed on noble metals (Au, Ag, Cu) are widely used to create surfaces with desirable properties [1, 2]. The functional performance of SAMs depends on its structure and stability on a surface. Surface enhanced Raman spectroscopy (SERS) is one of the most informative analytical method, it gives rich structural information on the bonding and orientation of the particular molecular group at the metal surface [2]. For better understanding of metal–adsorbate interactions and ordering it is important to investigate low frequency region. To determinate spectral markers, the positively charged SAM of N-(6-mercapto)hexylpyridinium (MHP) was formed on Au and Ag electrodes and quantum chemical calculations were performed. The low frequency vibrational modes observed at 260 cm^{-1} and 236 cm^{-1} belong to ν(Au–S) and ν(Ag–S) modes, respectively (Fig. 1A). Calculated bond lengths show correlation with frequency: Au–S calculated bond length (2.35 Å) is shorter comparing with silver (2.58 Å) electrode. Other useful marker for orientation analysis of C–S bond with respect to the electrode surface is intensity ratio $I_{\nu(C-S)T}/I_{\nu6b}$. The ratio $I_{\nu(C-S)T}/I_{\nu6b}$ was found to be 0.21 and 1.89 for Au and Ag electrodes, respectively.

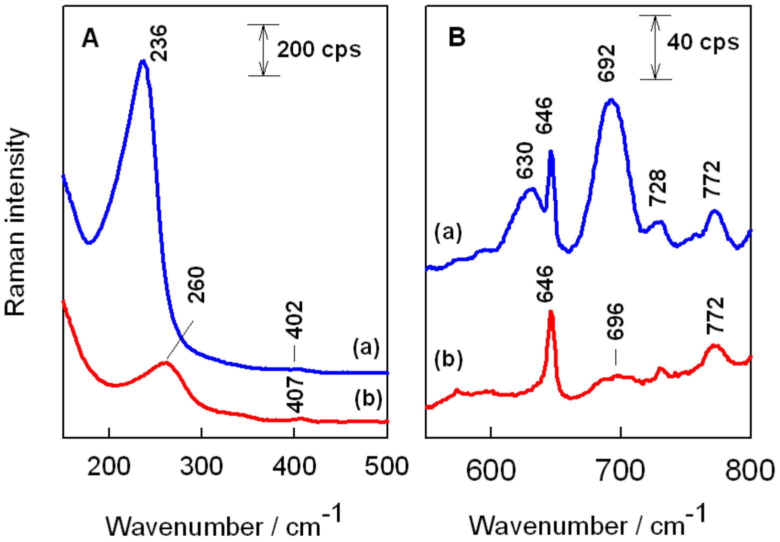

Figure 1. SERS spectra from (a) Ag/MHP and (b) Au/MHP monolayers in metal–sulfur (A) and C–S stretching (B) frequency regions.

To understand MHP interaction with environment, Raman spectra were recorded in different solvents and compared with SERS bands for adsorbed MHP at Au electrode in water. The pyridinium ring =C–H band (ν_2) was proposed to be a marker of dielectric constant at interfaces.

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MICROWAVE-ASSISTED SYNTHESIS OF NEW FLUORESCENT IMIDAZO[1,2-*a*]INDOLONE DERIVATIVES BY SUZUKI-MIYAURA CROSS-COUPLING REACTION IN AQUEOUS MEDIA

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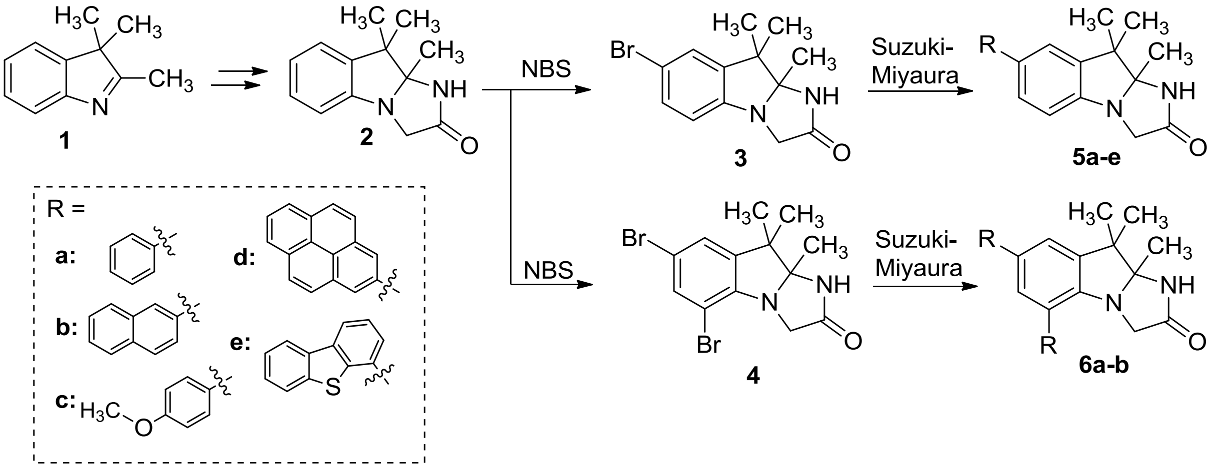
N-substituted 2,3,3-trimethyl-3*H*-indole derivatives are important heterocycles as they serve as building blocks for compounds which have many potential applications in fields ranging from biomedicine [1] to optoelectronics [2].

In this presentation, series of new 7-substituted and 5,7-disubstituted imidazo[1,2-*a*]indolones, which were prepared by bromination of starting compound **2** followed by Suzuki-Miyaura cross-coupling reactions, will be discussed.



Optical properties of the new imidazo[1,2-*a*]indolone derivatives **5-6** were investigated by performing fluorescence and UV-Vis absorption spectroscopy analysis.

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ORGANIC QUATERNARY AMMONIUM COMPOUNDS AS HOLE TRANSPORTING MATERIALS FOR OPTOELECTRONIC APPLICATIONS

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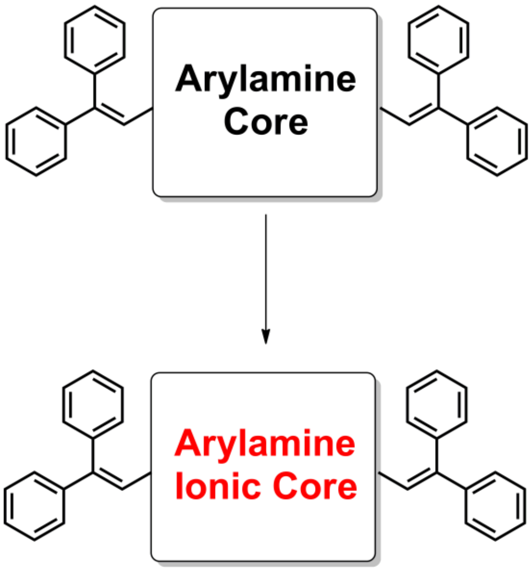
The gradual depletion of Earth's natural resources and the worlds growing energy needs has turned energy saving technology development into one of the greatest science challenges of today. Every second Sun outputs so much energy that it could satisfy the needs of humanity for roughly a million years. Such impressive data inspires scientist to create new devices which could convert this massive energy into electricity. That's where solar cells come in handy and engineering meets chemistry, which is charged with a task of utmost importance – creating the next generation of materials fit for constructing such devices. Said devices often consist of several layers, each having a specific function and made of materials that meet a certain set of requirements.



In this work several new diphenylethenyl substituted triphenylamine-based structures with and without ionic moieties are reported and their thermal, optical and photoelectric properties investigated. Comparatively high hole drift mobility achieved (up to 0.047×10^{-3} cm^2 V^{-1} s^{-1}) and possibility to vary energy levels of the molecules indicates that synthesized derivatives could be used as hole transporting materials in construction of various optoelectronic devices, such as organic light emitting devices, organic and hybrid solar cells, field effect transistors.

STUDY OF TEMPERATURE INFLUENCE ON MOLECULAR INTERACTIONS IN CHOLESTEROL USING RAMAN SPECTROSCOPY

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The important role of organization of both lipids and proteins in cellular membrane regulation and function is well-recognized [1]. Cholesterol has the important role of modulating the physical properties of the plasma membrane, of which it is a major component (30–40 mol%) in eukaryotic cells [2], in addition to its role in lipid metabolism and serving as a precursor of many biologically active compounds, such as bile acids, steroid hormones and vitamin D. The effects of cholesterol on model lipid membranes have been studied in great detail [3-5].

To study molecular interactions of cholesterol using Raman spectroscopy, identification of spectroscopic markers is first required. In this work we investigated the influence of temperature on Raman spectra of cholesterol and cholesterol-d7 (Figure 1) in order to identify specific markers which could give insight to molecular interactions and complement further studies of lipids using sum-frequency generation spectroscopy.

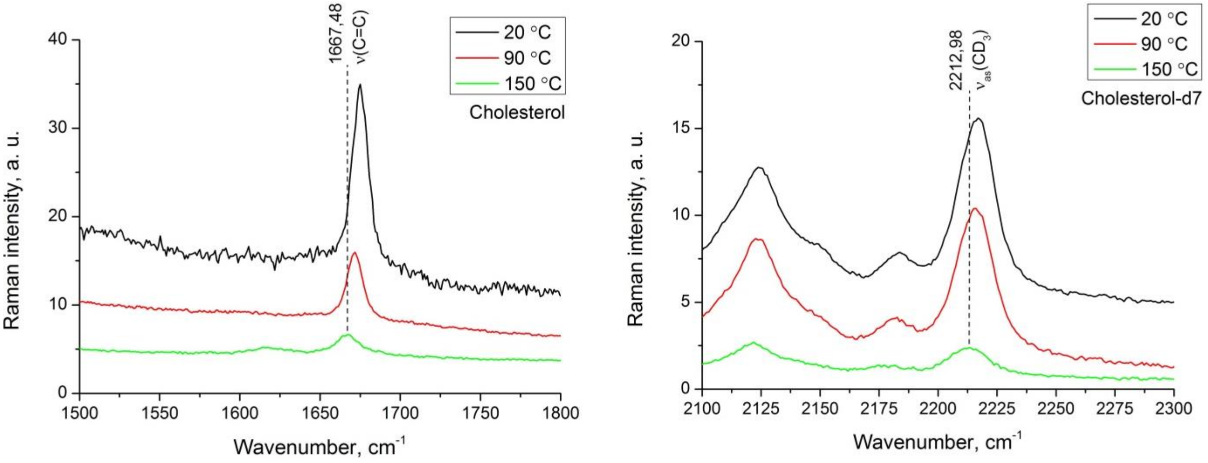

Figure 1. Selected spectral regions of cholesterol (left) and cholesterol-d7 (right) with assigned vibrational bands designated as potential markers.

In Figure 1 it is evident that temperature has an influence on vibrational band intensity and wavenumber: as temperature increases, the intensity of the vibrational band drops noticeably and the peak center is redshifted. This is evident in both ν(C=C) vibrational band of cholesterol and $\nu_{as}(CD_3)$ vibrational band of cholesterol-d7. These spectral features can be considered markers of intermolecular interaction. In this case, the interaction strength decreases with increasing temperature.

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PHOTORHEOMETRICAL STUDY OF COMPOSITIONS BASED ON GLYCEROL DIGLYCIDYL ETHER AND DI- OR TRIHYDROXYLIC ALCOHOLS

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Monomers such as epoxides which can produce stable cationic species on reaction with onium salts are generally used for cationic photopolymerization [1, 2]. Photoinitiated cationic polymerization has received tremendous attention in the recent years due to curing reaction occurring at ambient conditions, low volume shrinkage and less toxicity [3, 4]. Photorheometry allows one to monitor typical rheological properties such as viscosity and shear modulus while a coating or adhesive is irradiated with UV or visible light [5].

The cross-linked polymers were obtained by photopolymerization of glycerol diglycidyl ether with structurally different alcohols, e.g. 1,4-cyclohexanedimethanol, 1,1,1-tris(hydroxymethyl)propane, hydroquinone, and bisphenol A. The mixture of triarylsulfonium hexafluoroantimonates was used as photoinitiator. The 10, 20, and 30 mol. % concentration of the alcohols was used in the batches. Tetrahydrofuran was used as a solvent. The effect of the chemical structure and amount of the di- or trihydroxylic alcohol on the kinetics of photopolymerization was investigated. The dependencies of the reological properties, and the density of cross-links of the synthesized polymers on their chemical structure were studied.

The kinetics of photopolymerization was qualitatively evaluated by the measurements of storage modulus G‘ which was recorded as a function of irradiation time. The main effect of the decrease of the concentration of the alcohol in the batch and increase of the values of density of cross-links of the photocross-linked polymers was the reduction of the induction period and in the formation of the more rigid network. The reaction rate of the batches containing the fragments of the aromatic alcohols is longer compared with that of the batches containing the fragments of aliphatic alcohols due to the lower chain mobility caused by the steric hindrance of the aromatic alcohol molecules. Di- and trihydroxylic alcohols have an association with the proton, leading the higher concentration of alcohol to a decrease in the effective proton concentration, and thus inhibiting the rate of photopolymerization. The induction period of the photocross-linking of the batch without alcohol is significantly longer, and the reaction rate is lower in comparison with those of the batches containing the different amounts of the structurally different di- or trihydroxylic alcohols. The steric hindrance, proton-trapping effect, and electron cloud density of the oxygen atoms of added di- or trihydroxylic alcohols molecules will determine which factor plays the dominant role in the photopolymerization of glycerol diglycidyl ether [6].

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FTIR characterization of amyloids

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It is well known that main cause of pathogenesis of Alzheimer's disease is due to intercellular and extracellular accumulation of polypeptide compounds of low molecular mass – beta amyloid (Aβ). These molecules tend to aggregate and form different size and morphology complexes, varying from small soluble oligomers to insoluble fibrils [1]. There is evidence that small amyloid oligomers exhibit greater cytotoxicity [1, 2].

Secondary structure of β-amyloid oligomers prepared by two protocols has been characterized by infrared spectroscopy (FTIR).

Figure 1 compares FTIR spectra of Aβ(1-42) oligomers formed using different protocols in the Amide-I spectral region. Experimental spectra were fitted with Gaussian-Lorentzian form components, which can be assigned to different secondary structure elements of peptides. To determine the approximate position of fitted components, the second derivative spectra were calculated. The relative fraction of secondary structure elements derived from the analysis of Amide-I band and assignments of the components are given in Table 1. In both cases β-sheet is a dominant motive, visible as intense band at 1631 $cm^{—1}$ and less intensity high frequency band near 1695–1696 cm^{-1}. Such observations indicate presence of antiparallel β-sheet secondary form. β-sheet structure is more favorable in larger peptides, consisting approximately of 15 monomers. Importantly, small Aβ(1-42) oligomers exhibit considerably higher integrated intensity of α-helical structural domain in comparison with larger ones, 31.7 % and 12.6 %, respectively.

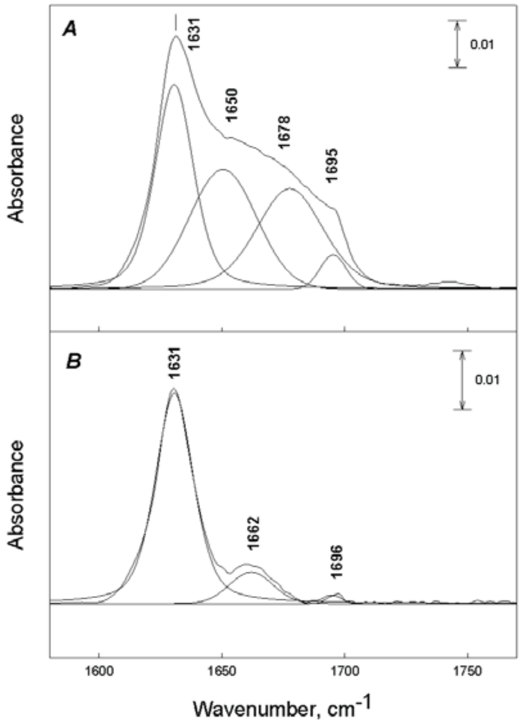

Fig 1. FTIR spectra of small (a) and large (b) Aβ(1-42) oligomers deposited at CaF_2 substrate in the Amide I spectral region

Table 1. Amide I peak positions and integrated intensities with corresponding band assignments of Aβ(1-42) peptide

Peptide Aβ(1-42)	α-helix cm^{-1} (%)	β-sheet cm^{-1} (%)	Unordered helix + random cm^{-1} (%)
Aβ(1-42) small oligomers protocol I	1650 (31.7)	1631 / 1696 (39.4)	1678 (28.9)
Aβ(1-42) larger oligomers protocol II	1662 (12.6)	1631 / 1695 (87.4)	- -

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SYNTHESIS OF 3’-SUBSTITUTED 1,1,3-TRIMETHYL-1,3-DIHYDRO-4’*H*-SPIRO[BENZO[*e*]INDOL-2,5’-[1,2]OXAZOLE] DERIVATIVES BY 1,3-DIPOLAR CYCLOADDITION

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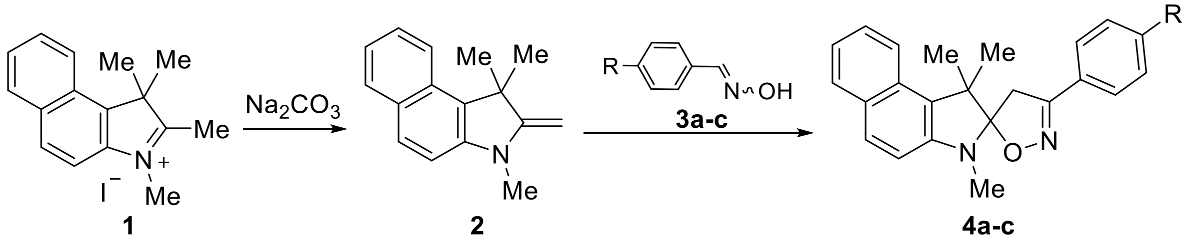
Functionalized benzo[*e*]indole derivatives are found in a considerable number of applications such as dye-sensitizers in photography [1] or fluorescent probes for biological imaging [2]. Notably, substituted isoxazolidines are important precursors to β-amino acids, β-lactams, 1,3-amino alcohols, and pyrrolidinones obtained through reductive N–O bond cleavage [3]. To good advantage, a literature survey on the synthesis of spiroindoline-isoxazoline derivatives, containing benzo[*e*]indole nucleus remain unexplored. In order to obtain the desired spirobenzo[*e*]indole-isoxazoline derivatives, we have examined 1,3-dipolar cycloaddition reactions of 1,1,3-trimethyl-2-methylene-2,3-dihydro-1*H*-benz[*e*]indole and benzaldehyde oximes.

Synthesis of starting compound was performed by alkylation of 1,1,2-trimethyl-1*H*-benzo[*e*]indole with methyl iodide and yielded benzo[*e*]indolium salt **1**, which after treatment with sodium carbonate gave the corresponding methylene indole **2**.



3,4a: R = H, **3,4b:** R = Br, **3,4 c:** R = N(Et)$_2$

Finally, the target spiro[benzo[*e*]indole-2,5'-[1,2]oxazole] derivatives **4a-c** were obtained via a 1,3-dipolar concerted thermal cycloaddition reaction. Methylene indole **2** reacts with a 1,3-dipolar molecule that contributes four electrons in the bond making process. The 1,3-dipolar molecule is a nitrile oxide generated *in situ* by oxidation of *syn*-benzaldehyde oximes **3a-c** using hypochlorite ion as the oxidizing agent. The structure assignments are based on extensive ^{1}H, ^{13}C spectroscopic studies.

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FLOW SYNTHESIS OF CYNNAMIC ACIDS DERIVATIVES

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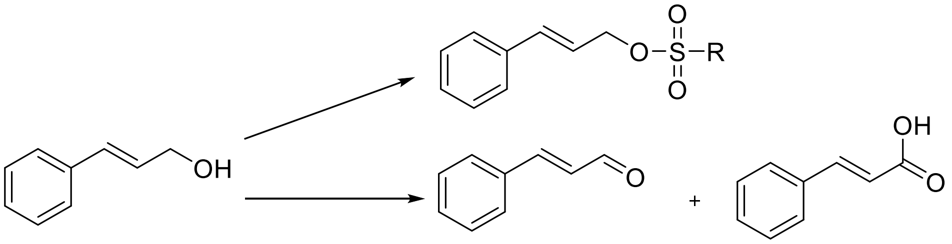
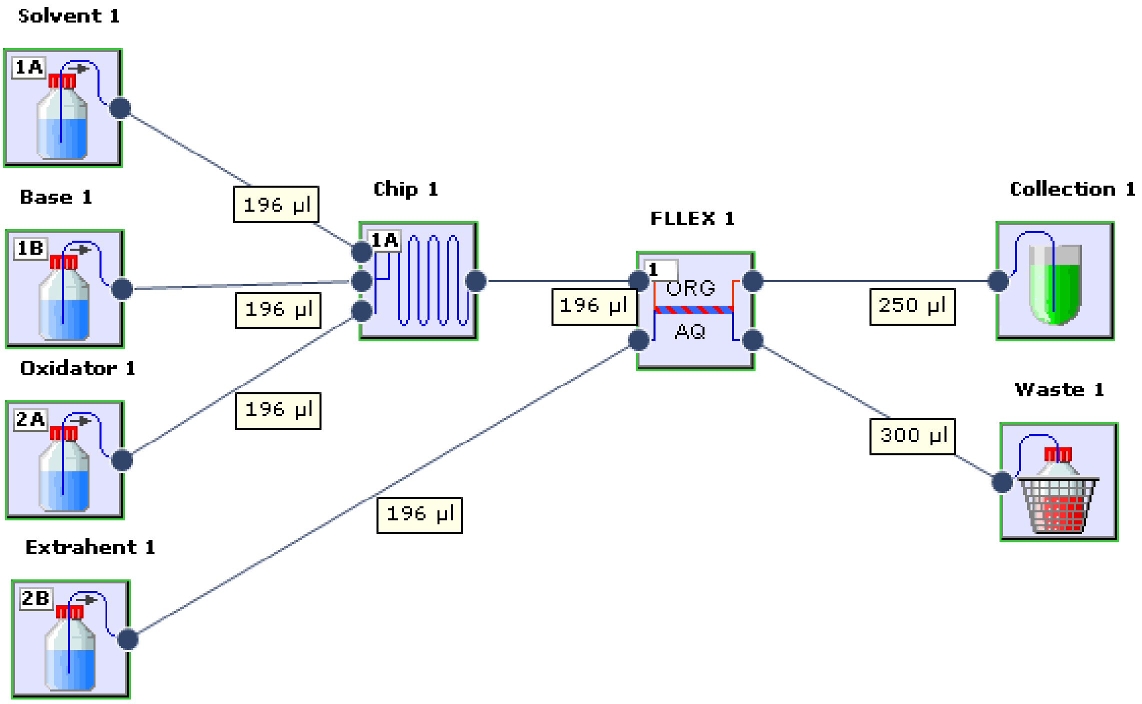
In conventional batch synthesis of organic compounds is not easy to control some kind of reactions. Due to week control fails repeatability rate and drops desirable product yield. For example oxidation reactions with oxygen, hydrogen peroxide, some nucleophilic reactions which builds instable intermediate compounds.

We decided to test chemistry of oxidation and nucleophilic addition of cinnamoyl alcohol in flow mode. Oxidation reactions were proceeded in various stoichiometry, temperature, residence time and concentrations on AFRICA reaction system. The sulphonated protecting group were attached as well in flow mode.



Synthesis technological scheme are given below.



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SYNTHESIS OF IONIC LIQUIDS FROM NATURAL AMINO ACIDS

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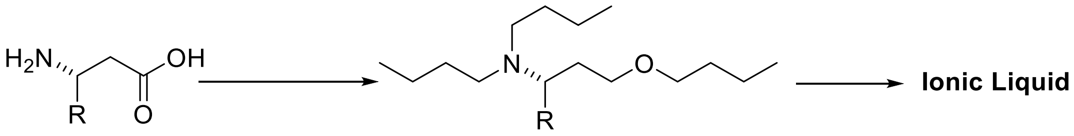
Ionic liquids involving choline and some natural amino acids are known in nature [1,2]. They plays role as phase transfer catalysts and metal ions chelating agents [3,4]. Natural sources and biodegradability makes them as very attractive research object.



We present synthesis of some butylated amino acids with further conversion to ionic liquids. Some of new compounds were successful tested in synthetic chemistry as catalysts.

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EFFECTS OF POLYOL ESTER STRUCTURE ON THEIR VISOCSITY AND SOLIDIFICATION TRENDS

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This research is dedicated to turning non-edible Camelina and Crambe oils into sustainable source of basestocks for lubricants, preferably hydraulic fluids. From diverse spectra of possible products, based on these non-food oils, medium chainlength fatty acids (MCFA) appear as promising candidates for basestock building blocks. Esters of polyhydric alcohols with tertiary β-carbon, a.k.a. polyols, are frequently used for the basestocks, because of improved thermal and oxidative stability. During this study, MCFA esters of neopentyl glycol (NP), trimethylol propane (TMP) and pentaerythritol (PE) were synthesized to investigate the influence of molecular structure on viscosity and low temperature solidification of obtained fluids. Kinematic viscosities at 40°C were measured using capillary viscometers. Pour points were determined using the same thermal cooling regime, as instructed by ASTM D97. The results are presented in Fig. 1.

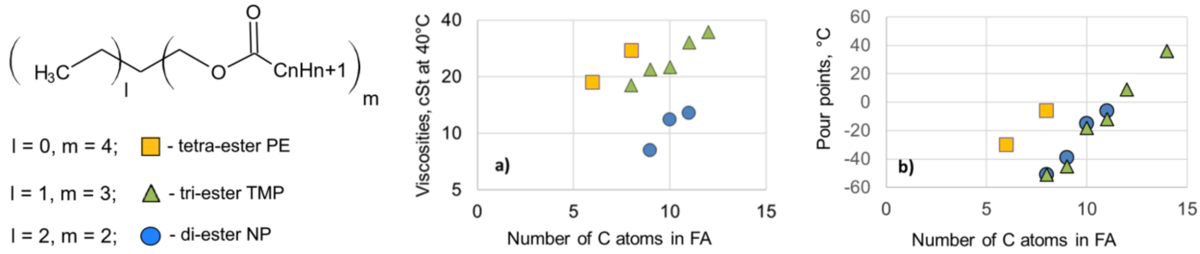

Figure 1. Structures of synthesized compounds as candidates for lubricant basestocks along with their viscosities (Fig. 1 a) and solidification tendencies (Fig. 1 b).

As expected, synthesized esters demonstrate a distinct tendency to increase in viscosity with higher molecular weights. In order to design a basestock of necessary viscosity grade, conventional methods of viscosity prediction can be used both for individual esters and their blends. The relationship between ester structure and pour points is much more complex (Fig. 1 b). Compared to tri-esters (i.e. TMP+MCFA), NP esters of the same MCFA (i.e. di-esters) solidify easier despite significantly lower mol. wt. Nearly as counterintuitive is the observation that tri-ester pour points are lower than those of tetra-esters of similar mol. wt. This suggests that polyol tri-esters, such as those of TMP, give more beneficial low temperature fluidity than polyol esters of NP or PE. Further improvement can be achieved by esterifying not one, but several MCFA during the synthesis. When NP and TMP esters were synthesized using a 1:1 blend of C9 and C11 MCFA, their pour points appeared in between of those for respective esters of pure MCFA, but much closer to those of C9 than C11. Synthesis iterations can provide further improvement in low temperature fluidity of MCFA esters and provide excellent opportunities to utilize Crambe and Camelina oils in industrial applications.

Acknowledgment
The project COSMOS has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 635405. Experimental assistance of D. Bražinskienė is cordially appreciated.

UTILIZATION OF ELASTOMER SWELLING TO EVALUATE RUBBER DE-VULCANIZED BY ENVIRONMENTALLY FRIENDLY METHOD

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The disposal of end of life tires (ELT) is complicated: they decompose slowly [1] and the reuse of once vulcanized rubber as raw material is restricted because of poor compatibility with virgin rubber in new rubber products [2]. De-vulcanization, or disruption of sulfur crosslinks in cured rubber, greatly improves the reusability of ELT [3]. A new mechano-chemical way of producing de-vulcanized material shows promising results, because the use of solvents and polluting chemicals is eliminated from its production [4].

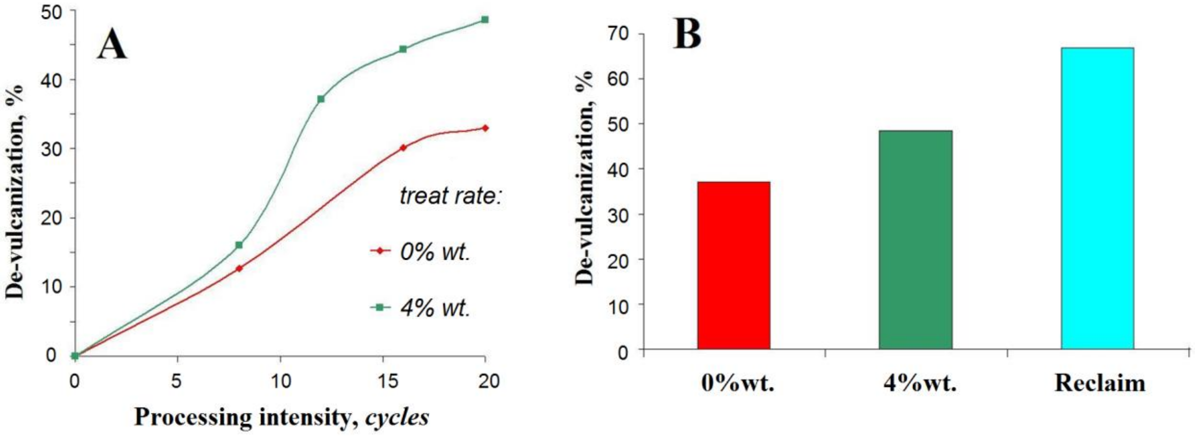

Fig. 1. Dependence of de-vulcanization extent on the intensity of the mechano-chemical processing (A) and the type of manufacturing (B) compared to traditional rubber Reclaim, produced thermochemically.

In this study a standard method (ASTM D6814) was modified to use a pycnometer for rubber density determination. Swelling properties of crosslinked polymers in benzene were translated into de-vulcanization extent per D6814 for three rubber samples. Two samples of mechano-chemically processed truck buffings were provided by Gumos Tech.: one was produced without the use of chemicals and the other utilized 4 % wt. de-vulcanizing agent during manufacture. The third sample was a traditional rubber Reclaim (Farmtrade, Ukraine), produced thermochemically [2]. Truck tire tread buffings were used as a rubber source for all samples. It is evident, Fig. 1, that the use of de-vulcanizing agent and the higher processing intensity increases the level of de-vulcanization. Even though mechano-chemically processed rubber does not possess the same level of de-vulcanization as the Reclaim sample, it has two major advantages: 1) it is in powder form, which improves mixing with virgin rubber and 2) it is produced much more environmentally friendly way. This creates great opportunities for the industrial spread of mechano-chemical processing of ELT.

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IMPROVEMENT IN RESISTANCE TO WEAR AND CORROSION OF ANODIZED ALUMINA BY IMPREGNATION IN BIOBASED FILLER

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Anodized alumina coatings (AA) improve surface hardness, corrosion resistance, paintability and other important properties. They are often employed in robotics, laser casings or other high-tech equipment, but their resistance to wear is poor. Sealing AA nanopores by hydroxylation in water or impregnation with various fillers, such as PTFE, MoS_2, or stearic acid is often used [1]. In this study impregnation with specially designed biobased filler 18Z was compared to AA sealing in hot water.

Hard AA coatings (Type III) were produced on 6082 alloy discs or plates [2]. Then they were immersed at 90°C without mixing either into deionized water for 20 min or 18Z for 1 h. Custom-built AA pistons for miniaturized 2-cycle engines were also impregnated in 18Z. Friction was tested using 6 mm OD steel ball-on-plate setup in CSM tribometer [2] at 10N load, reciprocal linear cycle of 8 mm total length at 2 cm/s. Corrosion resistance was tested at 50±2°C using Q-panel salt-spray cabinet according to ISO 9227:2012 with 5% NaCl plus 0.20±0.02 g/l $CuCl_2$, spiked with acetic a. to pH = 3.1 ~ 3.3. Onset of corrosion was determined using ISO 8993:2010 procedure. Friction and corrosion test results are displayed in Fig. 1.

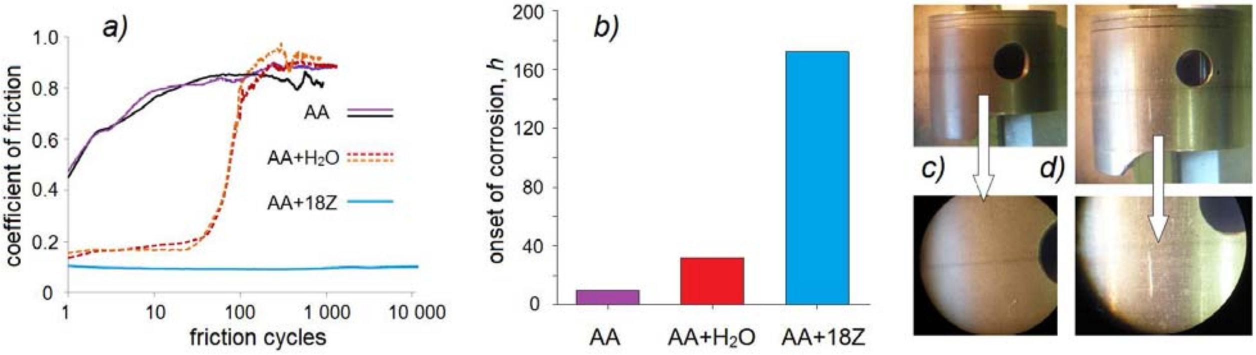

Fig. 1. Improvement in resistance to friction increase (a) and corrosion (b) after impregnating anodized coatings AA in 18Z. Wear scars on prototype pistons for 2 cycle engines, impregnated with 18Z (c) and without impregnation (d).

Both friction (Fig. 1 a) and corrosion (Fig. 1 b) resistance of AA with 18Z was much better than that of AA sealed by hydroxylation. Piston prototypes, impregnated with 18Z, (Fig. 1 c), were tested in the engines by Lithuanian Speed Model Car Federation [3]. They lasted 6-8 times longer than those without 18Z (Fig. 1 d), which usually break down due to friction increase. Impregnated ones appeared much less damaged by wear after dismantling the engines due to reasons, unrelated to piston friction. These results prove high commercial potential of the 18Z filler.

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HOLE-TRANSPORTING MOLECULAR GLASSES CONTAINING FLUORENE/TRIPHENYLAMINE MOIETIES

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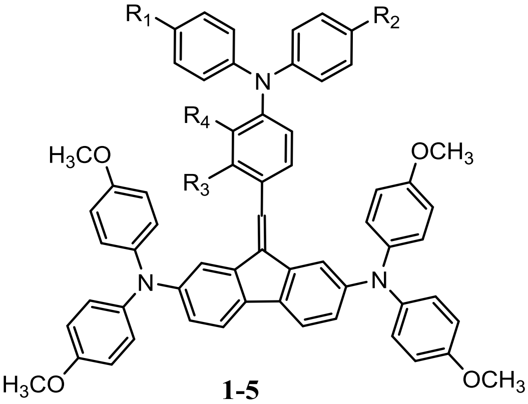
Electronic and optoelectronic devices using organic materials as active elements involve charge transport as an essential operation process and hence, require charge-transporting materials [1]. Therefore, development of high-performance charge-transporting materials is a key issue for the fabrication of high-performance devices. Among wide variety of organic semiconductors, usually possessing large conjugated π electron systems, there are some noteworthy small-system exceptions demonstrating semiconducting properties (especially charge mobility) rivaling those of counterpart compounds containing large π conjugated systems [2].

Here we report synthesis and properties of hole transporting materials (HTMs) possessing triphenylamine and fluorene chromophores (Figure 1). The target compounds were prepared by condensation of 2,7-dibromofluorene with appropriate carbaldehydes of triphenylamines followed by a Buchwald-Hartwig reaction of the obtained intermediates with bis(4-methoxyphenyl)amine. Thermal properties of the synthesized HTMs were measured by differential scanning calorimery. All obtained substances exhibit glass transition temperatures (T_g), ranging from 89 °C to 109 °C suggesting that these compounds tend to form amorphous glasses. The ionization potential values of the materials are 4.92-5.05 eV. HTM **2** exhibits the highest hole transport mobility up to $8\cdot10^{-4}$ $cm^2/V\cdot s$ at strong electric fields. Perovskite solar cells containing HTMs **1-5** were constructed and the preliminary results will be presented.



1-5

1 $R_1=R_2=R_3=R_4=H$;
2 $R_1=CH_3$, $R_2=R_3=R_4=H$;
3 $R_1=R_2=CH_3$, $R_3=R_4=H$;
4 $R_3=CH_3$, $R_1=R_2=R_4=H$;
5 $R_4=CH_3$, $R_1=R_2=R_3=H$.

Figure 1.HTMs **1-5**

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SYNTHESIS OF HIGHLY FLUORESCENT 3-SUBSTITUTED 4-STYRYL-1*H*-PYRAZOLE DERIVATIVES

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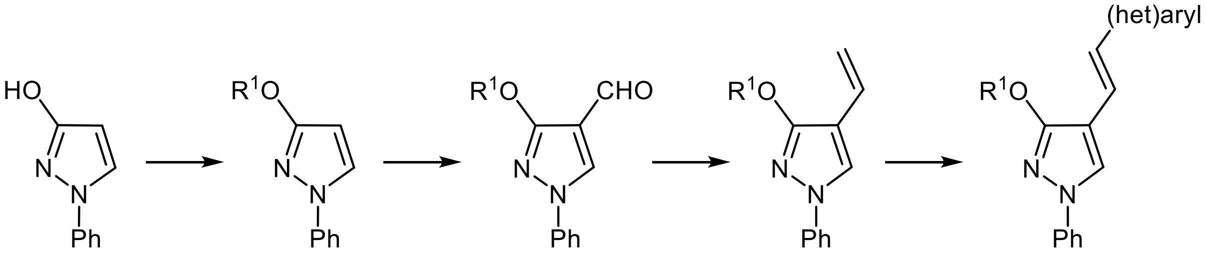
The pyrazole unit is an important substructure of many biologically active compounds.[1] Moreover, pyrazole derivatives found application in nanotechnologies, for example in the preparation of organic fluorescent nanoparticles.[2] The molecules consisting of polyconjugated structure end-capped with heteroaromatic or polycyclic aromatic chromophores are known to be highly fluorescent.[3] Vinylene linkage that is often employed in the design of the polyconjugated molecules serve not only as a “conjugated bridge”, it also improves electroluminescent properties by reducing steric interactions between aromatic rings, and thus, decreasing the free rotation between units.

The aim of the present work was to develop a method for the synthesis of 3-substituted-4-ethenyl-1*H*-pyrazole derivatives, which can be used as a building blocks or reactive intermediates for the preparation of highly fluorescent materials.



1 2 3 4 5

The starting material 1-phenyl-1*H*-pyrazol-3-ol (**1**) for the synthesis of 3-substituted 1-phenyl-1*H*-pyrazoles, was obtained by oxidation of the commercially available 1-phenylpyrazolidin-3-one. In order to obtain derivatives with different side chains of target structures, alkylation of (**1**) with various alkyl halides under the standard conditions in alkaline medium afforded 3-alkyloxy-1-phenyl-1*H*-pyrazoles (**2**). Formylation of intermediates (**2**) was performed by the Vilsmeier-Haack conditions. After heating compounds (**2**) with DMF/$POCl_3$ at 70 °C for appropriate time, the reaction gave the target carbaldehydes (**3**). These carbaldehydes (**3**) smoothly underwent the Wittig-type reaction to give our key compounds (**4**) in good yields.

The Heck reaction of 4-ethenyl-1*H*-pyrazoles (**4**) with halo(hetero)arenes afforded 4-styryl-1*H*-pyrazoles (**5**) as a highly fluorescent compounds with a quantum yields from 40% to 70% in THF solutions respectively.

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SOLID-STATE CHARACTERIZATION OF TRICYCLIC PHARMACEUTICAL COMPOUND AND CYCLODEXTRIN INCLUSION COMPLEX

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Cyclodextrins are cyclic (α-1,4)-linked oligosaccharides of α-D-glucopyranose obtained by enzymatic degradation of starch [1]. The molecular structure possess a truncated conical shape with a relatively hydrophobic central cavity and hydrophilic outer surface. Therefore, cyclodextrins can interact with appropriately sized molecules to result in the formation of inclusion complexes [2].

It has been scientifically proven that cyclodextrins improve the physicochemical and pharmacodynamic properties, including stability, solubility, dissolution rate, and drug bioavailability, of their guest molecules [3-5]. Those, inclusion complex between cyclodextrin and tricyclic pharmaceutical compound was formed. Drug/CD interactions in aqueous solution were examined by phase solubility studies. The solid complex was obtained and characterized by spectroscopic and thermal methods.

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UV/$S_2O_8^{2-}$ PROCESS FOR DEGRADING A TRICYCLIC MUSCLE RELAXANT PHARMACEUTICAL IN AQUEOUS SOLUTIONS

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Over the past decades, active pharmaceutical ingredients (APIs) have been increasingly manufactured and consumed. Unfortunately, medicines are often not completely metabolized by the human/animal body. As a result, they are excreted via urine and faeces as unchanged parent compound and as metabolites conjugates into sewage system. Due to partial removal of API during wastewater treatment, significant concentration of those compounds have been detected in surface water, underground water as well as in drinking water [2-3]. A number of studies have confirmed the negative impact of pharmaceutical contamination on aquatic organisms. Therefore, effective methods of API decomposition are still search.

Recently more attention has been paid on advances oxidation processes, including the UV/$S_2O_8^{2-}$ reaction. In the UV/$S_2O_8^{2-}$ process, $SO_4^{\bullet -}$ radicals characterized in high reduction potential ((E°= 2.6 V) are formed. The UV/peroxydisulfate oxidation provided effective decomposition of sulfamethazine [4], carbamazepine [5] and antipyrine [6]. Thus, in our study, UV/$S_2O_8^{2-}$ process has been used for degradation of a tricyclic pharmaceutical compound. The effects of various parameters, including different dosage of oxidant agent, API concentration, initial solution pH levels, and the presence of inorganic ions like chloride, nitrate, and carbonate have been evaluated.

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THE SHIFF BASES AS SENSITIVE ANALYTICAL REAGENTS FOR F^- AND $Cu^{2+,}$ $Pb^{2+,}$ Zn^{2+}, Al^{3+} IONS

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Two Schiff base derive from 2,3-diaminopyridine and 4-hydroxybenzaldehyde (**1**) and 3-nitrobenzaldehyde (**2**) were synthesized and characterized by spectroscopy methods (Figure 1). Ligands with different position of substituent attached to the molecule relative to C=N double bond are described and their selectivity for ions was compared. The binding affinity for ions was examined by naked-eye colour change, UV-Vis and ^{1}H NMR spectroscopy. Ligands **1** and **2** form stable complexes with Cu^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+} whereas ligand **1** binds also F^- ions. Titration plot indicated the formation of a 1:1 and 2:1 complexes (receptor : cation). Binding behavior of ligands towards several ions has been investigated using density functional theory calculations.

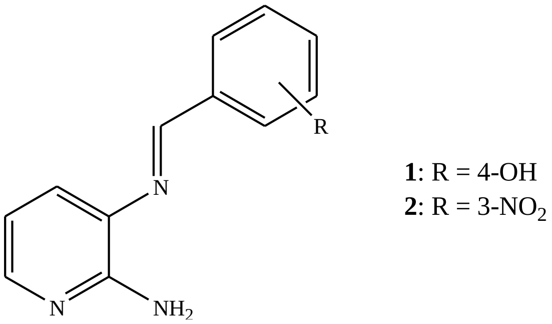

Fig. 1. Chemical structure of ligands **1** and **2**.

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PHYTOCHEMICAL ANALYSIS OF DIPLOID AND POLYPLOID FORMS OF *RIBES* USING SPECTROPHOTOMETRIC, LIQUID CHROMATOGRAPHIC AND GAS CHROMATOGRAPHIC METHODS

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Abstract

Polyploid plants can be created using biotechnological modification methods. New plant can differ from the primary form: anatomical features of the plant, different quality and quantity of secondary metabolites and different size fruits. Blackcurrants are cultivated as industrial applications and mainly used of berries. In folk medicine the leaves and buds of blackcurrant are used for tea. The tea can be used for treatment of rheumatism, arthritis and gastric disorders [1].

Blackcurrants diploid and polyploid forms that were grown in Lithuanian institute of horticulture were used for phytochemical research [2].

Volatile aroma compounds of diploid and polyploid forms of *Ribes* buds and stalks were analysed by gas chromotography. The qualitative analysis of total content of phenolic compounds was completed using spectrofotometric methods with Folin – Ciocalteu reagent. Flavonoid content was determined using reaction with aluminum chloride. Radical scavenging activity was measured using DPPH radical. With liquid chromatography were identified phenol compounds and their contents of blackcurrants methanol extract. Liquid chromatography was used with reversed – phase column with reaction detector.

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PRODUCTS OF CONDENSATION REACTIONS OF 5-OXO-1-[4-(PHENYLAMINO)PHENYL]PYRROLIDINE-3- CARBOXYLIC ACID AND THEIR ANTIOXIDANT ACTIVITY

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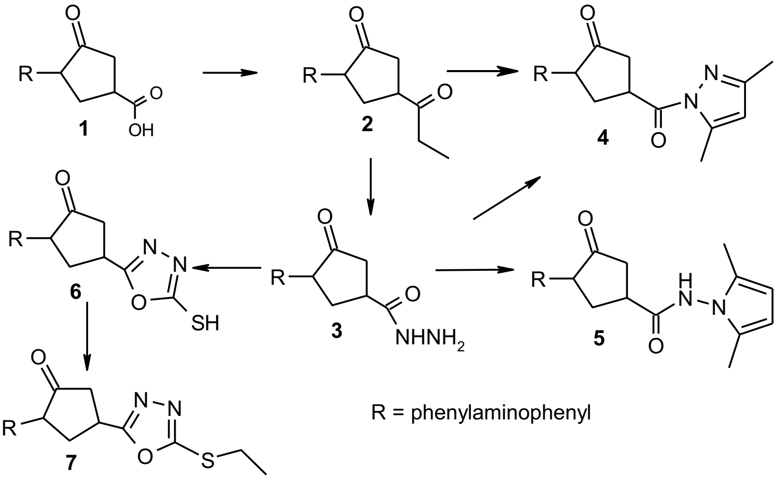
Carboxylic acid‘s hydrazides are easier to get from esters than from acids. That is why acid **1** is esterified with methanol and enough catalytic amount of concentrated sulfuric acid. Obtained ester **2** during heating in alcoholic solution together with hydrazide easily transforms to 5-oxo-1[4-(phenylamino)phenyl] pyrolidine-3-carbohydrate **(3)**. Hydrazide‘s **3** reaction with diketones forms: 3,5-dimethylpyrazol **4** and 2,5-dimethylppyrol **5**. 1,3,4 – oxodiazolthione **6** is obtained from hydrazide (3),during boiling process with carbon disulfide (CS_2) in alkalic – alcoholic solution and cyclized carbothyanate with acetic acid. The last one compound in alkylic process with CH_3CH_2I forms 4-[5-ethylsulfanyl)-1,3,4-oxodiazol-2-yl]-1-[4-(phenylamino)phenyl]pyrrolidine-2-one **(7)**. DPPH scavenging activity and FRAP methods were made for synthesized compounds. All compounds showed different antioxidant capacity. The highest results shows **6**. Compounds **4** and **7** are not strongly active as an antioxidants.



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PREPARATION AND CHARACTERISATION OF IONICALLY CROSS-LINKED ALGINATE/CUTTLEBONE BEADS

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In our work alginate/cuttlebone beads for drug administration via buccal route were prepared and characterized. The beads from sodium alginate were prepared by ionic cross-linking method of gelling, using cuttlebone microparticles as a source of calcium carbonate for slow and controlled gelation, as well as for osteoconductive properties. The formulations based on fully natural materials will probably have a perspective in the treatment of endodontic and periodontal diseases.

Keywords: alginate, cuttlebone, periodontal diseases.

Introduction

Nowadays recoil upon natural materials in biomedicine gain an enormous scale due to their high biocompatibility, non-toxicity, low immunogenicity, attractive cost and wide accessibility all over the world. A great demand is set towards innovative approaches in the treatment of periodontal diseases [1, 2]. The aim of our work was to prepare beads, possessing bioadhesive, antimicrobial, and bone regenerative properties as well. The main counterparts were from fully natural sources of marine origin, i.e. sodium alginate and cuttlebone.

Results and discussion

Elemental composition of CB measured by XFR technique appeared to be very similar to that of human bone tissue by means of macro- and microelements, such as Ca, P, Mg, Fe, Sr, Zn, etc., predicting good osteoconductive properties of biogenic material. Sodium alginate has been used for bead core formation, while pre-treated in alkali media CB microparticles served for regulation of gelling process [3], as well as for osteoconductive properties. Formulations showed average particle size of 1100 µm. Swelling of dried beads in artificial saliva increases with time and reaches maximum after 6 h, later the process of beads disintegration occurs.

Conclusion

Alginate/cuttlebone beads were successfully prepared by ionic cross-linking method using CB microparticles as a source of $CaCO_3$ for slow and controlled gelation. The obtained product resulted in sufficient swelling properties. Due to the enriched elemental composition of initial biogenic material as well as its predicted antimicrobial and mucoadhesive properties after treatment in alkali, the potential of prepared beads in treatment of periodontic diseases can be predicted. The antimicrobial and mucoadhesive properties of alginate/cuttlebone beads will be highlighted in our ongoing research.

Acknowledgements

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RAPID METHOD TO DETERMINE SUITABILITY OF ACRYLONITRILE-BUTADIENE-STYRENE PLASTIC FOR METALLIZATION

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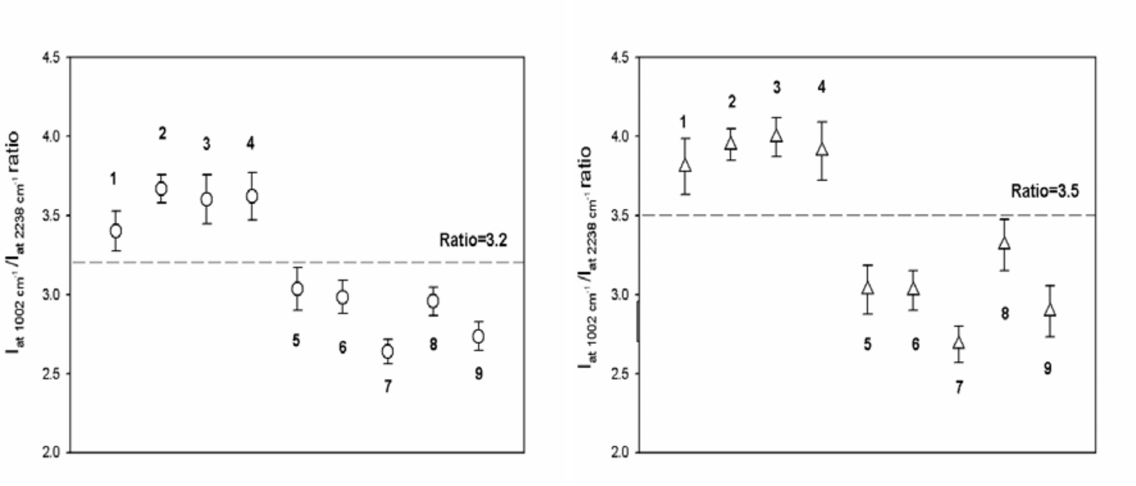
Industry shows an increasing interest in the deposition of metallic layers on products made of plastics and composite materials. Among all metal plated plastics acrylonitrile–butadiene–styrene (ABS) plastics comprise the greatest part, because they can easily be recycled and their surface is easily etched, which makes it possible to achieve a good adhesion of the metal coating to the plastic substrate [1-4].

In this study, the metallization of ABS plastics has been investigated. The adhesion of the metallic layer on ABS was studied by the cross-cut test. Raman spectroscopy was used to evaluate the components of ABS plastics.

It was assumed that the benzene ring of the styrene compound is more stable than the free C≡N group of acrylonitrile during or after the polymer preparation procedure and more resistant to air or/and light. So we decided to compare the Raman intensity of those functional groups. The results are shown in Fig.1.



(a) (b)

Fig.1. Dependence of ratio of Raman intensities of benzene and free cyanic groups on different nine sample of ABS polymer: (a) from surface and (b) from inside of polymer.

The present studies of ABS plastics by Raman spectroscopy method has shown that when a free C≡N vibration mode at 2238 cm^{-1} dominates on the surface of an ABS plastic and the ratio of $I_{at\ 1002\ cm^{-1}}/I_{at\ 2238\ cm^{-1}}$ is lower than 3.2, the adhesion between the surface of ABS and the metal layer is better than that when the ratio of $I_{at\ 1002\ cm^{-1}}/I_{at\ 2238\ cm^{-1}}$ is greater than 3.2.

So in practice this ratio can be used to decide which plastic will have a better adhesion with the metal layer before electrochemical deposition.

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SYNTHESIS AND INVESTIGATION OF V-SHAPED HOLE-TRANSPORTING MATERIALS CONTAINING TRÖGER`S BASE CORE AND PHENYLETHENYL BRANCHES

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Electronic and optoelectronic devices such as organic light-emitting diodes, organic photovoltaic devices and organic field-effect transistors involve charge transport as an essential operation process and hence require charge-transporting materials. Therefore, development of high-performance charge-transporting materials is a key issue for the fabrication of high-performance devices.[1]

We have demonstrated a simple synthesis procedure to obtain solution processable V-shaped hole-transporting materials based on Tröger's base core and phenylethenyl substituted triphenylamine moieties. Tröger's base core significantly increases glass transition temperatures and overall morphological stability of the HTMs. Investigated hole transporting materials are promising candidates for application in organic and hybrid optoelectronic devices as they can be handled in air, require no high temperature annealing steps, can be solution deposited, possess comparatively high mobility (up to 0.011 $cm^2\ V^{-1}\ s^{-1}$) and demonstrate very good thermal and morphological stability.

HTM materials are synthesized in two steps from relatively inexpensive starting materials. Respectable maximum power conversion efficiency of 11.09% was recorded in the perovskite device containing **HTM3** as hole transporting material.

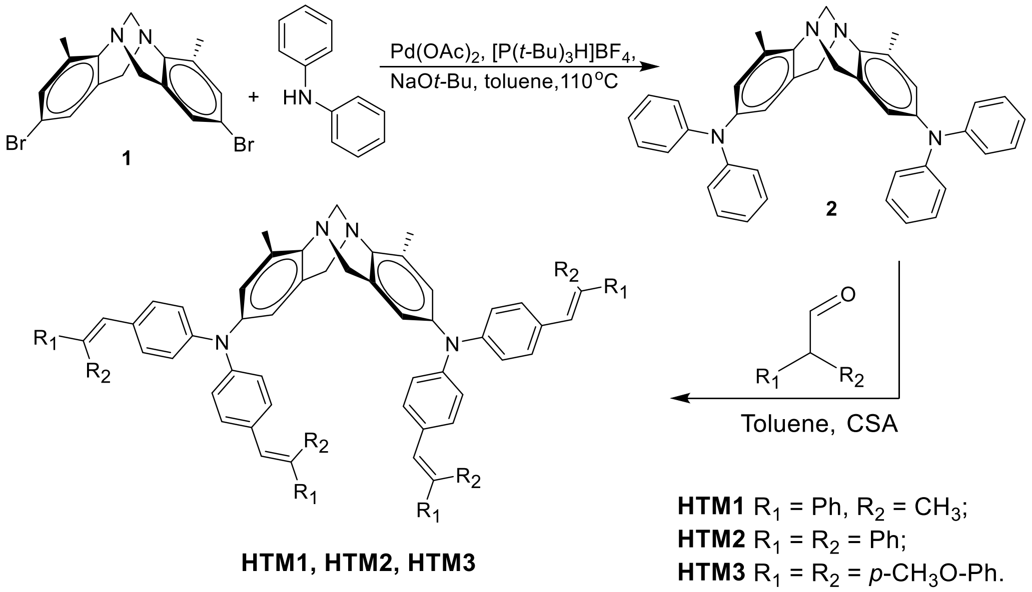

Figure 1. Synthesis of **HTM1-HTM3** with TB core

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LONG TERM OXIDATION AND HYDROLYSIS OF OLEATE FILMS ON STEEL

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Upon exposure to heat and air, fatty acid methyl esters (FAME) oxidize and produce a variety of oxygenated compounds such as hydroperoxides, aldehydes, alcohols, acids, epoxides and similar. Hydrolysis may also take place due to omnipresent humidity. Degradation products can be aggressive towards steel and attack many vehicle components, drastically reducing their service life [1]. Methyl oleate represents the main constituent of FAME, the basis of biodiesel. Better understanding of oleate degradation on metal surfaces can significantly improve biodiesel‘s technical acceptability.

Long term degradation tests were performed with cetane (a.k.a. n-hexadecane) acquired from Merck and FAME from Mestilla (Klaipėda). Low carbon steel coupons (98.8% wt. Fe, 0.8% wt. Mn and 0.4% wt. Si) were coated with 500 µm films as described [2]. The coupons were placed into a forced-draft oven HCP-108 at 50°C or 90°C under dry (<1% Relative Humidity) or humid (20% RH) atmosphere. Periodically, the coupons were taken out, cooled and weighed on the ALJ-160-4NM balance with ±0.1 mg accuracy to determine volatile losses, then placed back to the oven. After degradation residual films were washed off with i-propanol for acidity measurement. The rate of vaporization and acidity buildup are presented in Fig. 1.

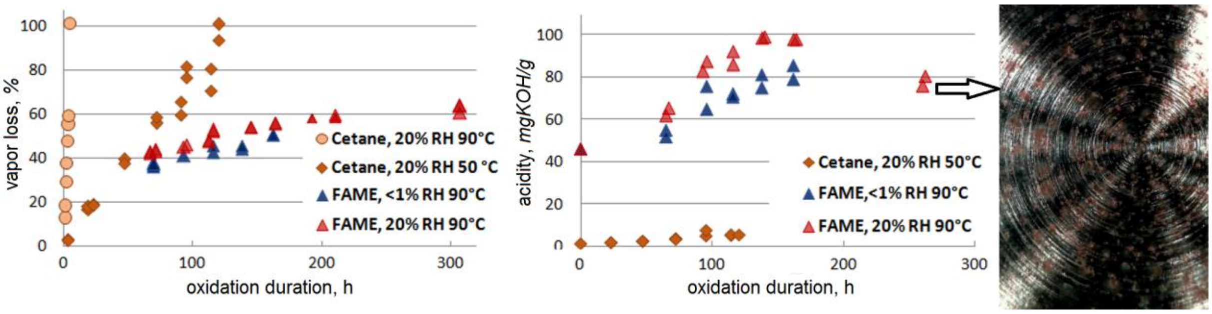

Figure 1. Vaporization and acidity buildup of cetane and FAME at 50°C and 90°C under dry and humid conditions. Right: appearance of steel surface after 100h + exposure to FAME film at 90°C and 20% RH.

Cetane vaporizes much more rapidly than FAME and its film disappears completely within 5-7 h at 90°C or less than 140 h at 50°C. FAME vaporizes rapidly initially, but later the rate slows down due to buildup of oxidation products of higher mol. weight. Increase in acidity is much faster in FAME than in cetane. Higher acidity as a result of oxidation reactions can cause corrosion. In case of cetane no visible signs of surface damage could be noticed on the coupons after degradation. However, after long-term exposure under humid conditions FAME films produced significant rust on the steel surface. No rust was observed after oxidizing FAME under dry atmosphere. Corrosion mechanisms on steel remain unclear. Both electrochemical corrosion and organo-metallic reactions might take place. Visual appearance of the rust spots suggests that the continuity of a passive film is interrupted, leading to the formation of active-passive galvanic cells and to the development of corrosion pits. However, more extensive studies are needed to obtain more details of corrosion mechanisms and possibly find a way to prevent these processes from taking place in equipment, which is exposed to biodiesel fuels.

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Preparation and study of antimicrobial water-soluble cationic starch iodophors

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Iodine is known as an antiseptic and has been used for more than 150 years [1]. Iodine solutions are not stable, whereas, a combination of iodine with natural or synthetic polymer complexes known as iodophors, are much more stable. Moreover, the antibacterial activity of these complexes is similar to the iodine solution, except that iodine is liberated into the solution at a slower rate. For this reason, irritation and allergenic effects on the skin are reduced. Iodophors are complexes of iodine and carriers, which are characterized by the following features: a) improved solubility of iodine; b) controlled release of iodine; c) reduced equilibrium concentration of free iodine. One of the suitable carriers for iodine may be starch. However, in order to utilize iodophors for mass production, the starch should be properly modified beforehand.

Antimicrobial iodine products are mainly used in a form of liquid, in which, the iodine concentration is more than 1 %. Due to a high molecular weight, natural and cationised starch polysaccharide aqueous pastes are quite viscous. So, in order to form iodine-iodophor aqueous solutions, which have low viscosity and are of high iodine concentration, the molecular weight of polysaccharide must be reduced. To that end, an oxidative destruction was performed on cationic starch (degree of substitution DS = 0.3) using different concentrations of an oxidizing agent (hydrogen peroxide) in the reaction mixture. Then, the obtained cationic dextrins (a group of low-molecular-weight polysaccharides produced by the hydrolysis of starch) were used to form iodophor solutions, whose stability was tested in opened containers and later compared to commercially available polyvinylpyrrolidone iodophor, and non-cationic dextrin iodophor. In addition, the stability of iodine was tested in potassium iodide-iodine in an aqueous solution, in which, no polymeric carrier was used. According to the results, iodine evaporates from potassium iodide-iodine solution during a period of 10 days. Meanwhile, some amount of iodine stored in opened containers was found to be present in polymeric iodophors' aqueous solutions even after 30-days period. This shows that the polymeric carriers effectively bind to molecular iodine and do not allow iodine to evaporate too quickly. From a cross-comparison of cationic starch dextrins, the conclusion can be drawn that the stability of iodophors in aqueous solutions decreases with decreasing molecular weight of cationic starch dextrins. Furthermore, all of the cationic starch dextrins investigated in this study, prevented iodine from evaporation more effectively, than compared to non-cationic starch dextrins. From the results obtained, it can be concluded that in order to produce stable iodophor solutions with a relatively high iodine concentration, the optimal molecular weight cationic starch dextrins must be used.

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SYNTHESIS ANDLUMINESCENCE PROPERTIES OF Eu^{3+}-DOPED $Y_{3-x}Nd_xAl_3O_{12}$

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$Y_3Al_5O_{12}$ is commonly called yttrium aluminium garnet (YAG) and adopts the cubic garnet structure. Rare earth doped yttrium aluminium garnet has been thoroughly investigated for application in various fields, such as laser, scintillators, cathode ray tubes (CRT), field-emission displays (FEDs), plasmas display panels (PDPs,) and optical windows, due to its attractive optical property, outstanding chemical stability, low creep rate and high thermal resistance. Luminescent materials based on YAG are stable under conditions of high irradiation with an electron beam. When YAG is doped with Nd^{3+}, it is reported that the near-infrared (NIR) laser output with high power and high slope efficiency were obtained in single crystals and polycrystalline transparent ceramic. The Nd^{3+}- doped YAG is one of the most popular laser active materials [1-3].

In this work YAG garnet samples doped with different amount of Nd^{3+} were prepared by sol-gel method. To our best knowledge, Nd:YAG garnets with various doping levels of europium have not been synthesized yet. Therefore, the main aim of this study was to fabricate these garnets and investigate their luminescence properties. The phase purity and crystallinity of synthesized samples were characterized by X-ray powder diffraction (XRD) analysis. The infrared spectroscopy (FTIR) was chosen as an additional tool to prove purity of garnets. The scanning electron microscope (SEM) was used to study the surface morphology and microstructure of the obtained ceramic samples. Luminescence properties were recognized using photoluminescence spectrometer.

It was confirmed from the XRD data that monophasic garnets can be easily synthesized at 1000 °C using the proposed sol-gel chemical approach. The results obtained by FTIR method are in a good agreement with XRD data and proves monophasic garnet structure compound existence. Luminescence spectrometry was used to investigate luminescence properties of garnets and allowed to compare dependence of peaks intensity on the concentration of dopant (Fig. 1).

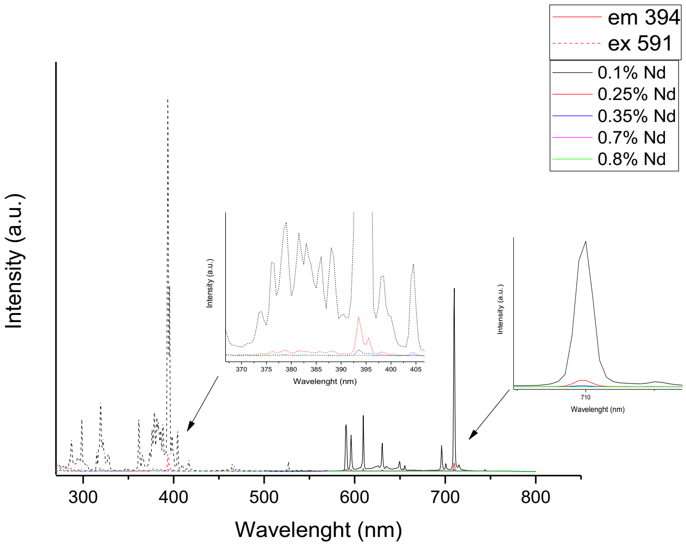

Fig. 1.Emission and excitation spectra of the $Y_{3-x}Nd_xAl_5O_{12}$:0,5% Eu garnets synthesized at 1000°C.

One of our aims was to analyze the influence of Nd^{3+}on the luminescencein garnetsat constant concentration of Eu^{3+} ions(0.5%). In Fig. 1 the characteristic emission of Eu^{3+} arising due to $^5D_0 \rightarrow ^7F_1$ (591 nm), $^5D_0 \rightarrow ^7F_2$ (611 nm) and $^5D_0 \rightarrow ^7F_4$ (710 nm) transitionsis seen. Nd^{3+} ion strongly affected distribution of $Eu^{3+}$and as a result, intensity of Eu^{3+}decreased with increasing amount of neodymium.

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Mössbauer Spectroscopy for Mixed-Metal Yttrium Aluminium-Iron Garnets

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Interest in the yttrium and metal-substituted iron garnets $Y_{3-x}MFe_5O_{12}$ continues to grow because of their magnetic and magneto-optical properties [1]. Magnetic and other physical properties can be changed by substitution of cations in the garnets. Replacement of Fe^{3+} ions with diamagnetic Al^{3+} ions is possible in $Y_3Fe_{5-x}Al_xO_{12}$ (YAIG). Mössbauer spectroscopy technique is a very useful tool for measuring the structural properties of the metal-substituted YIG [2].

In this study, mixed-metal yttrium aluminium-iron garnets in whole substitutional range were prepared by an aqueous sol-gel method. Mössbauer spectroscopy technique was used to analyze the obtained samples (Fig. 1, Table 1).

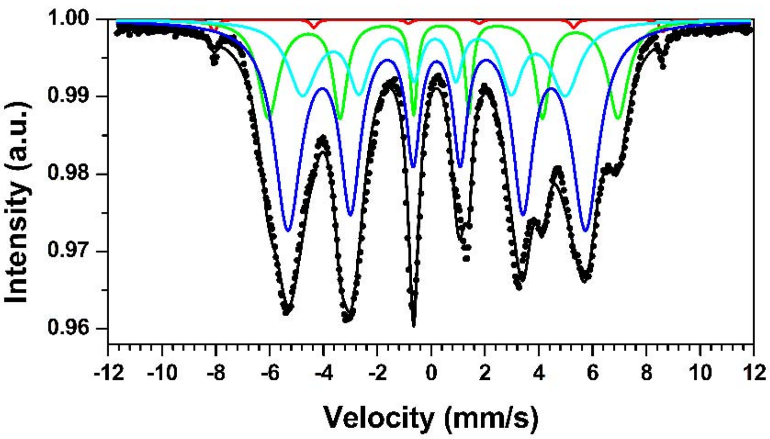

Fig. 1. Mössbauer spectrum of 3Y–1Al–4Fe–O precursor gel, annealed at 1000 °C for 10 h.

Table 1. Data from Mössbauer measurement at room temperature.

Subspectra color	Isomer shift δ	Quadrupole splitting ΔE_Q	Hyperfine field B_{Hf}	Full line width at half height (mm/s)	Relative area (%)	Interpretation
Red	0.37	-0.20	51.8 T	0.28	1	Fe^{3+} in hematite
Green	0.41	0.07	40.4 T	DIST (BHF)= 4.3 T	18	Fe^{3+} in garnet
Dark blue	0.21	0.00	34.4 T	DIST (BHF)= 4.3 T	50	Fe^{3+} in garnet
Blue	0.12	0.05	30.3 T	DIST (BHF)= 4.3 T	31	Fe^{3+} in garnet

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Natural pieces of Baltic Amber: Investigation into the Reasons for their Disintegration and Preventive Conservation

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The Palanga Amber Museum's collection is among the largest ones in Europe and it consists of about 29.000 exhibits: the largest raw amber piece and examples of other fossilized tree resins brought from all over the world, valuable amber pieces with trapped insects and plants inside, archaeological finds of amber, collections of ancient and modern decorative objects including jewelry. Over the last few years some of the amber pieces have been in the process of disintegration (fig. 1). Morphological pieces of amber and objects of decorative arts with amber which tend to disintegrate or crack have dark grey, light grey and whitish substances on their surfaces or these substances are inside the amber. The components of the substance on amber surface and inside were identified by combining the analytical methods (microchemical, optical microscopy, ATR-FTIR and XRD). The test of microbiological contamination of amber pieces was also performed.

Three phases have been identified in the X-ray diffraction pattern of the grey substance and they have been classified as the phases of pyrite, iron (II) sulfate hydrate and quartz. It was determined that the pH value of aqueous solution of grey masses are very acidic and can fluctuate between 2.69 and 3.15. In researches publications, it is specified that the conversion of pyrite into iron sulfate could be initiated by bacteria. Microbiological test refuted the theory that conversion is initiated by bacteria.

During long-term oxidation in humid environment, the mass of grey pyrite intruded into the pieces of amber where substances began to change into iron (II) sulfate hydrate (whitish). The result of this process is the spontaneous disintegration of amber pieces [1, 2]. Therefore, we conclude that such transformation of materials could be induced by the fluctuating, relative humidity of the museum environment. The optimum storage and exhibition conditions for amber are determined.

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SYNTHESIS OF MoS_2 THIN FILMS FROM AMMONIUM TETRATHIOMOLYBDATE

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In the past few years two dimensional transition metal dichalcogenides, especially molybdenum disulfide (MoS_2), have attracted much attention in scientific literature, leading to a quick rise in the number of publications on the subject [1]. MoS_2 is particularly appealing material due to its semiconducting nature and the number of stacked layers dependent band gap ranging from ~1.2 eV to ~1.8 eV [2], with potential applications in the fabrication of solar cells, sensors, photodetectors and flexible electronics, HER catalysis [3]. Thus it is of great importance to find a cost efficient and scalable synthetic method of producing single to a few layer MoS_2 thin films.

In recent literature it has been proposed that MoS_2 thin films (few monolayers thick) can be prepared by thermolysis of ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$), dissolved in different polar organic solvents, and spin or dip coated onto various insulating substrates [2,4,5] and annealed in reducing (H_2) atmosphere, or at low pressures (~1 Torr). However there are only few attempts to investigate coatings annealed in an inert (N_2) atmosphere. It is still not clear how the coating properties depend on the solvents, the deposition and annealing conditions.

In this work ammonium tetrathiomolybdate was synthesized by modified synthesis, based on substituting H_2S with thioacetamide, and proposed by J.W. McDonald et al. in [6]. The precursor, based on the organic solutions of $(NH_4)_2MoS_4$, were spin coated on silicon substrates (p and n type, 1-5 Ohmcm, (100)) that were cleaned with RCA method. The oxide layer was removed with hydrofluoric acid. After deposition the coatings were annealed at high temperatures (600-900 °C) in N_2 atmosphere. The morphology of the layers was investigated by the AFM (Fig. 1). The Raman spectra of the layers were studied.

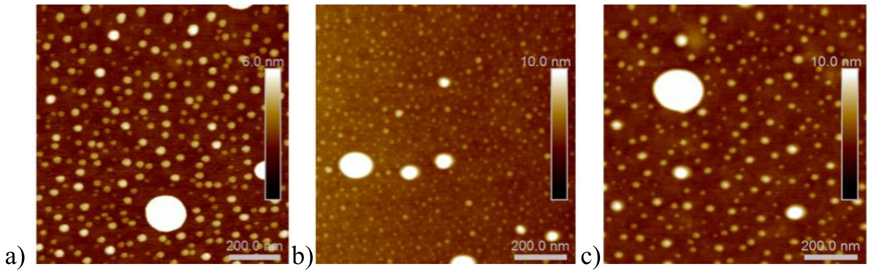

Figure 1. AFM topographic images of the coatings that were obtained from individual solutions by spin coating and annealing at 850°C: a) DMF 3500 rpm 60s, b) MeOH 3500 rpm 60 s, c) MeOH 6000 rpm 60 s.

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MORPHOLOGY OF CADMIUM SELENIDE BASED COATINGS FORMED ON POLYAMIDE SUBSTRATE

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Cadmium selenide (CdSe) based nanostructures very often are applied for various bioanalytical and analytical purposes [1], photoelectrochemical cells [2, 3], gas sensors [4], photoconductors [5], thin film transistors [6, 7], and gamma ray detectors [8]. In addition, CdSe-based films are very suitable for photovoltaic devices [9], because the CdSe is a promising photovoltaic material [10], which has high absorption coefficient, and high photosensitivity. All these applications are associated with extraordinary optical properties of CdSe, but these properties are significantly affected by substrates on which CdSe structures are deposited and sometime some optical properties, such as photoluminescence efficiency [1] are significantly reduced due to the interaction of CdSe-based structures with used substrates. Therefore from this point of view the deposition of metal chalcogenide films on the surface of organic polymer films is a promising approach to form films, which have advanced physical properties.

Cadmium selenide based coatings were formed on the surface of PA 6 (PA) film by treating PA film samples with potassium selenotrithionate, $K_2SeS_2O_6$, solution and then with cadmium (II) acetate, $Cd(CH_3COO)_2$, solution. The morphology of CdSe-based coatings was investigated by atomic force and scanning electron microscopies. It was determined that the formation of cadmium selenide coatings proceeds unevenly in the form of islands, which later grew into agglomerates. The surface of the layers formed is relatively uneven and rather rough. The tendencies of the decrease of the maximum height of CdSe-based coating (399, 348–296 nm) and of the average height of this coating (337-153 nm) with prolongation of polyamide treatment in $K_2SeS_2O_6$ were observed.

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XPS characterization of Mo-Cu-S layer on glass

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Mo-Cu-S heterometallic compounds have long been interest in bio-inorganic chemistry [1]. They have received much attention due to their fascinating properties such as catalysis, conductivity and strong nonlinear optical characteristic [2]. MoS_2 is a material which have excellent solid lubricating properties. Sputtered MoS_2 coatings were first developed for space applications to provide lubrication under vacuum conditions. More recently, MoS_2 has been starting to use for tool coating applications. This material exhibit low friction and good wear resistance and are thus capable of dry machining [3].

In this study Mo-Cu-S layers were formed on microscopic glass slides of dimension 10 mm×10 mm. Slides were thoroughly cleaned with cleaning liquid soap and ultra-sonic cleaning was carried out by dipping the glass slide into acetone at 40ºC for 10 min, then rinsed with distilled water and dried. Sulfur layers on glass have been formed by the use of elemental sulfur powders mixed with acetone. Then the mixture was placed on glass and annealed at 160°C for 10 min. For the formation of copper sulfide layers the sulfurized sample was treated with a 0.4 M copper (II/I) salt solution at 40 or 60ºC for 10–20 min. For the formation of Mo-Cu-S layers the sample was treated with a molybdenum (IV) salt solution at 40°C for 10 min. 0.05M Mo(IV) salt solution was made from crystalline $(NH_4)_6Mo_7O_{24}\times 4H_2O$ and a reducing agent–hydroxylamine hydrochloride [4].

Firstly Cu_xS layers were formed by the reaction:

$2xCu^+ + 1/8S_8 \rightarrow Cu_xS + xCu^{2+}$

After the reaction with Mo(IV) salt solution obtained Mo-Cu-S layers. Mo(IV) salt solution interaction with obtained Cu_xS layers may react accordingly:

$Mo^{4+} + Cu_2S + CuS \rightarrow CuMoS_2 + 2Cu^{2+}$,

$Mo^{4+} + 2Cu_2S \rightarrow MoS_2 + 4Cu^+$ or $Mo^{4+} + 2CuS \rightarrow MoS_2 + 2Cu^{2+}$

Obtained Mo-Cu-S layers composition were investigated by XPS analysis. XPS spectrum shows the presence of two highly intense peaks, separated by 3.25 eV, indicating Mo $3d_{5/2}$ at 232.35 eV and Mo $3d_{3/2}$ at 235.6 eV also having a peak at 227 eV because of S 2s in MoS_2. A huge peak at 232.35 eV corresponds to the Mo $3d_{5/2}$ in MoO_3. It suggests that a fraction of MoS_2 film is oxidized to MoO_3 due to the air exposition of the film. Also XPS spectrum shows the presence of on highly intense peak at 162.9 eV, indicating S 2p, which corresponds to $CuMoS_2$ [5]. Also having a shoulder peak at 164 eV which shows S^0. A peak at 169 eV shows in the sample left a little of $CuSO_4$. XPS spectrum shows one highly peak at 932.75 eV corresponds to the Cu $2p_{3/2}$ in $CuMoS_2$. Also having a shoulder peak at 934.35 eV, which shows $Cu(OH)_2$. Other shoulder peak at 935.9 eV shows $CuSO_4$. XPS study analyses that the peak positions of Mo, Cu and S are well matched. Also layer have some contamination of MoO_3 impurity.

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XPS studies of Cu-In-Se layers on glass

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Solar cells are one of the most prominent and promising energy technology today. It is not only sustainable, but also, renewable, clean, completely noise free, scalable, minimal amount of maintenance is required and it produces zero emissions.

$CuInSe_2$ is one of many potentially efficient materials for solar cell applications. Among these, it exhibits great optical absorption coefficient ($>10^5$ cm^{-1}) [1, 2], low direct band gap (1.04 eV) [2] and high thermal resilience [3]. Also, these optical properties do not get worse under highly intense irradiation [4]. Today, $CuInSe_2$ layers can reach 20.5% efficiency, while in solar cell 18.7% [5].

$CuInSe_2$ layers can be obtained using chemical or physical deposition. Chemical deposition offers low cost, homogeneous layers and is easy scalability for large surface area coatings. However, it usually requires annealing to obtain crystalline $CuInSe_2$ layers. Physical deposition, on the other hand, offers better quality layers, while often requiring high cost low-pressure, high-temperature equipment and it does not offer good scalability for large area coating. Physical deposition techniques often require annealing in H_2Se atmosphere, which results in reagent wastage, even lower cost efficiency and toxic work environment.

The glass substrate was washed with liquid soap and distilled water and dried. Then it was cleaned in ultrasonic cleaner bath in acetone for 10 min at 40 °C. The Cu-In-Se layer was obtained in three steps. At first, selenium layer was formed by submerging glass substrate into 0.4 M H_2SeO_3 and 1 M $KHSO_3$ 1:1 mixture at 60 °C for two and three hours. Secondly, sample was placed to 0.4 M $CuSO_4$ with addition of 1% hydroquinone. Sample was kept in solution for 5 min, 10 min, and 20 min, at 40 °C, and 60 °C. Next, it was submerged in $InCl_3$ solution for 10 min and 20 min at 40 °C. Possible $CuInSe_2$ layer formation reactions are:

$$Se + 2xCu^{+} \rightarrow Cu_xSe + xCu^{2+}$$

$$2Cu_2Se + In^{3+} \rightarrow CuInSe_2 + 3Cu^{+}$$

Obtained layers were studied using XPS analysis. One Se only layer sample was formed. According XPS graph shows Se^0 peak at 55.6 eV. Cu-In-Se layers were formed on glass with Se layer. A sample with corresponding XPS graph shows shifted Se^{2-} peak at 54,8 eV compared to Se only layer. Same sample XPS graph shows Cu^+ spectra $Cu2p_{3/2}$ at 932.4 eV and $Cu2p_{1/2}$ at 952.3 eV and it does agree with literature [6]. Negligible peak at 943 eV concludes the lack of Cu^{2+} [6]. Also peaks at 445.8 eV and 453.4 eV show presence of $In3d_{5/2}$. In^{3+} peaks are slightly shifted, then the ones found in the literature (444.4 eV and 452.2 eV accordingly) [6]. This might be due to layers being multiphase. Residual impurity elements, such as O, Cl and C was also found. Other samples data shows similar results.

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PROPERTIES OF LIQUID – MULTICOMPONENT SYSTEMS

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Fluid fertilizers are popular because of the ease of handling and use. Movement is by pump, and they usually require less labor to handle. Some pesticides and microelements can be injected into the fluid, saving trips across the field. Fertilizers custom blended to specifications are available. Properly applied, fluid fertilizers are no more or less efficient than solid fertilizers. Most fluid fertilizers contain the same basic ingredients as solid fertilizers. The only difference is that fluid fertilizers are dissolved in water, and solid fertilizers are not. The efficiency of fluid fertilizers is determined by the way they are applied.

The major types of fluid fertilizers are suspension fertilizers and liquid fertilizers. Liquid fertilizers are dissolved completely in water. Suspension fertilizers are partially dissolved in water, but some of the nutrients, particularly potash, are suspended in the water in the same way mud is suspended in water. True liquid fertilizers can be stored as long as the temperature stays above freezing [1].

Plants can absorb liquid fertilizers through both their roots and through leaf pores. Foliar feeding can supply nutrients when they are lacking or unavailable in the soil, or when roots are stressed. It is especially effective for giving fast-growing plants like vegetables an extra boost during the growing season [2].

The chemically pure substances of potassium chloride, ammonium dihydrophosphate and distilled water were used in this work. The solid phase has been obtained when carrying out the conversion reaction between potassium chloride and ammonium dihydrophosphate:

$$KCl_{(l)}+NH_4H_2PO_{4(l)} \leftrightarrow KH_2PO_{4(s)}+NH_4Cl_{(l)}$$

at temperatures of 20 °C, 40 °C, 60 °C and 80 °C. Aqueous solutions of these salines have been prepared by dissolving the starting materials – potassium chloride, ammonium dihydrophosphate – at a molar ratio of 0.8:0.2 [3]. The solid - crystalline potassium dihydrophosphate and liquid phase, which consist from K^+, NH_4^+, Cl^-, PO_4^{2-} ions were separated from the reaction products. These solutions can be used for the plants they are not sensitive to chlorine ions. So the aim of this work was to determine properties of liquid – multicomponent systems. To increase the nitrogen concentration in the liquid solutions was added urea from 1 to up 10 %. The test were made by seeding solutions with a small amount of crystals of the crystallizing phase. A series of solutions at different concentrations of $(NH_2)_2CO$ were cooled to 10 °C, and each solution was seeded with amount of some crystals. The solubility in the temperature range 10 to 20 °C, for the system was determined by visual - polythermal method. The solutions were cooled until crystallization occurred and then warmed very slowly with continuous stirring, until the last crystals disappeared.

It was determined, that when the concentration of urea in liquid solutions is 6 % the crystallization temperature is lowest (13 °C). It was measured other properties of the same solutions: viscosity, pH, density et al.

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PROPERTIES AND CHARACTERIZATION OF CZTS CRYSTALS PREPARED BY MICROWAVE HEATING IRRADIATION

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Rapid industrial growth and decline of fossil fuel resources is forcing search for sources of new alternative energy. Solar power is one of such solutions. Cu_2ZnSnS_4 (CZTS) is a potential absorber candidate for low cost thin film solar cells due to its favorable optoelectronic properties and the relatively high abundance of its constituent elements. The theoretical conversion efficiency of single-junction CZTS solar cell is 32.2% [1] and it has been considered as the most promising photon absorber materials to substitute CIGS [2]. Microwave irradiation is an emerging versatile technique for the controlled synthesis of various nanomaterials due to its distinct advantages like homogeneous nucleation, high reproducibility, better size control, improved yield, good purity and shorter crystallization time [3].

In the present study the CZTS crystals were prepared by microwave-assisted heating of $CuCl_2$ (0.1 M), $ZnCl_2$ (0.05 M), $SnCl_2$ (0.05 M) and CH_4N_2S (0.4 M) ethylene glycol – aqua solutions at 260ºC for 60 min. The synthesized compounds were annealed at different 400-600ºC temperatures for three hours in melted ampoules. Influence of annealing temperature on the crystallographic structure and phase purity of the CZTS was investigated by means of Field-Emission Scanning Electron Microscopy, Energy Dispersive X-ray analysis, X-ray Diffraction and Raman Spectroscopy.

It has been determined that the as-synthesized black powder of CZTS sample did not have crystal structure. Annealing of sample at temperatures greater than 500ºC results in formation of kesterite crystal structure and its stoichiometric composition. Energy Dispersive X-ray analysis of CZTS sample, annealed at 500ºC, confirms good stoichiometric composition of kesterite with ratio $Cu_{1.93}Zn_{1.00}Sn_{1.02}S_{3.98}$. It has been determined that increase in annealing temperature results in higher degree of crystallinity and appearance of purer CZTS phase as well as higher photoactivity.

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STUDIES OF ADSORBATE REACTIONS ON SINGLE AND ACTIVATED CuO BASED CATALYSTS

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One of the best available and commonly used abatement processes for volatile organic compounds (VOCs) is heterogeneous catalytic oxidation by air oxygen. The most active components for the oxidation reactions are transition metal (Cu, Cr, Co, Mn, etc.) oxides and precious metals (Pt, Pd) [1]. Though the latter ones are more expensive and possible implementation of transition metal oxides is investigated in order to substitute them. CuO is one the most active single metal oxides for decontamination of VOCs.

Activity of CuO catalysts was investigated in series of studies conducted at Department of Physical and Inorganic Chemistry. It was determined that the most active catalysts contain from 8 up to 12 % of CuO. Active component was dispersed on different supports that have high specific surface area: zeolite NaX, alumina γ-Al_2O_3 and a composite of γ-Al_2O_3-C_{act}. C_{act} stands for activated carbon and it was used as an additive to increase the specific surface area of γ-Al_2O_3. Some of investigated CuO based catalysts were promoted with Cr_2O_3, Co_3O_4, CeO_2 and La_2O_3 additives and methanol was used as a reference material for determination of catalytic activity in oxidation reactions. All synthesized catalyst managed to oxidize methanol although catalytic activity differs. Depending on the temperature range conversion of methanol was as follows: 35.0–92.2 % for CuO-Cr_2O_3-Co_3O_4/Al_2O_3-C_{act} (200–370 °C), 64.6–99.7 % for CuO/Al_2O_3 (160–250 °C), 65.9–98.5 % for CuO-La_2O_3/Al_2O_3 (160–250 °C), 81.2–99.8 % for CuO-CeO_2/Al_2O_3 (160–250 °C), 81.6–99.9 % for CuO/NaX (200–300 °C). As results show the most active is CuO-CeO_2/Al_2O_3 catalyst containing 9.32 % CuO and 1.94 % CeO_2. High methanol conversion values were attained even at lower temperatures compared to other investigated catalysts. The worst catalyst appeared to be CuO-Cr_2O_3-Co_3O_4/Al_2O_3-C_{act} which had lowest conversion and yielded greater number of undesired by-products – CO and formaldehyde. In this case CO_2 and H_2O are preferred as the only products of catalytic oxidation. High specific area is one of the key properties of any heterogeneous catalyst as it improves contact between dispersed active components and reactants. Among the tested catalysts it varies between 134.5 and 520.8 m^2/g. In our studies it doesn't play major role since there is no correlation between specific surface area and catalytic activity. Even more, high temperature (>500 °C) is detrimental to composite CuO-Cr_2O_3-Co_3O_4/Al_2O_3-C_{act} catalyst since specific surface area tends to decrease down to 16.45 m^2/g.

Commonly VOC oxidation over transition metal oxide catalysts undergoes redox cycle which is explained by Mars-van Krevelen mechanism [2]. Overall activity of catalyst depends on the rates of two processes: reduction of active sites by VOCs and subsequent chemisorption of oxygen. The highest activity of ceria promoted catalyst may be attributed to improved redox properties since CeO_2 has a large oxygen storage capacity and higher crystal lattice oxygen mobility. As our experiments show, sufficient amount of oxygen should be supplied in order to keep catalyst intact and operational. In the case of methanol the excess of oxygen should be 9 times larger than that of VOC. In comparison, when larger molecular mass alcohols are decontaminated larger amounts of oxygen are needed in the gaseous phase.

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ADSORPTION OF POTASSIUM, ZINC AND COPPER IONS ON CLINOPTILOLITE

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Natural zeolites, which are aluminosilicate minerals and found in volcanogenic sedimentary rocks, possess several important properties including adsorption, cation-exchange, dehydration–rehydration, and catalysis. Clinoptilolite $(Na_3K_3)(Al_6Si_{30}O_{72})\cdot 24H_2O$, are one of the naturally existing zeolites. The structure of natural clinoptilolite is ideal for sorption and ion exchange processes. Due to its structure and properties this natural, inert and non-toxic material can be used as a slowly releasing carrier of fertilizer, as well as other agrochemically, pharmaceutically and biochemically active compounds including disinfectants [1–3]. Sorption properties of natural zeolites for the Mn^{2+} ion were studied in comparison with various industrial adsorbents and some minerals. It was demonstrated that the sorption capacity of the natural zeolites grows with increasing temperature [4]. Potassium ion adsorption on clinoptilolite is not very dependent on the nature of the solution and adsorption proceeds very similarly when KCl and KNO_3 solutions are used. The adsorbed amounts of potassium ions are directly dependent on the concentration of potassium in the liquid phase [5]. Many works have been investigated influence of the presence of competing cations on the individual adsorption of Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Mn^{2+} from a solution containing a mixture of all these heavy metal ions, by natural zeolite [6, 7]. However, zinc and copper are used in fertilizers as trace elements [8], the aim of this work is the use of natural zeolite as a source of K^+, Cu^{2+}, Zn^{2+} ions for plants. In this case natural zeolites can be used in agriculture as special fertilizers not only by means of improving the soil's quality, but also obtained via adsorption of potassium, zinc and copper ions.

Clinoptilolite's adsorption capacity and desorption of K^+, Cu^{2+}, Zn^{2+} ions was investigated under conditions: the ratio between solid and liquid phase 5:200, adsorption duration 30 min. K^+ ion concentration in the solutions varied from 15 mg/ml to 40 mg/ml, while concentrations of Zn^{2+} and Cu^{2+} remained constant 15 mg/ml. 0.5–1.0 mm fraction of zeolite was immersed in solutions of every K-Zn-Cu-containing compound and stored at constant 25 °C temperature. Clinoptilolite's high adsorption capacity of potassium 163.4 mg/g, copper 73.58 mg/g and zinc 70.03 mg/g was determined under these conditions.

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THE CHEMOSORPTION PROPERTIES OF SYNTHETIC α-C_2S HYDRATE

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α-C_2S hydrate – dibasic calcium silicate hydrate with isolated tetrahedrons posses the lowest degree of polymerization, and is one of members of the neosilicates. α-C_2S hydrate does not exist in natural environment and forms during hydrothermal treatments [1]. Over three decades ago, by seeking to resolve various environmental problems including removal of toxic heavy metal ions, calcium silicate hydrates have been proposed as adsorbents. Due to their variety in chemical composition and crystalline lattice structure, which influence the calcium silicate hydrates adsorption capacity, a new family of inorganic cation exchangers was created [2-3].

The aim of this work was to determine synthetic α-C_2S hydrate ion exchange capacities and selectivity sequences for Cu^{+2} , Co^{+2}, Cr^{+3} ions.

It was determined that by using unstirred CaO – $SiO_2{\cdot}nH_2O$ – H_2O suspensions when the molar ration of CaO/SiO_2 was equal to 1.5, cured for 24 hours under saturated steam pressure at 175 °C, in the synthesis products α-C_2S hydrate was formed. Adsorption experiments were carried out at 25 °C temperature in the thermostatic absorber by stirring 5 g of synthetic α-C_2S hydrate in 500 ml of $Co(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ solutions containing 0.25 and 1 g Co^{2+},Cr^{3+}, Cu^{2+}/dm^3 for 0.5 – 30 min. The concentrations of heavy metal ions were determined by using AAS method. It was examined that the chemical nature of adsorptive had not a significant influence on the intercalation rate of heavy metal ions into α-C_2S hydrate structure because within 30 s all amount of Cr^{3+}, Cu^{2+} ions as well as Co^{2+} ions (within 5 min) were adsorbed. It was determined and proved by the kinetical calculations, that substitution reactions characteristic to the mentioned compounds are irreversible, i.e. almost all Cu^{2+}, Co^{2+} and Cr^{3+} ions was adsorbed by chemical interaction. Moreover, the selectivity sequence for heavy metals ions (1 g Co^{2+},Cr^{3+}, Cu^{2+}/dm^3) of α-C_2S hydrate can be written as follows: $Cr^{3+} > Co^{2+} > Cu^{2+}$. Synthesis and adsorption products were characterized by XRD, XRF and STA.

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C-S-H (I) SAMPLE STABILITY UNDER DIFFERENT PARTIAL WATER VAPOUR PRESSURE ENVIROMENT

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More than 30 crystalline calcium silicate hydrate phases are known, which structures range from semicrystalline to nearly amorphous, all of which are described by the generic term, ‘‘C-S-H“ [1]. Basicity of calcium silicate hydrates which are described by ratio of CaO/SiO_2 can vary from 0.3 to 3. In natural environment C-S-H (I) is formed in relatively low temperature (< 200˚C), hyper-alkaline, hydrothermal environments. In laboratory conditions C-S-H (I) is usually synthesized in CaO and SiO_2 mixture in dilute aqueous suspension [2]. C-S-H (I) has a layer structure, with the layers elongated in one direction that resulted in a fibrous structure, and showed similarities to tobermorite [3]. Nevertheless, no data have been published and it is completely unknown how the stability of synthetic C-S-H (I) structure changes during water vapour sorption in a different humidity. The aim of the present work was to determine the influence of partial pressure of water vapour on C-S-H (I) samples stability.

It was determined that C-S-H (I) type calcium silicate hydrate is dominating in CaO and SiO_2 mixture, when moral ratio of initial mixture is 1.5 after 16 h hydrothermal treatment in 200 ˚C. Furthermore, the compound which has calcium component – portlandite – did not react in synthesis conditions. It was observed that product has carbonised during drying process. Experiments of water vapour adsorption by synthetic C-S-H (I) samples were carried out at room temperature in desiccators over sulphuric acid for 96 h. It should be noticed that when the ratio of relative water vapour pressure (p/p_0) varied from 0.355 to 1.0, the heat of reaction increased from 113 to 147 J/g but there were no significant changes of mass loss in temperature range 40-210˚C. Furthermore, while the value of p/p_0 ratio equals to 1, portlandite completely reacted, because endothermic effect at temperature range 440-480˚C was not identified. Moreover, relative water vapour pressure has positive influence on structure properties of C-S-H (I) sample because of heat reaction of exothermic effect at temperature range 810-880˚C is increased till 30.41 J/g. Besides, samples were examined by simultaneous thermal analysis and X-ray powder diffraction.

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THE INFLUENCE OF GRAPHENE ADDITIVE ON THE HYDRATION PROPERTIES OF BINDER MATERIAL BASED ON α-C_2S HYDRATE

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Recently, synthesis, properties and structure of α-C_2S hydrate ($2CaO \cdot SiO_2 \cdot H_2O$) have obtained a new interest, because on its basis a new hydraulic cementitious materials family has been created [1]. The main feature of alternative hydraulic cementitious binder materials is the production in a two-step process: (1) hydrothermal preparation of the calcium silicate hydrates; (2) mechanochemical or thermal treatment of the hydrothermal products. Unlike ordinary PC, the C–S–H phase is formed during the production of the binder and not during the hardening of concrete [2]. In the past years, graphene and its derivatives have been investigated extensively. This is due its exceptional mechanical, electrical, thermal and optical properties, high surface area-to-volume ratio, and unique atomic structure [3]. All these processes of hydration kinetics plays an important role on microstructural development and final properties of hydrated cement pastes. Portland cement modified with nanomaterials has become a new alternative to traditional OPCs.

The influence of graphene additive on the hydration properties of binder material (BM) based on α-C_2S hydrate was examined. For this reason, BM was prepared from synthetic α-C_2S hydrate (C/S = 1.5; 16 h, 200 °C; because at these synthesis conditions in mixture portlandite already reacted) and quartz sand (the ratio of components was equal to 1:1 by mass). In order to create the hydraulically active binder material sample, the initial mixture was milled in a vibrating cup mill at 950 rpm for 5 min and thermally treated at 450 °C for 1 h.

It was determined that calorimetric curves of BM differ from the one of ordinary cements. The heat release curves obtained during hydration of BM samples produced with of α-C_2S hydrate components show only one distinctive peaks. In cement hydration, the rate of heat evolution first starts with an initial reaction, caused by the exothermic dissolution of the cement constituents. This results in the development of surface hydrates on cement particles. For that reason, the literature agrees that the rate of heat release in the first stage, which ends before the period of slow reaction, is controlled chemically. It was determined that BM with graphene additive show a little higher maximum heat release rate (0.0083 W/g) compare with pure BM samples (0.0064 W/g). At later stages of hydration, the calorimetric curve of BM showed the slower continued reaction, because the rate of heat evolution was decreased. It was determined that the total heat (67.22 J/g) for the BM samples with graphene additive after 72 hours is not significantly different to that of samples without additives (62.87 J/g). In the future research, the properties of mentioned binders materials such as compressive strength, mineralogical composition and porosity will be examined.

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THE INFLUENCE OF GRAPHENE ADDITIVE ON THE HYDRATION PROPERTIES OF OPC

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Every year a huge amount of ordinary Portland cement (OPC) is produced and used for the construction of building, roads and highways and other local purposes. For these reasons, the quality assurance of OPC has become an important and critical factor [1]. The hydration of this compound is quite a complicated process which includes dissolution and precipitation reactions. One important unresolved question is how to explain the influence of different factors on the hydration kinetics, as visible in typical heat flow diagrams [2]. Many research workers have used additives either as grinding aids for clinker or improving the properties of cement. Effect of additives on individual components of cements have been studied extensively to know the hydration behavior. Graphene is the most recent material discovered by scientists and is a star on the horizon of materials science and condensed matter physics [3]. This material has many potential applications in the real world and is about to change the future in a positive way.

In this work, the influence of graphene additive on the hydration properties of OPC sample was examined. It was determined that calorimetric curves of portlandcement differ from the one of ordinary cements hydration with water. The heat release curves obtained during hydration of OPC samples show two distinctive peaks. It was determined that OPC sample with graphene additive show a little higher maximum heat release rate (0.0058 W/g) compare with pure OPC samples (0.0035 W/g). It was observed that the second exothermic reaction processed from 3 to 10 h and, during this process, the total amount of heat of OPC samples was increased to 52.83 J/g. Meanwhile, in the samples with graphene component, the quantity of heat released within the same duration of hydration was equal to 57.54 J/g. At later stages of hydration, the calorimetric curves of both pure and with additive OPC samples showed the slower continued reaction, because the rate of heat evolution was decreased. It was determined that the total heat (250.89 J/g) for the OPC samples with graphene additive after 60 hours is not significantly different to that of samples without additives (238.16 J/g). Additionally, the hydration products were characterized by XRD, XRF and STA methods.

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THE SIMULTANEOUS ADSORPTION CAPACITY OF HYDROTALCITE FOR Co^{2+}, Cr^{3+}, Cu^{2+} IONS

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Hydrotalcite (HT) belong to a general group of materials called Layered Double Hydroxides (LDHs). These compounds had a general formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}[A_{x/n}]^{n-}\cdot mH_2O$ where M^{2+}, M^{3+} were di- and trivalent cations and A^{n-} could be an inorganic or organic anion, e. g. heteropolyacids or others. LDHs were recognised as valuable materials in multiple fields as catalysts, flame retardants, ion exchangers, drug releasers, anticorrosives and adsorbents [1-3]. It should be noted that multiple adsorbates are commonly found in waste waters, for this reason, the aim of this work was to investigate the simultaneous adsorption capacity of hydrotalcite for Co^{2+}, Cr^{3+} and Cu^{2+} ions.

Hydrothermal synthesis of hydrotalcite has been carried out in stirred suspensions in autoclave under the saturated steam pressure at 200 °C, when the duration of isothermal curing was 3 hours and the molar ratio of primary mixture was Mg/Al = 2:1. In order to evaluate the effect of mechanochemical treatment on hydrotalcite adsorption capacity, the synthesis products were grinded by using laboratory vibrating disc mill. Adsorption experiments were carried out at 25 °C temperature in the thermostatic absorber by stirring 5 g of hydrotalcite in 500 ml of $Co(NO_3)_2\cdot 6H_2O$, $Cr(NO_3)_3\cdot 9H_2O$ and $Cu(NO_3)_2\cdot 3H_2O$ solutions containing 1 g Co^{2+}, Cr^{3+}, Cu^{2+}/dm^3 for 0.5 – 30 min. The concentration of Co^{2+}, Cr^{3+} and Cu^{2+} ions in aqueous solution were determined using a Perkin Elmer AAnalyst 400 Atomic Absorption Spectrometer, while the products after synthesis and adsorption were characterized by XRD, XRF and granuliometric analyses.

The obtained results showed that the simultaneous adsorption depends on the chemical nature of adsorbate. It was determined that, in the beginning of the process, the uptake of Co^{2+} ions is very slow due to a small quantity of adsorbed ions, i. e. only 1.94 mg Co^{2+} /g is taken by hydrotalcite. However, the adsorption rate slightly increased, when the experiment was prolonged to 30 min, because the quantity of incorporated Co^{2+} ions was equal to 9.86 mg Co^{2+}/g. Meanwhile, the ion exchange reactions proceeded differently with Cr^{3+}, Cu^{2+} ions, because the total amount of adsorbed ions was equal to 31.16 mg Cr^{3+}/g and 36.27 mg Cu^{2+}/g. X-ray diffraction analysis showed that after simultaneous adsorption experiment the structure of hydrotalcite is disrupted, because the intensity of diffraction peaks typical to the latter compound is significantly decreased, which lead to the formation of new compounds ($Cu_2(NO_3)(OH)_2$, $MgAl(OH)_2(NO_3)\cdot 0.5\ H_2O$). These results were confirmed by XRF and granuliometric analyses data.

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Effect of partial water vapour on hydrotalcite sample structure

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Hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) can be ascribed to layered double hydroxides (LDH) group and can be used as chemical sensors, corrosion resistant coatings, components in optical and magnetic devices, for drug delivery and etc. [1, 2]. One of the most unique properties of LDH is memory effect (when LDH is heated, mixed metal oxides are able to restore layered LDH structure at room temperature) [3-5]. The aim of this work was to determine the influence of partial pressure of water vapour on crystal structure of hydrotalcite samples.

Hydrothermal synthesis of hydrotalcite has been carried out in stirred suspensions in autoclave under the saturated steam pressure at 200 °C, the duration of isothermal curing was 3 hours. Experiments of water vapour adsorption by hydrotalcite were carried out at room temperature in desiccators over sulphuric acid for 96 h.

It was determined that in aluminium oxide and magnesium carbonate mixture, when molar ratio of Mg/Al is 2, after 3 hours of isotermal curing at 200 °C temperature hydrotalcite and boehmite were formed. It should be noted that during synthesis conditions the compound which has magnium component – magnesite did not completely react. Furthermore, relative water vapour pressure in the environment has an influence on crystallinity of hydrotalcite: when the ratio of relative water vapour pressure (p/p_0) varied until 1, the area of main diffraction peak (d – 0.751 nm) and crystallite size increased from 75.6 to 114.4 a.u. and from 40.1 to 42.3 nm respectively. It was observed that by growing the value of p/p_0 ratio, the quantity of boehmite and magnesite were decreased: the heat of the endothermic effect at 530-620 °C temperature interval (which is typical for the decomposition of magnesite) decreased from 488.30 to 186.79 J/g and the mass loss – from 20.61 to 9.02 %. Besides, samples were examined by simultaneous thermal analysis and X-ray powder diffraction.

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SURFACE MICROSTRUCTURE AND SPECIFIC SURFACE AREA OF SYNTHETIC CALCIUM ALUMINIUM HYDRATE

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Geopolymers which are based on alumina/silicate ores presents a viable alternative for replacing ordinary Portland cement and are a novel “low-carbon” construction material [1]. In addition, geopolymers technology entails inexpensive and eco-friendly synthetic procedures involving raw materials. The one group of these compounds can be located in the $CaO–Al_2O_3–SiO_2–H_2O$ system. During hydrothermal synthesis the results the formation of compounds such as calcium silicate hydrates (CSH), calcium aluminium hydrates (CAH) and calcium aluminium silicate hydrates (CASH). The formation of mentioned structures with certain structural and physical properties is mainly affected by the synthesis conditions. In Ríos et al. work, the quantity of obtained CASH was reduced with increasing duration of hydrothermal synthesis (175 °C; 0-24 h) [2]. Meanwhile, Meller et al. found that the stability of obtained phases in $CaO–Al_2O_3–SiO_2–H_2O$ system can be altered radically even by small amounts of Al_2O_3 additive and the phase formation strongly depends on the synthesis temperature (from 200 to 350 °C) [3].

In this work the influence of aluminum additive quantity on the synthetic calcium aluminium hydrate surface microstructure and specific surface area were investigated. It was determined that, in $CaO–Al_2O_3–SiO_2–H_2O$ system, after 8 hours of isothermal curing at 130 ^{o}C temperature, when the molar ratios of primary mixtures $CaO/(SiO_2+Al_2O_3)$ and $Al_2O_3/(SiO_2+Al_2O_3)$ were equal to 0.55 and 0.1, respectively, calcium aluminium hydrate was dominating in the synthesis products. Meanwhile, alongside mentioned compound a broad basal reflection, without peaks, in 18 – 34º diffraction angles range was noticed and can be assigned to amorphous structure compounds, which mainly contain silicon, calcium and/or aluminium components. It should be noted that the quantity of Al_2O_3 additive in the primary mixtures affected the amount of formed CAH: the heat values of the CAH dehydration at ~281 °C temperature as well as the diffraction maximums were 1.5 times higher. Moreover, the carbonation appeared, when the products were dried in air conditioned chamber (50 ºC, 24 h), because the diffraction peaks characteristic to calcium carbonate were detected in the XRD patterns. It is clearly shown in TG curve: due to a larger amount of Al_2O_3 in synthesis products, the calculated quantity of calcium carbonate decreased from 2.11 % to 5.36 %.

It was determined that a stable monolayer of absorbed N_2 was formed on the surface of samples. Straight lines were obtained for all samples in BET coordination ($0.05 \le p/p_0 \le 0.30$) and correlation coefficients R^2 remains very close to the unit, i.e. 0.999. It was determined that increasing Al_2O_3 additive in primary mixture has influence on products structure and specific surface area. Specific surface area: decreased from 101.80 m^2/g to 53.16 m^2/g and C_{BET} constant values decreased from 65.96 m^2/g to 35.12 m^2/g. There parameters showed that to more orderly structure formed in products with a larger amount of Al_2O_3 additive. This assumption was confirmed by SEM analysis.

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THE FORMATION OF DIBASIC CALCIUM SILICATE HYDRATES IN CaO-WASTE SILICA GEL-H_2O MIXTURE

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According of the strict environmental regulations governing fluoride concentrations in water within many countries and safe disposal of fluoride containing wastes is still one of the critical environmental challenges [1, 2]. The industry of aluminium fluoride generates a large amount of silica gel contaminated with F^- ions as a by-product, which is not widely used or processed, but instead it is stored in a landfill site. One of the utilization method for silica gel waste could be its application as SiO_2 containing raw material for the synthesis of C-S-H [3]. For this reason, by choosing optimal conditions (temperature, raw materials and etc.) of isothermal curing, it is necessary to cheapen and improve the hydrothermal synthesis of C-S-H; to investigate properties of silica gel waste and the possibilities of this material application for the production of C-S-H.

The formation mechanism of calcium silicate hydrate under hydrothermal conditions, when primary mixtures consisted of CaO and amorphous $SiO_2{\cdot}nH_2O$ or silica gel waste, was examined in detail. The synthesis was carried out in unstirred suspensions, when molar ratio of the primary mixture was $CaO/SiO_2 = 2.5$ and the duration of isothermal curing in a 200 °C temperature range were 16, 24, 48 and 72 h. It was determined that, in CaO-SiO_2-H_2O mixture after 16 h of isothermal treatment, dicalcium silicate hydrates – α-C_2S hydrate and semi-crystalline calcium silicate hydrates C-S-H(I) were formed. After 48 h of isothermal curing, α-C_2S hydrate compound recrystallizes into hydroxyledgrewite. By prolonging the duration of synthesis, hydroxyledgrewite becomes unstable and recrystallizes into reinhardbraunsite. It should be noted that under these experimental conditions portlandite was not completely reacted. Meanwhile the mechanism of hydrothermal reactions and the sequence of the compounds formed in CaO-silica gel waste-H_2O mixtures are quite different because part of the CaO reacts with the F^- and Al^{3+} ions and forms cuspidine and hydrogarnet respectively. The previous results were confirmed by XRD and STA analysis.

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INFLUENCE OF FORMING PRESSURE ON THE SYNTHESIS OF CLINKER MINERALS

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Ordinary Portland cement (OPC) is the most popular binder used in concrete for construction because of its durability, universality and relatively low cost. Its annual worldwide production is approaching 4 billion tones [1]. However, all stages of OPC manufacture have negative impact on environment. Cement plants cause 5–7 % of global CO_2 emission, while 900 kg CO_2 is emitted to the atmosphere for producing one ton of cement [2]. Also about 111 kWh of electric energy is used to produce 1 ton of cement, while most of this energy is used for thermal treatment of clinker [3].

Due to the following reasons, it is a matter of great importance to seek for alternative approaches to reduce the adverse effects of the manufacture of OPC in an attempt to attain sustainable development. One of the ways to achieve lower energy consumption is to reduce clinker calcination temperature by 75-100 °C. This can be achieved by increasing the contact surface area of the reactants.

In this work, the influence of forming pressure on clinker mineral formation processes was determined. Cementitious binder specimens were prepared from “Akmenės cementas” clinker and “Nikiforovo” clay (Ukraine) to adjust the saturation coefficient. The samples were pressed to 4-20 MPa and burnt in temperatures of 1300, 1350, 1400 and 1450 °C for 20, 40 and 60 min. The mineral composition of the products was determined by XRD, chemical and Rietveld analysis.

Sample pressing at yet low pressures (4 MPa) accelerates synthesis of clinker minerals. In unpressed samples calcined at 1300 °C temperature for 20 min, amount of C_3S was 29,28 %. Due to pressing at yet low pressure, the amount of this main clinker mineral increased to 33,44 %. The obtained results were complimented by free lime investigation, which showed that amount of free CaO decreased from 8,25 % to 8,04 %. However, further increase of pressure had no positive influence, as the data of the samples pressed at various pressures were very similar: amount of C_3S was in range of 33–34 % and amount of free CaO varied around 8 %.

Similar result were obtained with extended combustion duration and temperature – pressing samples at yet low pressure, amount of free CaO decreased by ~0.5 % but further pressure increase had no influence. Far greater impact had the increase of temperature itself. In samples calcined at 1350, 1400 and 1450 °C for 20 min, amount of free CaO decreased respectively to 2,89; 1,6 and 0,75 %.

Even though raw material densification had a positive influence on synthesis of clinker minerals, however, it was not sufficient and should be supplemented with additional methods.

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PREPARATION OF CALCIUM TITANATE POWDERS AND THIN FILMS BY SOL-GEL METHOD

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One of the purposes of surface modifications for biomaterials is to improve tissue responses in a living body. Ceramic coatings are often applied to facilitate osteogenesis on metallic biomaterials. Calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (CHA) is the most popular coating material [1-3]. Recently, the calcium titanate $CaTiO_3$ (CT) coating has gained considerable attention as another surface modification technique for the activation of osteogenesis on titanium [4]. CT is chemically stable compound and has been proposed as an intermediate layer or an addition to improve the adhesion between CHA and substrates, i.e. increases the bond strength between Ti and CHA [5].

CT powders were prepared using Petchini sol-gel method. In the sol-gel processing, a citric acid (0.009 mol) was dissolved in 20 mL of DI water. After 15 min stirring titanium isopropoxide (0.003 mol) was added to the solution. The temperature was increased to 80-90 °C and mixed for another 30 min. The calcium acetate monohydrate (0.003 mol) and ethylene glycol (2 mL) were added to the clear solution. After mixing the sol for 1 h the solution was evaporated and obtained gel dried at room temperature. According to the TG data, CT phase starts to form in the range of 600-650 °C. The monophasic CT powders were obtained after calcination precursor gel at 650 °C for 5 h with heating rate of 1°C/min. The same sol-gel process was used for the preparation of CHA coatings on the Ti substrate. After cleaning Ti substrates were dip-coated with calcium and titanium ions containing sol and heated at 650 °C for 5 h with heating rate of 1°C/min. The thickness of CT layers increased by increasing number of dip-coating procedures. Titanium dioxide layers were formed on the same Ti substrate after heating as well. Different numbers of CT layers were prepared and characterized by the X-ray diffraction analysis, scanning electron microscopy and contact angle measurements. The phase purity, microstructure and wettability of CT thin films on titanium/titanium dioxide substrates were evaluated and discussed.

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FORMATION OF ZnO BY THE SILAR METHOD FOR THIN SOLAR CELLS

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Zinc oxide is low-cost and non-toxic material with various interesting properties having high stability, good optical and electrical properties. It is widely used in various applications like gas sensors, transparent conducting oxides, dye sensitized solar cells and buffer layers in $CuInS_2$ solar cells. ZnO is n-type semiconductor with wide band gap (3.3 eV) and transparency in visible range of solar spectrum. ZnO is widely used for manufacturing of thin film solar cells.

The thin ZnO layers were deposited by means of the successive ionic layer adsorption and reaction (SILAR) method. The morphology, structure and composition of the ZnO were examined by means of Field-Emission Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy. The optical properties of the ZnO thin films deposited onto glass substrates were investigated by means of UV/Vis spectrophotometric measurements.

It was found that obtained ZnO layers are composed of ZnO crystallites in size of ca. 25- 75 nm. Optical measurements show that the ZnO layer have band gap energy (E_b) of 3.2 eV. The transmittance of ZnO layer is ~100 %.

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The synthesis of 1.13 nm tobermorite from granite polish waste

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The minerals of calcium silicate hydrates group are found in nature. In addition, they are formed during the evaporation of silica bricks, aerated concrete, or thermal insulating materials [1]. The reaction pathway of calcium silicate hydrates is governed by various parameters such as temperature, stirring, the presence of foreign ions, which influence the kinetics of the reaction and even the microstructure of the products. Nevertheless, the effectiveness of synthesis first of all depends on the activity of used SiO_2. The best source for synthesis of 1.13 nm tobermorite is amorphous silica. It was also reported that tobermorite could be produced from different kinds of wastes, such as trachyte rock [2], municipal incineration bottom ash [3] and steel slag [4]. Unfortunately, there are no similar materials in our country. On the other hand, granite polish waste is a large amount of by-product from stone processing with low utilisation. According to its chemical and mineral composition it may be suitable for preparation of calcium silicate hydrates via hydrothermal reactions.

Granite polish waste was taken from JSC "Granitas" (Lithuania) and milled in ball mill until Sa = 905 m^2 kg^{-1}. Chemical composition of the material: SiO_2 – 58,4 %; Al_2O_3 – 15,4 %; Fe_2O_3 – 7,17 %; CaO – 3,95 %; K_2O – 3,86 %; Na_2O – 3,56 %; MgO – 2,87 %; others – 4,79 %. Reagent CaO was added to granite polish waste in necessary quantities to obtain mixtures with molar rations Ca/SiO_2 of 0.83 and 1.0. Dry primary mixtures were mixed with water to get suspension with water/solid ratio W/S = 10.0. Hydrothermal synthesis was carried out for 4; 8; 12; 24 and 72 h at 180 and 200 °C in unstirred suspension. The products were analysed by XRD, STA and SEM methods.

It was found, that at 180 °C the reactions of 1.13 nm tobermorite formation in the mixture with molar ratio Ca/SiO_2 = 0,83 are quite slow. After 4 h of isothermal curing only the traces of this compound together with semi-crystalline C–S–H(I) was formed. However, after extending the duration of treatment to 8 h the amount of formed 1.13 nm tobermorite noticeably increased. The quantity of 1.13 nm tobermorite narrowly but coherently augmented by prolonging the hydrothermal synthesis to 12 and 24 h. Nevertheless, the 1.13 nm tobermorite of the highest crystallinity degree was obtained only after 72 h of hydrothermal synthesis. In addition, these unreacted compounds from granite polish waste also were identified: annite from mica family and cordierite. Similar results were obtained when the molar ratio CaO/SiO_2 =1,0.

Elevating the temperature of the synthesis to 200 °C led to a significant acceleration of the hydrothermal reactions between CaO and granite polish waste. 1.13 nm tobermorite became a dominant compound in the product after 8 h of the synthesis and only a negligible amount of C-S-H(I) was identified in DSC curve. It should be underlined that 1.13 nm tobermorite was stable and do not start to recrystallize to xonotlite by prolonging the synthesis to 24 h. Therefore it can be state, that granite polish waste is suitable raw material for the synthesis of 1.13 nm tobermorite.

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SYNTHESIS OF $Sr_{1-x}Y_xF_{2+x}$ VIA CO – PRECIPITATION METHOD

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$Sr_{1-x}Y_xF_{2+x}$ is a promising as host matrix for up-converting process due to its low phonon energy lattice [1]. A low phonon energy lattice is essential in order to reduce the multiphonon relaxation (minimized energy losses) and to increase the lifetime of the intermediate states involved in upconversion (maximized radiative emission)[1]. Many features of fluoride nanoparticles also depend on their size and shape.

Strontium yttrium fluoride nanoparticles can be synthesized in different ways such as – thermolysis of metal trifluoroacetates, microwaving of metal nitrates in 1-butyl-3-methylimidazolium tetrafluoroborate and hydrothermal techniques. However, there is lack of information on the preparation of strontium yttrium fluoride nanoparticles by co-precipitation method [2].

It was found that the co-precipitation is a very productive method for the preparation of equilibrium and non-equilibrium nanophases of variable composition formed under ambient conditions. The effect of Y^{3+} ion concentration on phase structure of $Sr_{1-x}Y_xF_{2+x}$ system was studied. Concentration in crystal lattice was changed from 10 to 90 mol%. The effects of reaction conditions such as: concentration of starting materials, temperature, reaction time, viscosity of the reaction mixture which was changes by using PVP with different molar mass, on phase structure and morphology of products were investigated. The results showed that particular Y^{3+} ions content (10 – 50 mol %) is favorable for the formation of pure cubic phase with space group *Fm-3m* (#225). Moreover with higher yttrium content in compound (50-90 mol%) trigonal phase with space group P3c1 (#165) were formed. All samples were analyzed using X-Ray diffraction (XRD), scanning electron microscopy (SEM), dynamic light scattering (DLS) and infrared spectroscopy (FT-IR) methods. The influence of Y^{3+} ions content and synthesis conditions to phase structure, crystal size and morphology of $Sr_{1-x}Y_xF_{2+x}$ will be discussed.

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Doping effect of Tb^{3+} ions on luminescence properties of $Y_3Al_5O_{12}$:Cr^{3+} phosphor

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Since 1928, synthetic and natural compounds which have garnet structure were determined [1]. The yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) was one of the first synthetic garnets which received a huge interest in studies for different kind of applications till nowadays [2]. YAG has cubic garnet structure, stable crystal lattice, therefore YAG doped by rare earths elements and/or transition metal ions is widely used in optical technologies, luminescent and fiber-optic telecommunication systems [3-7]. Cr^{3+} doped garnets (YAG: Cr^{3+}) exhibit emission in red and far-red regions. It is known that there are three main processes in successful growth of plants, which require light in red, far-red and blue spectral ranges. YAG: Cr^{3+} is a potential candidate for application in phosphor-converted light-emitting diodes that meet photomorphogenetic needs of plants. Meanwhile, terbium doped YAG (YAG: Tb^{3+}) emits bright green color therefore is suitable for contrast-enhanced display application in high ambient illumination conditions [8-12]. YAG: Tb^{3+} also has potential to be used as phosphor materials such as cathode-ray and projection television tubes, X-ray phosphors and scintillators [13-15].
To our best knowledge in literature there are no reports on terbium–chromium co–doped yttrium aluminum garnets (YAG:Cr^{3+}, Tb^{3+}), which could be interesting compounds, because the excitation bands of terbium and chromium ions overlap in 250–300 nm range [16]. Therefore, in the present work synthesis and investigation of luminescence properties of terbium–chromium co–doped YAG compounds are discussed in details. The samples were synthesized by sol–gel route, which had a lot of advantages among other synthesis routes such as high reactivity, good homogeneity and probability to get phase pure garnets at low temperature range [3].

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FRICTION AND WEAR OF TITANIUM IN WATER AND FATTY ACIDS

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Titanium (Ti) alloys found many applications in aerospace and other high-tech industries. Their ability to prevent toxic or immunologic response make Ti a material of choice in medicine for orthopedic, dental and cardiovascular implants [1], which are exposed to blood plasma (95% water), proteins and lipids [2]. Since they may incur contacts with moving surfaces leading to tribological implications, wear of implants must be avoided in-vivo. In this study Ti friction was tested under dry conditions as well as in water and fatty acids, which are among major constituents in body fluids.

Plates of Ti alloy BT1-0 of 96.32% purity (1.75% Al, 0.11% Fe, 1.76% Mn, 0.06% Si) were polished to Ra of 1.15 to 1.35 μm and immersed into deionized water at room temperature or industrial oleic acid (70% pure) at 90ºC for 1 h. CSM tribometer was used in ball-on-plate linearly reciprocal configuration with 6 mm OD Al_2O_3 balls [3] at 10 N load, 2 cm/s velocity and 8 mm cycle length. Wear profiles were measured after 500 friction cycles with a contact profilometer Surtronic 25.

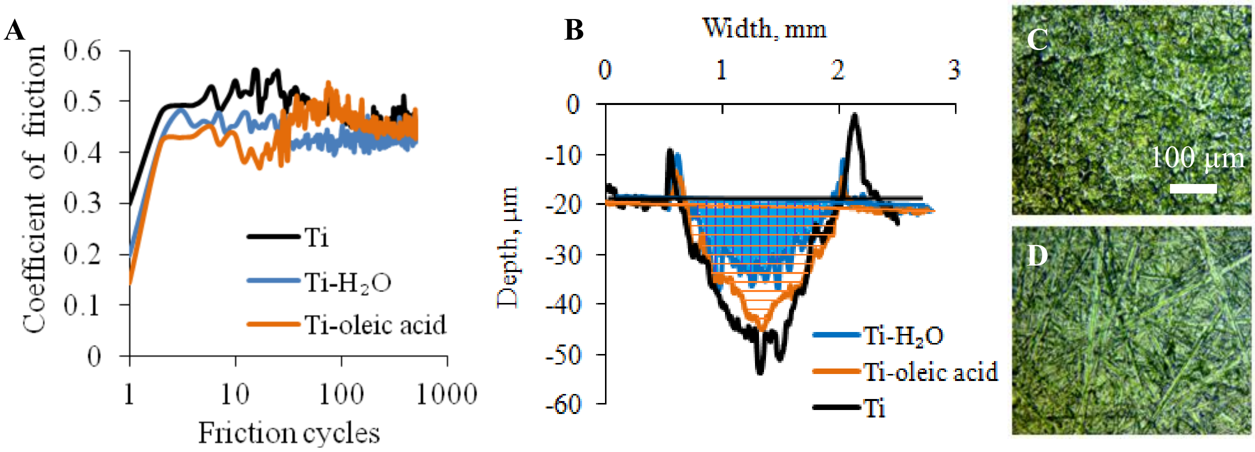

Fig 1. Friction (A) and wear (B) tendencies in dry and lubricated Ti surfaces. Optical microscope images of Ti surface without (C) and with (D) polishing before tribotests.

Water or oleic a. provided only slightly lower friction during initial cycles compared to dry Ti surfaces. The surfaces were polished with 600 grit abrasive cloth (Fig 1 C and D), however friction (Fig 1 A) and wear (Fig 1 B) did not change. Formation of any lubricating films appeared not likely. Coefficient of friction reached 0.5 nearly instantaneously both in dry and lubricated conditions. Furthermore, wear is very significant with scars clearly evident. Wear rates of dry surfaces are similar to those lubricated with oleic acid. This shows that occasional in-vivo tribological processes in implants might bear significant risks of wear and surface damage on titanium implants.

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COMMERCIAL AND SOL-GEL DERIVED COBALT CHROMITES AS CERAMIC PIGMENTS: A COMPARATIVE STUDY

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Factors affecting the appearance of glazes are diverse: the origin and the mesh size of raw materials, the clay body on which the glaze is fired, the duration of firing, the type of a kiln and others. Generally glazes are composed of several parts: pigment, silica (SiO_2), flux and alumina (Al_2O_3). The flux is used to lower the melting temperature of the silica and the alumina is used to increase the viscosity of the glaze and give it stability on the clay body. To give a colour for the glaze, colouring oxides are added [1, 2]. In this paper the dependence of the glaze colour and quality on the composition of the pigment is discussed. For this intent purchased cobalt chromium spinel with a commercial name Cobalt bottle green (CoBG, *Kremer Pigmente*) and sol-gel derived cobalt chromium spinel (SGCo) were chosen. For further investigation of colour variations, other sol-gel synthesized chromites MCr_2O_4 (M = Cu, Ni, Zn; SGCu, SGNi and SGZn, respectively) were selected.

According to producer, the dark green pigment CoBG is $CoCr_2O_4$, which was confirmed by XRD analysis. The diameter of the particles varies from 4 to 25 μm. However, CoBG distinguish more green tones than pure $CoCr_2O_4$ [3], which leads to assumption of impurities.

In the sol-gel synthesis, $Co(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$ were used as starting materials; 1,2-ethanediol was used as gelation agent. The produced gel samples were dried at 105 °C temperature for 20 h, triturated in an agate mortar and calcined at 700 °C for 3 h. The powders were ground repeatedly and annealed at 1000 °C temperature for 10 h [4]. Particle size of obtained powders were of 0.1-0.8 μm; colour pallete changing from bluish green for SGCo to black, green and yellowish green for SGCu, SGNi and SGZn, respectively.

For the preparation of glazes, 5 wt% of each pigment was mixed with base glaze (commercial ID P074 10), 0.5 g of each mixture was put on ceramic plates (3 x 4 cm), dried in air and burned in oxidising atmosphere at 1000 °C for 1h. The glaze with commercial pigment came to be homogeneous and in dark green colour. However, obtained glazes with sol-gel synthesized pigments were heterogeneous: the pigments were not uniformly distributed and the blue colour was dominant.

Produced pigments were characterised by Rigaku MiniFlex II diffractometer in a scanning range of $2\theta = 10–80°$, using Cu Kα radiation. The pigments and their glazes were characterised by the CIELab colorimetric method. The L*, a* and b* CIELab parameters were measured on a Perkin Elmer Lambda 950 spectrophotometer, in the 780–380 nm range, employing an illuminant D65 and a 10° standard observer. The morphology of glazes was determined through a scanning electron microscope Hitachi TM-3000.

Acknowledgement: The authors thank G. Kreiza and K. Kazlauskas for their assistance in CIELab measurements.

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2-PHENYLINDOLYLCARBAZOLE DERIVATIVES WITH REACTIVE FUNCTIONAL GROUPS AS ELECTROACTIVE MATERIALS

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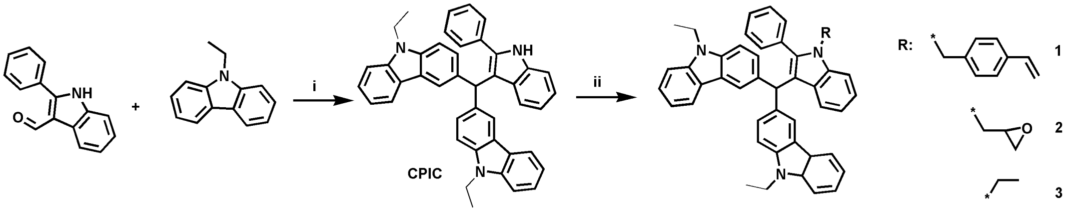
Low-molar-mass and polymer organic amorphous semiconductors are widely studied as the key components of organic optoelectronic devices such as organic light emitting diodes and organic and hybrid solar cells [1, 2]. Effective charge transport and excellent thermal stability are the reasons why electron-rich moieties such as carbazole [3] are widely used in the design of hole transporting materials. Much less investigations are reported on the derivatives having other electro-active moieties, such as 2-phenylindole [4]. In addition, indole derivatives usually show high triplet energy values and can be used as host materials in phosphorescent organic light emitting diodes.

In this work derivatives of 2-phenylindolylcarbazole with reactive epoxy and vinylbenzyl groups were synthesized and investigated in order to identify correlations between the molecular structures of the compounds and their thermal, optical, photophysical, electrochemical properties (Scheme 1). We also investigated the possibility of photo-polymerization of the synthesized derivatives.



Scheme 1. Synthesis of 2-phenylindolylcarbazole derivatives. (*i*) HCl (conc.), tetrahydrofuran/methanol, r.t., 5h; (*ii*) alkylhalide, K-*t*BuO, BTMAC, DMSO, r. t., 48h.

The thermal, optical, photophysical, electrochemical and photoelectrical properties of the materials will be reported.

Acknowledgments

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IMMOBILIZATION OF ROSEMARY OIL IN ELECTROSPUN CELLULOSE ACETATE FIBERS

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Recently, among various approaches for preparation of nano-materials, electrospinning is one of the most attractive methods for its continuous fabricating capability and facile operating process. Particularly, the electrospun fibers exhibit a large surface area to volume ratio due to the high porosity and nano to submicron structure, which is favorable for the sustained release of active agents [1].

In this work the electrospun cellulose acetate/rosemary essential oil (CA/RO) fibers were successfully fabricated under the optimal conditions by using single-needle electrospinning equipment. The cylindrical nanofibers (CA1/RO) with average diameter ranging from 255 to 617 nm were obtained by using acetone, dichloromethane and dimethylformamide as solvents in initial composition, meanwhile, the elimination of dimethylformamide from electrospinning solution yielded flat microfibers (CA2/RO) with average diameter varying from 1242 to 2939 nm (Fig.1). Moreover, the gas chromatography experiments confirmed the continuous release of bioactive components from CA1/RO nanofibers which could potentially be used in medicine or food packaging applications.

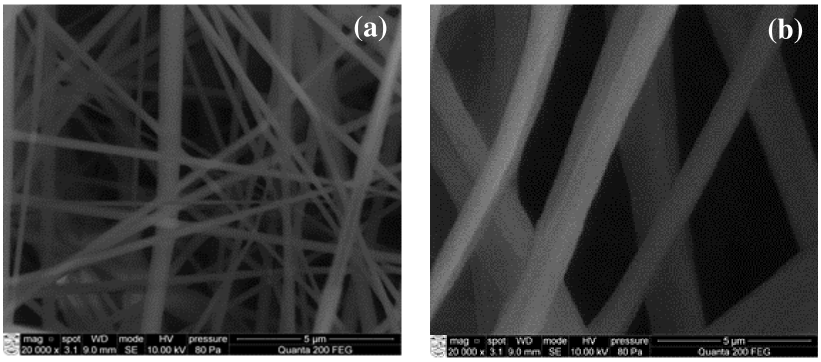

Fig. 1. SEM images of CA1/RO (a) and CA2/RO (b) fibers at x20000 magnification

Acknowledgment. The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP-055/2015.

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ELECTROSPUN CELLULOSE ACETATE FIBERS CONTAINING ESSENTIAL OILS FOR ACTIVE FOOD PACKAGING

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The most interesting and promising components of active packaging are antimicrobial and antioxidant species. Compared with synthetic active materials, natural compounds can be of great interest because of their safety and health characteristics. Furthermore, biopolymers such as cellulose, starch or chitosan can be used as safe and biodegradable carriers to incorporate and release active compounds in food packaging [1].

In this work the electrospun nanofibers of cellulose acetate (CA) and rosemary (RO), clove (CL) or thyme (TH) essential oils were produced by using needle-free Nanospider^{TM} electrospinning equipment. The data of Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) indicated the immobilization of essential oils into CA fibers. The CA3/RO, CA3/CL and CA3/TH nanofibers exhibited antimicrobial activity, and its minimum inhibitory concentration (MIC) against *Escherichia coli*, *Pseudomonas aeruginosa* and *Listeria monocytogenes* was approximate 5-10 mg/mL and minimum bactericidal concentration (MBC) was approximate 10-15 mg/mL (Table 1).

Furthermore, the electrospun nanofibers of CA3/RO, CA3/CL and CA3/TH secured excellent antioxidant activity as demonstrated by 2-2-diphenyl-1-picrylhydrazyl (DPPH) free radical inhibition (Table 1).

Table 1. Antimicrobial and antioxidant properties of cellulose acetate/essential oils fibers

Sample	MIC/MBC[a]			DPPH inhibition[b]
	E. coli	*P. aeruginosa*	*L. monocytogenes*	
CA3/RO nanofiber	5/15	5/15	5/15	16.2 ± 2.0
CA3/CL nanofiber	5/10	10/15	5/10	91.5 ± 0.1
CA3/TH nanofiber	5/10	5/10	5/10	58.9 ± 1.2

[a] MIC and MBC values as mg/mL for electrospun fiber
[b] Inhibition (%) of DPPH free radicals using electrospun fiber

Based on antioxidant activity results the CA3/CL nanofiber was chosen as most effective material for active food packaging test. Color analyzes showed that the CA3/CL nanofiber can effectively preserve the quality of fresh beef, indicating its potential for the application in antioxidant food packaging.

Acknowledgment. The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP-055/2015.

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REVIEW: BIODEGRADABLE POLYMERS AND MELT ELECTROSPINNING METHOD FOR NANOFIBER FABRICATION

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Electrospinning has been recognized as an efficient technique for the fabrication of polymer nanofibers. Most of the electrospun nanofibers are based on solution spinning. Risky chemicals are used to dissolve plentiful polymers. These solvents may leave residue that is not compatible with health issues. There has been a desire to produce fibers by concentrating on a cleaner process, through being environmentally safe and productive. Thus, an electrospinning system that uses molten polymer has gathered great excitement [1]. In this study we are aiming to review the potential of electrospun biodegradable nanofibers for filtration applications. We are focusing mainly on a different polymers and their features such as viscosity, strength and application availability.

Two significant properties of polymer melts that will influence their capacity to be electrospun are 1) they are nonconductive and 2) their viscosity is much greater than solutions. The first point is particularly important, as there are similarities in the electrostatic jets of both non-conductive fluids and polymer melts. Even within electrospun solutions, the conductivity of the polymer jet has a significant effect on the resulting morphology of electrospun polystyrene fibers [2]. The second issue of viscosity has been implicated in the eventual diameter of the fiber as well as the single, large Taylor cone formed, and reporting that the fibrous material collected is one continuous fiber [3].

A number of polymers have been used in melt electrospinning. Polymers that have been melt-electrospun include, poly(lactic acid) [4-5], poly(ethylene glycol) [6-7], polycaprolactone [8-9], poly(lactide-co-glycolide) [10-11] and polypropylene [12-13]. Most of them are biodegradable.

After analyzing research made in field of melt electrospinning it become clear, that this method has a huge potential as a way to make nanofibrous materials. Since there is no need for potentially toxic solvents and there is great variety of biodegradable polymers to choose from, there is no wonder that the greatest interest for melt electrospinning is shown in the field of biomedicine. However the potential of biodegradable melt electrospun nanofibrous materials for possible air filtration applications is not analyzed.

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SYNTHESIS AND PROPERTIES OF PHOTOCROSS-LINKABLE CARBAZOLE-BASED MONOMERS

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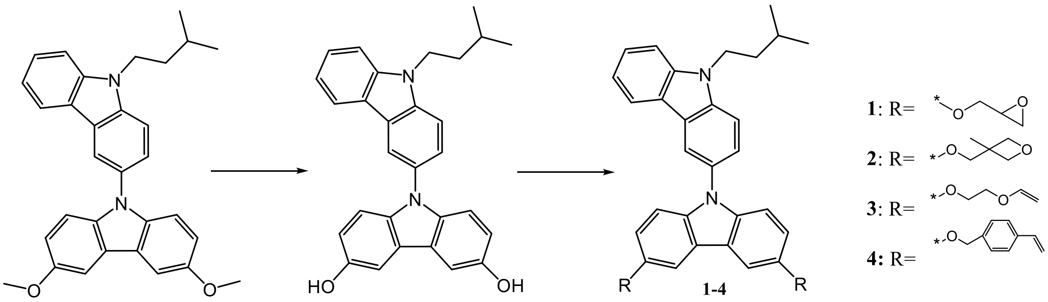
Ongoing improvement of organic (opto)electronic devices raises the increasing requirements to organic charge-transporting materials. Most of the modern optoelectronic devices are the multilayer systems. A severe difficulty which often occurs in the preparation of such devices is the solubility of material which forms the bottom layer onto which the top layer has to be cast, since most of organic semiconductors are soluble in the same organic solvents. The approach that is used to circumvent this problem is to render the material insoluble by using cross-linking reactions. In this presentation we report on the preparation of new glass-forming monomers containing carbazolyl groups and on their cationic photopolymerization. The work also aims the comparison of the reactivity of the different functional groups as well as the preparation of electro-active polymer networks.

The monomers containing two reactive functional groups such as vinyloxyethyl-, epoxypropyl-, oxetanyl- and vinylbenzyl-, were synthesized from 3-(3,6-dihydroxycarbazol-9-yl)-9-isopentylcarbazole.



The kinetics of UV curing of the monomers was monitored by real-time FT-IR technique. Comparative study on the thermal, optical, photophysical, and photoelectrical properties of the cross-linked systems will be presented.

Acknowledgments

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CARBAZOLE-BASED DERIVATIVES HAVING DONOR AND ACCEPTOR MOETIES

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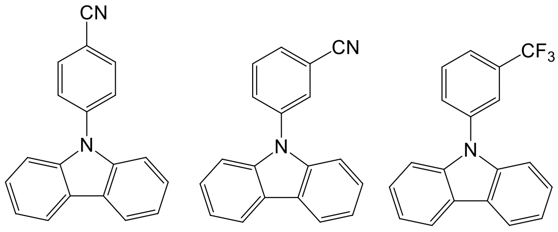
The materials are useful for the preparation of optoelectronic devices, such as light-emitting diodes, electrophotographic photoreceptors, solar cells as charge-transporting compounds [1,2].

In this report we are presenting the synthesis and studies of the series of carbazole derivatives there derivatives of benzene were merged with the 9th atom of carbazole by Ullmann or modified Ullmann coupling reactions (Fig 1).



1 **2** **3**

Fig. 1. Structures of **1-3**.

The structures of the synthesized compounds were proved by ^{1}H and ^{13}C NMR, IR and mass spectrometries. The thermal, optical, electrochemical and photophysical properties of the compounds were investigated.

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DERIVATIVES OF 9-PHENYL CARBAZOLE WITH INDOLE MOIETIES FOR ELECTROPHOSPHORECENT DEVICES

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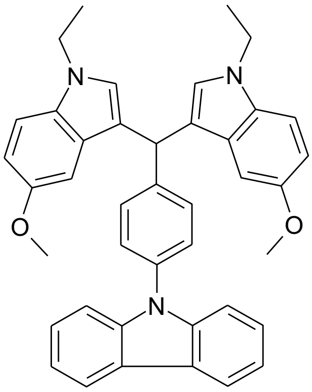
Derivatives with electroactive fragments are widely studied due to their good processability and applications in various (opto)electronic devices including organic light emitting diodes [1,2]. Their thin films on the different substrates can be fabricated by using simple techniques, i.e. casting or spin-coating from solutions. Such advantages are important in the fabrication of low cost and large area devices.

In this contribution the synthesis and properties of carbazole and indole derivatives **1-3** will be presented.



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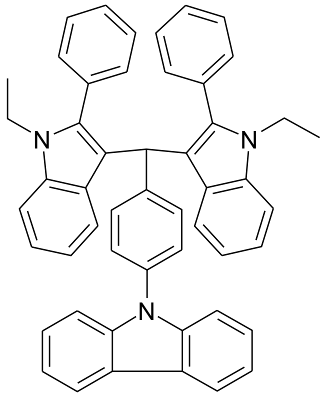

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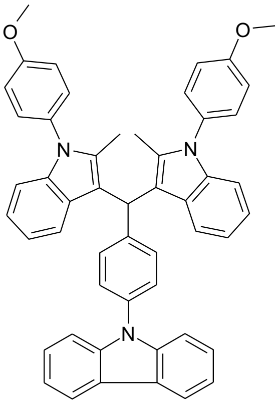

3

The thermal properties of the derivatives were examined by differential scanning calorimetry and thermogravimetric analysis. All the compounds demonstrated high thermal stability. Their 5% weight loss temperatures were found to be higher than 390 °C. The glass-transitions were observed in the range of 89-130 °C

Photophysical properties of the synthesized compounds were studied. The dilute solutions of **1** and **3** emit in the range of 350-400 nm when excited with ultraviolet radiation.

The ionization potentials of the derivatives were estimated by cyclic voltammetry. They were found to be comparable and ranged from 5,59–5,66 eV.

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CHEAP AND EFFICIENT CARBAZOLE-BASED HOLE TRANSPORTING MATERIALS FOR PEROVSKITE SOLAR CELLS

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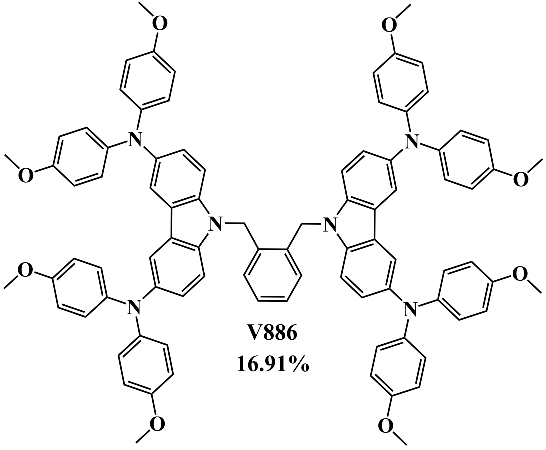
Over a last few years perovskite solar cells have reached 21% power conversion efficiency and due to simple production process are promising alternative for the conventional silicon solar cells. Apart perovskite light absorber in the best-performing devices hole transporting material (HTM) plays important role. Since the first successful application in ssDSSC [1] and consequentially in perovskite solar cells [2], currently the most studied and best performing small molecule HTM is 2,2',7,7'-tetrakis-(*N,N*-di-p-methoxyphenylamine)-9,9'-spirobifluorene (**Spiro-OMeTAD**). However due to long and complicated synthetic route [3] and purification by sublimation **Spiro-OMeTAD** price is very high.



Recently in our group new efficient HTM methoxydiphenylamine-substituted carbazole twin derivative was synthetised (**V886**). Perovskite solar cell with **V886** demonstrated 16.91% power conversion efficiency [4].

In this work more representatives of branched carbazole-based HTMs are presented. They were synthetised by a two-step synthetic procedure from the commertially availible starting materials. In the first step "click" reaction of brominated carbazole with (bromomethyl)benzene derivatives was used for the core synthesis. This stage is very fast (10 min), does not require high temperature and the product is purified by non-chromatographic methods. On the second step diphenylamine fragment is introduced by palladium-catalysed Buchwald−Hartwig reaction. Synthetized compounds are well soluble in common solvents (e.g. THF), are thermally stable and have suitable charge transporting properties for the application in perovskite solar cells. Some of the novel HTM's demonstrates very similar performance as **Spiro-OMeTAD**.

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EFFICIENCY ENHANCEMENT OF PEROVSKITE SOLAR CELLS *VIA* INCORPORATION OF PHENYLETHENYL SIDE ARMS INTO INDOLOCARBAZOLE-BASED HOLE TRANSPORTING MATERIALS

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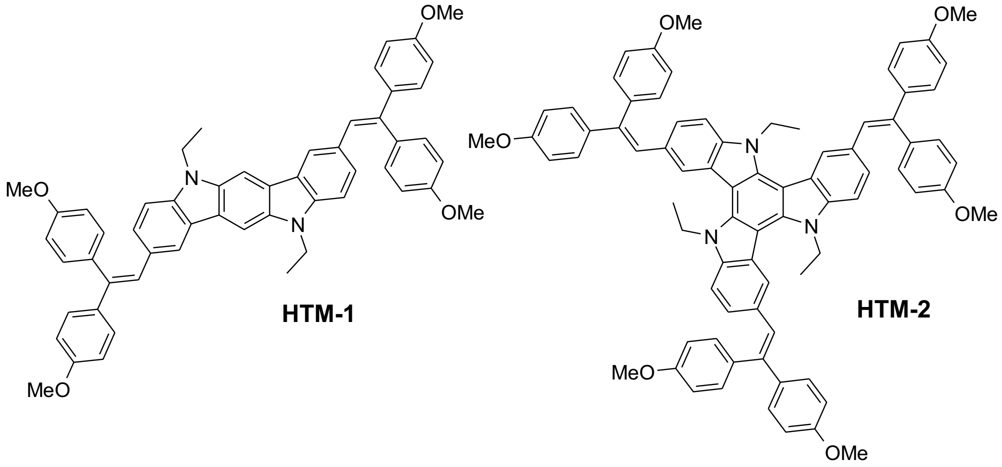
Perovskite-based solar cells are very promising new-generation photovoltaic devices for practical applications. It has been demonstrated that spiro-OMeTAD is an effective small-molecule hole transporting material (HTM) for perovskite solar cells but because of high price and recrystallization in based device, what gives negatively affects in performance at elevated temperatures and over longer periods of time, it's important to develop a cheaper alternative to spiro-OMeTAD for successful commercialization of hybrid perovskite solar cells [1]. This work is aimed to design and synthesize new cheaper and more efficient HTMs based on nitrogen-containing π-electron systems possessing diphenylethenyl substituents and apply it for perovskite-sensitized solid-state solar cells.

The small-molecule HTMs based on indolocarbazole core were synthesized and incorporated into perovskite solar cells, which displayed a power conversion efficiency of up to 15.24%. The investigated HTMs were synthesized in three steps from commercially available and relatively inexpensive starting materials without using expensive catalysts.



HTM-1

HTM-2

Figure 1. Indolocarbazole-based hole transporting materials

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ADSORPTION OF CHLOROGENIC ACID ON CATIONIC CROSS-LINKED STARCH WITH QUATERNARY AMINO GROUPS

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Chlorogenic acid (CGA) is a polyphenolic antioxidant distributed widely in fruits like apple, pears, berries, plum and vegetables like sweet potato, lettuce, spinach, coffee beans, tea, etc. [1, 2]. The antioxidant property of CGA is attributed to its double bond conjugated catechol structure of the phenyl ring. Several recent reports have shown its pharmacological properties that include anti-obese, anti-inflammatory, neuroprotective, anti-diabetic, antioxidant, anti-cancerous, radio protective, neuroprotective properties, and also for treating Alzheimer's disease [3]. Despite its safety and effectiveness the use of CGA is limited by its low bioavailability and stability [4, 5]. One of the ways to improve these disadvantages could be the adsorption of CGA on polymers having cationic groups, for example, on cationic cross-linked starches containing quaternary ammonium groups (CCS).

The aim of present work was to investigate the equilibrium adsorption of CGA on CCS with quaternary ammonium groups.

The equilibrium adsorption of CGA on CCS with degree of substitution of 0.42 was investigated at temperatures of 30, 40 and 60 °C. The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption models were applied to describe the adsorption isotherms of CGA (see Table).

Table. Influence of temperature on parameters of adsorption models for adsorption of CGA on CCS (DS=0.42)

Temperature, ^{0}C	Langmuir model			Freundlich model		Dubinin-Radushkevich model		Temkin model	
	Q_L, mmol/g	EF, mol/ekv	R^2	n_F	R^2	E_{DR}, kJ/mol	R^2	ΔE_T, kJ/mol	R^2
30	1.554	0.85	0.9980	4.42	0.9956	12.9	0.9969	17.17	0.9959
40	1.487	0.81	0.9961	4.55	0.9920	12.9	0.9930	18.33	0.9905
60	1.290	0.71	0.9973	3.02	0.9550	12.9	0.9625	22.13	0.9545

With the increase of adsorption temperature the values of the Langmuir sorption capacity Q_L, adsorption efficiency *EF* and Freundlich constant n_F decreased. Meanwhile, the calculated values of Dubinin-Radushkevich adsorption energy E_{DR} confirmed that CGA was adsorbed by ion exchange mechanism and values of n_F showed that conditions for CGA adsorption on CCS are favourable.

The thermodynamic parameters of the adsorption were calculated. The high negative values of the Gibbs free energy ΔG^o evidenced the great affinity of CGA to adsorbent. The positive values of changes of enthalpy and entropy suggested that adsorption was the endothermic process and the order of the system decreased during adsorption.

Acknowledgment. The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP-055/2015.

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STARCH DERIVATIVES WITH TERTIARY AMINO GROUPS FOR IMMOBILIZATION OF BIOACTIVE PHENOLIC ACIDS

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Due to their bioactive properties, phenolic acids are extensively studied and there is evidence of their role in food, nutritional and pharmaceutical sciences. However, the effectiveness of phenolic compounds depend on preserving the stability, bioactivity and bioavailability of active ingredients. One of the ways to protect the anionic phenols could be the immobilization on polymers having cationic groups.

Starch cross-linking with epichlorohydrin (EPCH) is the most common method used in polysaccharide chemistry. Reacting EPCH with NH_4OH is a convenient and inexpensive way of introducing weakly basic anion-exchange groups into polymer substrate [1]. Moreover, cross-linked polysaccharides containing tertiary amine groups have been used for the recovery of various anionic substances from aqueous solution. The sorption properties of such cationic starch derivatives depend both on the degree of cross-linking and degree of cationization [2].

The aim of present work was to evaluate the immobilization of phenolic acid on cross-linked cationic starches with tertiary amine groups (CSTA) as well as desorption into different medium.

CSTA was obtained in the reaction of native starch (NS) or preliminary cross-linked starch (CS) with EPCH in presence of NH_4OH. Preliminary cross-linking of starch avoids the gelatinization of starch in alkaline medium. As phenolic acid the chlorogenic acid have been used and its adsorption on CSTA was compared to that of methyl orange containing sulfate group.

The results showed that CSTA exhibit good sorption capacities which depended on both the type of starch (native or cross-linked) and amount of introduced nitrogen (see Table). Meanwhile, desorption of chlorogenic acid from CSTA depended on the desorption medium.

Table. Influence of type of modified starch and amount of introduced nitrogen on sorption capacity of CSTA

Type of starch	Starch:EPCH:NH_4OH:NaOH (molar ratio)	N (%)	Amount of adsorbed (mmol/g)	
			Chlorogenic acid	Methyl orange
NS	1 : 0.5 : 1 : 0.5	2.1	0.51	0.23
	1 : 0.5 : 1.5 : 0.5	1.6	0.41	0.28
CS	1 : 0.5 : 1 : 0.5	1.8	0.60	0.29
	1 : 0.5 : 1.5 : 0.5	0.9	0.38	0.36

Acknowledgment. The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP-055/2015

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STARCH-BASED BIODEGRADABLE FILMS FOR COATING UREA: PREPARATION AND PROPERTIES

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The fertilizers industry has developed modified fertilizers which help to avoid or at least reduce nutrient losses. Such fertilizers include: foliar fertilizers; slow release and controlled-release coated/encapsulated fertilizers; nitrification and urease inhibitors/stabilized fertilizers [1]. Controlled or slow nutrient release can be achieved through special chemical and physical characteristics which is especially important for mineral nitrogen fertilizers (urea, ammonium nitrate and etc.) [2]. With controlled-release fertilizers the principal procedure is one whereby conventional soluble fertilizer materials are given a protective coating or encapsulation (water insoluble, semipermeable or impermeable with pores), controlling water penetration and thus the rate of dissolution and nutrient release synchronized to the plants' needs [1]. Coated fertilizers are the fastest growing group of slow-release and controlled-release fertilizers. Polymer coated fertilizers are the most promising materials in CRFs, which have the best potential for optimal supply of nutrients during growth period of crops and their application is beneficial both in environmental and economic aspects. The disadvantages are that the most of the used coating polymers are non-biodegradable and get accumulated in the soil. That is an environmental problem. Problems can be avoided using natural, biodegradable polymers. Among the natural polymers, starch is of interest [4]. Starch is biodegradable, low cost and renewable. Glycerin, one of the polymers of starch, is easy to prepare, improves the plasticity of coating.

This work features preparation of film-forming composites from different kinds of native starch: potato (Berexfood, Germany), wheat (Amilina, Lithuania), Kollotex 1250 (Avebe, Netherlands). Their properties were determined and evaluated for applicability of encapsulation of nitrogen fertilizers as well as physical properties of the product. Mechanical, sorption properties of the composites and coated fertilizers solubility in water was studied. In order to determine water sorption by film forming urea fertilizers were kept in desiccators at different environmental conditions. Release of the coated fertilizers (amide nitrogen contents) were determined after 1, 7 and 14 days [1, 5, 6]. Determinations of crushing strength were made using a standard methodology [7] using a device IPG-2. Hygroscopic moisture and pH of solution were determined using standard procedures [6]. X-ray diffraction analysis of the product was carried out using the Dron-6 X-ray diffractometer [8]. Thermogravimetric and differential scanning calorimetry and infrared spectroscopy were also performed.

Coated nitrogen fertilizers were produced in laboratory conditions. Consequently stability, and physical properties were analyzed. It was determined that coatings on fertilizer, decrease the solubility of essential nutrients, which depends on the quantity of material used to form coatings. These results show that it is possible to change the thickness of the coating when producing fertilizer, which allows to manufacture product with different dissolution rate.

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Vinyl-functionalized phenanthroimidazole: synthesis, properties and self-polymerization

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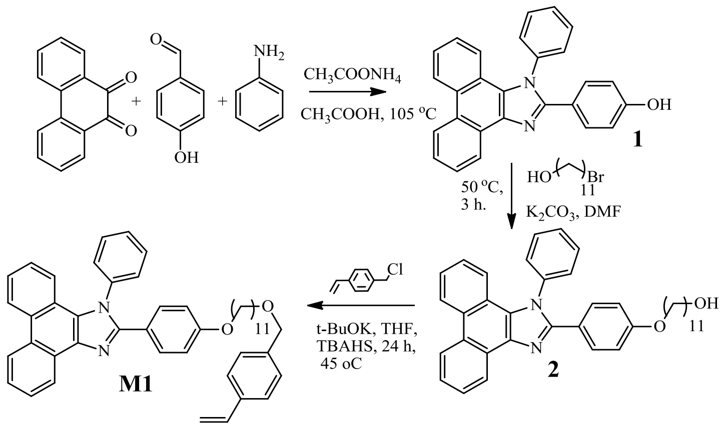
Efficient solid-state emission of organic materials is essential for their application in optoelectronic devices. The molecular design and development of new chromophores that emit visible light in the solid state with high efficiency are strongly desired for the development of organic light emitting diodes with superior performance [1]. Phenanthroimidazole derivatives are recognized as efficient emitting and/or charge transporting materials for various applications [2]. In this presentation we report on the synthesis and self-polymerization of new phenanthroimidazole-based monomer. Synthetic route to monomer 1-phenyl-2-(4-((11-(4-vinylphenoxy)undecyl)oxy)phenyl)-1H-phenanthro[9,10-d]imidazole (**M1)** is outlined in **Scheme 1**.



Scheme 1. Preparation of 1-phenyl-2-(4-((11-(4-vinylphenoxy)undecyl)oxy)phenyl)-1H-phenanthro[9,10-d]imidazole

The structures of the synthesized compounds **1**, **2** and **M1** were confirmed by ^{1}H NMR, ^{13}C NMR, IR spectroscopy, mass spectrometry and single-crystal X-ray diffraction analysis. The thermal properties of monomer **M1** and the polymer were investigated by the differential scanning calorimetry and thermogravimetry. Optical and photophysical properties were studied by UV and fluorescence spectroscopies. The polymerization kinetics was investigated by DSC and real time FT-IR technique. The average molecular weights were determined by GPC technique.

Acknowledgements. Financial support from the Research Council of Lithuania (project No. TAP LB-03/2015) is gratefully acknowledged.

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CATIONIC STARCH OBTAINED BY REACTIVE EXTRUSION

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Extrusion processing is a technology commonly used in the polymer industry [1]. Extrusion processes are applied to polysaccharides for specific purposes such as physical modification and chemical modification, e.g. reactive extrusion [2].

The aim of this work was to obtain the physically and chemically modified native potato starch by using reactor (Druvather® Reactor DVT5, Lödige, Germany) and twin-screw extruder (ZE25R x 40D UTXi, Krauss Maffei, Berstorff, Germany). Modification of starch was performed in two steps. First of all the reaction components were mixed in a high speed bath-reaction at the molar ratio starch:2,3-epoxypropyltrimethylammonium chloride:NaOH:H_2O = 1:0.125:0.04:3.5 and then the mixture was extruded. Processing conditions were as follows: the mixture of reaction components was added; temperature in the sections, 80–140 °C; screw speed, 50 rpm; feed rate, 1–2 kg/h. The physical modification and cationisation of starch in the extruder was carried out simultaneously. In such way four samples of cationic starches (CS) were obtained. The degree of substitution (DS) was determined by Kjeldahl method and the reaction efficiency (RE) was calculated. Also the swelling power (SP) and solubility index (SOL) at 75 °C temperature in distilled water of CS derivatives were determined and the particle size of 0.05 wt% CS aqueous dispersions was measured by using DelsaNano^{TR} C particle analyser (Beckman Coulter, Japan). The obtained results are shown in the Table. As we can see the RE of cationisation is higher than 90% and characteristics of physically modified CS derivatives depend on the temperature in the sections of extrusion. Extruded CS samples were compared with non-extruded CS (Control).

Table. The conditions of extrusion and characteristics of CS derivatives

CS sample Nr.	Temperature in the sections, °C					DS	RE, %	SP, g/g	SOL, %	Particle size	
	1	2–8	12	13	25					d, nm	PI
1	20	80	130	130	130	0.117	93.6	104±25	78±5	398	0.380
2	20	80	140	140	140	0.118	94.4	84±28	80±4	642	0.288
3	20	90	130	130	130	0.113	90.4	70±43	76±4	640	0.283
4	20	100	130	130	130	0.116	92.8	130±28	92±2	213	0.315
Control	-	-	-	-	-	0.100	90.0	918±66	43±4	$>1\cdot10^8$	-

Acknowledgments

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SEM investigation of polyethylene, polypropylene and polyester with Cu_xS layers

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As an important semiconductor, copper sulfides in different stoichiometries are widely used as p-type semiconductors in solar cells, as optical filters, and as superionic materials. Due to their unique optical and electrical properties, they also applies in thin films and composite materials.

Non-stoichiometric Cu_xS layers may be formatted on different polymers by using various sulfuring agents and methods. These composites are characterized by low electrical sheet resistance and they are elastic and have very low density.

The aim of this work was to investigate and compare surface morphology of isotactic polypropylene (iPP), polyethylene (PE) films, and polyester (PES) fiber coated with thin layers of copper sulfide with SEM. Cu_xS layers were prepared by the sorption-diffusion method using thiourea solution as a sulfuring agent on different polymers. Firstly, polymers were pretreated for surface activation, and then Cu_xS layers were formed.

All polymers were sulfurized in acidic solution of thiourea and treated at 80 °C with aqueous solution of Cu(I-II). Cu(I-II) solution was prepared using different reducing agents. Samples with sheet resistance till 1 kΩ were chosen for SEM investigation.

The cross-section analysis of the sulfurized polymers samples provides information about the thickness of the sulfurized layer, which was about 10-15 µm for PP, 7 µm for PE, and for PES sorption of sulfur was the whole volume.

After the formation of Cu_xS layers on the polymers, it can be see that they thickness are about 25 µm PP, 20 µm for PE, and for PES – in whole volume, but most amount of Cu_xS is on the surface.

SEM investigation of samples surface with Cu_xS layers showed that compact layer formed on PE film, and grain structure -on PP film and PES fibre, but on fibre grains structure was larger.

On the surface of all polymers we can also observe Cu_xS layer containing the remaining sulfur conglomerates.

COPOLYMERS OF N-VINYLFORMAMIDE AS SUPPORT FOR IMMOBILIZATION OF CELLULOLYTIC ENZYMES

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Cellulosic biomass is a plentiful source for developing renewable resources which can be serve as substrate for the production of second generation biofuels such as cellulosic ethanol. Enzymatic hydrolysis of cellulosic biomass performed to using immobilized enzymes allows to carry out this process in a more efficient and economical way [1]. The main advantages of use immobilized enzymes are: easier product separation and reuse of the catalyst, enabling continuous process, and improved stability. The carrier on which enzyme are immobilized should be selected in an appropriate manner. It should be adapt to enzyme, technology process and immobilization method. This will enable to fully exploit the enzyme activity, and minimize the cost of the obtained product [2].

In this work we demonstrate a method of immobilization which involves the adsorption of the biocatalyst on a surface of a water insoluble carrier, based on poly (N-vinylformamide). Adsorption interactions are relatively weak and do not cause protein conformational changes. Due to selected immobilization process this method is simple, cheap and fast so it could be important in technological application.

The carrier was obtained by radical polymerization of N-vinylformamide (NVF) in inverse suspension with the participation of hydrophilic crosslinking monomer [3], ethylene glycol dimethylacrylate (EGDMA). For one of the carrier, during the stage of crosslinking polymerization, was added a linear polyvinylamine (PVAm). As a result, first carrier was obtained with an amide groups and second carrier with an amide and an amino groups. Next stage of the research consisted immobilization of three different commercial cellulolytic enzymes on polymeric supports.

Determined efficiency of immobilization of enzymes on both investigated carriers. Obtained heterogeneous catalytic systems were tested in the reaction of paper (TNO, Delft, Holland), and wood pulp hydrolysis. Reaction rate constants and the activity of catalyst systems were determined during several hydrolysis cycles. It has been shown that the carriers can be successfully used for the immobilization of cellulolytic enzymes, in particular cellulases.

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OPTICAL PROPERTIES OF THALLIUM SELENIDE LAYERS ON THE POLYAMIDE FILM SURFACE

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Thin chalcogenide films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors etc. [1]. The chemical deposition methods are low cost processes and the films are found to be of comparable quality to those obtained by more sophisticated and expensive physical deposition process [2].

In present work the thin layers of thallium selenide on PA 6 films were formed by sorption-diffusion method via heterogeneous chemical reactions in two stages. First, PA 6 films were initially selenized for 1.5 h in 0.05 M $K_2SeS_2O_6$ at pH 2.15, adjusted using 0.1 M HCl at 60 °C. Next, to form Tl_xSe_y layers, selenized samples of PA 6 were treated in Tl_2SO_4 salt solution for 10 min at various pH and temperature. The aim of this study was to obtain the layers of thallium selenide of various compositions on the surface of PA film and to investigate their optical properties. Total amount of selenium and thallium in thallium selenide layers was determined using atomic absorption spectrophotometry. Tl/Se molar ratio increases with the increased temperature and pH value of Tl_2SO_4 solution. Optical properties of Tl_xSe_y layers were measure using UV/VIS spectroscopy. In this work, using the Tauc model [3], the absorption spectrum fitting method [4] was applied to estimate the optical band gap and width of the tail of localized states (Urbach energy) of Tl_xSe_y layers.

Tauc plots reveal a systematic shift toward lower optical bandgap values with the increasing pH, as well as the increase in temperature of the Tl_2SO_4 solution. Optical bandgap values of 3.07 eV for Tl_xSe_y (pH = 9.2) and 2.80 eV for Tl_xSe_y (pH = 13.0) were estimated from the Tauc plots showing rather small pH effect on the optical bandgap of the material. Temperature, on the other hand, had a more pronounced effect with the estimated optical bandgap of 3.02 and 2.09 eV for Tl_xSe_y (t = 50 °C) and Tl_xSe_y (t = 80 °C), respectively.

With the increasing pH, Urbach energy increases from 0.56 eV to 0.68–0.70 eV. With the increasing synthesis temperature, however, Urbach energy initially increases from 0.64 at 50 °C to 0.79 eV for 70 °C sample, but then decreases to 0.48 eV for 80 °C. This can be associated with the increasing structural order of the Tl_xSe_y at higher temperatures, as confirmed by the larger amount of thallium detected using AAS analysis.

Table. Optical properties of thallium selenide on polyamide 6

pH	t, °	E_{gap}, eV	R^2	E_{tail}, eV	R^2
9.2	60	3.07	0.9981	0.56	0.9986
11.3	60	2.86	0.9995	0.70	0.999
13.0	60	2.80	0.9985	0.68	0.9985
11.3	50	3.02	0.9945	0.64	0.9998
11.3	70	2.79	0.9992	0.79	0.9943
11.3	80	2.09	0.9988	0.48	0.9981

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CHARACTERIZATION OF LONG-TERM ATMOSPHERIC CORROSION PRODUCTS OF ZINC

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Characterization of destruction products formed on zinc surface after 10-year exposure in different environmental sites (rural, marine, industrial) has been presented. Specimens exposed to standard room condition (HN 69:2003) were used as reference (Control). Morphological and structural changes of surface were evaluated using optical, scanning electron, X-ray diffraction microscopy (XRD) and wavelength dispersive X-ray fluorescence spectroscopy. The corrosion level was determined using the weight loss method [1].

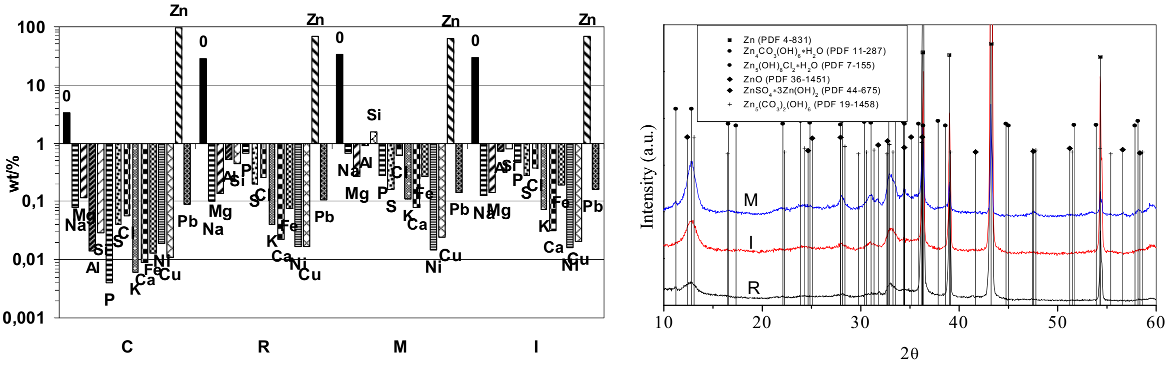

Fig. Distribution of microelements (wt-%) and XRD pattern on zinc after 10 years of exposure to rural (R), marine (M) and industrial (I) environments.

Zinc samples indicated the crystalline phases of zinc base, $Zn_4CO_3(OH)_6 \cdot H_2O$, $ZnSO_4 \cdot 3Zn(OH)_2$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$. The presence of ZnO and $Zn_5(CO_3)_2(OH)_6$ in some sites were detected. It has been noted that the mentioned bio-mineralization product gives anti-fouling film on the zinc surface [2]. The samples after exposure became siliceous. It should be noted, that silicon compounds existed on surface in non-crystalline alumina-silicates form.

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PROPERTIES OF CdSe FILMS DEPOSITED BY CBD-SILAR METHOD ON POLYMER

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CdSe nanoparticles have received a lot of attention due to their unique optical and electronic properties. The CdSe films on various polymers are usually deposited by combined CBD-SILAR method. The aim of present work was to deposit CdSe films on polyamide (PA-6) substrate applying H_2SeO_3 solution as a source of selenium. The Na_2SO_3 solution was used as the reducing agent [1]. The CdSe films composition morphology and optical properties can be controlled by varying $Cd(CH_3COO)_2$ solution temperature. The obtained composite materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Vis spectroscopy.

XRD analysis showed that CdSe (PDF No. 77-2307) and selenium (PDF No. 71-527) phases, respectively, a hexagonal and a monoclinic unit cell, which were incorporated into PA-6 polymer matrix. SEM micrographs analysis (Fig.) revealed that regardless of the synthesis temperature the spherical particles dominate.

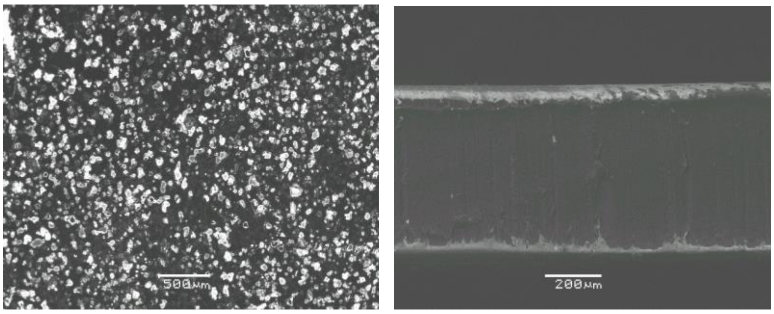

Fig. SEM images and cross section image of PA-6/Se/Cd composite obtained 60°C.

Optical constants of PA-6/Se/Cd composite materials were derived from UV-Vis absorption spectra using Tauc's model [2]. The relatively high values of the Urbach energy (Table) indicate that PA-6/Se/Cd composite materials are structurally disordered.

Table. Optical characteristics of PA-6/Se/Cd composite obtained at 60°C.

Parameter	
Thickness	89 ±1.5 µm
Absorption coefficient	$(5.62\text{-}6.46)\cdot10^4$, cm^{-1}
Band gap	1.68, eV
Fundamental absorption edge	742.5, nm
Urbach energy	0.673, eV
Constant B	$5.72\cdot10^5$, $cm^1\cdot eV^{-1}$

The resulting composites show optical properties that promise enhanced light harvesting for solar cell applications (Table).

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Influence of chloride concentration in thermofication water on formation of β-FeOOH on carbon steel

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Mild carbon steels are the base class of metals used in most hot- and ground-water piping systems first of all due to their low cost. However, due to modest surface self-passivity these steels are prone to electrochemical corrosion even in sufficiently low conductive waters. The protective ability of steels depends on the structure and composition (ion environment) of Fe oxides/hydroxides layers, which are formed during interaction with corrosive medium. On the other hand, the properties of developed oxide layers depend on water temperature, flow rate and chemical composition: hardness salts, dissolved gases, chlorides, sulfates, bicarbonates etc. The influence of chlorides on the properties of self-developed Fe oxide layers (first of all, corrosion resistance) is especially important for thermofication waters, which are characterized by high temperatures and pressure. Accurate identification of formed Fe oxides forms and their change tendencies can improve operating conditions, prevent corrosion development or select optimal constructing materials. An analytical capability of Mössbauer spectroscopy is most suitable for identification of Fe compounds [1, 2].

The samples of mild carbon steel (Si ~0.32, Mn ~ 0.5, C ~0.19 wt.%) were exposed in thermofication water used in practice. The concentration of chloride in water was varied from "natural" level 5 mg/L to 25 mg/L. The predominant formation and accumulation of β-FeOOH on steel substrate was determined by CEMS analysis (Fig. 1). The influence of Cl^- concentration in thermofication water on stability of pre-existing Fe oxide/hydroxide layers was evaluated by open circuit potential and dc-voltammetry electrochemical methods. The correlations between formation of β-FeOOH and corrosion behavior of steel were discussed.

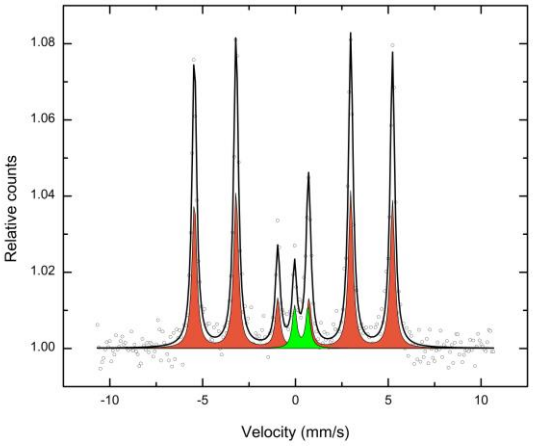

Figure 1. Mossbauer spectra of affected steel sample.

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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF RED-LUMINESCENT GOLD CLUSTERS

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Recently, fluorescent and luminescent gold clusters attract increasing attention due to chemical inertness, nontoxicity, extremely small size and strong luminescence, allowing prospective applications in nanomedicine. In this study, we present the results obtained investigating new red-luminescent gold cluster formation using a branched amino acids food supplement, namely BCAA'S, as a cheap and biocompatible gold ions reducer in an alkaline medium. Besides, several other protein-based food supplements were also tested for gold clusters formation. It was determined, that application of BCAA'S instead of well-known bovine serum albumin (BSA) [1, 2] allowed to synthesize quite similar red-luminescent gold clusters with higher quantum yield, long lifetime and good stability for weeks (Fig. 1). The stability of BCAA'S, as well as BSA-mediated gold clusters, was found to be dependent on the purity of these products performing by dialysis way.

Our findings imply that synthesized gold nanoclusters tend to accumulate in more tumorigenic breast cancer cells (line MDA-MB-213) being prospective for bio imagining.

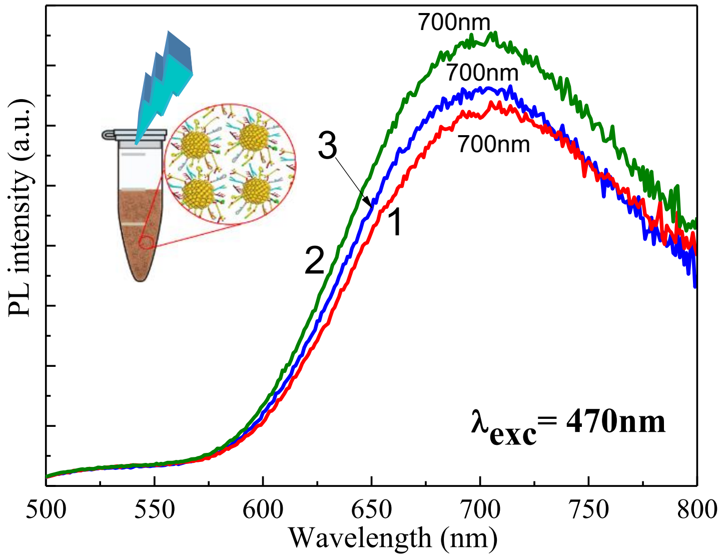

Fig. 1. Variation of the photoluminescence spectra of BCAA'S-mediated Au NCs formed in the solution containing 3 μmol/mL $HAuCl_4$ and 28 mg/mL BCAA'S at a pH 12.0 and *T* 37 ^{o}C for 24 h with exposition time: 1 as-grown; 2 after 3 days; 3 after 7 days.

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FLUORESCENCE QUANTUM YIELD OF PERYLENEDIIMIDE DERIVATIVES

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Organic materials with fluorescence in visible spectrum are investigated extensively due to their potential application in organic optoelectronics. For instance, perylenediimides (PDIs) are materials of high photo and thermal stability, high fluorescence quantum yields and chemical inertness. Therefore, they can be used in many organic optoelectronics devices like organic light emitting diodes, solid-state lasers and photovoltaic devices [1].

The fluorescence properties of a material may be characterized by determining the fluorescence spectra, lifetime and quantum yield. The fluorescence quantum yield is the ratio of the number of photons absorbed to the number of photons emitted through fluorescence. This parameter is important when choosing a material for organic optoelectronics applications. While measurements of the absolute quantum yield require sophisticated methods and instrumentation, one of the easiest ways to determine quantum yield is the comparative method [2]. The essence of this method is comparison of absorption and fluorescence spectra between a test sample and a standard sample with known fluorescence quantum yield.

In this research, the fluorescence quantum yields of eight different perylenediimide derivatives were determined employing the comparative method. Fluorescein and Rhodamine 101 were used as standards.

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STRUCTURAL AND FLUORESCENCE STUDIES OF POLYCRYSTALLINE A-AL$_2$O$_3$ OBTAINED ON ANODIC ALUMINA

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As is known, α-Al$_2$O$_3$ membranes due to their biocompability and high chemical resistance are of great demand [1]. Previous studies dealt with the investigation of physical chemical properties of anodic alumina. However, the formation of robust α-Al$_2$O$_3$ films from free-standing anodic alumina films and membranes remains quite a challenge [1]. In the present study we obtained robust α-Al$_2$O$_3$ films (144 µm thick) films by the heat treatment at 1200–1400 °C of free-standing anodic alumina and studied their physical chemical and fluorescence properties. The samples were obtained by double-sided anodizing of aluminum specimens in 2.0 M aqueous solution of sulfuric acid at constant current density of 32 A m^{-2} and temperature of (10.0 ± 0.1) °C up to the moment when aluminum was completely oxidized. At the steady state of oxide growth the voltage was at about 20 V, the anodizing time was of about 1.5 h. If indicated, the films were heat treated in the air at temperature range of 200–1400 °C.

According to differential scanning calorimetry data accomplished by *X*-ray analysis, the first step of crystallization occurs at around 944 °C, producing γ-Al$_2$O$_3$. The second one takes place at around 1236 °C, which corresponds to the formation of α-Al$_2$O$_3$. According to scanning electron microscopy analysis, the as-anodized anodic alumina films possess well-ordered porous structure with the pore diameter of 10.2 nm. After heat treatment at 1400 °C the samples lose their porous structure and certain crystallites with average size of 2.6 mm can be observed. In porous anodic alumina the surface structure transformation during high temperature treatment is caused by the reorganization of oxygen and aluminum sub-lattice and removal of impurities incorporated during anodizing. The changes in the surface structure of the films can be also observed by fluorescence microscope (Figure). The as-anodized film has uniform emission throughout the surface. At the same time for 1400 °C-treated film mainly emit only along the grain boundaries. It can be explained by the concentration of the defects of different type at grain boundaries of α-Al$_2$O$_3$. According to steady-state fluorescence measurements both the as-anodized and heat treated at 1400 °C films are characterized by a broad fluorescence in the wavelength range of 400–650 nm. The time-resolved fluorescence data show that with increasing treatment temperature the average life time of the centers increases from 3.5 to 4.5 ns. It is caused by the refining of alumina structure and formation of α-Al$_2$O$_3$. The origin of the fluorescence is believed to be due to the presence of hydroxyl groups.

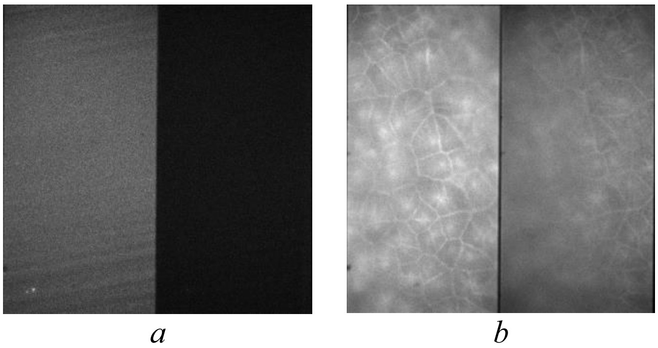
a *b*

Figure. The surface appearance of the as-anodized (a) and heat treated at 1400 °C (b) sulfuric acid anodic alumina films observed by the fluorescence microscope in (430-480 nm)/(485-630 nm) diapason under 405 nm excitation.

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Surface Active Materials for Paper Cleaning

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The deterioration of paper in books and archival materials due to the degradation of its cellulosic substrate has been recognized since the turn of the century. The principal changes that act in the structure of cellulose and that cause its alteration are biodegradation, photo degradation, acid hydrolysis and oxidation. Washing is a fundamental treatment that can improve appearance of document and reduce the acidity simultaneously thus stabilizing paper chemically.

Given the importance of the preservation of paper medium, the objective of this study is to adapt the surfactants in the washing process and to investigate their effect on paper properties. During this study the change of mechanical, thermo-resistance, acid and optical properties of the paper samples, which were affected by surfactant (Amytis, Tinuvetin JUN HC, Tween 20, Triton X-100, P3 – Triquart, Bromosept 50) aqueous solutions, was examined. The most suitable surfactant material for cleaning grease stains from paper medium was proposed. To conduct the research, a filter paper was chosen, made of 100 % cellulose. Paper samples were washed in surfactant aqueous solutions, dried at room temperature and thermal- aged to 500 h in a drying oven. Mass spectroscopy (MS), elemental analysis, electron paramagnetic resonance (EPR), infrared (IR) and UV/Vis spectroscopy, thermogravimetric analysis (TG), the tensile test, the contact angle, polymerization degree and acidity measurements methods were used for samples characterization.

This work showed that all tested surface-active and disinfection materials into washing procedures does not have significant impact on the acidity of the paper, degree of polymerization, it changes the paper sorption properties and thermal stability minimally, except Bromosept 50 solution. During the examination of paper specimen surface with SEM analysis methods, it was established, that during the washing the fiver swelling is not avoidable and change of paper medium dimensions is irreversible, but no signs of destruction were observed even after heat-aging of 500h. After thermal - aging, the intensity change of sample absorption in UV/Vis spectrum is very slight, except of the samples, affected by P3-Triquart solutions. It is observed that rinsing the samples for 3 times (each time 10 min.) in the distilled water bath, Surfactant material failed to be washed out completely from the samples, potential residue is 0,3 %- 0,4 %. The most effective way to remove oily stains is to clean the paper medium by hexane or acetone and then washing again with 1 % P3- Triquart and Triton aqueous solution.

Hardening and hydration properties of blended cements

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Cement industry is one of the most energy intensive industries in the world and generates approximately 5% of global anthropogenic CO_2 emissions. It has been one of the largest CO_2 emission sources [1]. Concrete is regarded as the second consumed construction material and hence massive quantities of cement needs to be annually produced. This production leads to pollute the environment by releasing significant quantities of CO_2 emission in addition to produce solid waste material known Cement Kiln Dust [2].

The aim of this investigation is to explore the possibility of using this material as a cement replacement in cement production. Also the purpose of this research is to identify hydration properties of the different configurations of a composite cement consisting of cement, slag and kiln dust. Recipes are created by reducing the amount of cement from 40% to 15% by replacing it with kiln dust. All formed samples with dimensions 30x30x30 mm were made of cement, slag, kiln dust and cured in 100 % r.h.at 20 °C for 24 hours, then removed from forms and hydrated for 6 months at 20 °C. The mineral change were determined with: XRD - Bruker X-ray S8 Tiger WD; FT-IR - Perkin Elmer FT–IR Spectrum; DSC-TG - Netzsch STA 409 PC Luxx (*data not shown in the abstract*).

1 table. Recipes of samples

Sample name	Blended cement composition, %		
	Slag	Cement	Kiln dust
SC	60	40	0
SC2,5D	60	37,5	2,5
SC5D	60	35	5
SC10D	60	30	10
SC15D	60	25	15
SC25D	60	15	25

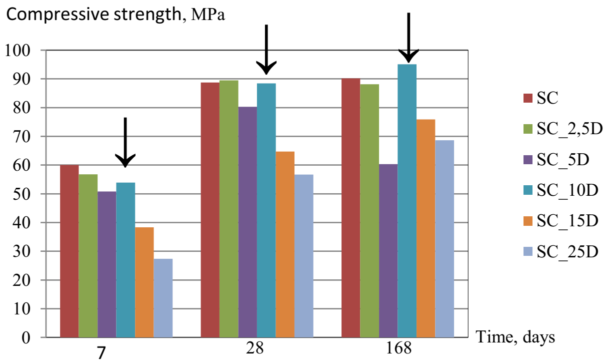

Fig. 1. The compressive strength results

It was established that the composite cement samples, which included 30% cement, 60% slag and 10% kiln dust had the highest growth of compressive strength after 6 month of hydration (95 MPa).

It was also determined that amount of $Ca(OH)_2$ decreases in samples with kiln dust, that shows that the reaction between the kiln dust and alkalis takes place to form bigger amount of CSH. With increase more than 10 % of kiln dust the compressive strength decrease because of the main binding material – clinker dilution in the system.

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THE INFLUENCE OF STRUCTURE AND MINERAL COMPOSITION ON PROPERTIES OF AUTOCLAVED AERATED CONCRETE

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Dense and porous concrete is the main construction material for a long time. Autoclaved aerated concrete (AAC) is getting more and more popular over other cement construction materials because of its outstanding properties, low cost and availability. AAC is obtained by using inorganic binders such as cement and/or lime combined with fine siliceous based material, cell-generating agent and water [1, 2]. The final stage of manufacturing is hydrothermal treatment at 170–200 °C temperature for several hours [3]. The main compound which influence the mechanical properties of products is 1.13 nm tobermorite $5CaO \cdot 6SiO_2 \cdot 5H_2O$ [4]. In addition, the structure of the air pores and the mechanical condition of the pore shells directly affect the properties of AAC [5].

AAC cakes with dimensions 6220x1580x670 mm were formed in the industrial GmbH Masa-Henke production technology line. Samples with dimensions 100x100x100 mm were cut from these AAC cakes and hardened at saturated steam pressure for 4–16 h at 170–200 °C temperature.

Mineral composition and structure analysis of AAC samples were carried out by X-ray diffraction (XRD), simultaneous thermal analysis (STA), optical microscopy, scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) methods.

It was determined that after 8 h of treatment at 180 °C temperature 1.13 nm tobermorite and C-S-H(I) are the main new formed compounds and AAC samples reached the highest compressive strength. Meanwhile, after changing the temperature and duration of isothermal curing, the formation of these compounds and values of compressive strength decreased. This phenomenon may be associated with changes in mineral composition and structure of new formed compounds. Furthermore, platy shape crystals characteristic to 1.13 nm tobermorite are formed on the surface of pores and in structure material. Besides, the morphology of crystals changed by increasing temperature to 200 °C – the surface of pores is covered only with fibrous shape crystals but in the structure material is formed a mixture of plate like shape crystals together with fibrous crystals and amorphous aggregates. The latest, presumably are associated with the formation of gyrolite gel, which was observed in the XRD curves. Moreover, micropores with diameter 0.6–0.0065 μm are dominated in all samples and these pores compose 49–52 % of all micropores in the samples autoclaved at 180 °C temperature. It should be noted that quantity of pores of mentioned diameter increased up to 8 % (54–58 %) after increment of curing temperature to 200 °C. In addition, thermal shrinkage of all AAC samples are similar till 800 °C temperature (1.05–1.36 %) but after increment of burning temperature to 1000 °C the later parameter of samples hardened at 200 °C decreased almost twice in comparison with samples treated at 180 °C.

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ANALYSIS OF PHYSICAL AND CHEMICAL COMPOSITION OF PROTEIN FIBRES

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Wool is a complex multicell system composed of inaminate cells which differ in composition, shape and properties. The crystal structure of wool fiber plays an important role in its mechanical, thermal and other physical properties. It is well known that keratin is the major structural fibrous protein providing outer covering, such as hair, wool, feathers, nails, and horns of mammals, reptiles, and birds [1]. Wool defines as protein fibre and very exclusive property of wool fibre is natural crimp, surface structure, cross-section and even chemical consist [2]. Wool is composed of a cuticle and cortex and a medulla only in the case of course wool. The cuticle has valine, disulfide bond groups and carboxyl groups, whereas the cortex makes up the main portion of the wool [3].

The geometrical properties of the wool fibers and diameter of medulla depend on many factors: nutrition, animal age, animal body region, the stage of hair growth, the time of cut the hair, nutrition, grazing place. So, wool fibre is a very complicated object of research. The best proof for it is the fact that in spite of many studies made over the last 70 years the problem of the structure of this system has not yet been fully resolved.

The purpose of present work was to identify some differences between sheep's wool and dog's hair fibres through investigating the crystal and chemical structures, macrochain conformation and surface morphology of them. Wide-angle X-ray diffraction (WAXD) and Fourier transform infrared spectrometry (FT-IR) were performed. Elemental analysis (C, H, N) of fibres were done on an Elemental Analyzer CE-440 and percentage nitrogen was estimated by the standard Total Kjeldahl Nitrogen (TKN) method.

The crystallinity of investigated fibres depending on the type of hairs varies from 6.7 % up to 30.0 %. But the crystallinity of the most dogs' fibres is lower than 20 %, while the sheep wool crystallinity is 27.1 %.

Sheep wool and eight dog's hairs IR spectra was plotted simultaneously. The obtained spectra were very similar and did not spotlight any unusual peaks. The main difference between sheep wool and dogs hair infrared spectra were in interval 3000–2800 cm^{-1}, which were assigned to the asymmetrical and symmetrical stretching vibrations of C–H in $–CH_3$ and $–CH_2–$ groups. The sheep wool spectrum has no visible peak at 2958 cm^{-1} meanwhile in the case of dog hair spectrums the peak in the similar frequency zone is obvious. The other two peaks in 2920 cm^{-1} and 2851 cm^{-1} shifted towards longer wavelengths direction and the change of their intensity are different. Also, it was estimated that all peaks of dog hair spectra in other intervals are more intensive and have the bigger areal.

The percentage amounts of C, H and N into sheep wool and dogs hair are of the same order of magnitude though slightly fluctuates at intervals: C – 43.8-48.0%, H – 5.7-6.3% and N – 13.8-15.6%.

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INCORPORATION OF SILVER SELENIDE INTO SILK MATRICE

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A composite material consisting of polymers modified by desirable semiconductors has attracted an increasing interest because of characteristic physical and chemical properties. These properties determine the potential application.

Silk is protein polymers, which possess excellent natural properties, such as strength, resistance to light, temperature and humidity. It is environment-friendly biodegradable polymer and can be used to produce a variety of materials, such as films, gels, fibres, nanofibres, granules on a micro or nano scale [1]. Silk has been used as a biomaterial in a variety of biological applications.

Silver selenide (Ag_2Se) is a well-known $A^I_2B^{VI}$ super-ionic conductor and can be used to make solar cells, magnetic field sensors, solid-state electrochemical sensors, and optical filters [2-5]. The aim of this study was incorporation of Ag_2Se into silk matrices.

Ag_2Se was synthesized easily via wet-chemical processing. This method is very attractive, since Ag_2Se can be deposited from solution, requires comparatively mild conditions, and aqueous solutions of H_2SeO_3, Na_2SO_3 [6] and $AgNO_3$ are employed.

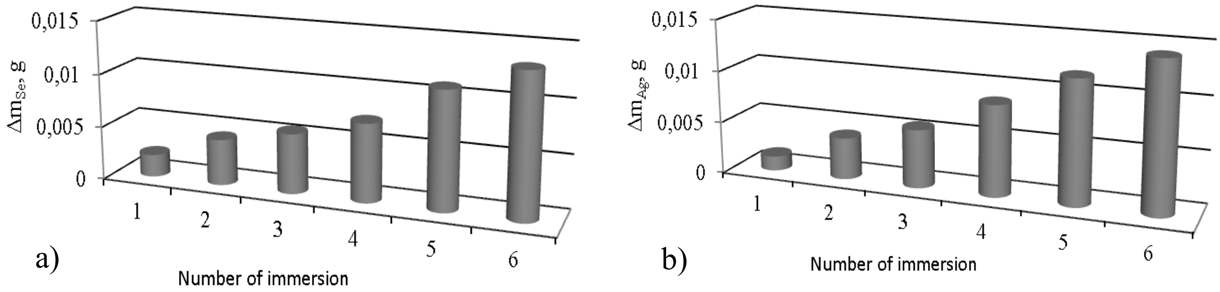

Fig. Se (a) and Ag (b) weight change as a function of the number of silk immersions in precursor solutions at room temperature. Time of immersion: in 0.2 M H_2SeO_3/0.3 M Na_2SO_3 solution – 2 h, in 0.05 M $AgNO_3$ – 1 h.

The samples of the silk were immersed into the precursor solutions several times in order to study the dependence of electrical characteristics of their surface on the incorporated Ag_2Se amount. As expected, the higher the number of immersions, the higher the amount of Se and Ag in silk (Fig.), thus the higher the surface conductivity.

The X-ray diffraction patterns for the different samples obtained after different number of immersion in the precursor solution, are characteristic of a crystalline material, which was subsequently identified as naumanite (JCPDS #71-2410).

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Influence of metal ions additives on enzymatic hide unhairing in oxidative medium

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Developing new and less polluting technologies of leather processing it is payed special attention to lime and sulphides, which is used for beamhouse processes, trying to decrease their amounts or replace them by other systems of materials. It is supposed that as the components of such systems can be enzymatic preparations (EP), which characterize by wide spectra of effect, and, also, oxidizing materials.

Usability and efficiency of enzymes are determined by various factors such as an activity of enzymes, a medium pH, and temperature, a proportion of the enzyme and a substrate, oxidation-reduction potential of the medium, ions or other components in a treatment medium.

It is very interesting interaction between enzymes and oxidative materials. For instance: such strong oxidizer as peracetic acid does not decrease opening up of derma capability and activity of some EP during limed hide bating process [1]. Andrioli et al. [2] report about hide unhairing with enzymes in oxidative medium.

Main aim of the research was to develop an efficient unhairing system containing EP and oxidative material.

Hydrogen peroxide was used as oxidative agent, and as EP was chosen alkaline protease *Aquaderm A (*Novo Nordisk, Denmark) having wide spectra of action. Soaked cow hide samples were used for the investigation of unhairing process.

Firstly, the addition of metal ions influence on decomposition rate of hydrogen peroxide was investigated. It was established that the rate of hydrogen peroxide decomposition can be regulated within required limits by a change of concentration of bivalent metal (Mn^{+2}, Fe^{+2}, Cu^{+2}) ions from 14 up to 56 μmol/L when pH is 9.0±0.2 at 20±1°C. According to their catalytic efficiency the metal ions can be inscribed in such way: $Mn^{+2} > Fe^{+2} > Cu^{+2}$.

Further, the oxidative-enzymatic hide unhairing system was developed. It contains hydrogen peroxide (2-4% of soaked hide mass), EP *Aquaderm A* and catalyser $(C_{(Mn^{2+}, Fe^{2+})}\text{ - }28\text{-}56\mu mol/L)$ Temperature of unhairing process is 20±1°C; duration 4 hours; medium pH 9.0±0.2; regime – run continuously. Epidermis after process is degraded and hair removed completely, grain is clean, and without injuries.

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CHARACTERIZATION OF HYDROGEL WITH ANTIBACTERIAL ACTIVITY

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Hydrogels are chemically or physically cross-linked synthetic or natural polymers with the ability to absorb and retain liquids in an aqueous medium. They form a flexible and permanent film permeable to water vapor and metabolites, absorbing wound exudates and preventing the entry of pathogens into the wound surface [1]. A natural polymer, such as sodium alginate is most suitable for the preparation of hydrogels, due to its non-toxicity, hydrophilicity and biocompatibility. The structure of alginate hydrogels is similar to the extracellular matrix in tissues; therefore they are perfect transporting systems and can by applied for the delivery of drugs and other active compounds delivery. Recently, due to such features the hydrogels are increasingly applied in medicine, especially for wound dressing and bacterial skin infection treatment [2]. One of most common skin diseases is acne vulgaris. Overgrowth of *Propionibacterium acnes* is an essential factor inducing the inflammation of hair follicles. Usually topical and oral antibiotics are used for the treatment of the advanced form of disease. Small peptides with antibacterial and anti-inflammatory properties can be applied as an alternative in acne vulgaris therapy [3].

In this study, the bacteriocin-like (BLIS) peptide, produced by *Staphylococcus xylosus* was isolated and studied against the spectrum of antibacterial activity. It was detected that the BLIS inhibits a growth of many gram-positive bacteria, including *Propionibacterium acnes*, and can be applied in the production of antibacterial preparations. Cross-linked poly(vinyl alcohol) (PVA) and sodium alginate (SA) hydrogels, loaded with BLIS as antibacterial agent, were prepared using freezing-thawing method and the main characteristics of hydrogels were studied.

Firstly, the influence of SA concentration (0, 10, 25 and 50 %) on hydrogel properties (content of water, gel fraction, swelling and weight loss) was evaluated. It was determined that the amount of gel fraction decreases with the increasing of SA content, however the swelling ability increases. The addition of SA might probably inhibit the implication reaction and gelation process. It was observed that the water content of different hydrogel compositions ranged between 80 % and 60 %. The weight loss of PVA hydrogel without SA was limited and reached only about 16 %, while for hydrogel with 50 % of SA reached 45 % after 48 hours. So, the degradation of such hydrogels is quite high. The PVA hydrogel composition with 25 % of sodium alginate was selected for further study.

PVA/SA hydrogel loaded with bacteriocin solution in glycerol was tested for its ability to treat *Propionibacterium acnes* and to release bacteriocins. The results of agar diffusion method against *P. acnes* bacterium showed that the hydrogel has antibacterial activity and effectively inhibits the growth of bacterium.

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YEAST PHEROMON AS AN EXAMPLE OF BIOLOGICALLY ACTIVE OLIGOPEPTIDES FORMING TERNARY COMPLEXES

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Currently, *Saccharomyces cerevisiae* (baker's yeast) is the most commonly used single cell laboratory organism. Such features as lack of toxity, non-pathogenic properties as well as the easiness of growth and maintenance of the culture under laboratory conditions, make the work with *Saccharomyces cerevisiae* safe and unexpensive.

Yeast cells can undergo vegetative (asexual) reproduction process (called budding) or generative (sexual) one. In the second case, a key role is played by specific biologically active substances known as yeast pheromones, which are produced and secreted by haploid cells enabling them rapprochement and subsequent fusion. *Saccharomyces cerevisiae* pheromone, factor-α, is the name of the group of four oligopeptides with high sequence homology known as: factor-α1, -α2, -α3 and -α4. The predominant variant of factor-α is factor-α1. It is a 13-residue long peptide with following amino acid sequence: WHWLQLKPGQPMY.

In living organisms peptides and proteins are very effective and often specific ligands for a variety of metal ions. They possess a range of potential donor atoms (nitrogen, oxygen, sulphur) that may participate in the metal ion binding. The histidine (H, His) residue is especially important in the case of Cu(II) complexation. The imidazole nitrogen of the histidine side chain provides the first and the most relevant anchoring point for Cu(II) ions in most His-containing peptides. Previous studies on model peptides indicated that peptides which own a His residue in second position (counting from the N-terminal end), such as factor-α1, are able to form highly stable complexes with Cu(II) ions. This chelate system uses only three of four equatorial coordination positions around the Cu(II) ion. This implies that the fourth position can be occupied by another ligand. Structures involving additionally molecule of a different ligand in fourth position (ternary complexes) are of great interest as they may reflect some more complex peptide-metal interactions present in living organisms.

The purpose of this study was to investigate the redox properties of factor-α analogue-Cu(II) complex using various voltammetric methods. The amino acid sequence of factor-α water soluble derivative was as follows: WHWSKNR. In order to acquire more detailed information about the free copper binding site, experiments with small molecules, such as imidazole, GGH tripeptide, phosphate anion, were carried out. Performed studies provided a better understanding of coordination process in the context of the formation of ternary complexes. Moreover, more advanced researches which assume clarifying the mechanism of interactions of copper(II) ions with peptides of biological importance can be continued on this basis.

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THE INFLUENCE OF MYCOBIOTA ON THE INTERFACE OF THE POLYANILINE COATINGS

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The aim of the presented study was to elucidate the effect of growth and metabolism of mycobiota on the physico-chemical properties of polyaniline modified surface. Polyaniline films were synthesized by potentiodynamic polymerization in an aqueous solution. Samples were placed in Petri dishes filled with a malt agar extract medium; medium was sown up with the mycobiota and incubated at 26°C. The mycobiota from ours culture collection were used during this study [1, 2]. The electrochemical analysis of the biomodified polymers was completed by X-ray photoelectron spectroscopy and wetability measurements.

These investigations shown, that the attachment of the polymer film via a metabolic products resulted in surface oxidation, formation different chemically novel compounds, which incorporated into the polymer film and changed the surface nanostructure. This investigation is especially interesting from the point of view of materials design and metabolic activity definition.

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COLLAGEN DERIVATIVES APPLICATION FOR BIODEGRADABLE FILMS FORMATION

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From the analysis of scientific literature, we can conclude that obtaining of hydrolyzates from collagen-based waste from various industries, including meat, fish and leather, with balanced amino acid composition is a precondition for the effective use of the product in stockbreeding, agriculture, food and pharmaceutical industries [1,2]. There are four main ways of obtaining protein hydrolysates: through acid hydrolysis (mostly dilute H_2SO_4, HCl or H_3PO_4), alkaline hydrolysis (e.g., NaOH, KOH or $Ba(OH)_2$), enzymatic hydrolysis or microbial breakdown [3].

Gelatin, which can be obtained from leather industry waste, has excellent biodegradability and can be used for biodegradable film formation. However due to the very close gap between the melting point and decomposition temperature, compositions are made in blends which consume large amounts of time, energy and water.

It has been suggested, that various materials may be incorporated in collagen compositions during their preparation to improve or modify the properties. Performing composites, except collagen, contain hydrophilic polymers, structural reagents (formaldehyde, glyoxal, glutaraldehyde, tanning agents or minerals), organic fillers (starch, cellulose and chitosan) and plasticizers, such as glycerin. As hydrophilic polymers polyvinyl alcohol (PVA), polyethylene glycol/polyethylene oxide (PEG/PEO), polyvinylpyrrolidone (PVP), propylene glycol alginate or a combination thereof can be used. Such combination allows adjusting the properties of the films, including moisture content, viscosity, strength, organoleptic properties and biodegradation ability. Modification of collagen-based polymers by chitosan - is a promising way to improve their properties, primarily due to the structuring ability of chitosan and its high affinity to collagen.

Polyvinyl alcohol (PVA) has been widely applied to the packaging industry due to its excellent gas barrier properties, mechanical properties and thermal properties. However, the degradation rate of PVA under natural environmental conditions is too slow. One of the simplest methods of speeding the biodegradation is incorporation PVA with biodegradable collagen-based materials [4].

To overcome the above-mentioned problems, and taking into account the sensitivity of collagen to temperature and mechanical influences, using extrusion methods provide higher and a broader range of viscosity, temperature control and more accurate and cheaper products.

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IMPACT OF 4-[(9-ALKYLCARBAZOL-3-YL)AMINO]-3-CARBOXYBUTYRIC ACID DISODIUM SALTS ON RAPE (BRASSICA NAPUS L.) GERMINATION *IN VITRO*

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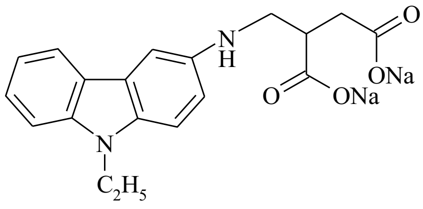
The predominant oil crop for food, industry, and renewable energy needs in Lithuania is oilseed rape (*Brassica napus*). Seed yield and fat concentration are the primary parameters in crop cultivation for both nutritional and industrial uses. High seed yield double-low rapeseed varieties developed in other countries (Sweden, Germany, Denmark) are cultivated in Lithuania, but they often cannot fully realize the productivity potential encoded in the variety genome because of unfavourable climatic and soil conditions [1]. Rapeseed requires a greater level of nitrogen (N) and other nutrients than cereal crops. Nitrogen nutrition remains the factor that significantly restricts plant also and rape productivity. Amino acids as organic nitrogenous compounds stimulated cell growth [2]. Nitrogen-containing five- and six-membered heterocyclic compounds and their derivatives often found in natural sources could be used as growth regulators [3].

The aim of the research was to investigate the influence of 4-[(9-alkylcarbazol-3-yl)amino]-3-carboxybutyric acid disodium salts on rape (*Brassica napus L.*) germination.



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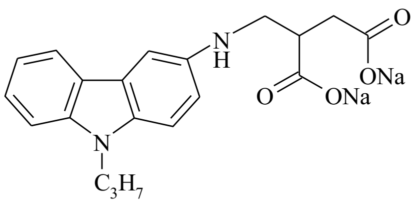

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