16th–21st
JUNE 2019

WEEM-2019

International WORKSHOP on Electrochemistry of Electroactive Materials

BOROVETS,
BULGARIA

Book of abstracts

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WELCOME

Dear WEEM participants, dear colleagues and friends,

WEEM-2019 is the ninth successive event of a series of International Workshops on Electrochemistry of Electroactive Materials (WEEM) started in Russia (Moscow, 1995) and followed by meetings in France (Dourdan, 1997), Poland (Poraj, 2000 and Szczyrk, 2009), Germany (Bad Herrenalb, 2003 and 2015), Russia (Repino, 2006), and Hungary (Szeged-Hódmezővásárhely, 2012). WEEMs are specifically designed conferences aiming at detailed analysis of the state-of-art and intensive discussions of key issues related to the research and applications of various electroactive systems. These systems include materials of quite different chemical natures, e.g. electron-conducting and redox polymers, mixed-valence transition-metal inorganic solids, solid ion conductors, lithium/sodium/potassium-cation intercalation systems as well as organic/polymeric-inorganic composites. Progress in the understanding of the complex mechanisms of their functioning and diverse applications requires bringing together leading scientists in various areas of research and providing them with the opportunity to combine presentations of original results with the possibility for extensive exchange of opinions. In-depth analysis of unresolved problems and identification of newly emerging issues is expected to occur so that it will result in further developments of the area as well as in the formation of competitive international teams able to face new scientific challenges.

We do hope that WEEM-2019 that has succeeded in bringing together more than 100 participants from Europe, North America and Asia will help revealing the progress made in the area of electrochemistry of electroactive materials and support the motivation for our future work.

We are glad to welcome many WEEM disciples and good friends at the present meeting and especially appreciate the participation of young scientists and newcomers that are expected to join the already large WEEM family for the future. We wish to all participants a most successful meeting with valuable exchange of knowledge, competence and new ideas, and, last but not least, a pleasant stay in Borovets,

Vessela Tsakova and Mikhail Vorotyntsev

Scientific Program

June 17, Monday

Morning session

Opening

Subsession I: Nanoparticles and nucleation.

D. Mandler

A Different Approach for Electrochemical Deposition: Starting with Nanomaterials as the Building Blocks

V.M. Mirsky

Detection and analysis of sub-micrometer particles by means of wide field surface plasmon microscopy

V.K. Laurinavichyute

Application of wide field surface plasmon microscopy for analysis of initial stages of electrochemical nucleation

Subsession II: Electroactive polymers I

T.V. Magdesieva

Targeted electrooxidation of Bulky Donor/Acceptor Diarylamines: a convenient route to multifunctional redox active materials

P. Mussini

"Inherently chiral" electrode surfaces: stereogenic elements and enantiodiscrimination performances

T. Ozturk

Synthesis and Properties of Polythienothiophene and Dithienothiophene Posessing Pendant Alkyl and Triphenylamine Groups

Afternoon session

Subsession I: Electroactive polymers and oligomers I

M.A. Vorotyntsev

Synthesis of novel transition-metal containing representatives of the polyporphine family

E. Sezer

Capacitive and electrochromic behaviours of polymers based on thiophene, 3,4-(ethylenedioxy)thiophene and electron-withdrawing group substituted phenyldithienothiophene

P. Rapta

Redox Properties of Thienoacene-Extended Tetrathiafulvalenes studied by EPR/UV-vis-NIR Spectroelectrochemistry

Subsession II: Electroactive polymers III

J. Heinze

Charging/Discharging Phenomena of Conducting Polymers - An Overview of Recent Studies

L. Ruhlmann

Photoelectrochemical properties of original hybrid organic – inorganic porphyrin – polyoxometalate copolymers: from flat to mesoporous ITO electrodes

A.A. Nekrasov

Angular Dependence in Raman Spectroelectrochemistry of Conducting Polymer Films

POSTER SESSION – oral presentations

June 18, Tuesday

Morning session

Subsession I: Electroactive polymers IV

T. Schoetz

Understanding the charge storage mechanism of conductive polymers as hybrid battery-capacitor materials in ionic liquids

A. Pailleret

Deepening of the characterisation of the electrochemo-mechanical behavior of conducting polymers using electrochemical atomic force microscopy

J.P. Correia

Evaluation of the pseudocationic doping character of PEDOT:PSS towards Na+ exchange. Discrimination of the mass transfer processes by coupling EQCM and PBD data

Subsession II: Electroactive polymers V

A.R. Hillman

Effect of deposition electrochemical control function on solvent content and spatial profile within conducting polymer films

O.L. Gribkova

The role of polyelectrolytes during electrosynthesis of conductive polymers

P. Chulkin

Electrochemical impedance spectroscopy monitoring of charge transport in conductive polymer film

Afternoon session

Subsession I: Applications of electroactive polymers and composites I

M. Sjodin

Conducting Redox Polymers as Electrical Energy Storage Materials

O.V. Levin

Organometallic electrode materials for new generation of batteries

B. Gupta

Bipolar Activity of Conducting Polymers to Induce Wireless Electromechanical Deformation

Subsession I: Applications of electroactive polymers and composites II

P.J. Kulesza

Hybrid Electrocatalytic and Photoelectrochemical Materials for Selective Conversion of Carbon Dioxide to Fuels and Utility Chemicals

A.S. Viana

Electrosynthesis of biomimetic poly(catecholamine) films with tunable properties for biosensing applications

V. Karabozhikova

Electroanalytical determination of caffeic acid and tryptophan on PEDOT-modified electrodes

POSTER SESSION I – exhibition

June 19, Wednesday

Morning session

Subsession I: Inorganic electroactive materials

I.A. Rutkowska

Mixed-Metal-Oxide-Supports for Noble Metal Nanoparticles: Enhancement of Electrocatalytic Oxidation of Simple Organic Fuels

Qingli Hao

Electrochemical Reduction of CO2 to Ethanol by Nanocomposite catalysts

S. Morin

Nanostructured mixed transition metal spinel oxide thin films as efficient electrocatalysts – composition, structure and properties

V.V. Kuznetsov

Promising nPt.mRu($H_{x-2n-3m}MoO_3$)*catalysis for both carbon monoxide and methanol oxidation reactions*

Subsession II: Inorganic electroactive materials II

M. Longhi

Synergistic Effects of Active Sites Nature and Hydrophilicity on Oxygen Reduction Reaction Activity of Pt-Free Catalysts

C. Zanardi

Role of oxidized functional groups in the electrocatalytic properties of carbon-based nanomaterials

L. Falciola

“Insulating” and mesoporous solid-templated silica films: electroanalytical signal amplification and selectivity properties

N. Cioffi

Electrodecoration of iron oxide nanoparticles with bioactive nanophases for 3rd generation targeted nanoantimicrobials

June 20, Thursday

Morning session

Subsession I: Inorganic electroactive materials III

D. Aurbach

New Horizons of EQCM-D-Based Surface-Acoustic-Wave Spectroscopy for Energy Storage and Conversion

R. Stoyanova

Electrode Materials for Hybrid Metal Ion Batteries

Yongyao Xia

Li Storage in a Low Intercalation Potential Li_2TiSiO_5

Subsession II: Inorganic electroactive materials IV

A.V. Kubarkov

Functional binders based on electron- and ion-conducting polymers for Li-ion battery electrodes

Xaogang Zhang

Two-dimensional porous carbon materials for high-performance supercapacitors

S. Ivanov

Electrochemical Deposition of Silicon From Sulfolane Electrolytes

V. Khomenko

On the Processes of Migration and Diffusion in the Systems with Solid-State Reagents

Afternoon session

Subsession I: Miscelleneous. Composite and oligomeric electroactive materials

F. Scholz

Electrochemical Age Determinations

P.G. Pickup

Pt/metal oxide/carbon composite films for ethanol oxidation

E.V. Zolotukhina

Selective Electrooxidation of Formaldehyde and Acetic Aldehyde in the Presence of Alcohols on Palladium-Polypyrrole Composites

Subsession II: Composite electroactive materials II

G. Ragoisha

Capacitive and non-capacitive currents in electroactive systems

V. Kondratiev

Poly(3,4-ethylenedioxythiophene)/tungsten oxide composites for high rate performance supercapacitor electrodes

R. Holze

Benefits from two worlds: Composites of intrinsicially conducting polymers and metal oxides as supercapacitor electrode materials

POSTER SESSION II – exhibition

June 21, Friday

Morning session

Session: Composite and hybrid electroactive materials III

A. Pron

UV-vis-NIR, Raman and EPR spectroelectrochemistry of organic semiconductors and their hybrids with inorganic semiconductor nanocrystals

M. Skompska

Photocatalytic and photoelectrocatalytic application ZnO/TiO2 core-shell composite decorated with Au nanoparticles

M. Jouini

Photo-Electrode Hybrid Materials for Energy-Related Applications

A. Kormányos

Effect of composition and applied bias on charge carrier dynamics in metal-oxide/nanocarbon hybrid photoelectrodes

A. Fedorczyk

Synthesis and Electrocatalytic Properties of Poly(1,8-diaminocarbazole)/Bimetallic Nanoparticles Composites

Closing ceremony

ORAL Presentations

A Different Approach for Electrochemical Deposition: Starting with Nanomaterials as the Building Blocks

O. Geuli, L. Liu, C. Liu and D. Mandler

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Electrochemical deposition (ED) dates back to Faraday and is a well-established approach for producing coatings. This presentation will summarize novel ED approaches, where nanostructured films are formed, starting with nanomaterials as building blocks, instead of molecular or ionic species. This “nano to nano” deposition concept has a significant advantage of directly transferring nano-objects from the dispersion to the coating, which maintains their unique nanoscale properties. It is achieved via destabilizing the nano-objects in the dispersions by applying electrochemical potential or current, which diminishes interparticle repulsion. Three different mechanisms have been explored, so far, for the ED of nanomaterials: (a) Direct redox induced deposition; (b) Indirect pH and ionic strength induced deposition; (c) Matrix induced co-deposition. With the latter two mechanisms, the “nano to nano” approach can be applied to electrochemically inactive and non-conductive nanomaterials. The deposition process is selective to conductive substrates and can be manipulated by potential/current and time, yielding films with thickness from nanometers to a few micrometers.

A variety of examples will be presented spanning from organic to inorganic nanomaterials and used in applications such as coating of medical implants and more. Furthermore, we will show how such deposited nanomaterials can be used as carriers.

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Detection and analysis of sub-micrometer particles by means of wide field surface plasmon microscopy

Shavkat Nizamov, Vladimir M. Mirsky

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The technology of Wide Field Surface Plasmon Microscopy (WF-SPRM) provides a real-time detection of interaction of single nanoparticles of different origin with a sensor surface. Adsorption of each nanoparticle leads to a characteristic image whose intensity depends on the size and chemical composition of the particle. A number of the nanoparticle - surface binding events per time and surface area characterizes volume concentration. A large monitored surface area of the sensor surface allows one to detect many hundreds of events in each frame or totally up to a million particles on the sensor surface; this leads to the very high dynamic range of counting and to the correspondingly high dynamic range in the concentration scale. Depending on the type of particles and experimental conditions, the detection limit for aqueous samples can be below 100 nanoparticles per microliter. Stable analysis of nanoparticles in very complex environments (fruit juice, cosmetics) was demonstrated. To determine chemical composition of single nanoparticles, the WF-SPRM was coupled with electrochemical analysis: applying a linear potential sweep, the adsorbed nanoparticles can be subjected to electrochemical conversion, leading to the change of their refractive index; the value of the electrical potential of this conversion characterizes the material of the particular nanoparticle. Notably, such analysis is performed simultaneously but independently for each adsorbed particle.

Although the WF-SPRM technology was initially developed for analytics of engineered nanoparticles, it can be also applied in many other fields of science, for example, in bioanalytics, colloid chemistry or electrochemistry. In another presentation of the WEEM-2019 an application of the WF-SPRM for investigation of initial stages of electrochemical nucleation will be shown.

[1] S. Nizamov, O. Kasian, V. M. Mirsky. Angew. Chemie, 55 (2016) 7247–7251.
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Application of wide field surface plasmon microscopy for analysis of initial stages of electrochemical nucleation

Veronika K. Laurinavichyute[1], Shavkat Nizamov[2], Vladimir M. Mirsky[2]

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An analysis of initial stages of electrochemical nucleation is crucial to understand the mechanism of this process and is of importance for the design and electrochemical synthesis of new materials. Here we suggest an application of the recently developed wide field surface plasmon microscopy (WF-SPRM) to trace electrochemical nucleation of copper at low overpotentials. An analysis of the WF-SPRM records gives time dependence of the surface density of the growing copper nuclei and their mutual positioning. The nuclei sizes were calculated using the linear dependence of optical signal on the copper nuclei size in the wide range of sizes starting from ~50 nm. The current transients, calculated from the analysis of optical data, correspond quantitatively to the independently measured experimental current-time dependences. An analysis of the growth curves of the copper nuclei together with their spatial distribution indicates a transition from the kinetic to the diffusion control of copper deposition.

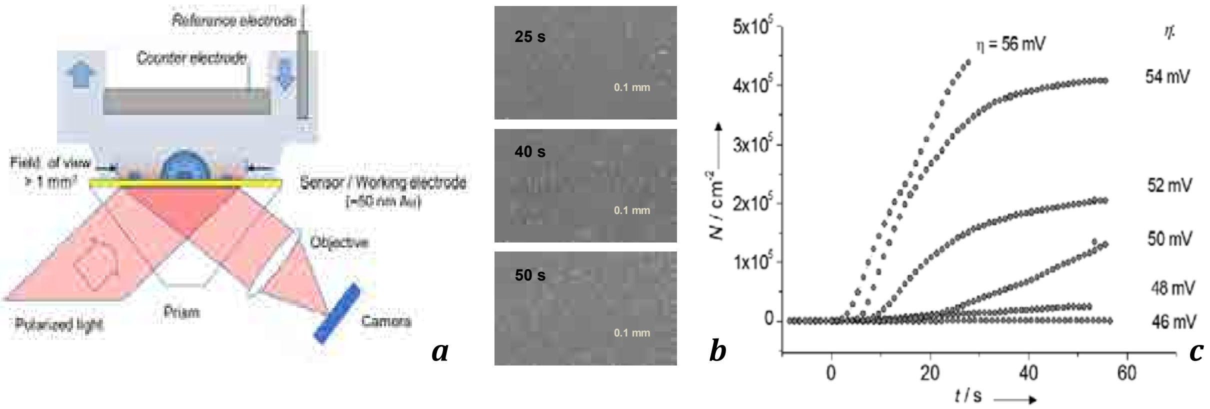

Fig. 1. Schematic view of wide field surface plasmon microscopy setup (*a*), *in-situ* WF-SPRM visualisation of growing copper nuclei (*b*) and corresponding time dependences of the surface density of copper nuclei (c).

Acknowledgments: V.L. is grateful to the financial support from DAAD (Program Ostpartnerschaft) and BTU (Research Professorship Grant for V.M.).

Targeted electrooxidation of bulky Donor/Acceptor diarylamines: a convenient route to multifunctional redox active materials

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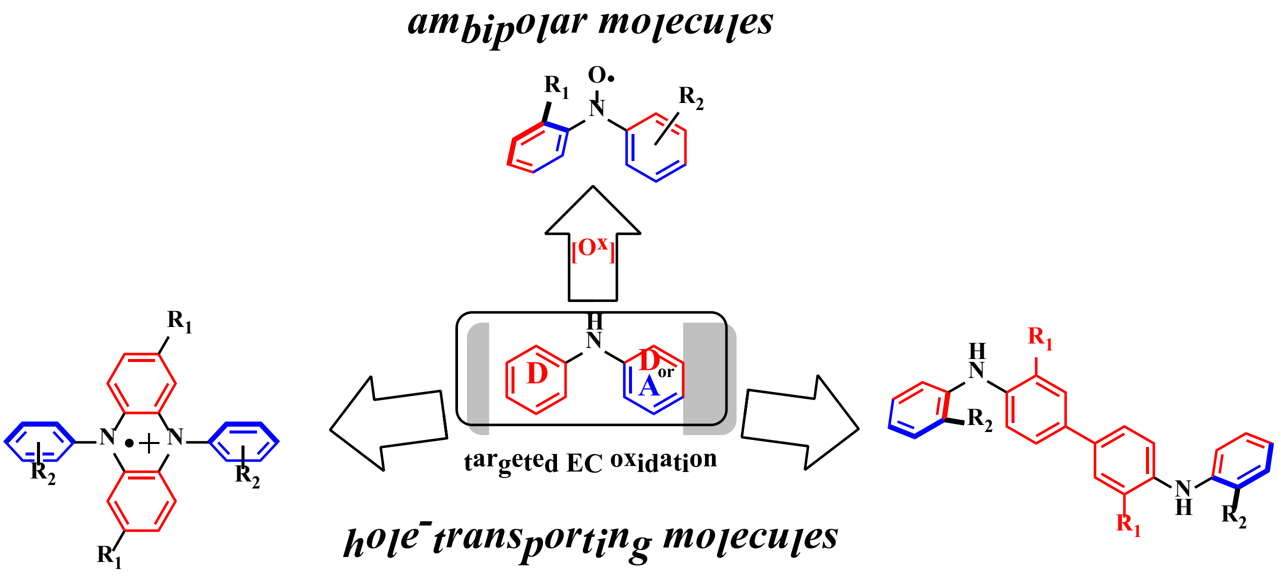
Ecologic situation dictates a necessity for gradual replacement of inorganic metal-containing materials for biodegradable and recyclable raw materials thus highlighting elaboration of new competitive redox- and photoredox active organic molecules as the main components for photo and electrochemical energy storage and conversion systems. Sustainable chemistry requirements as well as wide possibilities for targeted functionalization of a molecule for performing various practical tasks provided by organic compounds make them promising in this context. The key requirement determining applicability of a compound as electroactive material for energy conversion and storage systems is formation, at least, two relatively stable redox states. Purely organic metal-free molecules capable to form three stable redox states, e.g., stable cationic, neutral and anionic forms are rare since stabilization of antipodal charged states for the same molecule, such as anions and cations, is not an easy task. Meanwhile, this type of molecules is strongly required, e.g., for fabrication of ambipolar batteries. The application of a bipolar redox-active charge-storage material in a redox-flow battery has significant advantages, such as considerably reduced synthesis efforts, the simplified flow cell design (as both cell compartments use the same material) and a solution to the problematic cross-contamination, which prevents long-term capacity decay. Thus, a targeted search for new ambipolar molecules is a challenging task.

One of the possible approaches is to regulate the relative impact of donor/acceptor component in stabilization of the redox-active center, as dependent on its charge. To provide regulation, the conjugation between the functional group (NO, NH or some other) and electron-rich or electron-poor aromatic rings should be weakened. This can be achieved by insertion of a bulky substituent in the *ortho*-position of the ring. The bulky group facilitates formation of various conformational states related to the dihedral angle between electron-donating or electron-withdrawing aromatic ring and a functional group. This allows regulating intramolecular charge transfer from donating or withdrawing ring to the functional group, as dependent on its redox state.

As the objects for verification of the suggested approach, a new series of bulky donor/acceptor diarylamines were synthesized. These compounds can be considered as a convenient "starting platform" for further targeted oxidative functionalization leading to a variety of redox-active molecules (N,N-diarylbenzidines, N,N-diarylphenazines and diarylnitroxides) which can be considered as possible candidates for application as hole-transporting materials and ambipolar charge carriers (Scheme1).

Scheme 1



Systematic investigation of anodic oxidation of the series of bulky diarylamines containing electron donating and electron withdrawing substituents in various combinations was performed. It revealed that targeted electrooxidation of bulky donor/acceptor diarylamines can lead selectively to either N,N-diarylphenazines or N,N-diarylbenzidines, as dependent on the location and electronic properties of the substituents in both phenyl rings. Guidelines for the prediction of the dominant reaction path of initially formed radical cations were formulated. The conclusions developed will be useful for planning electrosynthesis of new types of hole-transporting materials since new phenazines can form extremely stable radical-cations as well as dicationic species upon electrooxidation. New donor/acceptor benzidines are photo active and exhibit interesting electrochemical and photophysical properties.

Chemical oxidation of the bulky donor/acceptor diarylamines allowed obtaining a new type of diaryl nitroxide radicals – so called “twisted” donor/acceptor diarylnitroxides with “adjustable” conjugation between aromatic rings and the NO group. They constitute rare example of “smart” purely organic molecules capable to change their geometry to regulate the relative impact of the donor/acceptor component in stabilization of the redox-active center, as dependent on its charge. Such molecular design allows to amplify stabilizing interaction and to minimize destabilizing effects leading to aromatic functional derivatives capable to provide stabilization of the nitroxyl radicals, their oxidized form (oxoammonium cations) and reduced form (aminoxyl anions). Furthermore, new compounds exhibit fast ET kinetics, as it was shown by voltammetric investigations. This allows considering new nitroxide radicals as perspective candidates for testing as ambipolar redox active materials for “poleless’ batteries as well as dual mediators for double-layer supercapacitors.

Acknowledgments: This work was supported by Russian Science Foundation (Project number 19-13-00094) .

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[2] O.A. Levitskiy, V.V. Sentyurin, T.V. Magdesieva, *Electrochimica Acta*, **2018**, 260, 459-467.

"*Inherently chiral*" electrode surfaces: stereogenic elements and enantiodiscrimination performances

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Electrochemical processes are intrinsically "intelligent" on account of the selectivity achievable in both analytical and preparative contexts through fine control of the electrode potential. They can become even smarter by addition of chirality, implying to discriminate between enantiomers of chiral electroactive probes, which requires the electron transfer process to take place at an enantiopure chiral interphase.[1,2]

A recently proposed groundbreaking strategy is based on the use of heterocycle-based "inherently chiral" molecular selectors, *i.e.* with chirality and key functional properties originating from the same structural element, which coincides with the main molecular backbone, featuring a tailored torsion with associated energy barrier too high to be overcome at room *T*. This concept has been successfully implemented by us in both electrode surfaces[3-10] and in ionic-liquid based media.[11,12]

We will particularly focus on preparation, features and performances of enantiopure electrode surfaces obtained starting from enantiopure monomers with atropisomeric 3,3'-bithiophene or 2,2'-biindole cores and oligothiophene wings[3-9] or from enantiopure helical monomers (tetrathiahelicenes).[10] By fast and regular electrooligomerization enantiopure inherently chiral films are obtained, often including attractive cyclic terms, with high electroactivity and, above all, impressive enantiodiscrimination ability as general-scope electrode surfaces in terms of large potential differences for the enantiomers of very different chiral probes, also of pharmaceutical interest. The film impressive enantioselectivìty also holds with circularly polarized light and electron spins, resulting in outstanding chiroptical and spin filter performances, suggesting fascinating correlations between the three contexts.[2,8-10]

Acknowledgements: The support is gratefully acknowledged of Regione Lombardia and Fondazione Cariplo (Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC-edizione 2016, Project 2016-0923).

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Synthesis and Properties of Polythienothiophene and Dithienothiophene Posessing Pendant Alkyl and Triphenylamine Groups

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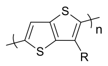
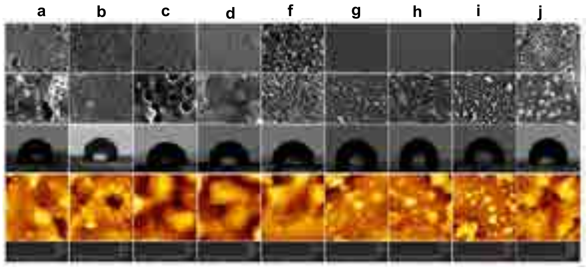
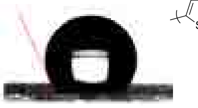
Small and polymeric organic semiconductors containing organic conjugated structures are important research topics in organic material chemistry. This is due to their possible applications as solar cells, OLEDs, transistors, energy storage, electrochromic devices and sensors [1]. Thiophene, thienothiophene (TT) and dithienothiophene (DTT) have an important place in the development of such materials [2]. In this study, electropolymers of polyTT and polyDTT, having pendant alkyl and triphenylamine groups were prepared. Their syntheses and properties, such as CV, CV-UV, SEM, AFM and CA, are presented.

R = **(a)** CH_3, **(b)** C_2H_5, **(c)** C_3H_7,
(d) C_4H_9, **(e)** i-C_5H_{11},
(f) n-C_5H_{11}, **(g)** C_6H_{13},
(h) C_7H_{15}, **(i)** C_8H_{17},
(j) C_9H_{19}, **(k)** $C_{10}H_{21}$



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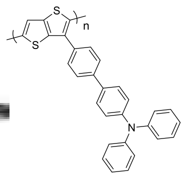

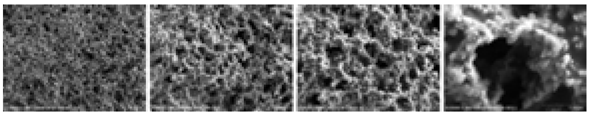

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Synthesis of novel transition-metal containing representatives of the polyporphine family

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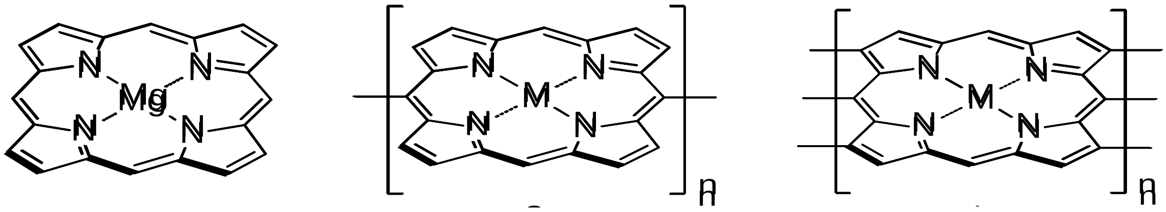

(a) MgP **(b) pMgP-I** **(c) pMgP-II**

Fig. 1. Monomeric Mg(II) porphine (a) and polyporphines of type I (b) and II (c)

The first representatives of ***polyporphines***, i.e. homopolymers composed of ***porphine*** (non-substituted porphyrin) units were synthesized [1,2] via oxidative electropolymerization of Mg(II) porphine in acetonitrile (Fig. 1a).

Owing to specific properties of the porphine macrocycle containing the Mg ion, this process may be carried out for a very low potential (below 0.4 V vs. Ag/0.01 M Ag^+ in CH_3CN), resulting in formation of polymeric chains of type I, **pMgP-I** (Fig. 1b, M = Mg^{2+}) where porphine units are linked in *meso-meso* positions while Mg ions are retained inside the units [1,3,4]. Electrode coated by pMgP-I film in contact with monomer-free electrolyte solution possesses a pronounced redox activity of both the *p-* and *n*-types in the course of multi-cycle potential variation if the anodic limit is within 0.4 V. If a more positive potential is imposed the pMgP-I polymer is irreversibly oxidized, with formation of polyporphine of type II, **pMgP-II**, having additional bonds in *beta-beta* positions (Fig. 1c, M = Mg^{2+}) [2]. Owing to its permanently planar "condensed tape" structure this polymer possesses unique properties, in particular its electronic energy structure is of the ***metallic*** type (Fermi level is located inside a broad energy band) so that it demonstrates both a strong redox activity and a high electronic conductivity within the whole range of potentials (over 3 V in width), without an insulating potential region in its neutral state.

Numerous applications of monomeric porphyrins are based on the presence of a ***transition metal ion***, M, inside the porphine macrocycle. One may expect that the corresponding polyporphines, pMP-I and/or pMP-II, would have certain advantages, compared to monomeric species, owing to the automatic immobilization of the polymer film at the substrate and a very high concentration of porphine units inside the polymer.

One can obtain porphine monomers containing the needed transition metal ion, M (Fig. 1a with M instead of Mg). However, their electropolymerization does not lead to desirable polyporphines of a *regular* molecular structure (either of type I or type II) since the oxidation potentials of such metalloporphines is over 0.4 V so that the bonds between the porphine units are formed in *all* positions: *meso-meso*, *meso-beta* and *beta-beta* ones.

To get polyporphines of regular structures we have applied the ***ion-exchange*** procedure [5-9] which consists of ***three steps***: ***demetalation*** of pMgP-I, then ***remetalation*** of the metal-free polymer of type I (pH_2P-I) to get pMP-I (Fig. 1b) and finally its ***irreversible oxidation*** into type II, pMP-II (Fig. 1c).

Crucial advantage of this approach consists in conservation of the molecular structure of the polymer of type I at first two stages of the procedure that is of importance for the reliable control of the ion exchange process, see below.

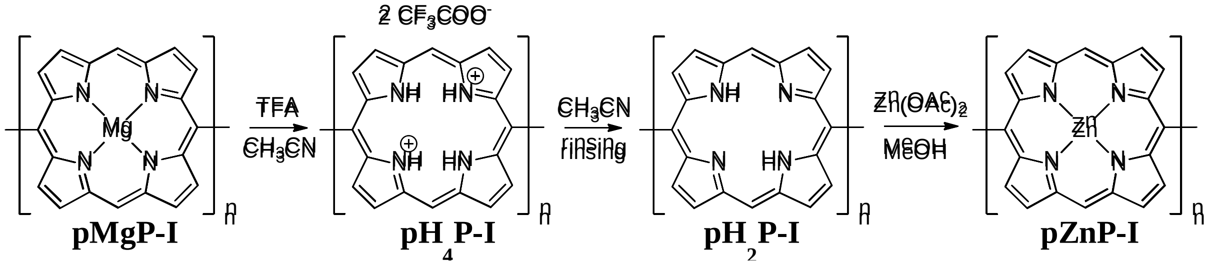

Fig. 2. Schematic illustration of the demetalation and remetalation steps.

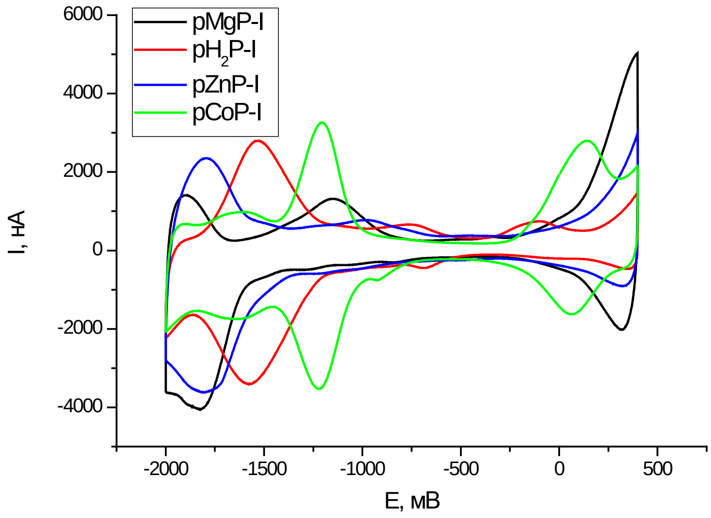

Fig. 3. CV response of various polyporphines of type I in monomer-free solution.

Demetalation step (Fig. 2) is performed by keeping the electrode coated by the pMgP-I film is contact with a dry in CH_3CN solution of concentrated TFA acid. It leads to replacement of Mg(II) ion by ***four*** protons, thus forming a charged polymer, pH_4P-I. Its rinsing removes excessive protons to give a metal-free polyporphine of type I. pH_2P-I, composed of neutral porphine units (Fig. 2).

Complete character of the ion replacement is controlled by the CV response (Fig. 3) as well as by IR and XPS spectra. In particular, treatment of PMgP-I film by acid results in a new couple of cathodic/anodic waves near - 1.6 V (red line) instead of the previous one near - 1.8 V (black line).

Two different methods have been used for the remetalation step (Fig. 2).

One of them [5-7] uses a procedure analogous to the one applied for the demetalation step, i.e. the metal-free polyporphine film, pH_2P-I, is kept in contact with dry concentrated solution of the corresponding metal salt. This process passes smoothly for Zn [5] while for transition metal ions (Co, Fe, Cu...) it requires to boil the saturated solution of the salt for extended duration [6,7].

The passage of the metal ion inclusion is again controlled by IR, XPS and CV methods. In particular, Fig. 3 shows the *proper* shift of the waves for Zn (blue line) and Co (green line), with appearance of characteristic responses due to Co(II)/Co(III) and Co(II)/Co(I) transitions inside the polymer units.

A serious drawback of this ***chemical*** approach to the ion exchange inside polyporphines [5-7] is the contamination of the resulting film by solid deposits of both the salt and its hydrolysis products which are difficult to remove by rinsing.

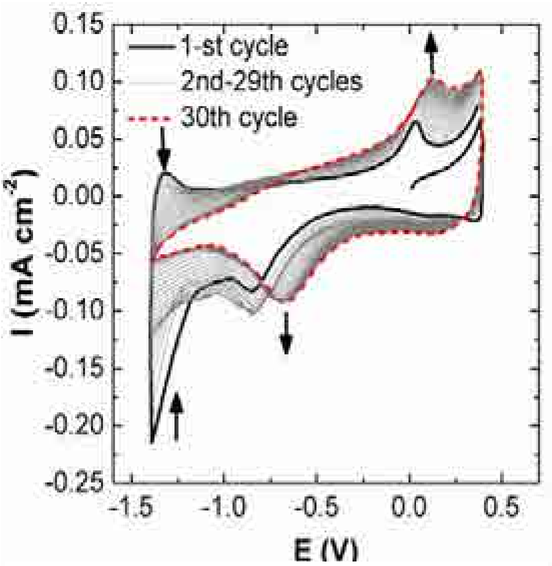

Fig. 4. Potential cycling of pH_2P-I film in 0.5 mM $Mn(ClO_4)_2$ solution leading to its transformation into pMnP-I one.

Alternative method towards insertion of transition metal ions inside porphine units of the polymer, ***electrochemically induced ion exchange***, has recently been elaborated [8,9]. The pH_2P-I film coated electrode is placed into a ***dilute*** (0.5 mM) solution of a salt of the corresponding metal ion and the potential is cycled within a properly chosen interval. Progressive evolution of the CV response enables one to monitor the process of protons' replacement inside porphine units by metal ions, see Fig. 4 for synthesis of the pMnP-I film.

Its advantage is to perform the transformation at ***room temperature*** as well as ***to diminish the salt concentration*** by around 1000 times, compared to the chemical method.

Similar to pMgP-I, all synthesized polyporphine films of type I, pMP-I (Fig. 1b, M = H_2, Zn, Co, Fe, Mn, Cu) have been successfully transformed into the corresponding ***polyporphines of type II***, pMP-II (Fig. 1c), by their electrooxidation.

Transition-metal containing polyporphines, pMP-I and pMP-II, have shown

high electrocatalytic activities in oxygen reduction and sulfite anion oxidation reactions [7,9].

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Capacitive and electrochromic behaviours of polymers based on thiophene, 3,4-(ethylenedioxy)thiophene and electron-withdrawing groups substituted phenyldithienothiophene

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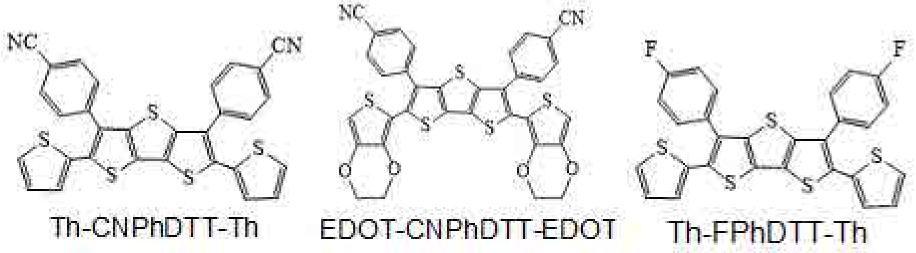
Polythiophene (PTh) and poly-3,4-(ethylenedioxy)thiophene (PEDOT) are common conjugated polymers due to their environmentally stabilities in their p-doped forms. Their high conductivities and superior electrochromic behaviors make them favorable materials for electrochromic devices, LEDs and capacitors [1,2].

Dithienothiophenes (DTT) are electron rich fused molecules, having flat and rigid delocalized systems, which make them appropriate candidates to be used in conjugated and low band gap semiconductors [3].

In this study, previously synthesised 4,4'-(2,6-Di(thiophen-2-yl)dithieno[3,2-b:2',3'-d] thiophene-3,5-diyl)dibenzonitrile (Th-CNPhDTT-Th) and 4,4'-(2,6-bis(2,3-dihydrothieno [3,4-b] [1,4]dioxin-5-yl) dithieno [3,2-b:2',3'-d] thiophene-3,5-diyl)dibenzonitrile (EDOT-CNPhDTT-EDOT) (Scheme 1) [4,5] were electrochemically polymerized by potentiodynamic method by applying different cycle numbers(Figure 1a and c) and redox behaviour was tested by cyclic voltammetry(CV) obtained at different scan rates (Figure 1 b and d).



Scheme 1. Structure of comonomers.

The redox and capacitive behaviors of polymeric films obtained at different thickness were compared and polymerization at 20 cycles were determined as optimum conditions for both polymer (Figure 2 and 3).

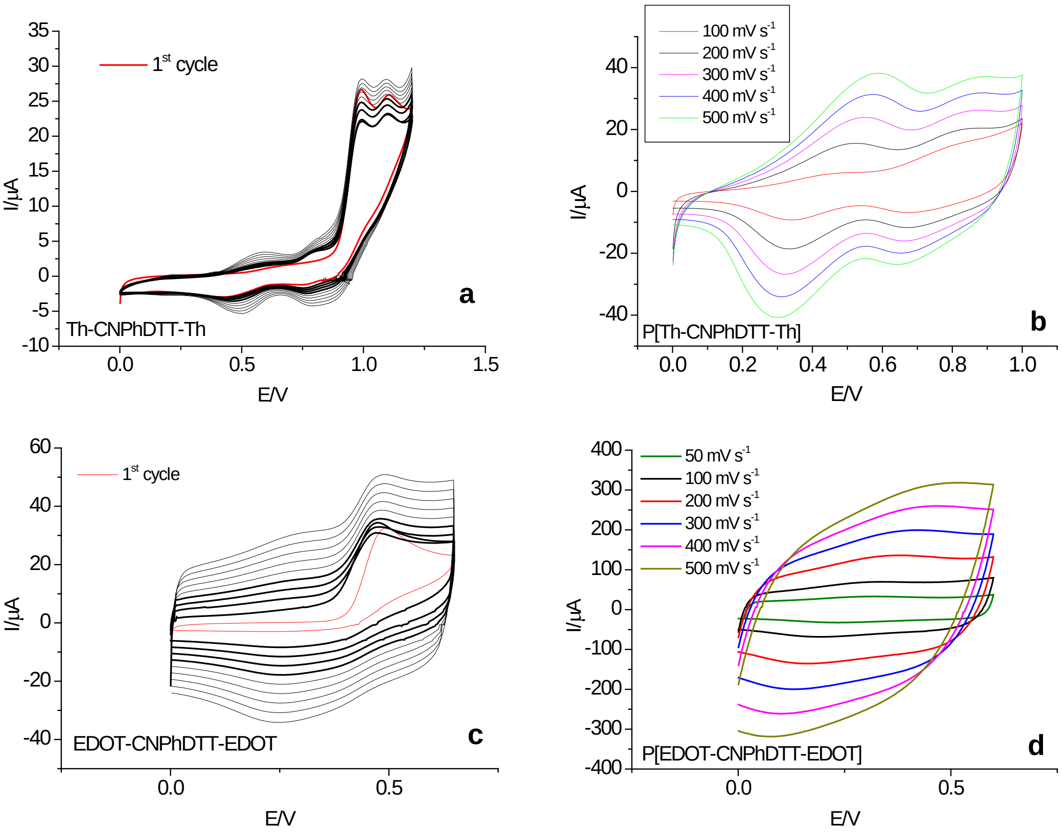


Figure 1. CV's of Th-CNPhDTT-Th and EDOT-CNPhDTT-EDOT during (a and c) and after polymerization(b and d) respectively in ACN:DCM (7:3) containing 0.05 M $NaClO_4$ and 0.05 M $LiClO_4$.

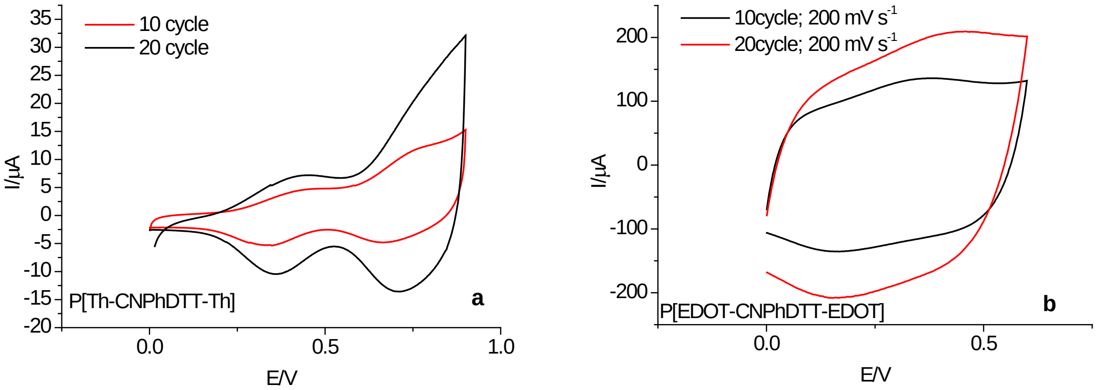


Figure 2. Comparison of CV's of P[Th-CNPhDTT-Th] **(a)** and P[EDOT-CNPhDTT-EDOT] **(b)** obtained by applying 10 and 20 cycles during polymerization. at 100 mV s^{-1} in ACN:DCM containing 0.05 M $NaClO_4$ and 0.05 M $LiClO_4$.

The simulation of the impedance behavior of the all films through the data obtained experimentally was investigated and the electrical equivalent circuit model with lowest error used to describe the experimental results (Figure 4).

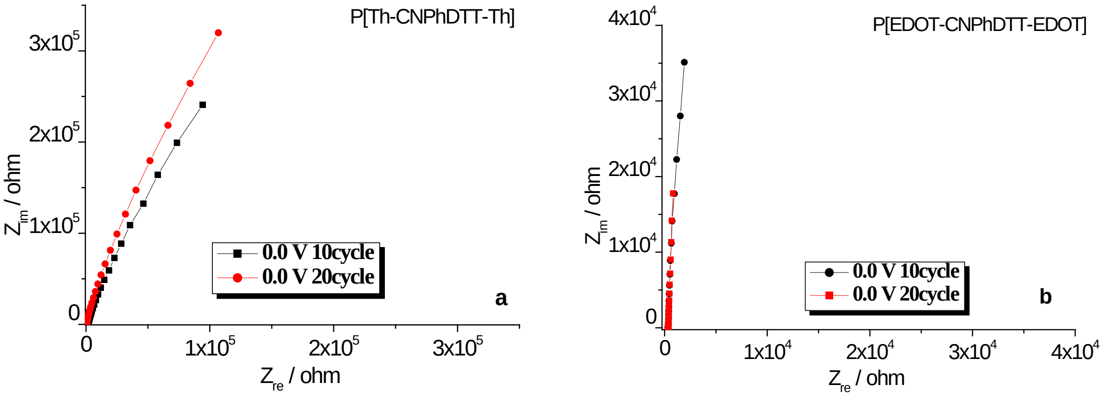


Figure 3. Comparison of Nyquist diagrams of P[Th-CNPhDTT-Th] **(a)** and P[EDOT-CNPhDTT-EDOT] **(b)** in ACN:DCM containing 0.05 M $NaClO_4$ and 0.05 M $LiClO_4$.

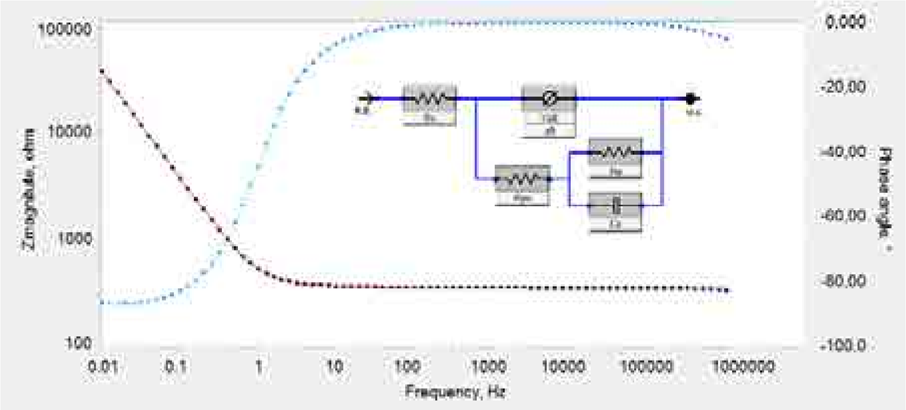


Figure. 4. Experimental (dots) and simulated (solid line) Bode plots of P[EDOT-CNPhDTT-EDOT] film.

Different capacitors and electrochromic devices were constructed. Results suggested that capacitors contructed from P[EDOT-CNPhDTT-EDOT] have better properties than P[Th-CNPhDTT-Th] for charge storage applications.

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Redox Properties of Thienoacene-Extended Tetrathiafulvalenes studied by EPR/UV-vis-NIR Spectroelectrochemistry

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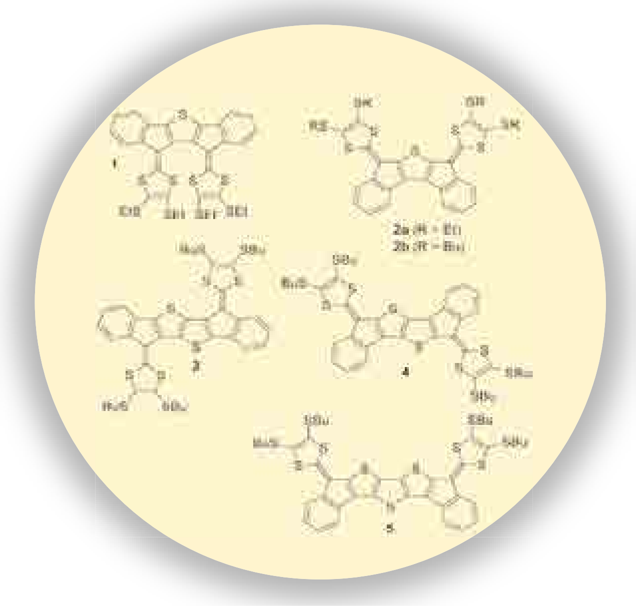
Turning on and off associations between molecules by a reversible change in their redox states is a convenient way of controlling self-assembly and hence for advancing supramolecular chemistry [1-3]. Here we present systematic studies on a selection of extended tetrathiafulvalenes with thienoacene spacers [1] (Scheme 1).



Scheme 1. Investigated extended tetrathiafulvalenes with thienoacene spacers.

By cyclic and differential pulse voltammetry and in situ EPR/UV-Vis-NIR spectroelectrochemistry, in combination with computations, we have elucidated how the number and orientations of thiophene rings in the spacer between the two dithiafulvene rings influence both the donor strength and association properties. The radical cations and their associates were found to cover a remarkable large region of the UV-Vis-NIR spectrum, but the appearance of the absorption spectrum of the radical cations as well as of the unassociated dications also depended strongly on the exact molecular structure (Figure 1).

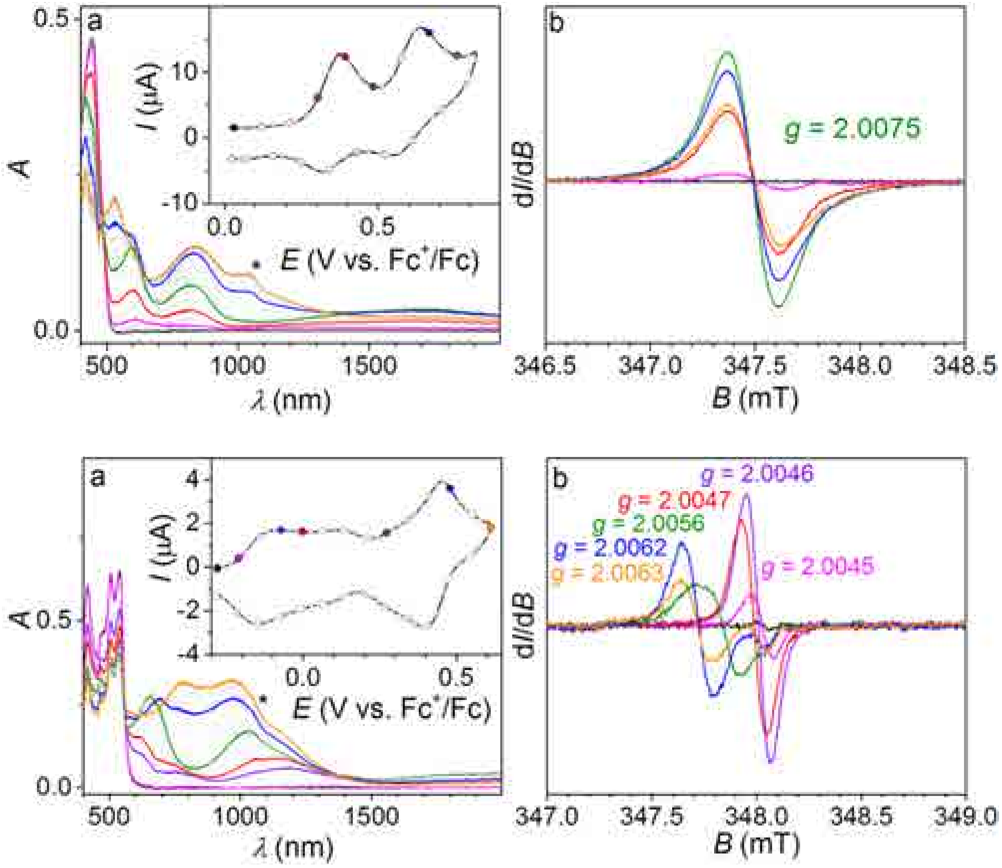


Figure 1. In situ EPR/UV-Vis-NIR spectroelectrochemistry of **1** and **5** (0.5 mM) in CH_2Cl_2 + 0.2 M n-Bu_4NPF_6. Optical (a) and EPR spectra (b) correspond to the potential marked with circles in the corresponding voltammogram shown as inset in (a). The color code is maintained throughout the figure. * in (a) marks a spectrometer artefact.

In this contribution we present detailed in situ EPR/UV-Vis-NIR spectroelectrochemical studies in order to obtain a more detailed description of the influence exerted by one or more central thiophene rings and the influence of connecting the two dithiafulvene units in a cross-conjugated or linearly conjugated manner. By systematic studies on the redox properties of a selection of thienoacene-extended tetrathiafulvalenes we have found that the donor strength depends strongly on the orientation of the central thiophene rings as the ability to delocalize the unpaired electron depends on whether the conjugation pathway is cross-conjugated or linearly conjugated. In the case of dicationic structures the paramagnetic dications might occur in two potential forms, depending on the extend of the mutual electron spin interaction. If the two electron spins are isolated in distant parts of the molecule (which for the symmetric structures would be magnetically equivalent), and experience no or only vague interaction, the bi-radical state is formed. Its EPR characteristics are then identical or very similar to those of the radical cations. However, if the two spins couple ferromagnetically and form a "true" triplet state, the coupling also induces enhanced electron spin relaxation, which results in EPR signal broadening. The EPR spectra of organic triplets are thus often broadened "beyond detection" in isotropic solutions at room temperature, and can be considered EPR silent under such experimental conditions. The intrinsic absorptions as well as those originating from associations of radical cations expand a remarkable broad region of the UV-Vis-NIR region, with absorption spectra that depend strongly on the structure of the spacer, and these thienoacene-extended tetrathiafulvalenes thus seem promising molecules for electrochromic materials applications.

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Charging/Discharging Phenomena of Conducting Polymers

- An Overview of Recent Studies-

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The voltammetric charging/discharging curves of conducting polymers (CP) have been described in numerous publications. Characteristic features of such voltammograms are a steep wave at the beginning of the charging followed by a broad, flat plateau as potential increases. Moreover, during discharging very often a hysteresis is observed (Fig.1) Different causes of these phenomena ranging from conformational effects to N-shaped free-energy curves as a consequence of phase transitions have been presented in the literature. A consistent interpretation is difficult because the voltammetric response under solid state conditions may depend on quite a large number of different factors such as intermolecular forces within the polymer, surface properties, overlapping redox steps, chemical reactions as well as ion and solvent transport. Furthermore, the experimental conditions during electropolymerization and electrochemical measurements also influence the charging/discharging behavior. Important experimental parameters are the formation potential, the temperature, the solvent and even the layer thickness,.

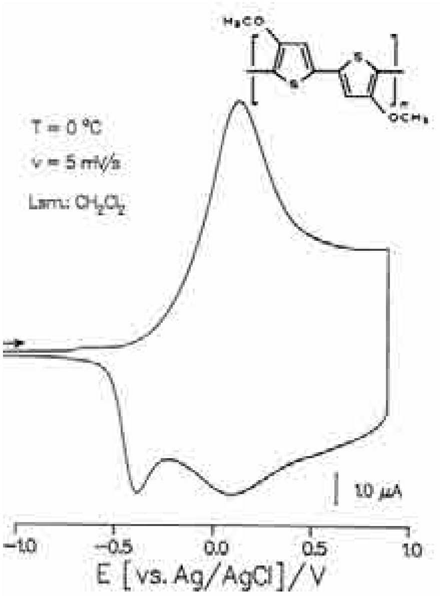

Fig.1: Cyclic voltammogram of conducting polymer (PDMOBT) in CH_2Cl_2/$TBAPF_6$, (potentiodynamic polymerization, 9 cycles)

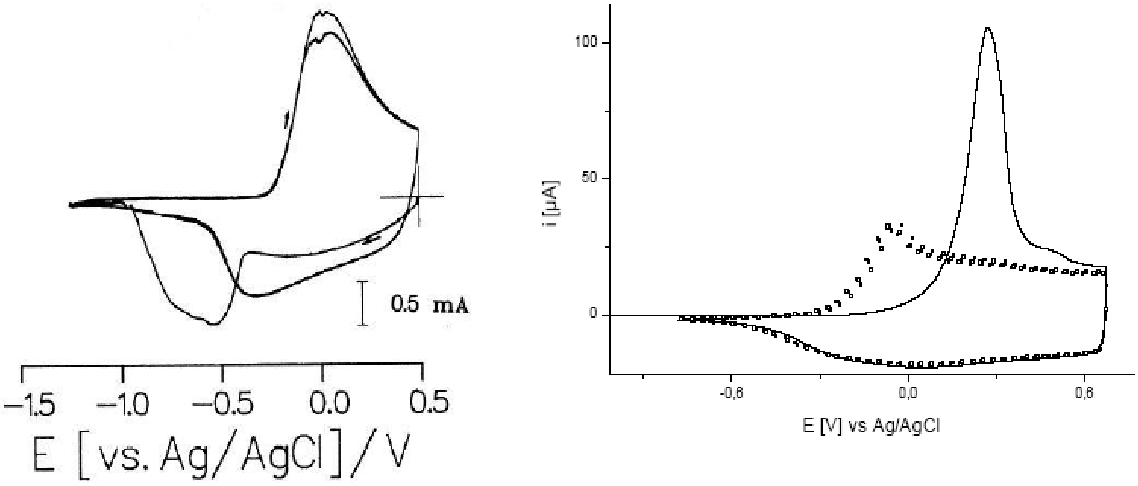

Fig. 2: Different types of charging/discharging processes in conducting polymers, left:: large overpotential of the first reduction of a polypyrrole film in propylene carbonate (0.1 M $LiClO_4$;); right:: memory effect of PEDOT in acetonitrile (0.1 M $TBAPF_6$), v = 0.1 V/s.

The aim of the lecture is to present a general overview and mechanistic interpretation of important charging/discharging phenomena in the field of CPs. This includes *inter alia* the memory effect, the overpotential phenomenon of the first reduction, the dimerization of chains during charging , or the cation vs. anion transport.(Fig. 2). The available experimental data support the view that dimerization reactions and surface effects in comparison to simple redox reactions mainly influence the charging/discharging mechanism of CPs. [1-4]

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Photoelectrochemical properties of original hybrid organic – inorganic porphyrin – polyoxometalate copolymers: from flat to mesoporous ITO electrodes

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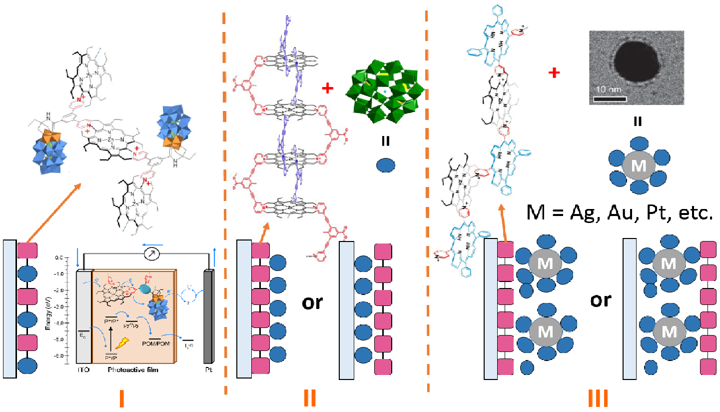

Figure 1 Various type of porphyrin-POM films.

The development of hybrid polymers incorporating polyoxometalates (POMs) is a promising approach to elaborate new functional materials. To expand the practical applications, their association to a visible-light photosensitizer is needed. In this context, we have developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin dications[1-2] or even radical cations.[3] Mechanisms of electrochemical routes to these electroactive copolymers will be presented. The formation of POM-porphyrin copolymeric films (Fig. 1, film I) can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Py-POM-Py).[4] This process is feasible for various type of POMs such as Dawson, Lindqvist or Keggin type POMs.[5-7] Other type of POMs with higher number of pyridyl groups (POM(py)$_6$) has been also used with success. A second methodology is also proposed to form hybrid POM-porphyrin films (Fig. 1, films II or III): first the formation of cationic polyporphyrin electropolymer. Then, by metathesis reaction, the (partial) exchange onto the surface of the initial counter ions by the POM^{n-} or by the nanoparticles stabilized with POM^{n-} (POM^{n-}@M, M = Ag, Au, Pt, etc.). The photovoltaic performances of these hybrid materials have been investigated as well as their impedance properties. [8-9] In order to increase the efficiency, mesoporous ITO electrodes (nanofiber formed by electrospun or porous ITO electrode obtained using a colloidal co-assembly approach) have been used and will be discussed.

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Angular Dependence in Raman Spectroelectrochemistry of Conducting Polymer Films

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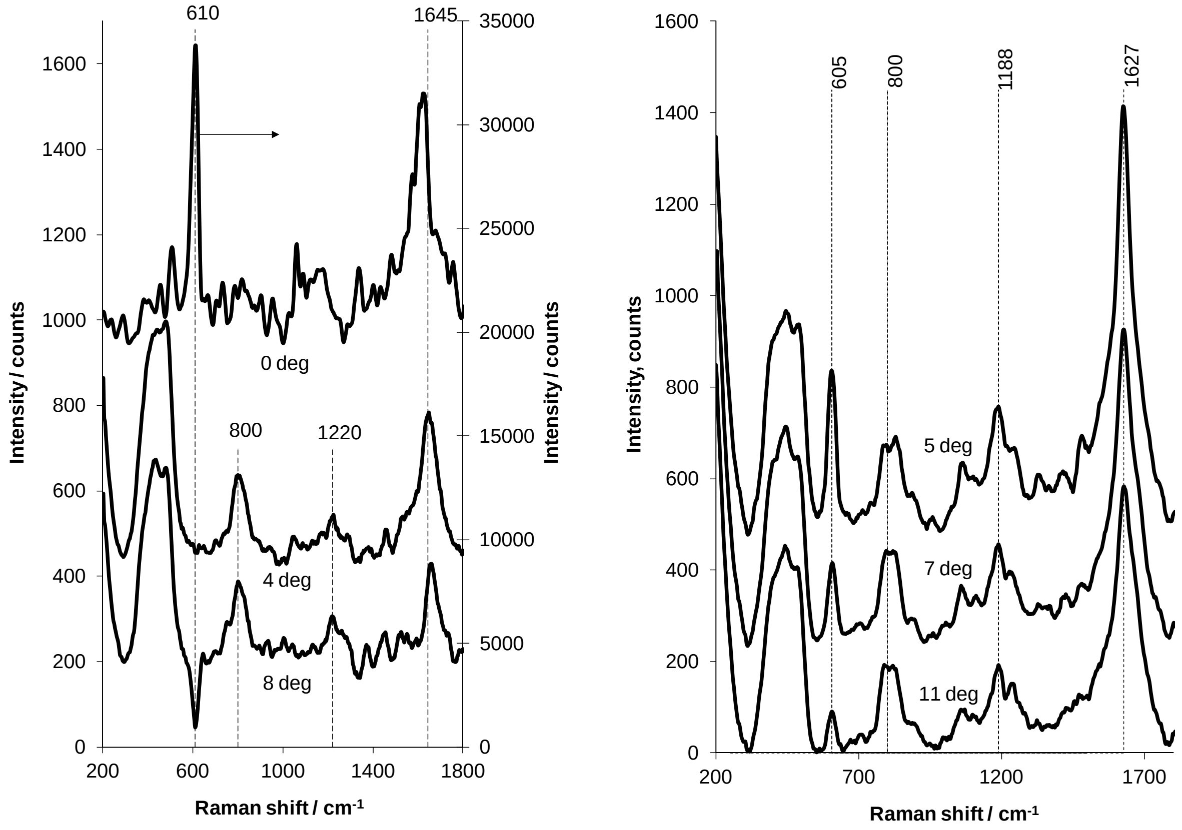
Raman spectroelectrochemistry is a powerful tool to monitor structural transformations during electrosynthesis and doping/dedoping of conducting polymers. However, the excitation laser beam passes several interfaces, where absorption, refraction and reflection processes may occur. These are: air/glass (the wall of spectroelectrochemical cell); glass/electrolyte; electrolyte/film (of conducting polymer); film/electrode. Noteworthy, the film of conducting polymer changes its thickness, absorption and refraction during the electrosynthesis and doping/dedoping. Moreover, conducing polymer films are inhomogeneous consisting of conductive domains distributed in non-conductive matrix, these domains changing their sizes during doping/dedoping. All these phenomena, as well as the electrode material, laser excitation wavelength and Raman resonance phenomena due to specific absorption of laser radiation, influence the shape of *in situ* Raman spectra and are also dependent on the incident angle of the laser beam.

These issues are illustrated on the example of electrosynthesis and redox transformations of thin (<150 nm) films of polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT). Fiber optics Raman spectrometer with 180° (back) scattering geometry, 532 nm laser excitation, Pt sheet and standard 2 cm quartz spectrophotomeric cell were used. It was shown that Pt electrode immersed into deionized water exhibits an intense Raman signal near 600 and 1650 cm^{-1}, as well as some other bands in the most informative Raman range of 600-1650 cm^{-1} (Fig. 1a). Similar vibrations can be found in the spectrum of Pt coated by reduced PANI film (-0.2V vs. Ag/AgCl), which is most transparent to 532 nm radiation (Fig. 1b).

By increasing incident angle of the laser beam from 0 (perpendicular) to 8-11 degrees one can minimize the intensity of 600 and 1645 cm^{-1} vibrations in the spectra of both bare Pt and reduced PANI film thus minimizing the influence of multiple interfaces on the spectrum shape. This is less evident for PEDOT films absorbing 532 nm radiation in all oxidation states.



a) b)

Fig. 1. Raman spectra of Pt electrode in deionized water (a) and Pt electrode covered by PANI film at the potential of -0,2 V (vs. Ag/AgCl) in 1M HCl (b) at different incident angles of laser beam.

The vibrations near 600, 800, 1200 and 1650 cm^{-1} most possibly belong to optical phenomena (reflection, refraction, interference) at the air/quartz/solution interfaces. This is supported by the fact that they are also present with different intensity in the spectra of quartz cell without Pt electrode filled with air or different solutions (including polymeric sulfonic acids), i.e., their intensity depends on the refraction index of the medium inside the cell. The remaining (after the angle adjustment) vibration near 1650 cm^{-1} most possibly belong to H-O-H bending vibration of water (Fig. 1a, 8 deg) and superposition of the water vibration and C-C stretching vibration in leucoemeraldine form of PANI (Fig. 1b, 11 deg). So, it is obvious that the optimal incident angle is unique for each system and should be determined before *in situ* Raman experiments on electrosynthesis (for bare Pt electrode) or electrochemical doping/dedoping (for the film in the most transparent oxidation state) of electroactive polymers.

Another advantage of purposeful adjustment of the incident angle of the laser beam can be illustrated on the example of electropolymerization of aniline (Ani) in the presence of different polymeric sulfonic acids: poly(2-acrylamido-2-methyl-1-

propanesulfonic acid), PAMPSA, and poly(styrenesulfonic acid), PSSA. The polymerization solution based on PSSA, as distinct to PAMPSA, exhibits an intense background signal due to fluorescence of intermolecular associates (Fig. 2).

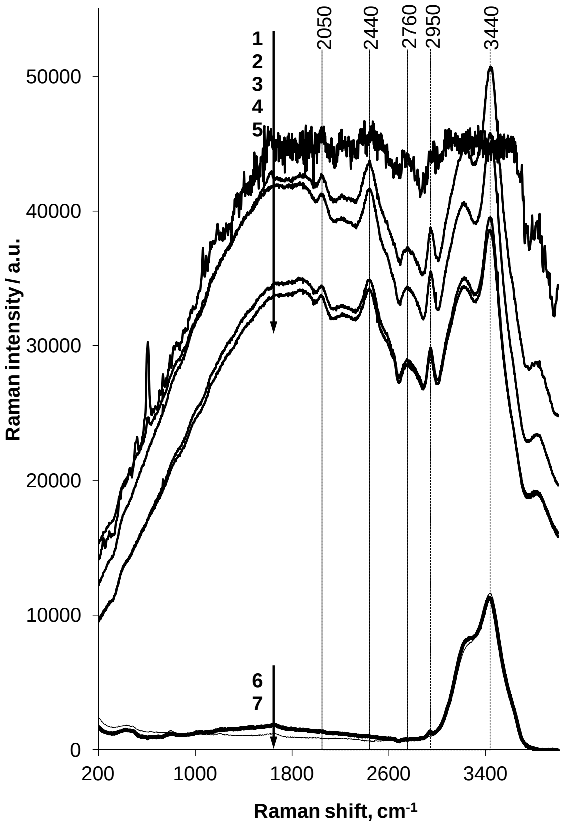


Fig. 2. Raman spectra of Pt electrode at different incident angles of the laser beam in aqueous solutions of 0,025M Ani and 0,05M PSSA (1 – 0 deg, 2 – 5 deg, 3 – 10 deg, 4 – 15 deg, 5 – 20 deg), 0,025M Ani and 0,05M PAMPSA (6 – 20 deg), 0,1M Ani and 1M HCl (7 – 20 deg)

By increasing the incident angle of the laser beam one can decrease the intensity of background signal and to exclude CCD detector overload making it possible to subtract the background before starting the electropolymerization. As distinct from common methods to reduce CCD overload (decrease of the laser intensity or energy (use of 633, 752 nm excitation) or spectrum integration time), the adjustment of indecent angle practically does not influence the sensitivity and accuracy of detection (see O-H stretching vibration in water near 3440 cm^{-1} and vibrations of PSSA backbone in the range of 2000-3000 cm^{-1}).

Conclusions

By adjusting incident angle of the laser beam during *in situ* Raman spectroelectrochemical studies of electrosynthesis or electrochemical doping/dedoping of conducting polymers on metallic electrodes one can minimize the influence of background signals originated from:

1) optical phenomena (reflection, refraction, interference) at multiple interfaces in Raman spectroelectrochemical cell;
2) fluorescent phenomena in the solution layer before the electrode;
3) changes in laser beam reflection from electrode due to growth of the laser-absorbing polymer film;
4) changes in laser beam reflection from electrode due to changes in laser absorbance in conducting polymer film during redox processes.

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Understanding the charge storage mechanism of conductive polymers as hybrid battery-capacitor materials in ionic liquids

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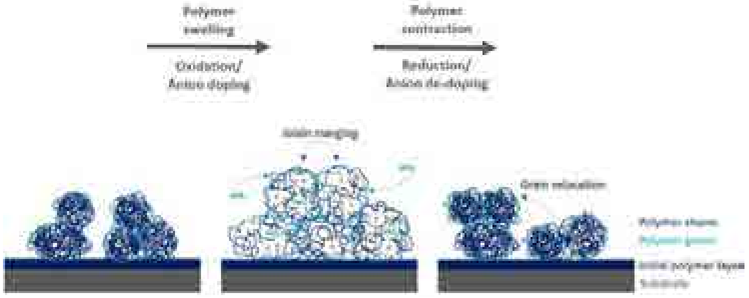
Safe and sustainable energy storage, distinguished by high-performance, outlines the main objectives of near future energy storage technologies. The closing of the gap between high power and energy per unit weight, characteristics which are especially required for electromobility, demands new materials acting as battery and capacitor at the same time. Conductive polymers attracted attention as hybrid battery-(pseudo-)capacitor material [1,2]. However, their potential impact has not yet been fully investigated as their behaviour, especially in non-aqueous electrolytes such as ionic liquids, is not fully understood. Here, we aim to clarify the fundamental functionality of the hybrid characteristics while studying the interaction between a conductive polymer and an ionic liquid by in-operando atomic force microscopy and electrochemical quartz crystal microbalance measurements. The main achievement is the visualisation of reversible morphological modifications of the conductive polymer depending on the state of charge, influencing significantly the viscoelastic material properties. The combination of the findings provides in turn a model, explaining why conductive polymers behave like a (pseudo-)capacitor at a high state of charge and as battery at a lower state of charge [3]. To put it in context, the knowledge enables the application-orientated synthesis and use of conductive polymers as high-performance energy storage material.



Schematic model of the morphological changes of a conductive polymer in ionic liquid during charging (oxidation) and discharging (reduction).

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Deepening of the characterisation of the electrochemo-mechanical behavior of conducting polymers using electrochemical atomic force microscopy

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Electronically Conducting Polymers (ECPs) keep attracting the attention of numerous research groups worldwide as a consequence of their exciting and interdependent properties among which one can cite their mixed ionic/electronic conductivity, their redox activity, their ion and solvent exchanger behaviour, their electrochromic properties and their electrochemo-mechanical behaviour [1]. All the abovementioned properties of ECPs are electrochemically tunable, which justifies that ECPs are widely involved in a large number of applications, among which one can cite, in a non-exhaustive list, supercapacitors, batteries, artificial muscles and ion-selective membranes, tissue engineering, organic electrochemical transistors, or protection against corrosion.

The electrochemo-mechanical behaviour of ECPs has been surprisingly much less investigated than any other of the properties recalled above for this well-known family of insertion materials. It is though well established that ECPs are likely to swell and shrink as a consequence of ion and solvent exchanges occurring necessarily during the electrochemically driven switching of their redox state so as to maintain a global electroneutrality in the bulk of these materials. As a consequence of these thickness variations, one can also predict density and elasticity modulus variations of such films during these ion and solvent transfer processes. ElectroChemical Atomic Force Microscopy (EC-AFM) appears to be fully adapted to the time follow-up of thickness variations of ECPs thin films placed under an electrochemical conditioning, thanks to ideal time and spatial (vertical) resolutions and a very soft and tunable mechanical interaction between the AFM tip and the polymer film [2].

In this presentation, recent investigations involving in-situ atomic force microscopy ant its coupling with different electrochemical techniques will be reported. Original observations will be introduced and discussed in the light of various phenomena related to the electrochemo-mechanical behaviour of conducting polymers, most of which are still debated in literature nowadays and among which one can cite the memory effect [3-4], the electrochemically stimulated conformational relaxation (ESCR) [5] or electro-osmosis [6].

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Evaluation of the pseudocationic doping character of PEDOT:PSS towards Na^+ exchange. Discrimination of the mass transfer processes by coupling EQCM and PBD data

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The growing lack of non-refractory lithium minerals and the high cost of recycling lithium batteries have led the energy storage industry to try to adapt the already mature technology of lithium-ion batteries to sodium-ion. However, the conventional cathodes, that perform a high performance lithium ion exchange, cannot accommodate the sodium ion in its structure due to its larger size. A solution to this problem can go through the use of materials with some structural elasticity such as Poly(3,4-ethylenedioxythiophene) doped with poly(styrene-4-sulfonate) (PEDOT:PSS) that exhibits, in some extent, pseudo-cationic doping character. Besides the stability, the easiness of mass transfer and the level of the cation participation during the charge/discharge processes of the polymer, are then a crucial parameter for the performance of such devices.

In this work PEDOT:PSS films were electrosynthesized onto platinum electrodes from aqueous solutions containing the monomer and PSS. The mass transfer phenomena taking place during the redox conversion of the modified electrodes in organic media containing $NaClO_4$, were probed by electromicrogravimetry (EQCM) and Probe Beam Deflection (PBD). By cooperatively using the data collected by PBD and EQCM allows distinguishing the solvent mass fluxes from that of the ions, which were resolved individually by using the mathematical tool of temporal convolution of PBD data. The gathered results revealed an exceptionally fast redox conversion with >95% pseudo-cationic redox behaviour (in contrast with the ≈60% recorded for Li^+). Long runs of potentiostatic deep charging/discharging conversions of the PEDOT:PSS demonstrated the high stability of electric and mass transfer responses of the modified electrodes.

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Effect of deposition electrochemical control function on solvent content and spatial profile within conducting polymer films

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The electrochemical deposition and properties of conducting polymer filmsand their application in electronic, optical, sensing and energy storage devices have attracted huge interest. However, the literature describing this research contains many apparent inconsistencies: nominally the same material prepared by different researchers is commonly found to have different properties. This is problematic in the development of these materials for practical applications. Qualitatively, this is often attributed to variations in film structure, but without defining the nature of these variations, their origins or their resilience (or otherwise) to redox cycling that would be typical of a functioning device.

One hypothesis that has been invoked is that different electrochemical control functions result in different nucleation and growth mechanisms and/or dynamics, generating films with different internal spatial structures and solvent profiles. However, since electrochemical techniques, spectroscopic methods and surface imaging methods are unable to probe these aspects, there has been little evidence produced to test this hypothesis.

Here we describe the use of *in situ* neutron reflectivity (NR) measurements to determine both overall film solvent content and its spatial profile through polypyrrole (PPy) and poly(3,4-ethylenedoxythiophene) (PEDOT) films. The NR technique is sensitive to isotopic substitution (“contrast variation”), which we exploit via H/D substitution in polymer or solvent (*e.g.*, d_4-pyrrole polymerised from H_2O solution) to provide contrast between the polymer and solvent components of the film. Measurements were made under conditions that generated films of similar *total* polymer population to eliminate effects due solely to film thickness.

In both PPy and PEDOT cases, we determinedquantitative film solvation (both spatially resolved and integrated) for films deposited under potentiostatic (PS), potentiodynamic (PD) and galvanostatic (GS) conditions. These observations provide insights into film homogeneity and evolution during deposition, and the sharpness of the film/solution interface. *During deposition*, the effect of electrochemical control function is greater for PPy than for PEDOT. The longevity of these distinctions was explored *via* analogous observations *subsequent to deposition* (after transfer to background electrolyte),during which the films were redox cycled and allowed to relax. Interestingly, the outcomes for PPy and PEDOT were quite different. We discuss these findings in the context of applications in which film solvent distribution controls the dynamics of mobile species transport (*e.g.*dopant in an electro/optical device or analyte in a sensor) and of polymer spinal motion (*e.g.*in an actuator).

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Specific role of polyelectrolytes during electrosynthesis of different conductive polymers

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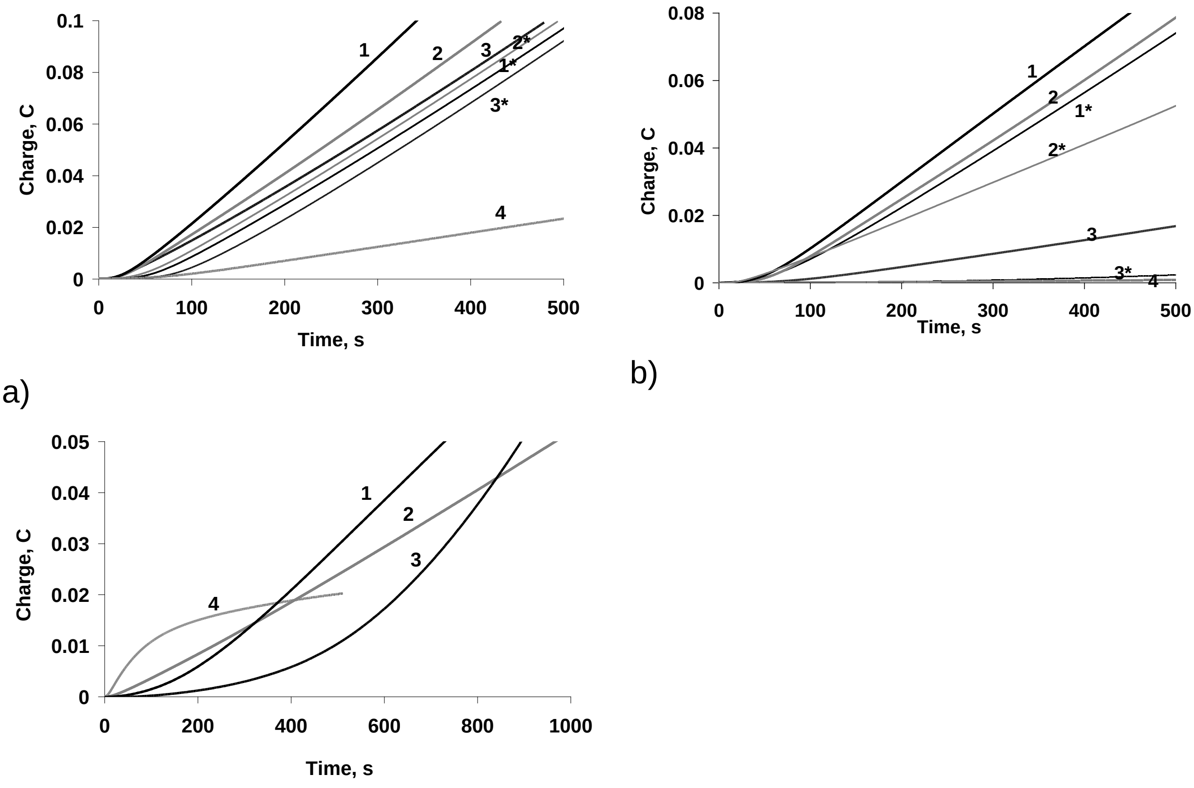
The main advantage of the using of water-soluble polyelectrolytes during electrosynthesis of conducting polymers is the possibility to modify their structure with the purpose to change optical, electrochemical and spectroelectrochemical properties. The presence of polyelectrolytes during electrochemical synthesis: 1) reduces the oxidation potential of the monomer; 2) accelerates polymerization; 3) allows to perform the synthesis at lower reagent concentrations; 4) influences the structure and morphology of the electrodeposited polymer films; 5) improves the surface uniformity and mechanical properties of the films.

The goal was to generalize results on the role of polyelectrolytes during electrosynthesis of conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and poly-(3,4-ethylenedioxythiophene) (PEDOT). The polymers were electrodeposited in potentiostatic (PS), galvanostatic (GS) and cyclic voltammetry (CV) regimes in the presence of sulfonated polyelectrolytes with different structure and different molecular weight: poly(styrene-4-sulfonic acid) (PSSA), poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA), and their sodium salts in the case of PPy and PEDOT. The course of electropolymerization was monitored by *in situ* Raman and UV-Vis spectroscopy. The films obtained were characterized by cyclic voltammetry, Vis-NIR spectroelectrochemistry.

Only slight influence of polyelectrolytes structure and their molecular weight on PPy and PEDOT electrosynthesis was found. We observed slightly higher rate of PS synthesis (Fig. 1a,b), lower onset potential of monomer oxidation and lower potential of GS-synthesis for PSSA(Na) compared to PAMPSA(Na). Also, higher rate of PS synthesis was observed in the presence of low molecular weight (LMW) PSSA(Na) compared to high molecular weight (HMW) PSSA(Na). Contrarily, the synthesis of PPy and PEDOT proceeds at higher rate in the presence of HMW PAMPSA than in the presence of LMW PAMPSA. We suppose that it is due to more pronounced hydrophobic properties and more regular distribution of hydrophobic fragments and sulfoacid groups in the coil domains of PSSA(Na). On the opposite, the sulfoacid groups of PAMPSA are distributed both inside and outside the macromolecule coils, thus less effectively compensating the cation-radical charges on the growing polymer chain.

Also the lower onset potential of monomer oxidation and higher synthesis rate of PPy and PEDOT electrodeposition was observed in the presence of polyelectrolytes in the acid form then in the salt form (Fig.1 a,b).

The spectroelectrochemical and electrochemical behavior of PPy and PEDOT films obtained in the presence of polyelectrolytes both in the acid and the salt forms, as well as polyelectrolytes of different MW, are similar to that of PPy and PEDOT obtained in non-aqueous media or aqueous inorganic electrolytes.



a)

b)

c)

Fig. 1. Time dependences of the charge during PS synthesis of PPY (a), PEDOT (b) and PANI (c) in aqueous solutions containing LMW PSSA - 1, LMW PSSNa– 1*, HMW PSSA - 2, HMW PSSNa– 2*, HMW PAMPSA - 3, HMW PAMPSNa– 3*, LMW PAMPSA– 4.

The crucial influence of the polyacid molecular weight on the electrosynthesis kinetics and properties of the films obtained was observed for PANI-PAMPSA films. In the case of LMW PAMPSA the non-autocatalytic character of PS synthesis (Fig.1 c), growth of the potential during GS synthesis and intense “middle peak” during CV synthesis were observed. These syntheses resemble aniline electropolymerization in inorganic acid medium with high pH>2.8 (insufficient protonation) or low aniline concentration. The resulting films have abnormal electrochemical and electrochemical behavior. PANI synthesis in HMW PAMPSA has pronounced autocatalytic character and the films have common electrochemical and spectroelectrochemical properties of the traditional PANI electrodeposited in inorganic acid with low pH. More coiled conformation of HMW PAMPSA chains and distribution of some sulfoacid groups inside the coils is more preferable for local aniline concentrating in the vicinity of polyelectrolyte and higher degree of aniline protonation.

In the case of PSSA there is no significant influence of the polyacid molecular weight on the character of aniline electropolymerization and the properties of PANI films thus obtained. Comparing the electrochemical properties of PANI-PSSA films with those of PANI-PAMPSA we observed hindered formation of the quinoid structures for PANI-PSSA possibly due to more rigid side chains of PSSA.

So, we suppose that in the case of PANI electrosynthesis the degree of aniline protonation, which depends on the polyacid structure, plays the crucial role. The higher degree of protonation and higher local concentration of the monomer in the vicinity of HMW PAMPSA chains leads to the acceleration of the synthesis and formation of PANI films having common electrochemical and spectroelectrochemical properties. In the case of PPy and PEDOT the crucial role belongs to the effective compensation of the positive charges of cation-radical fragments formed in the initial stage of the polymer formation by negative sulfoacid groups of polyelectrolytes. The efficiency of this charge compensation is also dependent on the polyacid structure and conformation.

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Electrochemical impedance spectroscopy monitoring of charge transport in conductive polymer film

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The work presents a novel impedance spectroscopy based technique for conductive polymer film characterization with a particular emphasis on determination of mobility and concentration of mobile charge carriers. Electrochemical impedance spectroscopy method is known for its ability to explore individual steps of electrochemical processes by frequency response analysis. However, the well-performing procedure has been worked out for investigations of relatively simple electrochemical reactions, the universal approach to study non-uniform complex systems is still to be developed.

Conductive polymers are an object of intensive electrochemical study due to unique characteristics and unlimited possibility of structure modification. Thorough investigation of charge transport in this type of materials, including acquisition of quantitative data about charge carriers, makes up an attractive, but elusive goal. The challenge has been undertaken by many electrochemistry groups with the noticeable milestones achieved by Gabrieli [1], Tanguy [2], Vorotyntsev and Inzelt [3].

Polyaniline and poly-(3,4-ethylenedioxythiophene) (PEDOT) were chosen as the most known and broadly used conductive polymers to demonstrate capability of the technique. A number of films of different thickness were deposited onto Pt electrode surface and consequently investigated in water and dichloromethane solution. The difficulties related with non-uniformity of the film, potential and concentration distributions has been overcome by separate analysis of resistive and capacitive properties in different ac frequency ranges. A mathematical model describing impedance of conductive polymer film has been worked out. It was applied for estimation of concentration and diffusion coefficients of charged species as functions of electrode potential and film thickness.

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Conducting Redox Polymers as Electrical Energy Storage Materials

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Conducting redox polymers (CRPs) is an attractive alternative as organic matter based electrical energy storage materials as they provide means of combining the favorable charge transport properties of conducting polymers with the high capacity and well defined redox chemistry of small redox active groups. In general CRPs are composed of a conducting polymer backbone where each or some of the monomers building up the polymer is bearing a redox active functional group. Although the working principle of CRPs is straightforward several key criteria need to be met in the CRP design in order to benefit from synergetic effects of the conducting polymer backbone and the pendent group in CRPs that will be outlined in this presentation: 1) As conducting polymers are only conducting in their charged state successful polymer-pendent group combinations rely on that the pendant group has a redox potential within the conducting region of the polymer backbone. This condition is referred to as redox matching and the requirement in the CRP design will be explicitly proven.[1] 2) The purpose of the polymer backbone is to provide efficient electron transport through the material. We have previously shown the polymer conductivity can be severely compromised by the pendant group.[2] This could be overcome by judicious choice of polymer backbone and results will be presented that show that non-activated (semi-metallic) electron transport can be achieved in CRPs.[3-4] 3) A final design principle that will be discussed is related to the polymerizability and how it is affected by the nature of the link between the polymer backbone and the pendent.[5] In addition a novel polymerization method for CRP monomers will be presented that allow bulk processing even for insoluble CRP-materials.

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Organometallic electrode materials for new generation of batteries

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At present, several conceptions of electrochemical energy storage devices are known. Most of them are based on inorganic active materials restricted by limited mineral resources, waste treatment processes, as well as large energy consumption in their synthesis. A possible next step in power sources development might be creation of novel organic and metalorganic "soft" materials with designed functionality.

Among advantages of the organic compounds, one can mention relatively low impact on the environment and wide scope of possible modulations of electrochemical properties by structural manipulations [1]. In particular, various functional polymers, such as conducting polymers with extended π-systems [2], and nitroxide radical tetramethylpiperidine-N-oxyl (TEMPO)-based polymers [3] are explored as potential cathode materials.

In this report we discuss organic cathode materials based on π-conjugated polymer complexes of transition metals modified by TEMPO-type functional groups with potentially high capacitance. We have tested two approaches, leading to the increase of electron and ion conductivity of organic materials. The first approach represents mechanic mixture of conductive polymers with redox-active polymers. The second approach implies chemical linkage of the redox-active centers to the polymer chain. As a result, we have demonstrated the possibility to create electrode materials with overall capacitance more than 80 mAh/g, capable to fast charge/discharge at currents more than 5 C, even at temperatures below -30 ºC.

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Bipolar Activity of Conducting Polymers to Induce Wireless Electromechanical Deformation

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For electromechanical deformation of conducting polymers, two basic requirements are needed *i.e.* an electrical contact between the polymer and the power supply, and a bilayer structure of the polymer.[1] Both of these requirements limit the range of applications of such actuators. An intrinsic bilayer structure of the conducting polymer which can be electrochemically addressed without any physical connection to a power supply should open completely new perspectives, among others for wireless (micro-)robotics. In bipolar electrochemistry, a global electric field induces wireless electrochemical reactions at the two extremities of the conducting polymer, leading for example to a colour gradient.[2] Here, we demonstrate wireless actuation of electrochemically grown polypyrrole objects based on bipolar electrochemistry. The intrinsic asymmetric morphology of the two polymer interfaces constitutes the required bilayer structure, being a key factor for the directional bending in the presence of a static electric field.[3] Furthermore, electric fields of alternative polarity allow triggering a crawling motion of a polypyrrole strip.[4] The movement is the result of a triple symmetry breaking due to unequal oxidation states of the two extremities of the polypyrrole. By further tuning and optimizing the electrochemical reactions, the wireless actuation can be employed in a straight forward way as an optical read out of chemical and biochemical information.[5] The peculiar features of these new concepts open up original pathways for the development of electrically and/or chemically triggered biomimetic actuators.

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Hybrid Electrocatalytic and Photoelectrochemical Materials for Selective Conversion of Carbon Dioxide to Fuels and Utility Chemicals

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There has been growing interest in the photoelectrochemical conversion of carbon dioxide (a potent greenhouse gas and a contributor to global climate change) to useful carbon-based fuels or chemicals. The reaction products are of potential importance to energy technology, food research, medical applications and fabrication of plastic materials. Given the fact that the CO_2 molecule is very stable, its electroreduction processes are characterized by large over-potentials. It is often postulated that, during electroreduction, the rate limiting step is the protonation of the adsorbed CO product to form the CHO adsorbate. In this respect, the proton availability and its mobility at the photo(electro)chemical interface has to be addressed. On the other hand, competition between such parallel processes as hydrogen evolution and carbon dioxide reduction has also to be considered. By proper combination of certain metal (Au, Ag, Cu) nanoparticles with nonstoichiometric mixed-metal (WO_3+ZrO_2) selective reduction of CO_2 to alcohols is in acid media feasible.

Recently, we have concentrated on the development of hybrid materials by utilizing combination of metal oxide semiconductors thus capable of effective photoelectrochemical reduction of carbon dioxide. For example, the combination of conducting polymers, or titanium (IV) oxide, and copper (I) oxide has been considered before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH_3OH) as demonstrated upon identification of final products. Among important issue is intentional stabilization, activation, and functionalization of the mixed-metal-oxide-based photoelectrochemcal interface toward better long-term performance and selectivity production of small organic molecules (C1-C4) and other chemicals. In this respect, ultra-thin films of conducting polymers (simple or polyoxometallate-derivatized) and supramolecular complexes (with nitrogen containing ligands and certain transition metal sites), sub-monolayers of metals (Cu, Au), networks of noble metal (Au, Ag) nanoparticles or layers of robust bacterial biofilms have been considered.

The photo-biocathode with Cu-containing enzyme has induced the reduction of not only oxygen but carbon dioxide as well, under illuminations with photon energies higher than silicon band gap.

In the presentation, special attention will be paid to mechanistic aspects of electroreduction of carbon dioxide, fabrication and characterization of highly selective and durable semiconductor photoelectrode materials and to importance of the reaction conditions.

Electrosynthesis of biomimetic poly(catecholamine) films with tunable properties for biosensing applications

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Dopamine is the most commonly used catechol derivative inspired on mussel-chemistry to prepare biomimetic adhesive polymers [1,2]. It spontaneously polymerizes in aerated alkaline conditions, effectively coating any type of surface with a melanin-like semiconducting thin film: polydopamine. Due to the limiting amount of oxygen in solution, other chemical approaches have been used to increase polymerization rate [3]. Nevertheless, it is still difficult to control film organization, homogeneity, oxidation state and conductivity, compromising the technological performance of this material. A very promising, yet much less explored strategy for better tuning the chemical and physical properties of polydopamine is the use of electrochemical methods for its formation [4].

Hereby, we report a comprehensive study, and novel insights on the mechanism of the electrosynthesis (potentiodynamic and potentiostatic) of distinct catecholamine monomers (dopamine, L-DOPA and norepinephrine). By electrochemical tuning, the chemical composition, redox properties, wettability, thickness can be modulated in order to have extremely biocompatible films and suitable electrochemical transducer matrixes. This work highlights the advantages of the electrochemical routes, often overlooked in poly(catecholamine) synthesis, over standard chemical methods. The performance of the biomimetic coatings on distinct electrode materials with appropriate bio-functionalizations is demonstrated for electrochemical and optical biosensors.

Acknowledgments: This work was funded by Fundação para a Ciência e a Tecnologia through PhD scholarship SFRH/BD/129566/2017 and projects: IF/00808/2013/CP1159/CT0003, UID/MULTI/00612/2013 and PTDC/CTM-NAN/0994/2014.

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Electroanalytical determination of caffeic acid and tryptophan on PEDOT-modified electrodes

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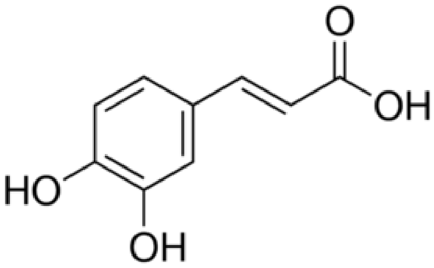
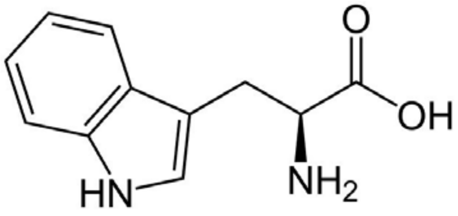
PEDOT is often used for electroanalytical studies for determination of various bioactive compounds including amino acids, antioxidants and drugs. In many cases complex multicomponent sensing materials are involved without revealing the role of the individual components for the electroanalytical reaction. The aim of the present study is to reveal the intrinsic role of PEDOT for the electrooxidation of two analytes: caffeic acid (CA) [1], an antioxidant present in wines, teas, coffee, olive oils, etc. and tryptophan (TRP), one of the five essential amino acids (Fig.1).



caffeic acid



tryptophan

Poly(3,4-ethylenedioxythiophene) (PEDOT) layers are obtained by electropolymerization in the presence of perchlorate ions and one of the two organic anions, polystyrene sulfonate (PSS) or dodecyl sulfate (SDS). Thin and thick PEDOT layers are deposited by varying the polymerization charge. Electrooxidation of TRP and CA are studied by means of cyclic voltammetry and differential pulse voltammetry (DPV). It is found that PEDOT is sensitive for both electrooxidation reactions irrespective of the doping anions used for its synthesis. Nevertheless, a marked difference in the electroanalytical performance of PEDOT is observed for both analytes.

In the case of CA it is found that depending on the thickness of the polymer layer different factors, i.e. adsorption for thin layers and diffusion for thick layers, are rate determining. In terms of electroanalytical characteristics it is established that adsorption control provides the opportunity to obtain higher electroanalytical sensitivity (23.2 μAμM^{-1}cm^{-2}) in a narrow concentration range (up to approximately 4 μM) of pseudo-linear response. A hyperbolic equation of the Langmuir/Michaelis–Menten type is suggested to model the experimentally obtained non-linear concentration dependence of the peak currents in an extended concentration range up to up to 30 μM. Diffusion control found out at thick PEDOT coatings results in markedly lower sensitivity (about 3.0 µAµM^{-1}cm^{-2}) but a further extension of the linear range up to 50 µM CA. The values for LOD found for thin and thick PEDOT layers are 0.11 µM and 1.5 µM, respectively.

On the other hand in the case of TRP oxidation cyclic voltammetry is used to obtain a linear concentration dependence of the voltammetric peak currents in the concentration range 10 to 400 µM, relevant for practical studies. The sensitivity and LOD are found to be 0.031 µA/µM and 7.5 µM, respectively. No adsorption effects are observed after long-term exposure to the analyte species. This advantageous situation is used for studying possible interference of co-analytes such as dopamine, ascorbic and uric acids. No interference effects of dopamine and uric acid are observed whereas ascorbic acid is found to add a diffusive current component to the peak current of TRP.

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Mixed-Metal-Oxide-Supports for Noble Metal Nanoparticles: Enhancement of Electroctalytic Oxidation of Simple Organic Fuels

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There has been growing interest in utilizing small (simple) organic molecules, as alternative fuels to hydrogen, in electrochemical energy conversion systems. In addition to ethanol (biofuel), that can be ideally oxidized to carbon dioxide thus delivering twelve electrons, recent important systems include dimethyl ether as well. But realistically the respective reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. PtRu) during electrooxidation of methanol and ethanol. Among important issues is incorporation of Rh nanostructures capable of weakening, or even breaking, the C-C bond in the ethanol molecules. On the other hand, rhodium itself is not directly electrocatalytic toward oxidation of ethanol. The oxides and noble metal nanoparticles have been deposited in a controlled manner using the layer-by-layer method. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites. In addition, formation of “nanoreactors” where ethanol is partitioned (at Rh) to methanolic residues further oxidized at PtRu cannot be excluded.

Electrochemical Reduction of CO_2 to Ethanol by Nanocomposite catalysts

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The increase of CO_2 concentration has become one of the most urgent environmental problems in the world. Capturing, storing and transforming CO_2 into clean energy can not only reduce the environmental problems, but also alleviate the energy crisis[1,2]. Electrochemical reduction is one of efficient methods for CO_2 utilization and recycling, which may be carried out at moderate temperature and atmospheric pressure. It also shows relatively high product selectivity compared with other reduction methods, such as chemical and thermochemical methods. However, the high over-potential for the electroreduction of CO_2 is the critical bottleneck and the main conversion products are CO, CH_4, HCOOH, and C1-related chemicals, but few C2-related chemicals or polycarbons. Herein, we reported an electrocatalyst of CuO-$CuCo_2O_4$ hollow nanospheres prepared by a hydrothermal method. It shows excellent catalytic performance in CO_2 reduction reaction, where ethanol is the only liquid production after long time reduction reaction. It`s faradic efficiency reaches more than 70%, far higher than those of C2 products in other present work. Furthermore, it is the first time to combine copper catalysts with cobalt catalysts, two widely used electrocatalytic materials. The composite metals indeed play a good synergistic role and are excellent in both morphology and catalytic performance.

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Nanostructured mixed transition metal spinel oxide thin films as efficient electrocatalysts – composition, structure and properties

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Introduction

Transition metal oxides have received renewed attention with their demonstrated usefulness as cathodes in dye-sensitized solar cells and as anodes in fuel cells. In addition, careful selection of the synthesis method and experimental conditions allow for the tailoring of the film nanostructure and surface area. However, it is clear from the literature [1-3] that the experimental parameters used for the oxide material preparation can greatly affect its electrocatalytic properties and this often makes it difficult to compare material performances. In this work, various binary and ternary cobalt oxide spinel thin films were prepared by thermal decomposition method.The films were analyzed, using several structural, chemical and electrochemical methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-rayphotoelectron spectroscopy (XPS) and cyclic voltammetry (CV). The oxygen evolution reaction (OER) was used as model reactions to determine the electrocatalytic activity of thesebinary and ternary cobalt oxide spinel electrodesand the results are compared to those obtained for Co_3O_4 spinel.

Experimental

The thermal decomposition method is a successful method for the preparation of $Cu_xCo_{3-x}O_4$ [3,4], $Ni_{1-x}Cu_xCo_2O_4$ with high x values ($0 \leq x \geq 1$) [5,6]as well as $Fe_yNi_{x-y}Co_{3-x}O_4$with high x values ($0.5 \leq x \geq 1$) and ($0 \leq y \geq 0.15$) [5]. The salt precursors were prepared by dissolving $Co(NO_3)_2.6H_2O$ (ACS Sigma Aldrich ≥ 98%), $Fe(NO_3)_3.9H_2O$ (ACS Sigma Aldrich ≥ 98%), $Ni(NO_3)_2.6H_2O$ (ACS Sigma Aldrich ≥ 98%)and $Cu(NO_3)_2$. $3H_2O$ (Sigma Aldrich 99.0% - 100.5%) in an appropriate molar ratio in a solvent mixture of isopropanol: ultrapure water in (4:1) ratiowith 10 µl ofTriton X-100.The samples were directly deposited on a clean fluorine doped tin oxide coated transparent conductive glass (FTO coated glass). The solvent was evaporated by heating at 60ºC and subsequently calcined at 300ºC (T = 400ºC for Fe containing samples) for 10 minutes. Up to five layers were prepared by repeating this procedure, and a final annealing step was carried out at 300ºC for one hour (T = 400ºC for Fe containing samples).

The surface morphology of the films was examined with a scanning electron microscope (FEI, QUANTA 3D PEG) and the composition of the prepared films were analyzed by energy-dispersive spectroscopy(EDAX GENESIS). The XRD data was collected on the X- ray diffractometer Bruker D8 DISCOVER with DAVINCI. DESIGN using Co Kα radiation (λ = 1.79026 Å). The unit cell refinement was carried out using Topas Version 4.0 software.X-ray Photoelectron Spectroscopy (XPS)experiments were performed using Instrumental Model – PHI Quantera SXM. The XPS spectra was recorded using Monochromatic Al Kα radiation of energy 1486.6 eV anda Shirley background subtraction was used for background correction. Electrochemical studies were carried out in a cylindrical Teflon cell, the potentials of the working electrode were measured against the saturated calomel electrode(SCE). Platinum wire was used as the counter electrode. The geometrical area of the electrode used in the studies was ca.0.983±0.008cm^2. The catalytic activity of the prepared electrodes for the O_2evolution reaction was assessed using cyclic voltammetry (CV). Cyclic voltammograms were recorded at room temperature using 1 M KOH. The electrochemical surface area of the electrode was determined from double layer charging curve using cyclic voltammetry by scanning the electrode potential between -100 mV to 100 mV(SCE) in 1M KOH at various scan rates. The charging current density was plotted as a function of scan rate to obtain the electrode capacitance. A value of 60 μF.cm^{-2} was used to calculate the ratio of the measured double layer capacitance and that of a smooth surface. All current densities are surface area corrected.

Results and Discussion

The addition of Cu to Co_3O_4 to form $Cu_xCo_{3-x}O_4$ resulted in an increase in roughness for x values from 0.25 to 1. When Ni is added to form the ternary oxides, the roughness more than doubles. For spinel oxides containing iron, nickel and cobalt, the roughness is much lower, i.e., around 80. EDS analysis shows that there is a reasonable correlation between stoichiometric and real composition. However,for allof our $Cu_xCo_{3-x}O_4$materialsthere is a tendency for more copper to be incorporated in the films, while for $Ni_{1-x}Cu_xCo_2O_4$ an excess of Coand a deficiency of Cu is observed. The latter effect is more pronounced as the Ni content increases.

The formation of the spinel structure is confirmed by XRD analysis. For $Cu_xCo_{3-x}O_4$ an increase of the lattice parameter with increasing copper content supports the incorporation of the copper in the spinel structure. For$Ni_{1-x}Cu_xCo_2O_4$, the lattice parameters increases with Ni content (decrease in Cu). However, the lattice parameter for $Ni_{0.25}Cu_{0.75}Co_2O_4$ does not follow the expected trend.

Figure 1 a), shows the CV over the double layer charging region and onset of oxygen evolutionfor a primary, secondary and ternary spinel oxides. While the CVs can provide some insights into the redox properties of the films (peaks around 400 mV in Fig. 1 a)), their assignment is more difficult for secondary and ternary spinel oxides. The CVs for the oxygen evolution are compared in Fig. 1 b), note that only the positive scan is shown for clarity.

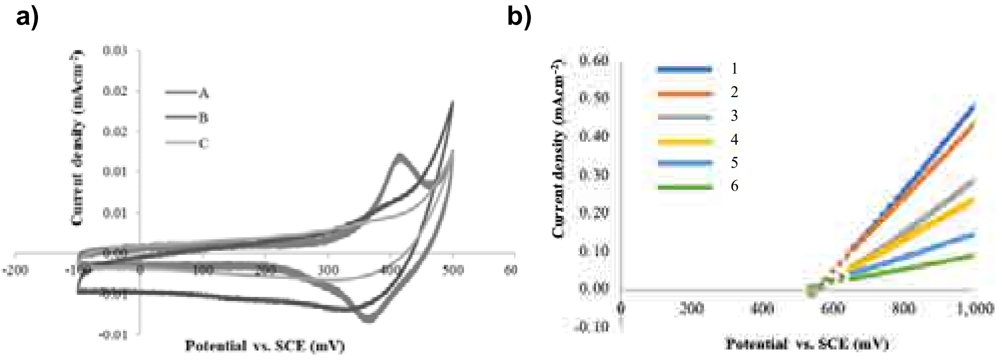

Figure 1 Cyclic voltammograms a) of A) Co_3O_4, B) $CuCo_2O_4$ and C) $Ni_{0.25}Cu_{0.75}Co_2O_4$ electrodes in 1M KOH at a scan rate of 10 mV s^{-1} and b) of 1) $Fe_{0.15}Ni_{0.35}Co_{2.5}O_4$, 2) $Fe_{0.1}Ni_{0.9}Co_2O_4$, 3) Co_3O_4, 4) $CuCo_2O_4$, 5) $Ni_{0.25}Cu_{0.75}Co_2O_4$, and 6) $Ni_{0.5}Cu_{0.5}Co_2O_4$ electrodes in 1M KOH at a scan rate of 50 mV s^{-1}.

Another important aspect of these materials is the distribution of metal cations among octahedral and tetrahedral sites available in the spinel structure. Since electrocatalytic processes depend on surface sites, XPS was used to characterize the as-prepared materials in terms of site occupancy at and near the surface. Figure 2 a) to c) compares the XPS spectra of Co 2p, Cu 2p and O 1s for Co_3O_4, $CuCo_2O_4$ and $Ni_{0.25-0.5}Cu_{0.75-0.5}Co_2O_4$.

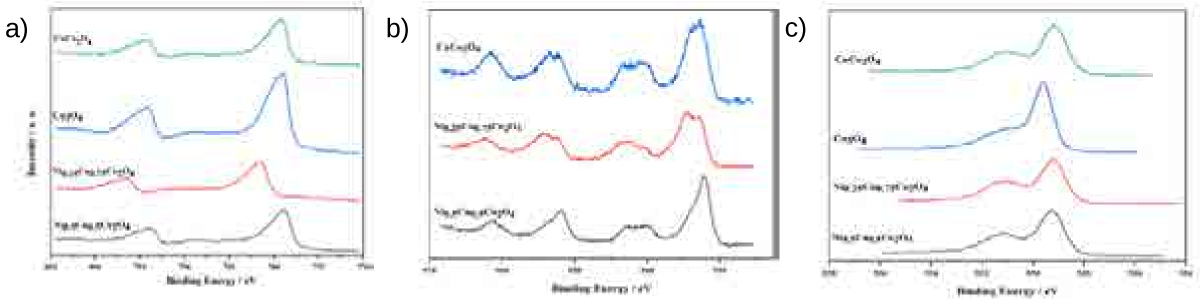

Figure 2XPS spectra of a) Co 2p, b) Cu 2p and c) O 1s for Co_3O_4, $CuCo_2O_4$, $Ni_{0.25}Cu_{0.75}Co_2O_4$ and $Ni_{0.5}Cu_{0.5}Co_2O_4$.

XPS preliminary data shows marked differences between the bulk and surface compositions of our materials (data not shown). The high resolution spectra for the Co and Cu 2p peaks also display differences, which are indicative of the existence of different Co^{2+}/Co^{3+} and Cu^{+}/Cu^{2+}ratios in these materials [7,8]. A detailed quantitative analysis will be provided in our presentation.

Adding Cu to Co_3O_4 to form $Cu_xCo_{3-x}O_4$ and Ni to $CuCo_2O_4$ to form $Ni_{1-x}Cu_xCo_2O_4$ does not increase the material's electrocatalytic activity towards the oxygen evolution reaction, when the current is corrected for the real surface area. However,compared to Co_3O_4,our $Fe_{0.15}Ni_{0.35}Co_{2.5}O_4$, and $Fe_{0.1}Ni_{0.9}Co_2O_4$ ternary spinel oxides show significant enhancement with almost double the current densityfor the oxygen evolution reaction at 1 V under the same conditions. Our results will be compared with the morphology, structure, surface and bulk compositions, and electrochemical properties of spinel oxides films of similar compositions reported in the literature.

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Promising nPt.mRu($H_{x-2n-3m}MoO_3$) catalysis for both carbon monoxide and methanol oxidation reaction

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A new method for the synthesis of nRu·mPt·($H_{x-3n-2m}MoO_3$) composite based on the redox reaction under open-circuit conditions between the reduced forms of molybdenum bronzes and solutions containing platinum and ruthenium species is proposed. Two different synthetic routes: namely, codepostion and step-wise deposition of platinum and ruthenium onto the surface of reduced hydrogen-containing molybdenum bronzes were tested. As follows from microscopy data, the uniform distribution of Pt and Ru over the electrode surface was observed in the case of their codeposition from the solution containing both platinum and ruthenium compounds. Therefore, using codeposition method for nRu·mPt·($H_{x-3n-2m}MoO_3$) catalysts preparing seems preferable.

The prepared composites were examined by the complex of physical methods included XRD, XPS, SEM, AES ICP. It was found that the maximum content of ruthenium in obtained materials did not exceed 17 at. %. XRD data showed that platinum was formed as a separate phase in the course of deposition under open-circuit conditions with red molybdenum bronzes used as a reducing agent. Other reflexes observed in the diffractogram corresponded to different types of hydrogen-containing molybdenum bronzes.

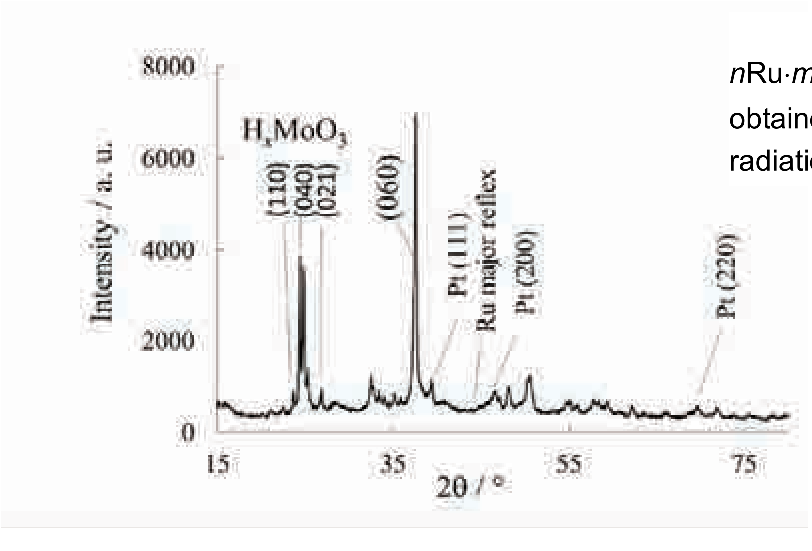

Fig. 1 Diffractogram of nRu·mPt·($H_{x-3n-2m}MoO_3$) composite obtained by codeposition. CuKα radiation.

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No ruthenium reflexes were detected in the diffractograms of obtained catalysts. Apparently, the absence of Ru reflexes is due to its low mass. It may be assumed that PtRu alloys with platinum lattice are formed in the course of currentless deposition. The formation of such alloys is typical for PtRu catalyst prepared by different methods.

Catalysts contained platinum mainly in the metallic state, while ruthenium was found in both metallic and oxidized states.

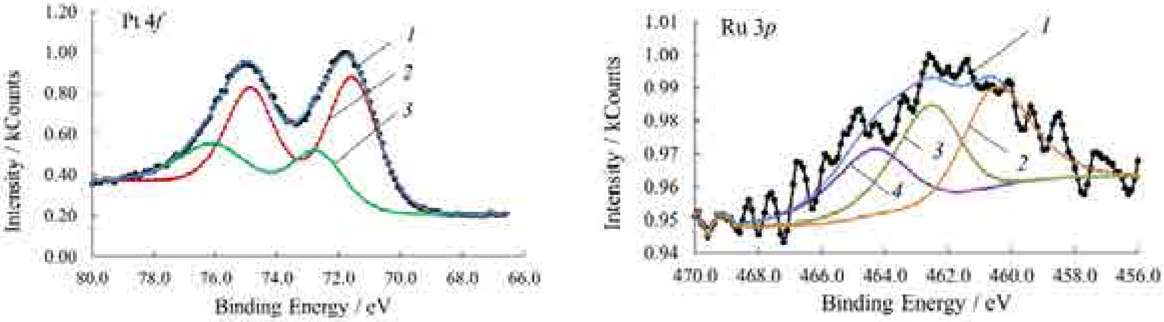

Fig 2. High-resolution Pt 4*f* (*1* – experimental data, *2* – Pt(0), *3* – Pt(2+)) and Ru 3*p* (*1* – experimental data, *2* – Ru(0), *3* – Ru(2+), *4* – Ru(3+)) XPS spectra.

The manufactured electrodes were characterized by a high catalytic activity in the reactions of carbon monoxide and methanol oxidation. CO monolayer desorption started at very low electrode potential (0.26 V vs. RHE). This fact is very promising for both carbon monoxide and methanol oxidation reactions [1].

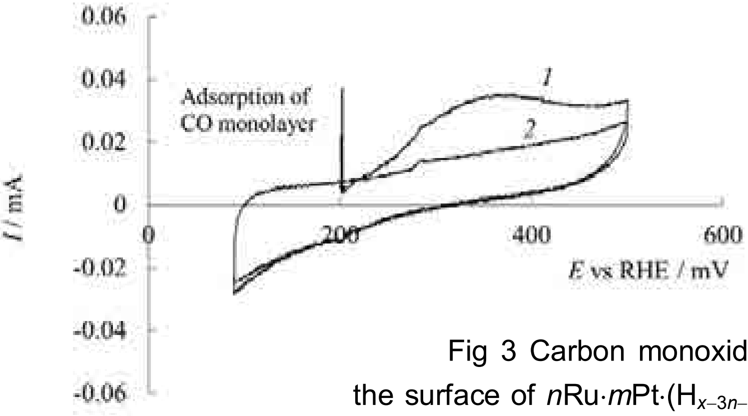

Fig 3 Carbon monoxide monolayer desorption from the surface of nRu·mPt·($H_{x-3n-2m}MoO_3$) composite (17 at. % Ru). The number near the curve indicates the number of the cycle.

nRu·mPt·($H_{x-3n-2m}MoO_3$) electrodes demonstrated high catalytic activity in both dissolved carbon monoxide and methanol oxidation reactions. The rate of the methanol oxidation reaction (MOR) on nRu·mPt·($H_{x-3n-2m}MoO_3$) was 4–5 times higher in comparison with that on nPt·($H_{x-2n}MoO_3$) [2] and ∼30 times higher as compared with that on Pt_{ed}/GC. On the basis of the obtained data, one can state the additive effect of ruthenium and molybdenum species on methanol electrooxidation. The accelerating effect is due to tightly bonded with electrode surface species (CO_{ads}, HCO_{ads}, and others [3]). This facilitates methanol oxidation through the weakly bonded with electrode surface adsorbates.

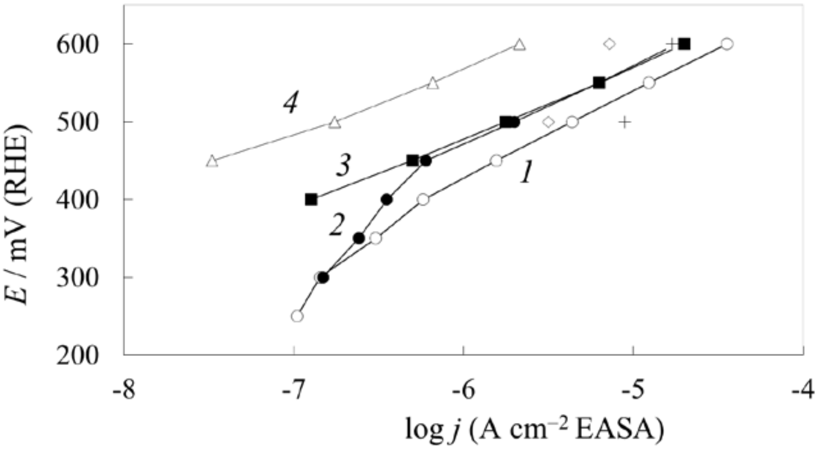

Fig. 4. Steady-state polarization curves of CH_3OH oxidation in 1.0 M CH_3OH + 0.5 M H_2SO_4 solution: *1* – nRu·mPt·($H_{x-3n-2m}MoO_3$)/GC (Composite I), *2* – nRu·mPt·($H_{x-3n-2m}MoO_3$)/GC (Composite II), *3* – nPt($H_{x-2n}MoO_3$)/GC, *4* – Pt_{ed}/GC.

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Synergistic Effects of Active Sites Nature and Hydrophilicity on Oxygen Reduction Reaction Activity of Pt-Free Catalysts

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Oxygen reduction reaction (ORR) is a fundamental step in many electrochemical applications, e.g. fuel cells and zinc/air batteries. Being kinetically hindered, ORR requires efficient catalysts typically based on Platinum Group Metals. These materials, though very efficient, present some drawbacks such as costs, availability and technological problems. Finding cheaper substitutes with similar or better electrocatalytic properties and stability is a challenge for the scientific community. Effective candidates are based on metal-nitrogen-carbon catalysts, in which metal is usually iron or cobalt.

In this work we highlight the importance of the hydrophilicity of the catalyst active sites on oxygen reduction reaction (ORR) through an electrochemical and physico-chemical study on catalysts based on nitrogen-modified carbon doped with different metals (Fe, Cu, and a mixture of them). BET, XRPD, micro-Raman, XPS, SEM, STEM and hydrophilicity measurements were performed. All synthesized catalysts are characterized not only by a porous structure, with porosity distribution centered in mesoporosity range, but also by the presence of carbon nanostructures. In iron-doped materials these nanostructures are bamboo-like structures typical of nitrogen carbon nanotubes, which are better organized, in larger amount and longer than those in the copper-doped material. Electrochemical ORR results highlight that the presence of iron and nitrogen carbon nanotubes is beneficial to the electroactivity of these materials, but also hydrophilicity of the active site is an important parameter affecting electrocatalytic properties. The most active material contains the mixture of Fe and Cu.

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Role of oxidized functional groups in the electrocatalytic properties of carbon-based nanomaterials

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Carbon-based nanomaterials, namely graphene oxide, carbon nanotubes and carbon black, are attracting the interest of the scientific community dealing with the development of electrochemical sensors. It is recognized, in fact, that when these materials are used as the sensing element of amperometric sensors, they can activate efficient electrocatalytic processes on different chemical species. These effects are of primary importance when considering the analytical performance of the final devices, in terms of sensitivity, selectivity and detection limit. Despite the importance of similar effects, their origin is often unclear and even not studied at all. This limits the development of electroactive materials in the direction sought. The possible arising of radial diffusion regimes occurring at nanostructured surfaces complicates the frame: they are often invoked in scientific literature to explain the increase of the observed peak current.

Trying to shed light to all these aspects, we are exploiting electrode surfaces possessing well-defined chemical compositions to define the correlation between the functional groups at the electrode|solution interface and the electrochemical behavior of the material with respect to oxidation of selected chemical species, namely β-nicotinamide adenine dinucleotide (NADH) and polyphenol derivatives. The rapid and effective detection of these species, in fact, is of meaningful analytical interest due to their presence in different frames, including human body and food matrices. A flat electrode surface possessing well-defined chemical composition was also used as the reference system with respect to the presence of functional groups on the carbon-based surface, in absence of radial diffusion regimes. Results coming from electrochemical, spectroscopic and morphologic analyses have been combined to obtain new insights on the role played by different moieties.

By following this approach, we could define the role played by different oxygenated functional groups present on carbon-based surfaces in the electrocatalytic oxidation of NADH: hydroxyl and carboxyl moieties on carbon-based surfaces are responsible for this quite peculiar electrochemical process. Very interestingly, hydroxyl moieties can induce strong anticipation of the NADH oxidation process from +0.47 to +0.18 V *vs*. Ag/AgCl. Shift of the electrochemical response at less positive potentials is considered an added value for the performance of the sensing element, since it increases the resolution of responses due to different electroactive species in solution and to solvent medium. For this reason, we also synthesized carbon-based nanomaterials whose surface was enriched of -OH residues. To such a purpose, we employed both a chemical and an electrochemical synthesis, exploiting, in any case, carboxylic residues already present on the edge plane of these nanomaterials. The chemical functionalization was achieved by the reaction with dopamine molecules, after activation of the carboxylic residues by N-hydroxysuccinimide and 1-ethyl-3-(dimethylaminopropyl) carbodiimide hydrochloride mixture. On the other hand, the electrochemical functionalization was obtained by Michael addition of caffeic acid molecules to carboxylic residues. The success of the proposed -OH enriching procedures was confirmed by electrochemical tests, evidencing, in any case, the arising of a reversible redox system due to 1,2-dihydroxyphenyl residues introduced as a consequence of the functionalization of the material. In addition, voltammetric tests in the presence of NADH were performed, also aiming at checking the stability of the chemical/electrochemical functionalization and the reproducibility of the preparation of the electrode coating.

By following a similar systematic approach, we are also trying to define the influence of oxidized moieties naturally present on carbon-based surfaces toward the electrochemical oxidation of various phenol derivatives. In particular, we could observe that the peak intensity due to hydroquinone and catechol oxidation significantly increases on passing from graphite to carbon nanostructured surfaces. A similar effect was also observed for morphine oxidation, which also consists in the electrochemical oxidation of the hydroxyphenyl moiety to the relevant ketone. Conversely, the oxidation peak of a reversible redox probe is not significantly affected by the variation of the electrochemical surface, indicating that the electroactive area does not change as a consequence of the modification of the surface. Although we are conscious that the different dimension of the hydrated radius of the redox probe can also affect this result, the strong difference observed on passing from bare to modified surfaces lets us conclude that oxidized residues on carbon based surface may play a role in this effect: a higher number of oxidized residues should be exposed at the electrode|solution interface at carbon nanostructured surfaces. Again, we are trying to deconvolve the contribution due to similar functional groups by using flat electrode surfaces possessing well-defined chemical composition. The study of oxidation processes of hydroquinone, catechol and resorcinol is in progress, by considering these species as model systems for more complex molecules, *e.g.* anthocyanins and flavonoids present in food matrices or drugs of abuse like morphine and heroin.

“Insulating” and mesoporous solid-templated silica films: electroanalytical signal amplification and selectivity properties

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Mesoporous silica materials characterized by well-ordered microstructure and size- and shape-controlled pores have attracted much attention in the last years for the possibility of developing functional thin films for advanced applications [1-2].

In this work, “insulating” and mesoporous silica films were prepared by spin coating a home-made silica sol on a conductive support, controlling the mesoporosity by using template Polystyrene (PS) latex beads with 30-60-100 nm dimensions. Successive multi-layer depositions were done (1-2-3-5 layers) obtaining stable, homogeneous and reproducible transparent films, characterized by an interconnected porous structure. The morphological features and the physicochemical and optical properties of the films were studied by DLS, FE-SEM, AFM, UV-vis transmittance spectroscopy and wettability analyses. A deep electrochemical characterization was also performed by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS), using two redox probes [($K_4Fe(CN)_6$) and ($Ru(NH_3)_6Cl_3$)], presenting opposite charge and different diffusional behaviour, and evidencing the effects of spatial confinement and charge selection.

In the case of “insulating” films prepared without the use of PS latexes, we proved an experimental evidence for theoretical models [3] concerning electroinactive layer-modified electrodes, with a complex balance between diverging effects (higher hydrophilicity and insulating behaviour effects of silica) when increasing the numbers of layers [4]. In the case of mesoporous layers, a better electrochemical response of smaller pores and of thicker layers was found, due to different cooperative phenomena [5].

The final devices were used in trace electroanalytical applications in real matrices, exploiting the selectivity feature (exclusion of interfering molecules) and biofouling prevention, during the determination of dopamine [5].

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Electrodecoration of iron oxide nanoparticles with bioactive nanophases for 3rd generation targeted nanoantimicrobials

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In its most general clinical sense, hyperthermia is a therapeutic procedure in which tissues are heated above normal physiological ranges. It is most often considered as an alternative therapy for illness treatment, especially when it is coupled to the use of magnetic particles (MNPs) [1]. In this respect, this class of nanomaterials attracted lot of interest for life science and biomedical applications. Some papers have demonstrated how magnetic hyperthermia can be used to selectively target sick cells, in addition to the most used therapies [2].

In our work, aiming at exploiting the characteristics of MNPs in a synergistic way with the antibacterial action provided by copper NPs, we have investigated the possible electro-decoration of magnetite NPs by CuNPs [3]. The Sacrificial Anode Electrolysis (SAE) method [4] has been used to electrodecorate Fe_3O_4 by CuNPs, by introducing preformed Fe_3O_4 NPs which were capped by different polymers, including polyacrylic acid (PAA) and polyethylenimine (PEI) in the electrochemical cell .

The morphology of pristine Fe_3O_4 and electrodecorated NPs was studied by Transmission Electron Microscopy (TEM), while the investigation on the surface chemical composition was performed through x-ray Photoelectron Spectroscopy (XPS). The atomic percentages for the electrodecorated nanomaterials are reported in Table 1.

	% C	**% N**	**% O**	**% Cl**	***% Fe***	***% Cu***
Cu@Fe_3O_4PAA	85.8	5.2	5.0	2.5	*0.8*	*0.7*
Cu@Fe_3O_4PEI	59.8	1.2	30.4	1.5	*1.2*	*5.3*

Tab. 1 Atomic surface percentages in Cu-modified Fe_3O_4 stabilized by PAA and PEI. The error is equal to 0,2% for Fe and Cu, 0,5% for all the other elements.

Data in the table show that a significant amount of copper is present on the surface of the composite nanophases. Since the resulting nanomaterials retain the

Fe_3O_4 NP magnetic properties, a possible interaction between copper and iron NPs can be hypothesized.

Further information can be derived from $Cu2p_{3/2}$ and Fe2p XP high resolution spectral regions, reported in Figure 1.

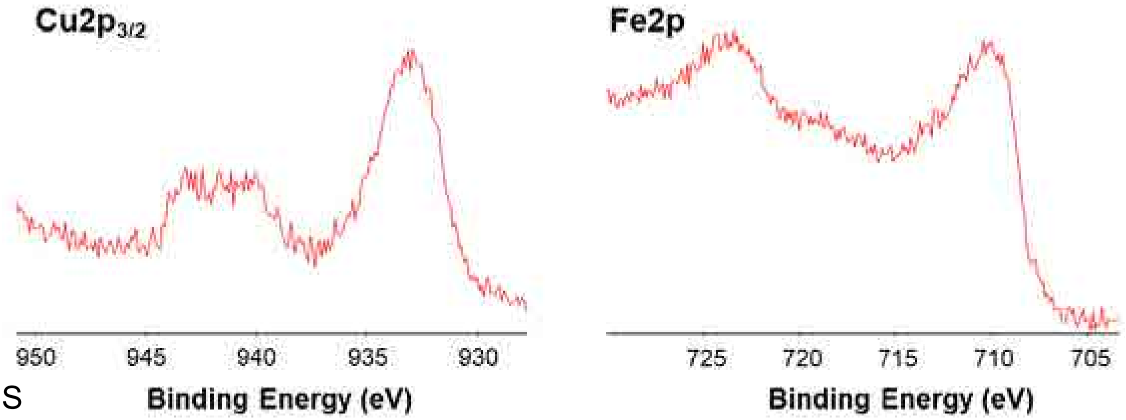

Fig. 1 Typical $Cu2p_{3/2}$ and Fe2p XP spectra for electrodecorated magnetite.

Signal shape and Binding Energy values demonstrated no evidence of a specific interaction involving the *cores* of the two inorganic nanophases (e.g. copper-iron oxide interactions). On the contrary, the combination of XPS and TEM analyses suggested that the interactions between the different nanophases involves lipophilic shells, when both the nanophases possess an inorganic core/organic shell structure. Further studies involving valence band and vibrational spectroscopy investigations will be performed to fully understand the nanocomposite nature.

Work is in progress to quantify the antibacterial effects of the nanocomposite materials and to outline how their ionic release (and, consequently, their antibacterial effect) can be influenced by magnetic fields.

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New Horizons of EQCM-D-Based Surface-Acoustic-Wave Spectroscopy for Energy Storage and Conversion

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With the increased importance of sustainable electrochemical systems for energy storage and conversion in our fast paced world, development of new *in-situ* techniques for characterization of batteries and supercapacitors are becoming in high demand. Over the recent years, the use of Electrochemical Quartz Crystal Microbalance with Dissipation Monitoring (EQCM-D) was further advanced beyond its gravimetric operation mode to be a unique and powerful tool for real-time probing of morphological and mechanical changes in operated electrodes [1]. Based on the multi harmonic responses of the resonance frequency and resonance width (or dissipation) a suitable morphological and viscoelastic modeling can be performed to extract mechanical and structural characteristics of the electrochemical processes [2-4]. The ability of EQCM-D to track formation and viscoelastic variations in the solid-electrolyte interface (SEI) formed on $Li_4Ti_5O_{12}$ (LTO) in contact with different organic electrolytes was demonstrated to be an effective method for fast evaluation of cycling performance of this electrode [5]. Recently, we presented an EQCM-D diagnostic of the particle-binder interactions in $LiFePO_4$ (LFP) and $NaFePO_4$ (NFP) battery electrodes. While relatively small volume changes are developed during Li insertion into the $FePO_4$ matrix (~6%), insertion of the larger Na ion resulting in stronger deformations in the host material (~17%), accommodation of the intercalation-induced volume changes significantly depends on the stiffness/softness of the binder used, [6] on one hand, and on the extent to which the size of the guest cation matches the size of the host sites in which the cations are accommodated. Based on the observed EQCM-D signature (i.e. a characteristic coupling of frequency and dissipation changes) during the insertion of both ions we have found a progressive softening of the NFP during cycling resulted from disintegration of the PVDF binder having a rigid nature in aqueous based electrolytes. On the contrary, the soft character of the binder in contact with organic solvents was found to be beneficial for a better accommodation of the large volume changes occurring in NFP. Our presented analytical approach can be expended for mechanical investigation of new binders, electrolyte solutions, and additives as well as for advanced high power and energy electrodes.

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Electrode Materials for Hybrid Metal Ion Batteries

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The energy storage by redox intercalation reactions is, nowadays, the most effective technology. When lithium is used as intercalating agents, the high energy density is achieved at an expense of non-sustainability. The replacement of Li^+ with cheaper monovalent ions enables to make greener battery alternatives [1]. The utilization of polyvalent ions instead of Li^+ permits to multiplying the battery capacity [2]. Contrary to Li^+, the realization of quick and reversible intercalation of bigger monovalent and of polyvalent ions is a scientific challenge due to kinetic constraints, polarizing ion effects and Coulomb interactions [3].

Herein we demonstrate how to make the intercalation of cheaper Na^+ and bivalent Mg^{2+} ions feasible. The idea is to perform dual intercalation of Li^+/Na^+ and Li^+/Mg^{2+} ions having different radii, charges, preferred coordination and diffusion pathway topology. All these features are illustrated by our recent studies on selective and non-selective intercalation properties of oxides and polyanion compounds with layered and tunnel structures [3-5]. Based on dual intercalation properties, the fabrication of hybrid metal ion batteries is presented and discussed [6].

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Li Storage in a Low Intercalation Potential i$_2$TiSiO$_5$

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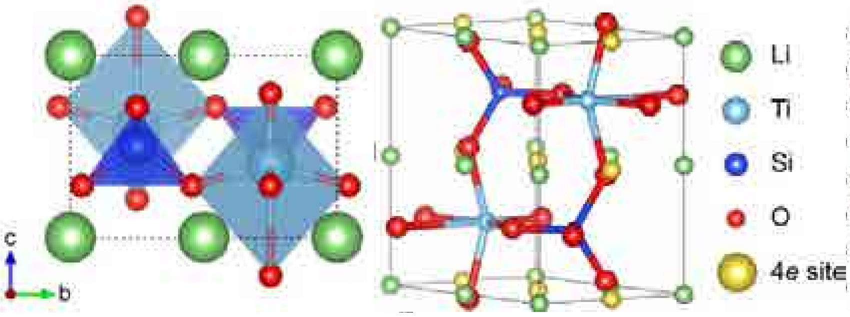
Today's anode for lithium ion batteries is dominated by graphite, with a low operate voltage at 0.1 V *vs.* Li$^+$/Li, easy to format lithium dendrite and cause to safety risk. As an alternative anode material, the "zero-strain" spinel structure $Li_4Ti_5O_{12}$ could avoid Li plating with a relative high intercalation potential (1.55 V *vs.* Li$^+$/Li) and exhibits an excellent cycling stability. However, the slightly low capacity and high voltage of $Li_4Ti_5O_{12}$ result in low energy density. Herein, we report a new anode material of Li_2TiSiO_5 as anode material for LIBs. The electrochemical profile, structure and Li storage mechanism were extensively studied [1-3].

The crystal structure of Li_2TiSiO_5 is illustrated as a layered structure with infinite sheets of distorted TiO_6 octahedra and SiO_4 tetrahedra, linked by Li atoms. The distorted TiO_6 octahedral and SiO_4 tetrahedral networks are thought to be the origin of the structural stability of this material. Along with the refined structure of Li_2TiSiO_5, the nuclear-density difference (Fourier) map in Fig. 1 reveals negative nuclear density only at the 4*d*, 4*e*, and Ti (2*c*) sites, implying that lithium can only reside at these sites. Figure 2 give the typical charge/discharge curve of $L_{i2}TiSiO_5$ at between 0 and 3 V (*vs.* Li$^+$/Li), delivers a reversible charge capacity (Li-ion extraction) of 308 mAh/g, with a voltage plateau below 1.0 V.



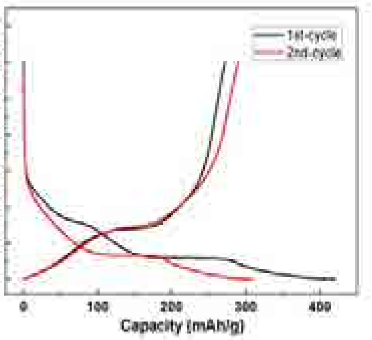


Fig. 1 Crystal structure of Li_2TiSiO_5 and Fig. 2 Typical charge/discharge curve

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Functional polymer binders for Li-ion battery electrodes

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The enhancement of volumetric energy density of Li-ion batteries is critical to meet the requirements of electric vehicles and energy storage grids. The energy density of conventional $LiFePO_4$ cathodes is limited by the amount of the added carbon conductor and inert PVdF binder which make up significant weight and volume fraction of the cathode. The performance of the electrodes can be improved by using conductive polymer binders combining adhesive properties with high electronic and ionic conductivity.

We have developed composite binders based on poly(ethylene oxide) (PEO), polyphenylene oxide (PPO), or sulfonated poly(phenylene oxide) (sPPO) as ionically conducting binders and poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT:PSS) polymer or carbon nanotubes (CNT) as electrically conducting components. Both PEDOT:PSS and CNT formed stable dispersions in PEO and sPPO solutions in “green” aqueous solvents but demonstrated poorer compatibility with PPO. The resulting composite binders have exhibited film-forming properties with electronic conductivity (1–40 S cm^{-1}), Li^+ ionic conductivity (10^{-5}–10^{-4} S cm^{-1}), and electrochemical stability over the potential range of 2.0–4.2 V vs. Li/Li^+.

The developed binders were used to fabricate $LiFePO_4$-based cathode composites. The cathodes prepared with ionically conducting PEO and sPPO binders demonstrated lower charge transfer resistance comparing to conventional PVdF binder. It has been found that both PEDOT:PSS and CNT increased the macroscopic electronic conductivity of cathode blends, resulting in improved utilization of active material capacity. Even small amounts of PEDOT:PSS and CNT (2 wt.% and 0.5 wt.%, respectively) provided sufficient electronic conductivity of the cathode material (~10^{-2} S cm^{-1}). Due to the low fraction of the electrically conductive components, the loading of the active material could be increased up to 95 wt.% resulting in enhanced energy density of the electrode. Carbon-free electrodes prepared with PEDOT:PSS and CNT also exhibited stronger adhesion to the aluminum current collector provided by sPPO and PEO co-binders. As a result, the cyclic stability of the developed cathodes was improved comparing to conventional binders.

The PEO-based binders have revealed poor cyclic performance with conventional carbonate electrolytes due to PEO solubility of in the electrolyte solution. However, that issue has been resolved by using sulfolane-based electrolytes. The PPO and sPPO binders can be used in conventional carbonate electrolytes, showing higher stability and cyclability. The PPO binder revealed improved electrochemical stability comparing to sPPO binders.

The rate capability of the cathodes is highly influenced by the cathode porosity. The cathode containing 2.5 wt.% of PEDOT:PSS, 2.5 wt.% of sPPO, and 95 wt.% of $LiFePO_4/C$ has demonstrated the optimal porosity of 43%. The packing density of the active material has been increased in the presence of sPPO binder, and the resulting cathodes have exhibited enhanced volumetric energy density at discharge rates 0.1C–50C

In summary, the developed polymer binders can replace conventionally used carbon black and PVdF in the $LiFePO_4$ cathode composition to enhance its specific capacity, cyclic performance and volumetric energy density.

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Two-dimensional porous carbon materials for high-performance supercapacitors

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Two-dimensional (2D) carbon materials have received much research interest in using as electrodes for supercapacitors by virtue of the large surface area, high electrical conductivity and well-defined structure. However, 2D carbon nanosheets tend to aggregate and restack during the electrodes pressure compaction process, leading to reduce the available specific surface and limit transport of ions.[1] Hence, it is extremely challenging to controllably design and prepare appropriate carbon nanostructure with high accessible surface area and packing density. [2] To pursue the aforementioned aims, our group developed a series of strategies (**Figure 1**) to construct the 2D carbon materials with designed morphology and pore structure, including (1) carbon nanosheets with crumpled structure, [3] (2) crumple carbon balls assembled by 2D carbon sheets, (3) monolayer carbon nanosheets with in-plane ordered mesopores, [4] (4) 2D-ZIF derived porous carbon sheets. [5] These strategies mentioned before can overcome the restacking and blocking of 2D nanomaterials, increase the ion-accessible surface area and improve the ion transport efficiency. The obtained 2D carbon materials as supercapacitor electrodes all have shown excellent electrochemical performance demonstrated by high capacitance, good rate capability, and long cycle life. These strategies presented here are promising in a wide range of applications such as supercapacitors and batteries.

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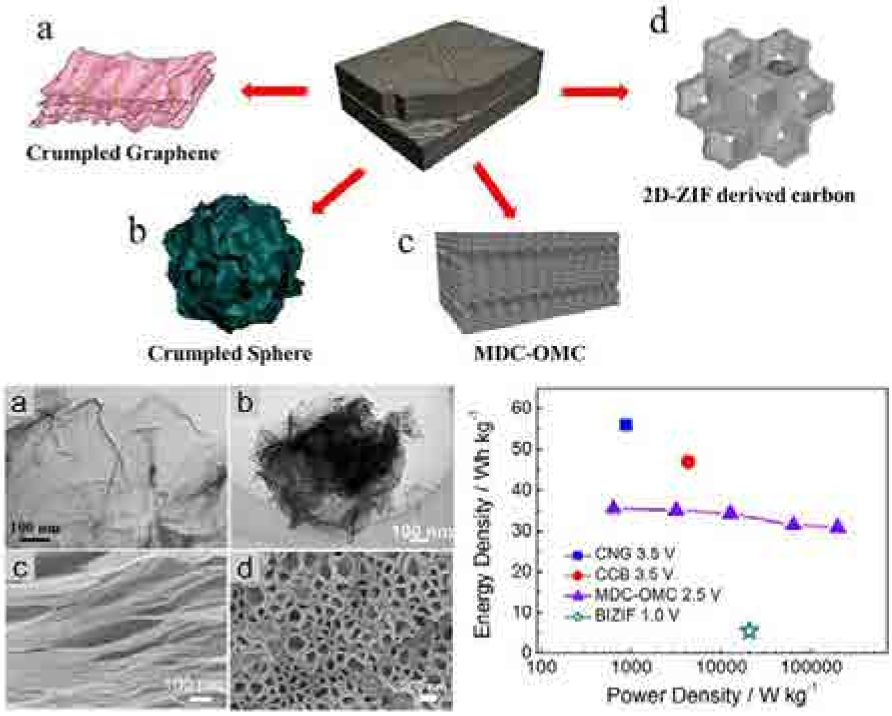

Figure 1. Schematic illustration of preparation 2D porous carbon materials and their electrochemical performance for supercapacitor.

Electrochemical Deposition of Silicon From Sulfolane Electrolytes

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Elemental silicon (Si) is one of the most important materials for the modern society, finding multiple applications in electronic industry, solar cell production technology and electrochemical energy storage. Si electrodeposition cannot be realized in water-based electrolytes due to its very low reduction potential and high reactivity of the Si precursors. As a result, a large number of unconventional media, including high temperature molten salts (HTMS) [1], room temperature ionic liquids (RTIL) [2] and other organic electrolyte solutions has been proposed. Although offering the possibility to deposit elemental Si, these electrolytes display certain drawbacks. Serious precautions must be undertaken when using volatile solvents, since they have a high vapor pressure and extreme flammability. The HTMS require high energy consumption and are very reactive. Considerable deposit contamination due to electrolyte decomposition has been observed for Si deposition from most of the organic media [2].

Sulfolane, rarely used in electrochemical applications, has a remarkable chemical and thermal stability, high polarity and very low protolytic constant. Therefore, this compound can be used as a medium to perform many chemical processes, which are in general affected by the reactivity of conventional solvents. In addition, sulfolane is an environmental friendly substance, displaying a low vapor pressure and minimal toxicity. The current contribution aims to deliver the first report on the electrodeposition of Si from sulfolane based electrolytes. Electrochemical methods, coupled with quartz crystal microbalance measurements, have been used to perform and characterise the deposition process. X-ray photoelectron spectroscopy reveals that the composition of the Si-containing deposit strongly depends on the nature of the used substrate. The electrochemical Li^+ storage in the Si material will be demonstrated.

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On the Processes of Migration and Diffusion in the Systems with Solid-State Reagents

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Solid-state insoluble and difficulty soluble reagents are common in electrochemical practice and are widely used as anode and cathode materials in many batteries, non-soluble anodes in electroplating, corrosion protection systems, electrochemical analyses, electrochemical sensors, chemtronics, etc.

However, the theory of charge transfer processes in solid-state systems is developed insufficiently and is based mainly on the classical theoretical assumptions formulated essentially for the reactions at the interface “electrolyte - solid phase”. In particular, ideas about the diffusion of protons (or ions of lithium and sodium) in solid state, for example in the battery electrodes with a solid-state reagent, can be frequently found in modern electrochemical literature. This approach is not justified for a few reasons, namely:

1. It is the difference of applied potentials and corresponding electric field strength in the bulk solid phase and at the interfaces that are, in the first place, a driving force of charge transfer in any solid-state electrochemical system. So, charge transfer in solid state in any case occurs mainly by migration but not diffusion.
2. Typical diffusion processes in solid state are too slow. For example, caused by a difference in concentrations, penetration of metallic ions into another metal on their direct “ideal” contact lasts for several months or even years (depending on the nature of the metals). Therefore, the time characteristic of diffusion processes is not comparable to the duration of electrode processes at discharge (charge) of batteries (tens of minutes, hours) and especially supercapacitors (fractions of seconds).

In many real systems involving solid-state reagents, the process of diffusion in solid phase is absent as such. The existence of such alternatives as the Grothuss, tunnel, and other fast mechanisms of cation migration in various solid-state systems often makes considering the long-duration, non-competitive and energy-consuming process of diffusion of heavy, charged particles in solid phase unnecessary.

In their attempt to justify the model of diffusion of protons (cations) in the solid phase some authors cite the linear relationship between peak currents, $I_{\max}$, in voltammetric curves and the square root of potential scan rate $\sqrt{\vartheta}$ by way of proof.

We have shown in this work that the existing linear dependence of the peak currents, $I_{\max}$, on $\sqrt{\vartheta}$ and potential difference between the anode and cathode peaks, $\Delta E_{\max}$, does not provide evidence for diffusion limitations in the reactions with a solid-state reagent but rather indicates that there is a limited stock of capacity, Q, of the active material in systems like that.

Electrochemical Age Determinations

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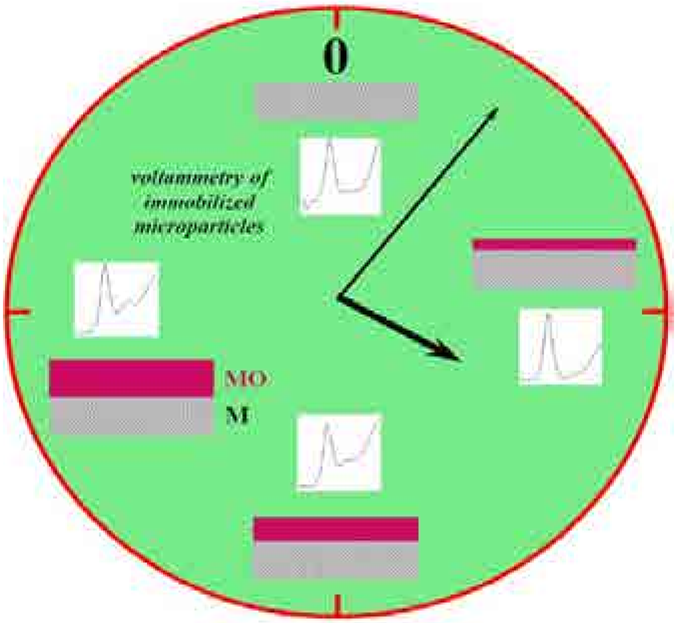
> *"What, then, is time? If no one asks me, I know what it is. If I wish to explain it to him who asks me, I do not know." Augustine of Hippo (354 – 430)*



Early in 1995, an age dependent signal of ceramic materials has been observed [1]; however, only in the last decade, a number of quantitative dating procedures have been developed for metallic and nonmetallic objects. These procedures are based on electrochemical responses of immobilized solid particles [2].

In case of metallic samples, the age determinations rely on the growth of corrosion layers, or in case of gold on time dependent alterations of the corrosion layer. So far, dating procedures of lead [3], copper/bronze [4, 5], leaded bronze [6, 7], and gold [8, 9] have been developed. Despite the dating of metals, an electrochemical approach has also been developed to quantify the aging of tars [10].

Electrochemical dating and authentification based on studies of solid samples is a vividly developing research topic opening new horizons for electroanalysis, and providing new and powerful tools for archaeometry and conservation sciences [11-15].

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Pt/metal oxide/carbon composite films for ethanol oxidation

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Metal oxides such as RuO_2 and SnO_2 can promote the oxidation of organic fuels at Pt nanoparticles in a number of ways. These include changing the d-band level of the Pt via electron transfer (electronic effect) and providing surface –OH functionality for the oxidation of adsorbed CO (bi-functional effect) [1]. Carbon black coated with a mixture of Ru and Sn oxides has been shown to increase the activity of Pt for ethanol oxidation without a significant loss of selectivity for its complete oxidation to CO_2 [2].

Here we report on the use of metal oxides prepared by thermal decomposition of metal acetylacetonate complexes ($M(acac)_n$). Oxide layers were deposited onto Ti foil and high surface area carbon electrodes, and drop coated with preformed Pt nanoparticles. Cyclic voltammetry in H_2SO_4(aq) and polarization experiments in a proton exchange membrane cell were used to study the co-catalytic effects of the oxide layers. The use of acetylacetonate precursors provides a versatile method for screening oxide supported catalysts, as well as the production of electrodes for fuel cells.

Previously, mixed Ru and Sn oxides were deposited onto Vulcan XC-72 carbon black from $KRuO_4$ and $SnCl_4$ in 0.1M KOH [2, 3]. Hydrous Ru oxides films deposited in this way are uniform, and have high electronic and proton conductivities [4]. However, it is difficult to control the incorporation of Sn into the mixed oxide, and the synthesis conditions strongly influence the activities of catalysts prepared using this method [3]. Consequently, thermal decomposition of $M(acac)_n$ complexes has been explored as an alternative and more versatile method to produce oxide coated support materials.

Initially, decomposition of $Ru(acac)_3$ and $Sn(acac)_2$ and their mixtures on Ti foil electrodes was investigated. These experiments reproduced the effects previously observed with oxide layers deposited on glassy carbon from $KRuO_4$ and $SnCl_4$ [5]. Deposits formed from both complexes increased the activity for ethanol oxidation of Pt nanoparticles drop coated onto their surfaces, while use of mixtures produced a strong synergistic effect. Deposits formed by thermal decomposition of a variety of other acac complexes, including $Ga(acac)_3$, $Zr(acac)_4$, and $In(acac)_3$, also increased the activity of Pt nanoparticles for ethanol oxidation.

Mixed Ru+Sn oxides were also produced by thermal decomposition of Ru(acac)$_3$ and Sn(acac)$_2$ on carbon black, in order to better characterize the oxide deposits and produce catalysts that could be used in fuel cells. X-ray diffraction and energy dispersive X-ray spectrometry confirmed the presence of a mixed oxide. Preformed Pt nanoparticles were adsorbed onto the oxide coated carbon, supported on carbon fiber paper, and the resulting electrodes were evaluated for ethanol oxidation in a proton exchange membrane cell at 80 °C.

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Selective Electrooxidation of Formaldehyde and Acetic Aldehyde in the Presence of Alcohols on Palladium-Polypyrrole Composites

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Palladium-polypyrrole (Pd-PPy) composites synthesized via one-step and one-pot redox procedure have been tested as electrocatalysts for formaldehyde oxidation in aqueous solution both under inert and oxygen atmospheres. It has clearly been shown that inert electrode coated by Pd-PPy composites demonstrates a high catalytic activity. Electrochemical response of Pd-PPy modified electrodes depends on the anodic potential range, pH and concentration of formaldehyde in solution as well as on the presence of oxygen in reaction atmosphere. It has been demonstrated that Pd-PPy composites are prospective materials for amperometric detection of formaldehyde in water solution even under oxygen atmosphere as well as in the presence of methanol or/and formate-anion [1].

Some interesting results have also been obtained in the case of acetic aldehyde electrooxidation in aqueous solutions, in particular in the presence of 4 or 12 M ethanol. It was shown, that silver oxide and palladium under certain conditions showed selectivity to acetic aldehyde in the presence of ethanol.

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Capacitive and non-capacitive currents in electroactive systems

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A great and rapidly increasing number of articles report capacitive origin of the current in electroactive systems with voltammetric profiles of typical electrochemically irreversible reactions [1,2]. A snapshot of errors in attribution of faradaic current to pseudocapacitance charging in a three-month period of 2016 was given in [2]. Here we present a further analysis of the problem, its origins and possible solutions based on potentiodynamic electrochemical impedance spectroscopy (PDEIS) of electroactive systems. Unlike cyclic voltammetry which leaves much uncertainty to the discrimination between capacitive and non-capacitive currents in electroactive system, the frequency response analysis provides a clear criterion of a non-capacitive current – its correspondence to branches of equivalent electric circuit composed of dissipative elements.

A capacitor charging is a reversible process with no dissipation and with possibility of charge transfer in both directions at the same potential. For the latter reason, cyclic voltammogram of a capacitive or pseudocapacitive electrode shows mirror symmetry with respect to the potential axis [3]. The Conway’s criterion of “mirror symmetry” of pseudocapacitive system cyclic voltammogram was later [1,4] transformed into an excessive requirement of a rectangular shape. The excessiveness consists in the implicit assumption of the capacitance independence on the potential (variable capacitance would not give rectangular voltammogram). Electrochemical double layer capacitances and pseudocapacitances are in fact typically potential dependent [5], so a non-rectangular shape of cyclic voltammogram does not exclude possibility of its capacitive origin. A rectangular shape can result occasionally from superposition on several pseudocapacitances distributed along the potential [3], but each of the contributing pseudocapacitances is potential dependent, as the pseudocapacitance results from intrinsically potential dependent electrochemical kinetics. The electrochemical pseudocapacitance originates typically from fast reversible electrochemical adsorption, due to surface coverage response to the variation of the potential which gives the corresponding current and frequency responses indistinguishable from those of a real capacitor [5,6].

Various indistinct meanings had been ascribed to pseudocapacitance and sometimes differential capacitance had been called pseudocapacitance, before the term “pseudocapacitance” was firmly related in electrochemistry to the capacitance originated in the electrochemical kinetics (this was substantially due to Conway’s [3] analysis of supercapacitors in terms of impedance spectroscopy in accord with the earlier [7] analysis of adsorption capacitance by Frumkin and Melik-Gaykazyan). The heritage of polysemantic use of the term “pseudocapacitance” affects present situation in applied electrochemistry, especially in supercapacitor research [1,2]. The problem is that incompatible properties of differently interpreted “pseudocapacitance” are often ascribed to the same object, e.g. a widely used scheme of article about supercapacitors combines the emphasis on pseudocapacitive system advantage as the object which can be charged and discharged fast and without energy losses with the following presentation of charge transport using equivalent electric circuit with essential contribution of dissipative elements – resistors, Warburg elements. The quantitative characteristic of supercapacitor – “specific capacitance” is widely derived by relation of total charge to the potential difference and mass without discrimination of capacitive and non-capacitive currents, though the unit used for specific capacitance of supercapacitor (farad per gram) assumes entirely capacitive origin of the current. The derivation of capacitance from the current on dissipative elements is in fact a physical nonsense. Great current at negligible potential difference is characteristic e.g. for strongly leaking capacitor which stores no energy as capacitor at all. Thus, comparison of efficiency of energy storage in various supercapacitors by their specific capacitances presented in literature appears to be practically impossible and theoretically not productive.

We also analyze the use in literature of “frequency-dependent capacitance”. The frequency dependence of capacitance normally refers to the dependence of the capacitance value on the range of frequencies used in frequency response analyses. In strict terms, a frequency-dependent capacitor has to be presented by a circuit which contains additional elements. In practical terms, however, a concept of frequency-dependent capacitance can be fruitful in certain cases, provided a researcher realizes its restrictions. There are two major cases, in which derivation of capacitance from frequency response in limited frequency range appears to be helpful. First, if capacitor is being developed for use in a certain frequency range and the frequency response analysis gives a capacitor in that particular range, then the object may be treated as capacitor, even though the circuit may appear to be more complex outside this range. Second, the decomposition of the electrochemical response into components related to double layer, interfacial charge transfer, mass transport, etc. in systems with complex mass transport was proved to be much easier with exclusion of very low frequencies [5]. Complex models of diffusion may require too many parameters to present accurately impedance contribution related to mass transport in a system with complex geometry (accounting diameter and length of pores, etc.). When the complexity of the diffusional part of impedance hinders analysis of contribution of other elements to the impedance spectrum, the rational practical solution consists in the cutting off the low-frequency part of impedance spectrum (the part which characterizes peculiarities of the spatially restricted mass transport) with the further analysis of the truncated spectrum. Complex models of diffusion impedance reduce to simpler models of the kind of Warburg element with exclusion of low frequencies, and this facilitates derivation of parameters of other contributing processes – double layer and adsorption capacitance charging, interfacial charge transfer. We have used the latter approach systematically in PDEIS [5], as the PDEIS spectrum inherently lacks information on low-frequency response at normal scan rates. In the presentation we will consider both the advantages and disadvantages of information derivation from frequency responses in limited frequency ranges.

Frequency response analysis in the extreme case of a single frequency turns to be impossible; nevertheless, in certain fields, e.g. in polymer electrochemistry a substitution of the frequency response analysis by calculation of a “fictional capacitance” (the term was coined by Fletcher et al [8]) at fixed frequencies has become accustomed with assumption of “fictional” *RC* model which is deliberately different from real model of the object under investigation in any frequency range (the assumption of *RC* model is often introduced implicitly in the form of the capacitance calculation from imaginary impedance). As the *RC* model can fit to only very limited range of real electrochemical systems, we consider the use of fictional capacitance to be generally not productive.

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Poly(3,4-ethylenedioxythiophene)/tungsten oxide composites for high rate performance supercapacitor electrodes

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Tungsten oxide was electrochemically deposited from a metastable acidic solution of isopolytungstate on glassy carbon electrodes modified with the film of conducting polymer poly(3,4-ethylenedioxythiophene). The electrochemical synthesis of PEDOT film and the formation PEDOT/WO_3 composite film was gravimetrically monitored by EQCM method. The morphology of deposits was studied using SEM and EDX analysis, including element mapping and depth concentration profile of main elements. SEM images of PEDOT/WO_3 composites show disperse distribution of WO_3 precipitates in the porous matrix of PEDOT, possessing high surface area and pore volume, effective for charge transport. Electrochemical behavior of composites was investigated in 0.5M H_2SO_4 by CV and EIS methods. CVs of composite films with different ratio of components combine pseudo-capacitive PEDOT responses and sharp symmetrical peaks of single redox couple of WO_3. Electrochemical measurements reveal high rate of charge transfer into composites, without diffusion limitations up to scan rate 0,5 V/s. One can suppose, that this fast process proceeds on the mechanism of adsorption-desorption of hydrogen charge compensating ions H^+*.* This feature is far from usually observed behavior of WO_3 deposits with diffusion controlled charge propagation.

The average value of specific capacitance of composite was found of about 324 $F \cdot g^{-1}$, whereas the specific capacitance, related to contribution of WO_3 component- 689 $F \cdot g^{-1}$. The values of specific capacitance of electrodes and their maintenance at high currents indicate that PEDOT/WO_3 could be promising electrode material for supercapacitor applications.

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Benefits from two worlds: Composites of intrinsically conducting polymers and metal oxides as supercapacitor electrode materials

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Supercapacitors used as passive electronic components on many levels from very small appliances up to vehicles and grid-connected installations are of quickly growing importance. Their high current capability makes them an almost perfect complement of batteries and fuel cells; in some cases (starter batteries) they can even replace conventional secondary batteries.

The discovery of the huge electrochemical double capacity of porous carbons in contact with electrolyte solutions has resulted in devices we now use as supercapacitors, more precisely electrochemical double layer capacitors[1 - 8]. Unfortunately the large capacity and associated high power comes with a low energy (density). As a temporary solution the combination of a battery or another electrochemical energy converter like a fuel cell with a supercapacitor is already successfully in use, but in the long run materials enabling higher energy densities are highly desirable. Various approaches ranging from tailored carbons with optimized pore sizes and pore size distributions enabling best use of the interfacial area between electronically conducting carbon and ionically conducting electrolyte solution to alternative materials utilizing superficial redox processes on electrochemically active materials are pursued.

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Almost starting with the first reports on the particular properties and capabilities of intrinsically conducting polymers ICPs their use in devices for electrochemical energy storage and conversion was suggested. At that time primary and secondary batteries were the intended application. Although the storage capabilities were not overwhelming research was pursued, but products finally failed in the market mostly.[9 - 13] More recently the redox activity of ICPs suggested their use as active masses in supercapacitor electrodes. [14,15] Somehow again now real breakthrough and success in practical application has been observed so far. Following the observation of pseudocapacitive behavior[16] of some superficial redox reactions of several metal oxides (e.g., RuO_2) the use of numerous metal chalcogenides as active masses in supercapacitor electrodes has been examined.[17,18] Perceived and real drawbacks and limitations of both materials, ICPs and metal chalcogenides, have stimulated research into their combinations.[19,20] Numerous reports on a wide variety of material combinations have attempted to take care of at least two challenges: To provide a sufficiently stable and electrochemically active material with a large electrochemically active surface area large enabling the high currents expected from a supercapacitor electrode. The second challenge has resulted in manifold architectures created by elaborate as well as by very simple one-pot synthetic procedures. They all share the same aim graphically illustrated in Fig. 1: Large interfacial area with efficient electron and ion transport. The first challenge requires a closer look at the used etal chalcogenide and ICPs. The question for their respective tasks in the com-

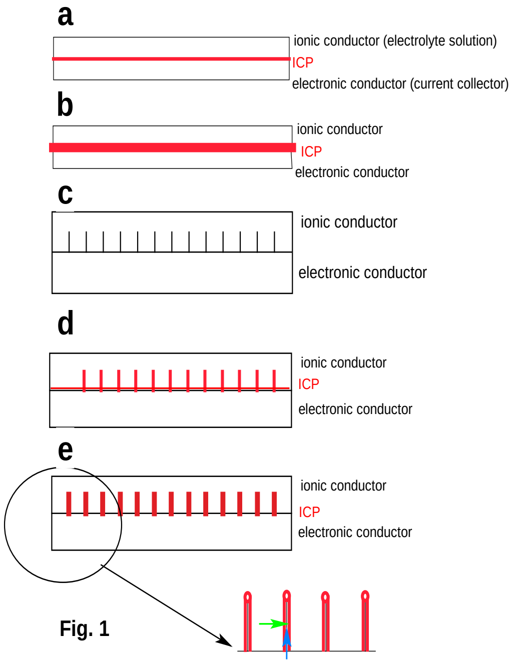

Fig. 1

(bottom right: black: electronically conducting support, red: active mass with ion (→) and electron (→) pathway)

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posites sounds very logical and rational, but is asked only infrequently. Conceivable tasks are:

- metal oxide
  - charge storage material
  - template for structuring ICP morphology
  - structural/mechanical support for ICP
- ICP
  - charge storage material
  - mechanical binder
  - mechanical stabilizer compensating volume changes
  - electronic conductance enhancer
  - dissolution inhibitor

Starting from the most frequently reported limitations of single-material electrode masses: insufficient stability, insufficient electronic conductivity (many metal chalcogenides are wide bandgap semiconductors or outright insulators) and too low storage capabilities the reported studies are focused on these properties. Unfortunately experimental parameters and settings for examining stability and storage capabilities appear to be poorly defined.[21 - 24] Accordingly reported numbers should be taken with precaution. Claims for overwhelming stability based on storage capability losses of 10 or more percent within 1000 cycles are hardly acceptable given the purpose of a capacitor (as compared to a battery).

This presentation will provide an overview, will highlight reached successes, outline general principles and suggest further lines of research and development.[25]

Acknowledgments: Preparation of this overview has been supported in various ways by the Alexander von Humboldt-Foundation, Deutscher Akademischer Austauschdienst, Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, National Basic Research Program of China, and National Materials Genome Project (2016YFB0700600), National Natural Science Foundation of China (51502137, U1601214, 51772147 and distinguished youth scientist of 51425301), and Jiangsu Distinguished Professorship Program (2016). Further support was provided by research grant No. 26455158 of St. Petersburg State University.

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UV-vis-NIR, Raman and EPR spectroelectrochemistry of organic semiconductors and their hybrids with inorganic semiconductor nanocrystals

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The progress in organic and hybrid (organic/inorganic) electronics stimulated intensive research on new organic semiconductors and hybrid nanomaterials consisting of organic semiconductors attached to inorganic semiconductor nanocrystals. Redox properties of these compounds are of crucial importance for their electronic and electrochemical properties and by consequence determine the type of their potential applications. To elucidate this problem we have performed electrochemical and spectroelectrochemical (cv, dpv, UV-vis-NIR, Raman, EPR) investigations on two groups of ambipolar organic semiconductors, namely arylene diimides and diketopyrrolopyrroles functionalized with electrodonating substituents. We have also studied by electrochemical means the effect of their binding to the surface of inorganic semiconductor nanocrystals, demonstrating that under appropriate conditions they can retain their electrochemical activity, albeit modified by electron withdrawing properties of the nanocrystal.

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Photocatalytic and photoelectrocatalytic application ZnO/TiO_2 core-shell composite decorated with Au nanoparticles

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Modification of semiconductor surfaces with Au nanoparticles (NPs) is a well-known and effective way for improvement of photocatalytic performance due to several effects: (i) increased absorption due to surface plasmons and light-scattering effects, (ii) improved charge separation and (iii) promoting electron transfer to adsorbed species [1]. On the other hand, modification of the electrode with Au NPs enhance electroreduction of oxygen to active oxygen species.

In this work we present the procedure of decoration of ZnO nanorods deposited on FTO substrate and ZnO/TiO_2 core-shell composite, with Au nanoparticles. We show that Au NPs bring an additional increase in activity of the system in photoelectrochemical water oxidation as well as in photocatalytic methylene blue (MB) decolorization. We present that the latter reaction can be considerably accelerated if a small negative potential is applied to the ZnO/TiO_2/Au composite electrode [2]. We discuss this effect in terms of the role of O_2 reduction products in MB photodegradation process. We also present that the cathodic polarization of ZnO/TiO_2/Au electrode allows overcoming the problem of inhibition of MB degradation in the presence of inorganic salt (Na_2SO_4) in the solution.

Acknowledgments: The authors thank for financial support provided by the National Science Centre (Poland) within project: DEC2012/07/B/ST5/02431 and the French Government for financial support of the Co-tutelle PhD program (MK).

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Photo-Electrode Hybrid Materials for Energy-Related Applications

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Our interest in hybrid materials is focused on the elaboration of photoelectrodes and on their integration in solar-energy conversion devices, such as solid-state Dye-sensitized Solar Cells (ss-DSCs, for photovoltaic conversion) and Dye-sensitized PhotoElectrosynthesis Cells (DSPECs, for photocatalytic conversion to "Solar Fuels").

In order to improve charge transfers and transport within photoelectrodes, along with overall stability and efficiency, we use controlled-deposition electrochemical techniques (for example, *in situ* electro-assisted PhotoElectroPolymerization (*PEP*)) for the preparation of the Hole-Transporting Material (HTM, used as a charge carrier within the device) on the photosensitized mesoporous semi-conductor of the electrode. This allows a better filling of mesoporous materials and a better contact between the components of the hybrid material/electrode.[1] Beside, using molecular engineering of bifunctional conjugates, we performed a significant improvement by removing the physical interface between the Dye and the HTM through the introduction of a covalent bond between components.[2]

We will present our recent progress in photoelectrodes design, based on photovoltaic and electrocatalytic/photoelectrochemical approaches.

Acknowledgments: This work is in part supported by PHC Polonium 2018 (n. 40588YM), the CNRS and the Université Paris Diderot - Sorbonne Paris Cité.

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Effect of composition and applied bias on charge carrier dynamics in metal-oxide/nanocarbon hybrid photoelectrodes

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One of the most critical challenges of the 21st century is the shift in energy use from fossil fuels to renewable sources. Photoelectrochemical solar energy conversion, as a potentially attractive candidate, has gained an increased momentum during the recent years. Although both water-splitting (hydrogen evolution) and carbon dioxide reduction are promising avenues, they both have substantial shortcomings to be addressed. A common virtue of these two processes is that a good photoelectrode has to concurrently fulfill many attributes to drive these reactions efficiently. One of the most important is the efficient charge carrier transport, which ensures that most of the photogenerated charge carriers can be extracted both toward the electrode/electrolyte junction and toward the back contact. Numerous promising photoelectrode material showed poor performance due to extensive charge carrier recombination both in the bulk and at the surface. A well-known example is α-Fe_2O_3 (hematite), in which the hole-diffusion length is only 2-4 nm. One possible way to improve charge carrier transport properties is to deposit the metal-oxide on an interconnected nanocarbon network (e.g., carbon nanotubes or graphene). These highly conductive nanoscaffolds can improve the transport of the photogenerated charge carriers, which in turn, results in an enhanced photoelectrochemical performance.

In my presentation, I am going to discuss how charge carrier dynamics of various hematite and hematite/nanocarbon composites is affected by the composition of the nanohybrids and by the applied bias. Nanocomposite photoelectrodes were synthesized by a two-step method: first the nanocarbon layer was spray-coated on the surface of the substrate electrode, and hematite was electrodeposited in a subsequent step. The metal-oxide/nanocarbon ratio was precisely controlled by the deposition charge density. To investigate charge carrier dynamics on a timescale ranging from seconds to femtoseconds three different techniques were employed: (i) transient absorption spectroscopy, employing a fs pump-probe setup, (ii) intensity-modulated photocurrent spectroscopy, and finally (iii) fast chronoamperometry. By covering this broad timescale, it was possible to study charge carrier transport, trapping and recombination processes, which were greatly affected by both the applied potential and the presence of the nanocarbons.

Synthesis and Electrocatalytic Properties of Poly(1,8-diaminocarbazole)/Bimetallic Nanoparticles Composites

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Organic-inorganic hybrid materials composed of conducting polymer films and metal nanoparticles dispersed in the polymer matrix focus an increasing interest due to their catalytic and electrocatalytic properties. In these composite systems the polymer plays the role of solid support for nanostructures as well as their stabilizer preventing from aggregation. One important area, where the development of highly effective catalyst is crucial, is fuel cell technology, where aqueous solution of formic acid is a promising fuel for fuel cells [1]. Among noble metal catalysts, platinum shows the highest catalytic activity for electrooxidation of formic acid but is poisoned by CO intermediate. In order to avoid it and achieve enhancement of catalytic efficiency, bimetallic Pt-Me systems are formed, in which Me=Ru, Pd or Au [2].

Poly(1,8-diaminocarbazole) (PDACz) is a polymer which combines properties of polyaniline (PANI) and polycarbazole (PCz). The monomer units in this polymer are linked mainly via C-(NH)-C head-to-tail coupling, as in the case of PANI, but only one of amino groups of each monomer molecule is involved in the coupling. Owing to presence of ‘free’ amino groups in polymer chain as well as sufficiently high difference between redox potential of the PDACz, and equilibrium potential of metal/metal ion couple, this polymer has been proposed as matrix in which metal nanoparticles can be prepared *in-situ* via electroless deposition [3]. The aim of this work was to synthesize the hybrid system in which bimetallic core-shell Pt-Me nanoparticles are uniformly dispersed in the thin polymer film, with enhanced electrocatalytic properties with respect to oxidation of formic acid. It was shown that activity of the system depends strongly on the strategy of incorporation of metal nanoparticles into the polymer matrix. The mechanism of formation of bimetallic nanoparticles has been also discussed.

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POSTERS I

Dithienopyrroles and their Derivatives as Electrochemically Active Monomers

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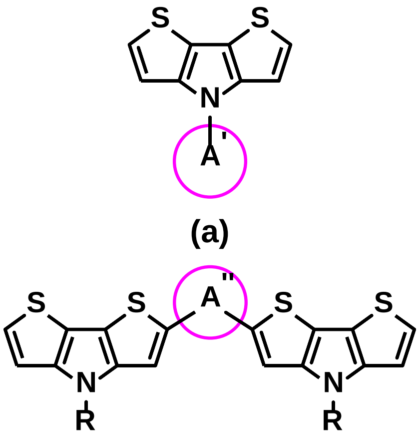
Several new conjugated polymers containing dithieno(3,2-b:2',3'-d)pyrrole (DTP) units were obtained by electropolymerization of the corresponding monomers. Redox and electronic properties of these polymers were tuned by *N*-substituting of the monomer with electron accepting groups (**A'** in Fig. 1a) [1] or by using tailor – made monomers containing an electron acceptor groups (**A"**) linked to DTP (Fig. 1b). Dithieno-substituted diketopyrrolopyrrole, thiadiazole, benzothiadiazole and tetrazine were introduced as central moieties. Upon their electropolymerization, all D-A"-D compounds, except the diketopyrrolepyrrole derivative, yielded alternating polymers of –(D-A-D)$_n$– type.



(a)

(b)

Fig.1. General chemical structure of investigated DTP derivatives.

Dithieno[3,2-b:2',3'-d]pyrrole *N*-functionalized with 4-(2-heptylthiazol-4-yl)phenyl (DTP1) and 4-(5-octylthiophen-2-yl)phenyl (DTP2) as **A'** groups readily electropolymerize to yield the corresponding polyDTP1 and polyDTP2. Thin polymeric films deposited on platinum or ITO electrodes exhibit electrochromic behavior. As evidenced by UV-vis-NIR spectroelectrochemistry, both polymers undergo classical (for conjugated polymers) oxidation, involving the formation of polarons in the first step and bipolarons in the second one. An interesting feature of the oxidation of polyDTP2 is the highly delocalized nature of bipolarons, indicative of the metallic state (featureless absorption tail extending towards NIR part of the spectrum). In order to elucidate the exact nature of the electrochemical oxidation process detailed Raman spectroelectrochemical investigations of polyDTP2 were carried out, supported by the vibrational model calculations using two methods: DFT and General Valence Force Field (GVFF). The results show that the polarons (radical cations) are formed in the pyrrole ring whereas bipolarons (dications) exhibit classical configuration with charges located in Cα positions of the thiophene rings [1].

Electrochemical and optical properties of D-**A”**-D monomers as well as corresponding electrochemically obtained $^{-}$(D-**A”**-D)$_{n}$$^{-}$ films depend on the accepting strength of the central **A”** unit. All obtained polymers exhibit ambipolar properties and electrochromic behavior in the oxidation and in the reduction processes. The smallest band gap of *ca*. 1 eV was determined for the polymer containing tetrazine moiety. This value is comparable to that previously obtained by us for dithienopyrrole–naphthalene bisimide donor–acceptor compounds [2].

Acknowledgments: Financial support from National Science Centre (NCN), Poland, Grant No 2015/17/B/ST5/00179 is acknowledged.

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The Design of Conducting Materials based on Polyaniline and Polypyrrole

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Conducting polymers, such as polyaniline and polypyrrole are obtained by the chemical oxidation of respective monomers are intractable powders with limited application potential. Yet, the control of their morphology – globules, nanofibres of nanotubes – is of substantial interest for their electrical properties [1,2]. The conducting polymers can be deposited as thin films on virtually any conducting or non-conducting surface. Various organic materials, *e.g.*, textiles, and inorganic particles, e.g. ferrites, sulfides or oxides, can be coated with conducting polymers. Colloidal dispersions and macroporous cryogels [3] (Fig. 1) are additional material forms of interest.

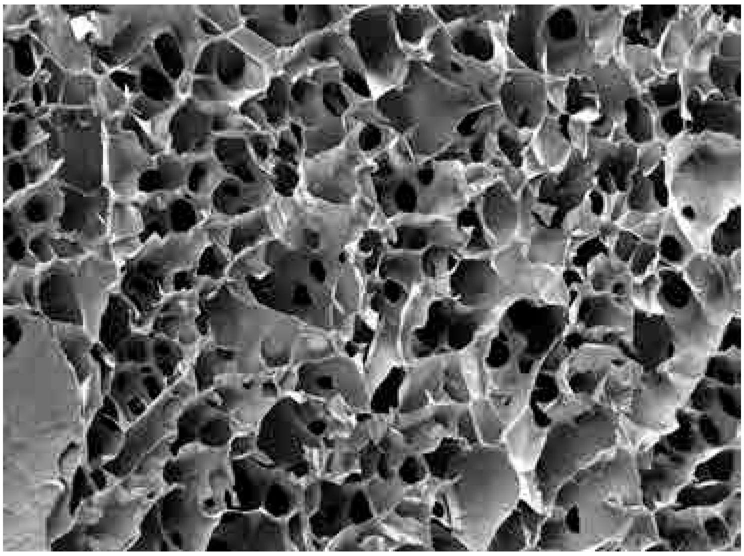

Figure 1. Freeze-dried polypyrrole cryogel stabilized with gelatin.

The carbonization of conducting polymers yields nitrogen-containing carbons, the reaction with noble-metal ions provides composites with noble-metal nanoparticles [4] applicable in electrocatalysis. Since conducting polymers are also electroactive, their composites open new possibilities also to electrochemists.

The conducting polymers may find uses because of their electrical and electrochemical properties, e.g. in corrosion protection of metals or in monitoring or electrostimulation of biological objects [5] (Fig. 2). Other properties are equally important: conducting polymers are excellent adsorbents of organic dyes and may become applicable in environmental issues, such as water-pollution treatment. Biocompatibility of conducting polymers [6] is another important feature for the design of scaffolds for biomedical applications.

Figure 2. Monitoring the response of carnivorous plant *Venus flytrap.*

Acknowledgments: The authors wish to thank the Czech Science Foundation (17-05095S) for financial support.

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Vibration Spectroscopy of Conducting Polymers: Polyaniline and Polypyrrole

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The contribution represents a set of selected studies that have been produced in last several years of active and intensive studies on conducting polymers, *viz.* polyaniline and polypyrrole, by infrared and Raman spectroscopies [1–9]. Its goal consists in the effort to guide the interested parties through the exciting pilgrimage of scientific research, which has been undertaken in the last decade, during which we have concentrated on investigations of the molecular structure of polyaniline and polypyrrole in its various forms and modifications.

Some interesting examples of the using of the vibration spectroscopic facilities in the Department of Vibrational Spectroscopy and their advantage for other scientists will be demonstrated:

- Advanced spectroscopic methods of FTIR spectroscopy have been used to detect *in-situ* time evolution of the spectra during aniline oxidation or temperature dependent spectra of samples in temperature-controlled cell.
- Resonance Raman scattering has been used to study the molecular structure of polypyrrole nanotubes. Surface-enhanced effect allowed for the detection of aniline oligomers on gold support.
- Mapping of polyaniline films with laser beam using Raman scattering.

The progress of the oxidation of aniline with ammonium peroxydisulfate in an alkaline aqueous medium has been monitored *in situ* by attenuated total reflection (ATR) Fourier transform infrared spectroscopy. The growth of the oligomer microspheres (Fig. 1) and of the film at the ATR crystal surface, as well as the changes proceeding in the surrounding aqueous medium, are reflected in the spectra (Fig. 2). The evolution of the spectra and the changes in the molecular structure occurring during aniline oxidation in alkaline medium are discussed with the help of differential spectra.

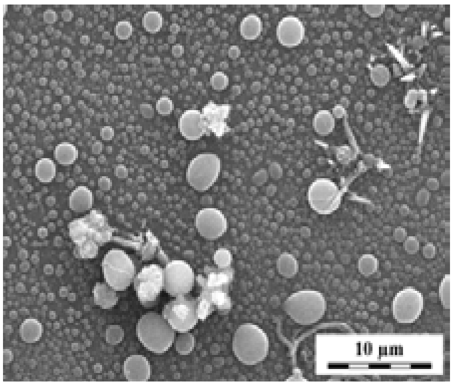

Figure 1. Aniline oligomer microspheres have been prepared during oxidation of aniline with ammonium peroxydisulfate under alkaline conditions in ammonium hydroxide solution.

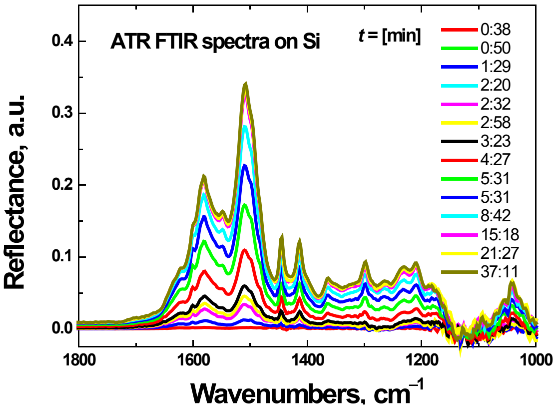

Figure 2. *In-situ* infrared spectroscopy of oligoaniline intermediates produced under alkaline conditions.

Acknowledgments: The authors wish to thank the Czech Science Foundation (17-04109S) for financial support.

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Peculiarities of Aniline Oxidative Polymerization within and on the Surface of Perfluorinated Sulfocationic Membranes

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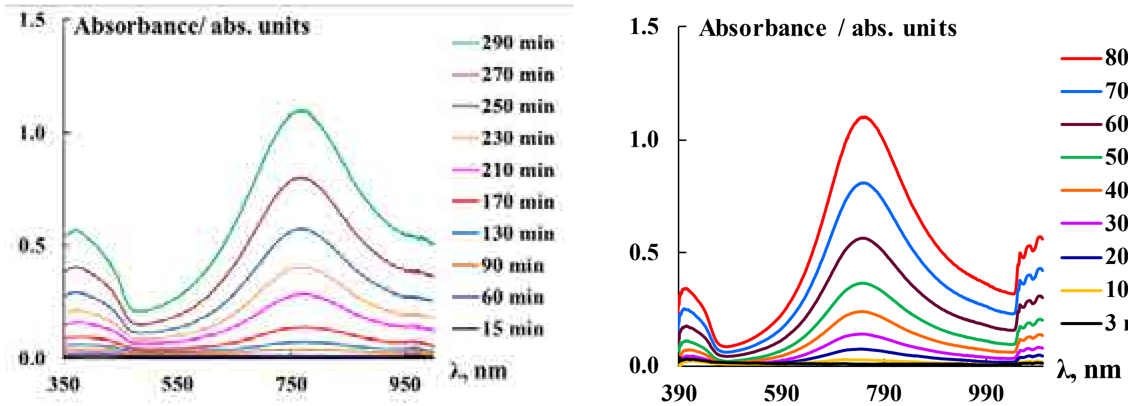
Composites based on Nafion-type ion exchange membranes and polyaniline are of great interest due to the synergy of the properties of these polymers. Understanding the mechanisms of polyaniline formation in the matrix of perfluorinated membranes makes it possible to find the way to control the preparation of composites with a given set of properties most suitable to the particular processes [1]. However, this requires research into the peculiarities of polyaniline synthesis in the perfluorinated membranes. Therefore the purpose of this work is the investigation into the sorption and kinetics of oxidative polymerization of aniline in the matrix of perfluorinated Nafion-type membranes during the preparation of optically transparent composites.

Based on systematic investigation into sorption of the monomer at every stage of polyaniline synthesis we calculated the membrane saturation degree by monomer, which was around 20% of the ion exchange capacity or 1% by weight. It was found that a portion of the non-polymerized sorbed monomer remains inside the membrane after the action of the oxidant for an extended period that makes it difficult to carry out a quantitative calculation of modifier content inside the membrane.

The kinetics of the aniline polymerization in membrane under the action of different oxidants: counter-ion ($FeCl_3$) and co-ion ($(NH_4)_2S_2O_8$) in relation to the basic matrix was studied. Fig. shows the electronic absorption spectra measured at set time intervals. Increasing the contact time of the membrane with the oxidant solution leads to a rise in the optical densities of the samples at wavelengths around 800 and 400 nm, which indicates the formation of PANI in emeraldine form almost in the first minutes of contact of the monomer-saturated membrane with the oxidant solution. From the spectral data, we calculated the average relative rate of aniline polymerization reaction for each time interval. Both dependencies have a clear power character. The polymer formation rate at the initial stage is significantly lower than at the final one. The unusual trend of kinetic curves indicates that the limiting stage of the reaction inside the membrane is the diffusion of the oxidant. Thus, the limiting stage of PANI synthesis is the diffusion of the oxidant into the membrane matrix regardless of the oxidant nature.



a b

Fig. UV-vis absorption spectra of MF-4SK membranes during the aniline polymerization in $(NH_4)_2S_2O_8$ (a) and $FeCl_3$ (b) solutions with equal equivalent concentrations. Legend defines the duration of the membrane contact with the oxidant solution.

The FTIR-spectra of surfaces of the anisotropic composite obtained by diffusion of the oxidant solution through the membrane in water were studied [2]. It was shown that in the case of ammonium peroxydisulfate shown that on the spectra of the surface contacted with the oxidant solution during synthesis there are peaks at 1500 and 1581 cm^{-1} corresponding to the vibration of structural fragments of PANI macromolecules: benzene and quinoid rings. The spectrum of the opposite side of the membrane is identical to that of the initial membrane. When using Fe^{3+}-ions as the oxidant, the penetration of the PANI chains through the membrane has taken place after 30 minutes and the spectra of both sides of the membrane are identical.

Thus, polyaniline synthesis takes place differently depending on the nature of the oxidant used: if the oxidizer is a co-ion in relation to the initial membrane the reaction proceeds in the solution near the membrane surface similarly to polyaniline synthesis on an inert support [3], but when the oxidizer is counter-ion the polymerization takes place within the membrane. This opens up the possibility to control the structure of the composite by choosing an appropriate oxidant.

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Chemical and electrochemical synthesis of polyaniline doped with camphorosulfonic and polystyrenosulfonic acids for the use as hole transporting layer in organic solar cells

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Organic photovoltaic (OPV) cells are very promising devices for low-cost and large area solar energy conversion. An efficiency of these devices depends not only on the composition of photoactive material (a donor-acceptor couple of conjugated polymer and fullerene derivative) but also on the properties of other components of the cell, especially a hole transporting layer (HTL) and electron transporting layer (ETL) [1]. Specifically, the HTL is organic or inorganic p-type semiconductor, while ETL is a thin layer of electron conducting (and hole blocking) material (such as ZnO or TiO_2). PEDOT:PSS is the most popular HTL in OPV cells owing to high transparency in the visible region, high electrical conductivity, and compatibility with thiophene derivatives used as components of active layers. However, there are some significant drawbacks of PEDOT:PSS such as hygroscopic properties and long term instability, and therefore, the alternative materials are required. Polyaniline (PANI) is considered as one of possible materials [2]. Since, the properties of the HTL depends not only on the kind of the polymer but also on the type of doping anion as well as method of synthesis, the goal of this work is to perform a comparative studies of PANI:PSS and PANI:CSA (camphorosulfonic acid) obtained by chemical and electrochemical synthesis. The parameters which are taken into account is electrochemical activity, conductivity, thermal and long term stability as well as optical properties. The OPV cells will be prepared in two geometries: standard and inverted. In the first one, PANI:PSS and PANI:CSA will be formed on FTO substrate by electrodeposition from aqueous solutions, while in the inverted cells the HTL film will be spincoated using PANI soluble in water or in organic solvent (m-cresol, chloroform, dichloromethane). In the latter case the crucial parameter will be good adhesion to photoactive layer. The method of synthesis and HTL properties will be correlated with efficiency of the resultant solar cell.

Acknowledgments:

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Pyrrole electropolymerization in the presence of sulfonated polyelectrolytes of different structure

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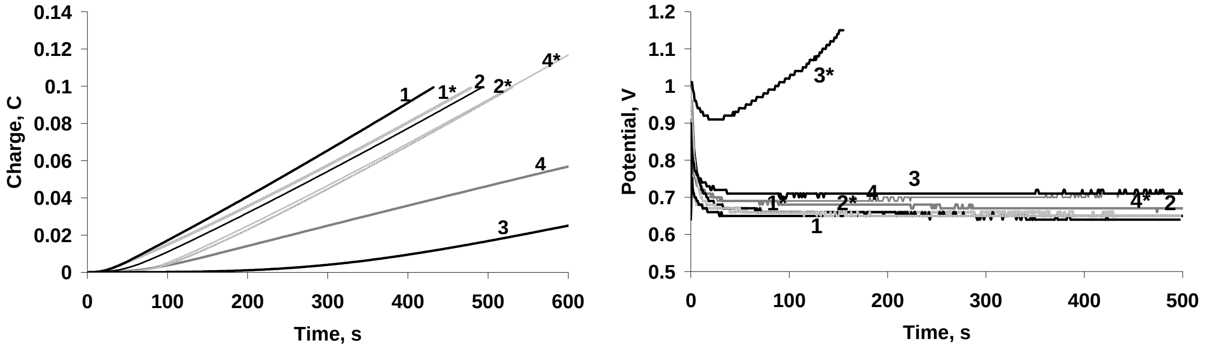
Polypyrrole (PPy) films were electrochemically synthesized in the presence of water-soluble polysulfonic acids and their sodium salts: poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, flexible-chain); poly(styrene-4-sulfonic acid) (PSSA, flexible-chain), poly-(p,p'-(2,2'-disulfonic acid)-diphenylene-iso-phthalamide) (i-PASA, semi-rigid-chain) in aqueous solutions. The pyrrole electropolymerization was performed in potentiostatic (PS), galvanostatic (GS) and cyclic voltammetry (CV) regimes and the results were compared with common synthesis of PPy in aqueous solutions of inorganic electrolytes. It was shown that the use of polyelectrolytes both in acid and salt form in PPy electrosynthesis leads to its acceleration and the possibility of using lower concentrations of reagents compared to electrosynthesis in inorganic acids and salts (Fig. 1).



a) b)

Fig. 1. Time dependences of the charge during PS synthesis (a) and potential during GS synthesis (b) of PPY in aqueous solutions containing PAMPSA - 1, PAMPSNa – 1*, PSSA - 2, PSSNa – 2*, H_2SO_4 - 3, Na_2SO_4 – 3*, i-PASA – 4 and i-PASNa – 4*.

Using Vis-NIR spectroscopy, cyclic voltammetry and spectroelectrichemistry it was shown that the course of synthesis and electronic structure of PPy depends strictly on the structure of polyelectrolyte and the nature of its cation. Shorter induction period of PS electropolymerization and lower potential of GS electropolymerization were observed in the presence of acid forms of flexible-chain polyelectrolytes compared to the syntheses in the presence of their sodium salt forms (Fig. 1). In the presence of acid forms of flexible-chain polyelectrolytes films are formed with higher degree of charge carriers' delocalization (Fig. 2), with rougher surface and spectroelectrochemical properties similar to those of PPy films obtained in inorganic electrolytes. Contrarily, in the presence of acid form of semi-rigid-chain polyelectrolyte PPy films are formed at lower rate; they are characterized by lesser roughness and lesser degree of charge carriers' delocalization (Fig. 2).

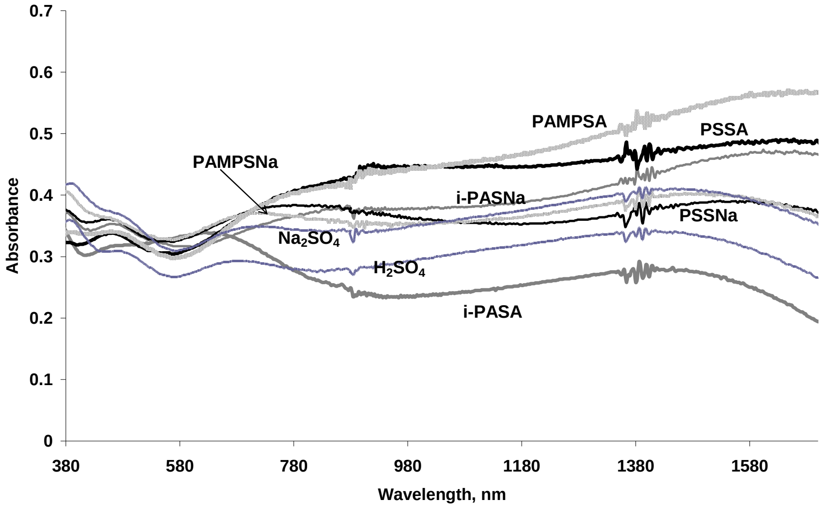


Fig. 2. UV-Vis-NIR spectra of the PPy films, electrodeposited in the presence of sulfonated polyelectrolytes of different structure, H_2SO_4 and Na_2SO_4.

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Synthesis of Polypyrrole Films Possessing an Extended Potential Range of Their Electroactivity

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Polypyrrole (pPy) polymer materials attract much attention of researchers due to their original properties. Proposed methods for deposition of pPy coatings as well as for synthesis of various pPy-containing composite materials has opened prospects for their use in a wide range of practical applications, such as molecular electronics, electrochemical sensors, supercapacitors, etc. [1-3]. One of the main methods of polypyrrole synthesis is the electrochemical method, the essence of which consists in electro-oxidation of the dissolved monomer on the electrode surface with formation of a polymer film.

The overwhelming majority of papers on electrodeposited polypyrrole arrives to the conclusion that the resulting conjugated polymer possesses an electrochemical activity potential region of about 1 V in width, the potential shift in the negative direction leads to the transition of this material into a neutral/insulator state while its shift in the positive direction results in "overoxidation" processes related to irreversible degradation. Such a narrow window of potentials of electroactivity is a disadvantage of this material, limiting its applicability, for example, as an active element of supercapacitors or a matrix for electrodeposition of most metals in the synthesis of composite metal-polymer catalysts / sensors. However, it was mentioned in [4] that using low deposition potentials and low monomer concentrations quite different polypyrrole films can be prepared, which exhibit electroactivity in a wider range of potentials. This change is irreversible and can occur either immediately after synthesis (electropolymerization) or during repeated cycling of the film in an extended range of potentials.

The goal of this work is to study and to optimize the method of electrodeposition of polypyrrole under non-conventional conditions (ensuring a low rate of polymer formation on the electrode surface), as well as to investigate the structure and properties of the obtained promising materials. To do this, we have studied the conditions in which there is an extension of the electroactivity region of polypyrrole for the subsequent purposeful enhancement of this effect (varied and measured parameters: concentration of pyrrole during electrodeposition within a sub-mmol range, low oxidation potential small thickness of the polymer coating, multi-scan parameters of the obtained polymer film). Resulting films have also been studied via cyclic voltammetry, UV and IR spectroscopies and SEM microscopy.

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Study of Polypyrrole Films Possessing an Extended Potential Range by the Method of Electrochemical Quartz Crystal Microbalance (EQCM) and the Spectroelectrochemical Method

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Polypyrrole (pPy) is widely used in various electronic, electrochemical and membrane technologies as an electroactive polymer with high electrical conductivity and high chemical stability [1].

There are two main ways of synthesis of conducting polymers based on heterocycles. In the first method, the dissolved monomer is oxidized at the electrode surface with the formation of the polymer film. In the second method, the monomer is oxidized in a solution of a chemical agent with a deposition polymer in powder.

Polypyrrole films synthesized by the electrochemical method have a relatively small window of electroactivity potentials. The authors of work [2] have revealed the possibility of obtaining polypyrrole having electroactivity in a wider range of potentials, unlike polypyrrole obtained under traditional conditions (having an electroactivity potential window of about 1 V). To achieve this effect, it is necessary to use low polypyrrole electrooxidation potentials, low monomer concentrations in the electropolymerization medium and multiscan of the obtained polypyrrole film in a monomer-free solution.

The goal of this work was to study the effect of expanding the region of electroactivity potentials of polypyrrole during its multicycling using the method of electrochemical quartz crystal microbalance (EQCM) and the spectroelectrochemical method. The first method allowed to estimate the input and output of ions of the background electrolyte when cycling the polypyrrole-modified electrode. The spectroelectrochemical method made it possible to track changes in the absorption spectra of a polypyrrole film when it was multiscanned in a background electrolyte solution.

Acknowledgments: This work was supported by the Russian Foundation for Basic Research (project no. 19-33-01303 mol_a).

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Synthesis and Electropolymerization of 3-arylthieno[3,2-b]thiophenes and Triphenylamine based Comonomers

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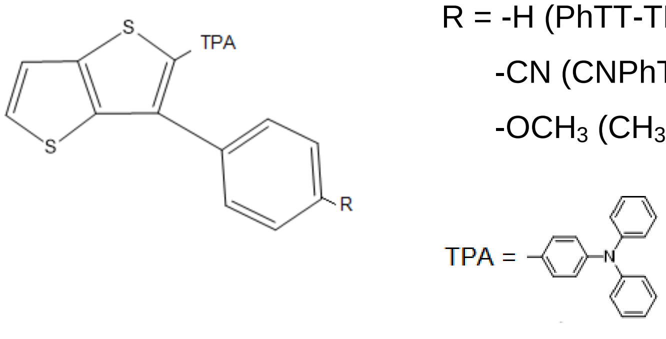
Electropolymerization is a useful tool for the synthesis of new conjugated polymer films for various applications in material chemistry. Thieno[3,2-b]thiophene, (TT) plays an important role on designing conducting polymers, due to its rigid structure and good π-conjugation system [1]. 3-phenylthieno[3,2-b]thiophene (PhTT) can be obtained by para-substitution with phenyl groups at C-3 of TT and properties of TT can be improved for applications [2].

Triphenylamine (TPA), possessing a three–dimensional propeller structure having a good hole transporting ability, Enhancement of light emitting efficiencies was attempted through the incorporation of PhTT and TPA[3,4].

Herein, electrochemical polymerizations of TT's possessing, cyano(CN) and methoxy(OCH_3) substituted phenyl and TPA were conducted. Polymeric films were characterized by cyclic voltammetry(CV), electrochemical impedance spectroscopy (EIS) and spectroelectrochemical measurements with a Gamry 600 model potentiostat.



R = -H (PhTT-TPA)
-CN (CNPhTT-TPA)
-OCH_3 (CH_3OPhTT-TPA)

Scheme 1. Structure of phenylthieno[3,2-*b*]thiophenes.

A Pt button(0.022 cm^2), a platinum and a silver wires were used as working, counter and pseudo reference electrodes respectively. The electrolyte was DCM:ACN(1:9) including 0.1 M sodium perchlorate($NaClO_4$).

Spectroelectrochemical data were recorded on a Schimadzu 160 A model UV–visible spectrophotometer. A three-electrode cell system was used where the working electrode was ITO, counter electrode was a Pt wire and pseudo-reference electrode was Ag wire.CV's of PhTTTPA, CH_3OPhTTTPA and CNPhTTTPA obtained during polymerization and the reversible redox behaviours of the resulting polymers(P[PhTTTPA], P[CH_3OPhTTTPA] and P[CNPhTTTPA]) were given in Figure 1 and the comparison of first scans of the CV's obtained during and after polymerization were compared in Figure 2 . The highest onset potential of monomer was found in the case of CH_3OPhTTTPA(Figure 2a). This might be due to the electron donor property of -CH_3O substitution of the PhTTTPA.

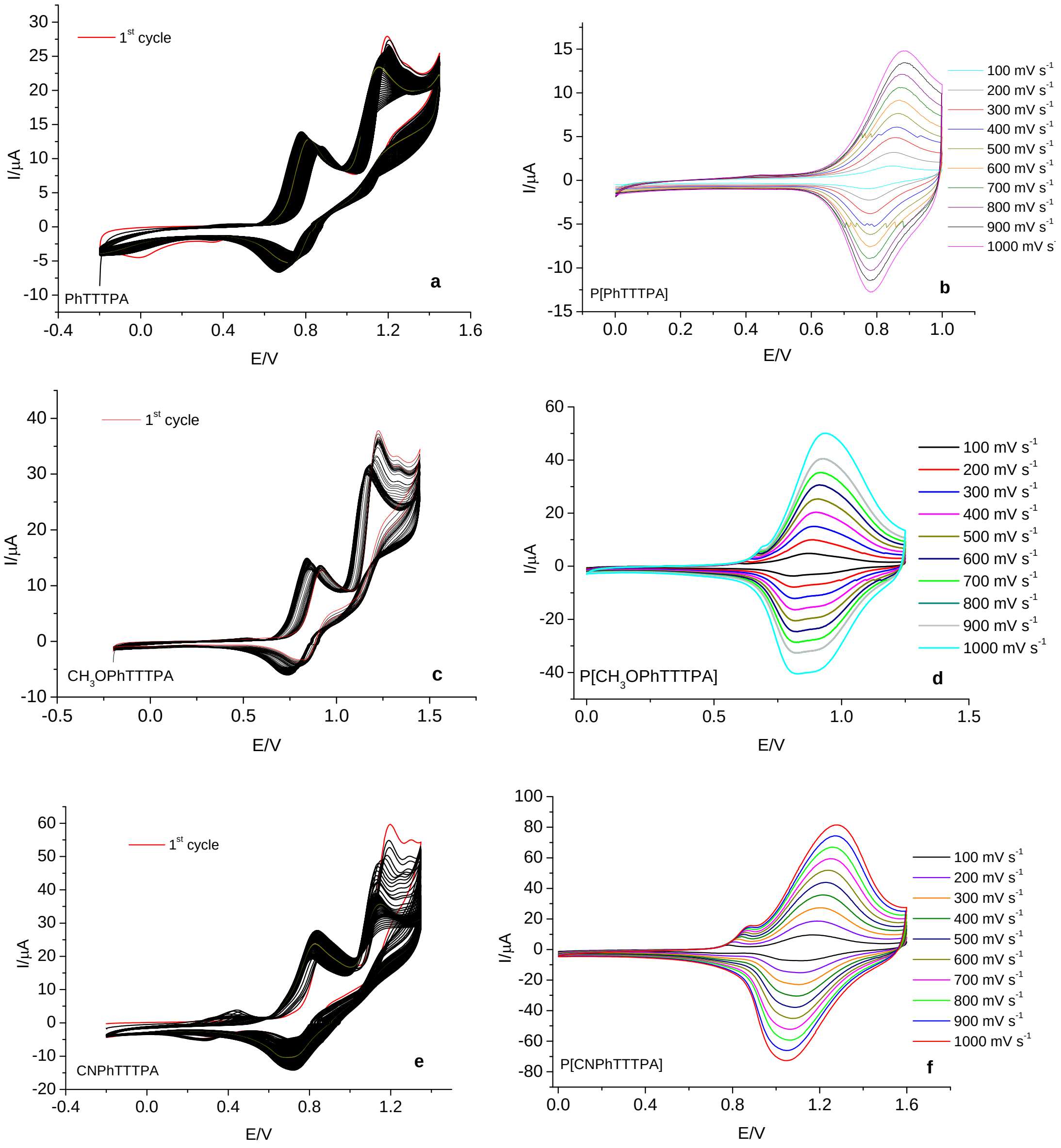


Figure 1. Cyclic voltammograms of PhTTTPA (a,b) ,CH_3OPhTTTPA (c,d) and CNPhTTTPA (e,f) during and after polymerization in 0.1 M $NaClO_4$ respectively.

The comparison of redox behaviour of polymer films in monomer free solution suggested that, due to electron witdrawing character of –CN group, slightly lower oxidation potential of CNPhTTTPA(Figure 2a) resulting higher thickness of the film and slightly higher oxidation potential were obtained for P[CNPhTTTPA] (Figure 2b).

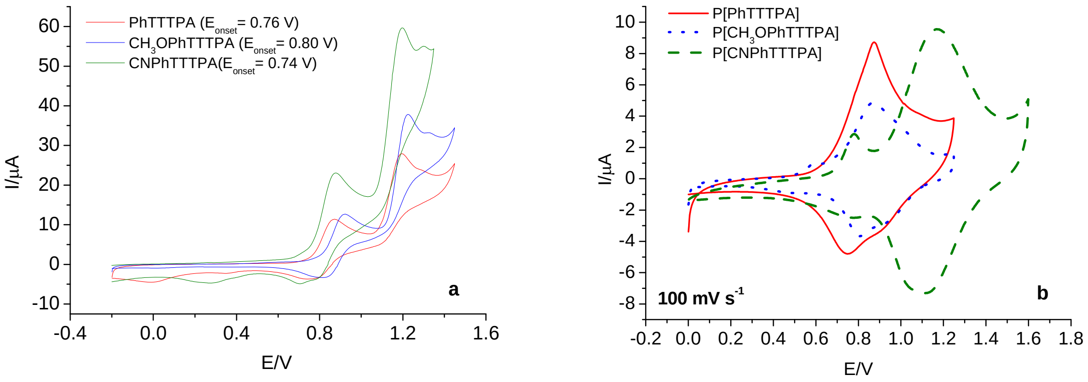


Figure 2. Comparison of and first cycle of CV's obtained during polymerization (a) of PhTTTPA, CH_3OPhTTTPA, CNPhTTTPA and of P[PhTTTPA, P[CH_3OPhTTTPA] and P[CNPhTTTPA] in monomer free solution (b).

EIS measuremenst of polymers were performed at different direct potential applications (E_{dc} = 0.0 V-1.0V) and results were compared (Figure 3). Results suggested that P[CH_3OPhTTTPA] shows better capacitive properties than the others.

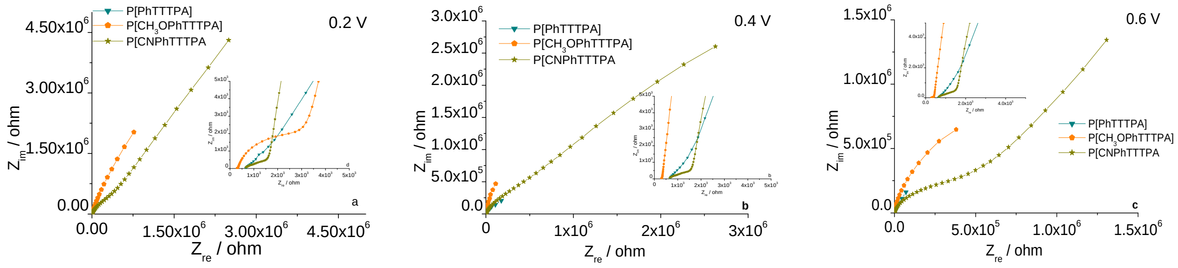


Figure 3. Comparison of Nyquist diagrams of P[PhTTTPA], P[CH_3OPhTTTPA] and P[CNPhTTTPA] at different E_{dc}; 0.2 V**(a)** 0.4 V**(b)** and 0.6 V **(c)** in $NaClO_4$.

Comparison of spectroelectrochemical behaviours of polymers showed that, E_g values of P[PhTTTPA], P[CNPhTTTPA] and P[CH_3OTTTPA] are 2.58, 2.15 and 1.96 eV, respectively.

As a conclusion in this study, P[PhTTTPA], P[CNPhTTTPA] and P[CH_3OTTTPA] were obtained by electropolymerization, redox and capacitive behaviours of polymers were compared. Results suggested that presence of TPA unit give better electrochemical reversibility to polymers and –CH_3O group lowers the band gap, enchanced the charge storage chracteristics, while oxidation potential can be decreased by -CN substitution.

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Electrochemical polymerization and characterization of 4,4'-(Dithieno[3,2-b;2',3'-d]thiophene-3,5-diyl)dibenzonfloride and copolymerization with 3,4-(ethylenedioxy)thiophene

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Designing proper materials by introducing donor and acceptor units to tune the band gap of the conjugated polymers is extremely important. Dithienothiophenes (DTT) are electron rich, planar, and rigid π-conjugated materials, which have been crucial building blocks of many materials for electronic and optical applications like electroluminescence, photochromism, nonlinear optical chromophores, and transistors with high mobilities of on/off ratios, and conducting polymers [1]. Also, DTTs are fluorescence molecules due to the easily oxidized sulfur of the middle of the thiophene ring and this feature allows them to be used in different applications [2]. 3,4-ethylenedioxythiophene (EDOT) has appeared as thiophene derivative combining high conductivity, low band gap, good electrochemical properties [3,4].

In this study, 4,4'-(2,6-di(thiophen-2-yl)dithieno[3,2-b:2',3'-d]thiophene-3,5-diyl)dibenzofloride (Th-FPhDTT-Th) was synthesized and electrochemically polymerized and P[Th-FPhDTT-Th] was obtained. In order to improve the properties, it was also copolymerize with EDOT to obtain P[(Th-FPhDTT-Th)-EDOT]. The resulting polymers were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), ATR-FTIR, UV-Visible and fluorescence spectrophotometric measurements.

Electrochemical measurements were performed with a 2263 Parstat model potentiostat interfaced to a PC. A glassy carbon (GC) electrode (2 mm^2), a platinum wire and a silver wire were used as working, counter and pseudo reference electrodes respectively. Spectroelectrochemical data were recorded on a Schimadzu 160 A model UV–visible spectrophotometer. A three-electrode cell system was used where the working electrode was ITO-coated glass slide, counter electrode was a Pt wire and pseudo-reference electrode was Ag wire. Sodium perchlorate ($NaClO_4$), lithium perchlorate ($LiClO_4$), acetonitrile (ACN) and dichloromethane (DCM) were analytical grade chemicals.

Copolymerization of Th-FPhDTT-Th with EDOT were also performed in ACN:DCM (7:3) containing 0.05 M $NaClO_4$ and 0.05 M $LiClO_4$ at 6 cycles in the range of 0-1.6 V at the scan rate of 50 mV/s comparatively with homopolymers (Fig. 1). Homopolymers and copolymer (P[(Th-FPhDTT-Th)-co-EDOT]) showed good redox behaviour even at very high scan rates (Fig. 2). By clear contribution of Th-FPhDTT-Th unit to pseudocapacitive humps within the CV around 0.7 V and non-faradic current of PEDOT blocks, P[(Th-FPhDTT-Th)-EDOT] shows improved supercapacitor behavior.

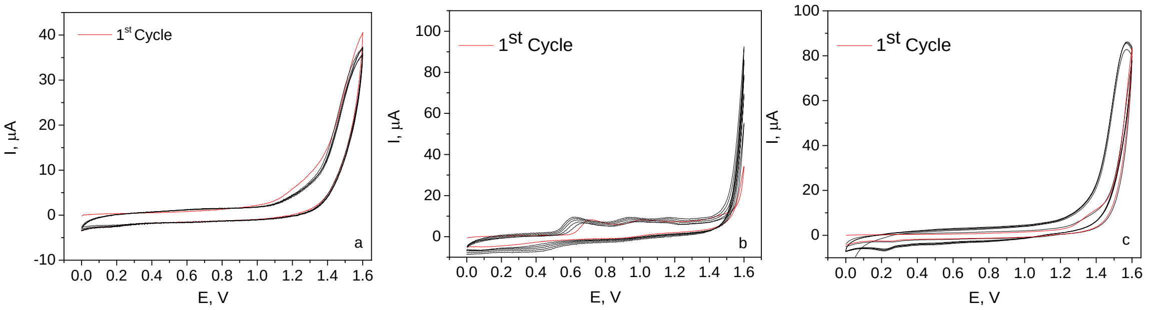

Figure 1. Polymerization of a) Th-FPhDTT-Th, b) EDOT and c) [(Th-FPhDTT-Th)-EDOT] in ACN:DCM (7:3) containing 0.05 M $NaClO_4$ and 0.05 M $LiClO_4$ at 6 cycles in the range of 0-1.6 V.

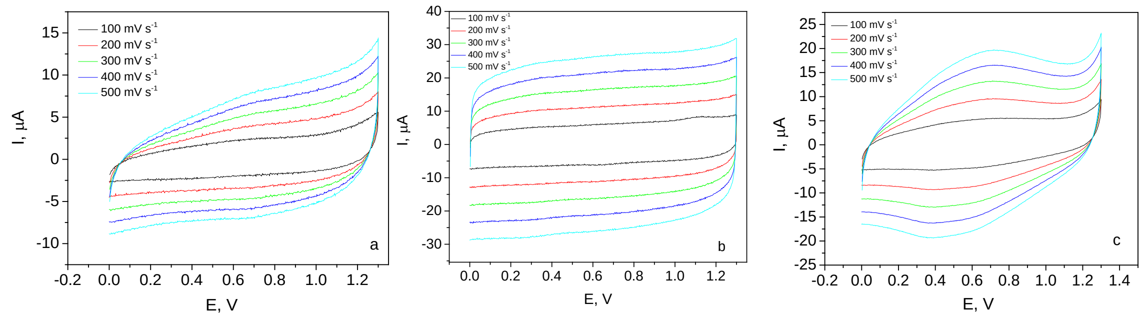

Figure 2. Scan rate dependence of a) P(Th-FPhDTT-Th), b)PEDOT and c) P[(Th-FPhDTT-Th)-EDOT] in ACN:DCM (7:3) containing 0.05 M $NaClO_4$ and 0.05 M $LiClO_4$.

Nyquist and Bode diagrams of polymers were shown in Fig. 3 and Fig. 4. When E_{dc} is equal or higher than 0.6 V for P(Th-FPhDTT-Th) and P[(Th-FPhDTT-Th)-EDOT] and 0.8 V for PEDOT, this capacitive behaviour was destroyed, (Fig. 3). In the case of E_{dc} = 0.0V, polymer shows generally capacitive behaviour in the frequency range of 0.01-100 Hz (Fig. 4).

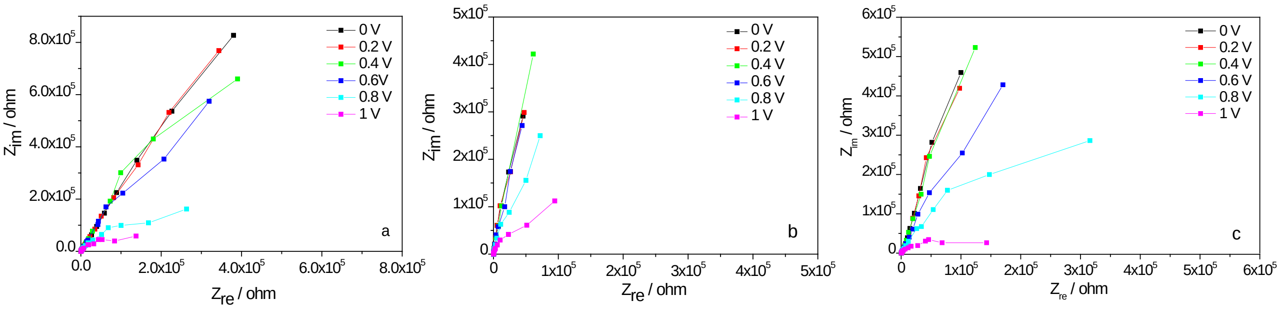

Figure 3. Nyquist plots of a) P(Th-FPhDTT-Th) b) PEDOT and c) P[(Th-FPhDTT-Th)-co-EDOT].

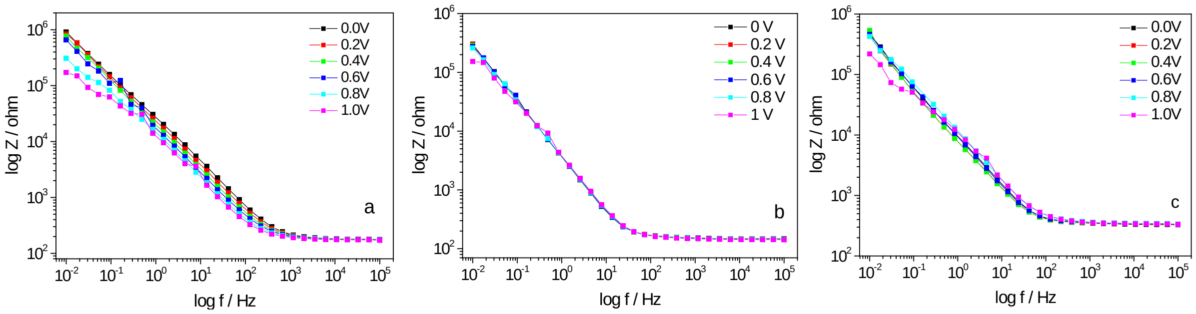

Figure 4. Bode plots of a) P(Th-FPhDTT-Th) b) PEDOT and c) P[(Th-FPhDTT-Th)-co-EDOT].

As a conclusion, in this study Th-FPhDTT-Th alone and in the presence of EDOT were electropolymerized by potentiodynamic polymerization at different polymerization charges. Results suggested that the film obtained by applying 6 cycles shows the best reversible redox behaviour. Inclusion of EDOT to the structure has an advantage for charge storage ability at low potentials and at E_{dc}= 0.4 V the highest value was obtained. Optimize capacitance of P[(Th-FPhDTT-Th)-co-EDOT] was achieved by the interaction between faradic charge transfer characteristic of P[Th-FPhDTT-Th] and double-layer type charge storage characteristic of PEDOT.

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Synthesis and Optoelectronic Application of Thienothiophene and Dithienothiophene Molecules

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1. INTRODUCTION

Thieno[3,2-b]thiophene (TT) and dithienothiophenes (DTT) are important molecules for the electronic and optoelectronic materials chemistry. These heterocyclic compounds have electron rich structures and planarity of fused thiophene conformation. Compared to thiophene(Th), fused Th rings, in the polymer form, is advantageous with lower band gap, extended π conjugation systems and high mobility on carrying charge.[1,2] TT and DTT can be used as a donor in the variety device structures such as organic light emitting diod(OLED), solar cell, electrochromic device (ECD) and capacitor etc.

In this work, TT and DTT structures combined with phenyl (Ph) group containing strong electron attractant fluorine (F) atom. Eventually, FPhTT and FPhDTT compounds were obtained, polymerized and characterized by electrochemical and spectrophotometric measurements.

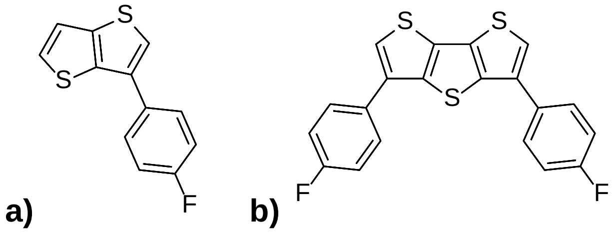


Figure 1. Used Monomers **a)** FPhTT and **b)** FPhDTT

2. EXPERIMENTAL

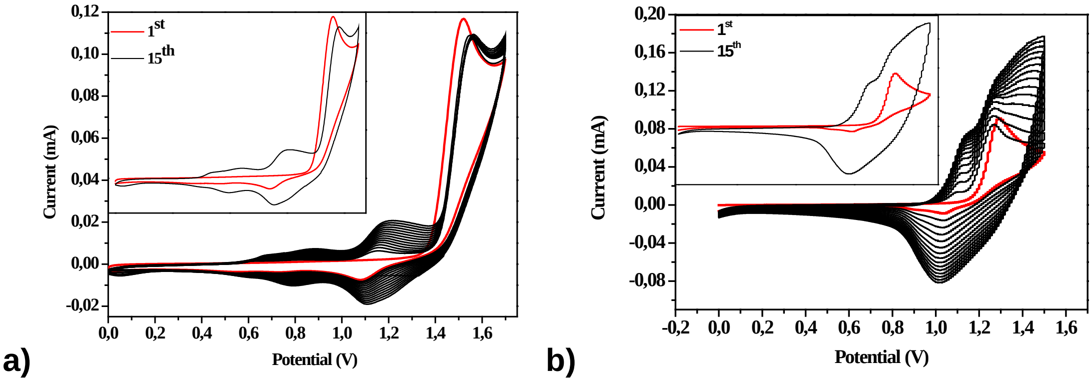
Materials: FPhTT and FPhDTT were synthesized as suggested for similar analogues in literature.[3,4] Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), acetonitrile (ACN), and other chemical were analytical grade chemicals and used without further purifications.

Methods: Electrochemical measurements were performed with a Gamry Instruments Reference 600 potentiostat/galvanostat interfaced to computer and controlled Gamry Framework software. UV measurements were performed on Hitachi U-0080D spectrophotometer. For electrochemical measurements GC electrode, for spectroelectrochemical measurements, indium tin oxide (ITO) electrode were used as working electrode. Polymers were further characterized by AFM, SEM and contact angle measurements.

3. RESULT AND DISCUSSION

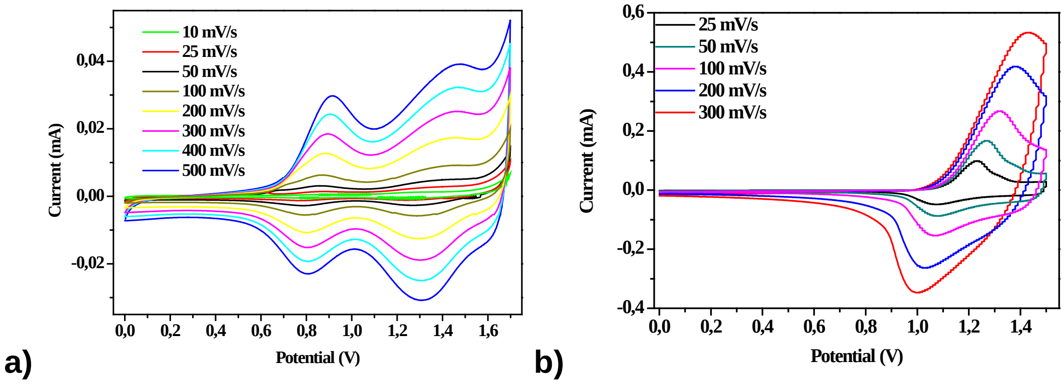
FPhTT and FPhDTT molecules were electropolymerized on glassy carbon (GC) electrode by potantiodynamic methods (Figure 2). While oxidation of FPhTT starts at 1.32 V, it shift to 1.02 V for FPhDTT due to inclusion of another Th ring to the monomer unit. Resulting electroactive P[FPhTT] and P[FPhDTT] polymer films were characterized with CV, and spectroelectrochemical measurements .

The CV's of P[FPhTT] at different scan rates (even at 2 V/s) show two reversible redox peaks at 0.9 and 1.45 V (Figure 3a). However, P[FPhDTT] shows only one redox peak near at 1.32 V (Figure 3b). These results are in agreement with previous results on similar analogues. [5,6]



a) b)

Figure 2. Cyclic voltammograms for the polymerization of **a)** FPhTT and **b)** FPhDTT monomers respectively, in ACN containing 0.1 M [Bu_4NPF_6], on GC electrode (area=0.022 cm^2), by applying 100 mV/s.



a) b)

Figure 3. CV's of **a)** P[FPhTT] and **b)** P[FPhDTT] films obtained at different scan rates in ACN containing 0.1 M Bu_4NPF_6.

FPhTT and FPhDTT were electropolymerized also on indium tin oxide (ITO) electrode and spectroelectrochemical measurements of P[FPhTT] and P[FPhDTT] films were given in Figure 4. P[FPhTT] and P[FPhDTT] have absorption at 450 nm and 455 nm respectively, due to $\pi - \pi^*$ transition at neutral state. At oxidized state, new absorptions at higher wavelength which indicates the polaron and bipolaron formation were observed. The band gaps (E_g) of polymer film (on ITO) and monomers (in solution) were estimated by extrapolation of the low energy edge of the absorption spectrum to the baseline.

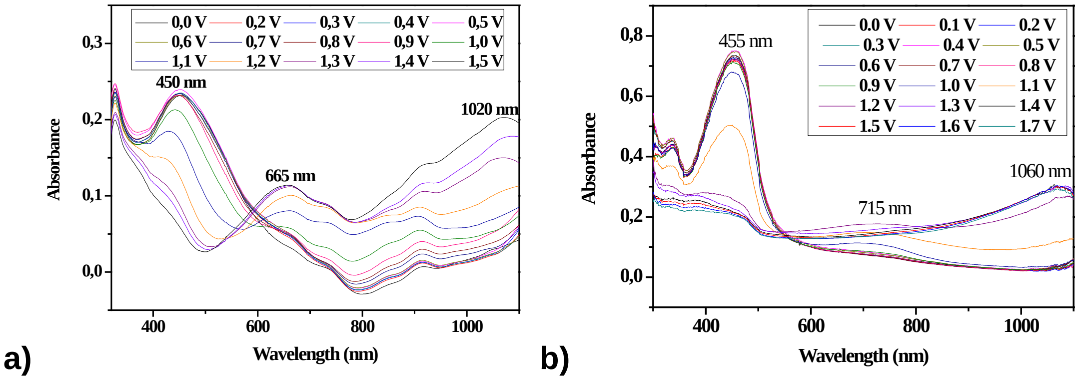


Figure 4. UV-Visible absorption spectra of **a)** P[FPhTT] and **b)** P[FPhDTT] on ITO electrodes at different applied potentials.

4. CONCLUSION

Electrochemical behavior of P[FPhTT] and P[FPhDTT] was investigated comparitevely. Results suggested that, polymerization rate of FPhDTT is higher than FPhTT due to having symmetric and more conjugated structure. Consequently resulting P[FPhDTT] has higher current density and P[FPhTT] has more reversible electron transfer reaction, since the thickness of the film at the same polymerization charge is higher in the case of P[FPhDTT] . All results suggested that P[FPhTT] and P[FPhDTT] show promising properties for ECD applications.

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Synthesis of Thienpthiophene Posessing Tetraphenylethylene and Their Electronic and Optoelectronic Applications

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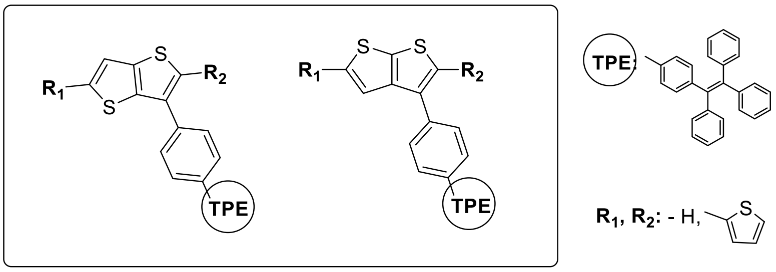
Thienothiophenes (TT) are used in various electronic and optoelectronic applications, such as solar cell, organic light emitting diode (OLED), organic field effective transistor (OFET), energy storage device, electrochromic device (ECD) etc. [1,2] Their electron rich character, supported by their rigid conjugate π system and planar structure, make them attractive molecules for material chemistry. Tetraphenylethylene (TPE) molecules are generally used for OLED fabrication due to their aggregation induced emission (AIE) feature. As such molecules exhibit interesting chemical and physical properties, they can be used as electron catalyst. Moreover, π-systems, having TPE are useful devices for organic optoelectronic storage.[3]

In this work, TT molecules were introduced with TPE and thiophene groups applying Suzuki coupling reaction. Their electroactive polymer films were obtained by electropolymerization on glassy carbon (GC) and ITO electrodes. These polymers were characterized by electrochemical (cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) etc.), UV, AFM and SEM etc. Diverse device applications (ECD, capacitor, hybrid batteries) were studied using different techniques.



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Electrochemical Investigation of Dimers and Fluorinated Derivatives of 1,3-Diphenylisobenzofuran as Chromophores for Singlet Fission

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Solar cell (The Dye Sensitized Solar Cell) [1] is a complex system which consists of three different components: semiconductor, the chromophore and the electrolyte. These components are brought together to generate electric power from light without suffering from any permanent chemical transformation. Nowadays, design and studies of systems that would be useful in solar cells is very important. It was found out that the principle of singlet fission would increase the efficiency of solar cells. Singlet fission [2] is a photophysical process in which an organic chromophore in excited singlet state shares its excitation energy with a neighbouring ground-state chromophore and both are converted into two triplet states. The phenomenon of the singlet fission is known for over a decade but only in molecular crystals which still represent the best example for such a study. The understanding of singlet fission in isolated molecules is much less developed. But those molecules might be advantageous for use as solar cell sensitizers.

1,3-Diphenylisobenzofuran (DPIBF) is a known and commercially available compound which has been considered as a model chromophore for singlet fission. [2,3] Therefore molecules on the base of DPIBF attract interest. Singlet fission can be described as an exchange of electrons among two molecules which does not require change of spin of any from the molecules. The redox properties of molecules for singlet fission are critical for their use in solar cells hence, the electrochemical study of various DPIBF derivatives is very important. [4] In our electrochemical study we focused on a) the nature of bridging of two DPIBF units (DPIBF "dimers"), and b) fluorinated derivatives of DPIBF. For characterization of redox properties of these molecules classical electrochemical techniques, and *in situ* UV-vis and EPR spectroscopy were used.

The oxidation as well as reduction patterns of all studied derivatives are mostly analogous to the parent DPIBF. Its oxidation proceeds in one irreversible step involving two electrons. On the other hand, reduction is more complicated.

The observed reduction pattern is apparently of the EEC type. Because the most important experimental data for the mentioned application are the first (or second) oxidative and reductive electron transfer potentials being reversible (before any follow-up chemical reaction), only the first two steps are discussed. More detailed study of the reduction mechanism which would be necessary for interpretation of other reduction steps is beyond the aim of this contribution.

The first reduction step of the parent DPIBF is a one-electron reversible process followed by another one-electron step. Upon the course of the first reduction step formation of the stable anion radical was proved and the corresponding change on UV-vis spectra in the range 1000 – 450 nm was observed.

When two DPIBF units are interconnected by a covalent bridging unit [5], an effect of intramolecular electronic communication between the two π systems through the bridge is followed. In the case of CH_2 bridge, a small effect on the redox potentials is observed, the two DPIBF units are reduced and oxidized independently, without mutual communication and the methylene unit serves as a delocalization stopper.

On the other hand the extended π-electron delocalization over whole molecule of *mm*, *mp*, *pp* and “quasi” dimer (figure 1) causes easier oxidization and reduction. The most particular molecule is the “quasi” dimer, which represents a single delocalized system with two redox centres where the reduction of one reduction centre influences the reduction of the second one. The UV-vis spectra show that the distribution of electrons and the shape of LUMO are very different from other dimers. The further investigation is under way.

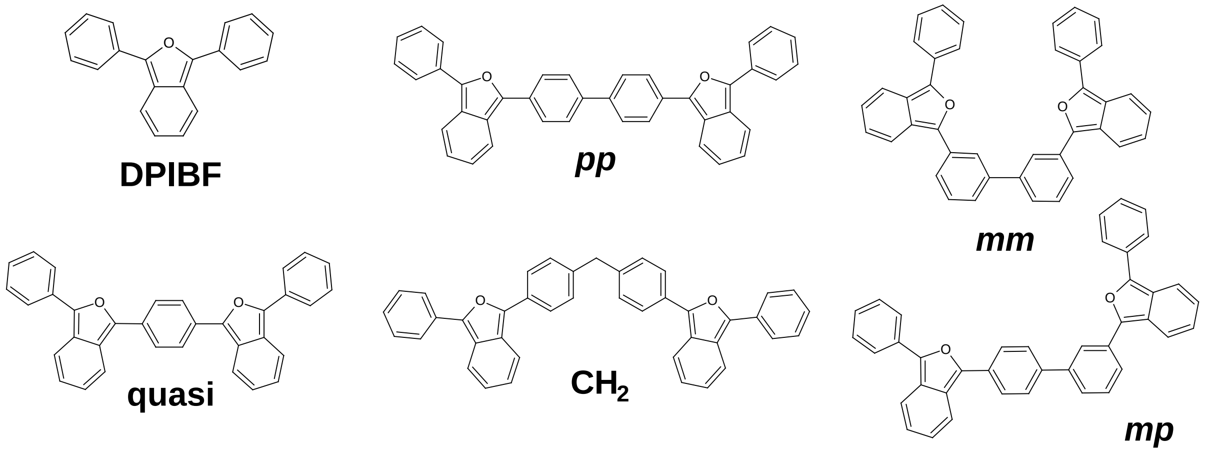

Figure 1

In the series of 11 fluorinated DPIBF (figure 2), contribution of each fluorine atom is generally more or less additive [6]. The fluorine in *p*-position has negligible influence on potential values. On the other hand the contribution of each fluorine atom in *m*-position, due to its strong inductive effect, is high and causes a shift of both reduction and oxidation potentials (the reduction potential is moved by about 70–85 mV to less negative values and the oxidation potential is shifted by about 50–60 mV to higher positive values). It is remarkable that the expected strong steric interaction of the fluorine atoms in *o*-position with the central heterocycle has no influence on reduction potentials in comparison with oxidation pattern. DPIBFs with 5 and 10 fluorine atoms differ substantially from the rest of the series of fluorinated DPIBFs. The additive contribution of each F-atom is converted to a total change of mechanism.

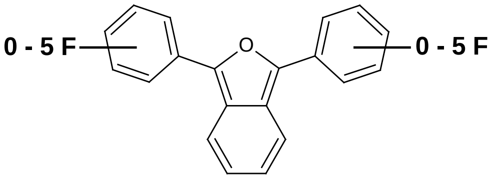

Figure 2

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B3LYP/6-31G(d,p) calculations of thienoacene tetrathiafulvalenes in different oxidation and spin states

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The structural differences among the investigated thienoacene tetrathiafulvalenes (**1-5**, see ref. [1]) were crucial for the understanding of electrochemical and spectroscopic results. We have found a good agreement between the geometries obtained from crystal structures and the DFT-optimized conformations. The non-planarity of several of the investigated structures has a large impact on the compound's electrochemical and optical properties [1]. The calculated geometries in the first and second oxidation states exhibit similar characteristics as for the neutral species. Upon oxidation, the positive charge is predicted to reside in the dithiafulvalene (DTF) unit, while the unpaired electron is delocalized to a larger or minor degree in the central skeleton (Figure 1).

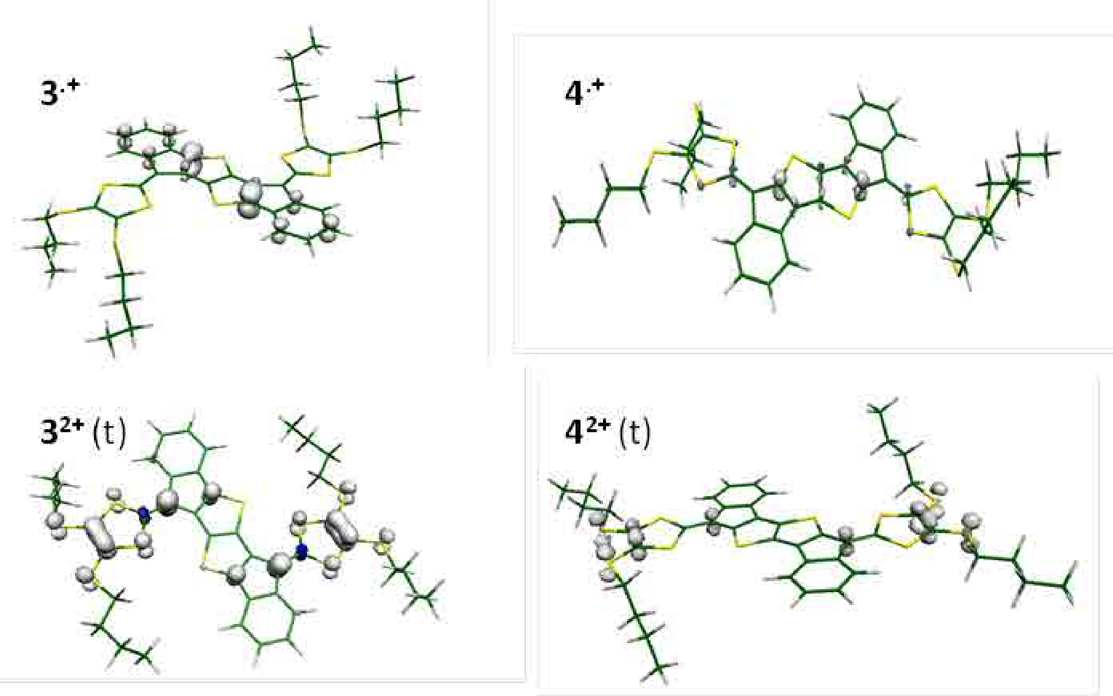

Figure 1. The B3LYP/6-31G(d,p) spin densities calculated for the optimal geometries of **3** and **4** for the corresponding radical cation and triplet (t) dication. The depicted iso-contour is 0.005 atomic units.

Focusing on the dicationic oxidation state, a direct conjugated pathway can be drawn between the two DTF units of **2a**, **4** and **5**, allowing the electrons to pair. However, for the dications of **1** and **3,** where the DTF units are connected in a cross-conjugated pathway, no closed shell bond structure with all electrons paired can be proposed. The B3LYP/6-31G(d,p) calculated Gibbs energy differences between the triplet and singlet ground states were calculated for all isolated dications and selected tetrathiafulvalene $\mathrm{TTF}^{+\bullet}$•••$\mathrm{TTF}^{+\bullet}$ associates (Figure 2).

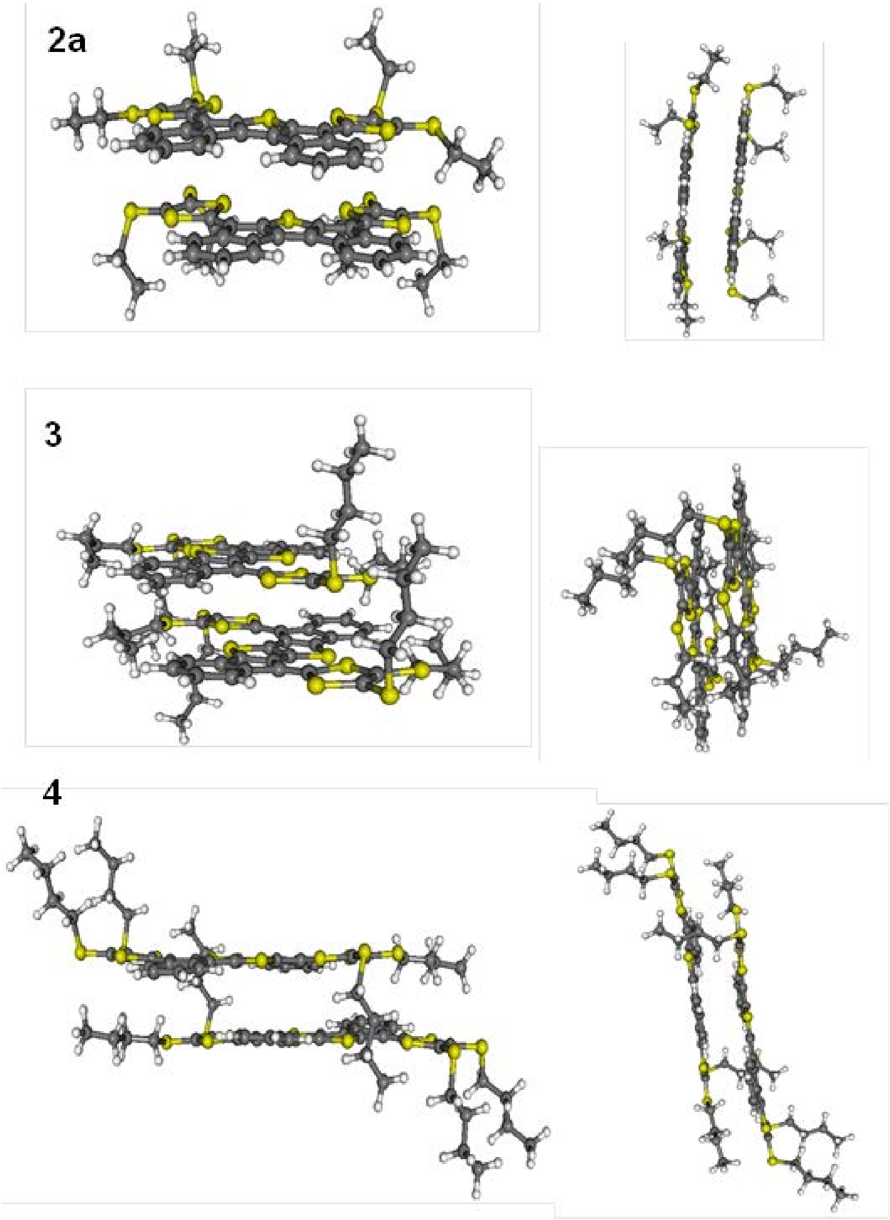

Figure 2. The B3LYP/6-31G(d,p) optimal geometries (front and side views) of model neutral TTF…TTF associates for **2a**, **3** and **4** (the starting geometries were taken from X-ray structures). Negligible associate geometrical changes were found upon the charging.

The calculations reveal that the triplet ground state is more stable than the singlet for $\mathbf{1}^{2+}$ and $\mathbf{3}^{2+}$, and the compounds are best described as biradicals. On the other hand, the ground states of the doubly charged **2a** and **5** are predicted to be open-shell singlets, while $\mathbf{4}^{2+}$ is found to be in the closed-shell singlet state.

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Influence of the structure of polyelectrolytes on electrosynthesis and properties of poly(3,4-ethylenedioxythiophene)

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The purpose of the work was an electrochemical polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) in the presence of water-soluble sulfonated polyelectrolytes with rigid and flexiblechains. Flexible-chain poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) or poly(styrene sulfonic acid) (PSSA) and rigid-chain poly-4,4’-(2,2’-disulfoacid)-diphenylene-iso-phthalamide (iso-PASA) or poly-4,4’-(2,2’-disulfoacid)-diphenylene-tere-phthalamide (tere-PASA) and their sodium salts were chosen as polyelectrolytes. In addition, we investigated the synthesis of PEDOT in the presence of mixtures of rigid-chain and flexible-chain polyelectrolyte in order to see which polyelectrolyte has a dominating influence on the course of the polymer synthesis and on its spectroelectrochemical properties and morphology. The electrochemical deposition was carried out in galvanostatic and potentiostatic regimes.

It was found that the polyelectrolyte structure and the nature of its counterion affected the kinetics of the electrosynthesis (Fig.1.).

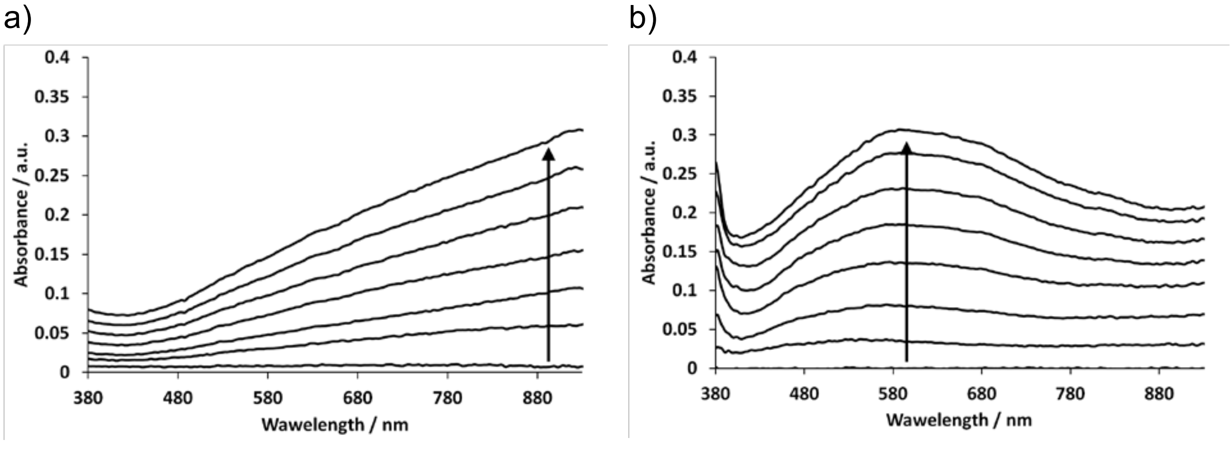

Fig.1. Evolution of absorption spectra during electropolymerisation of EDOT in the presence of PAMPSA (a), tere-PASA (similar to PAMPSA-tere-PASA 1:1) (b).

The character of evolution of absorption spectra of PEDOT film during the electrosynthesis in the presence of the flexible-chain polyelectrolytes and the rigid-chain polyelectrolytes in salt form is similar and characterized by intensive growth of absorption in the NIR-region, which corresponds to the formation of bipolarons. This significantly differs from the character of EDOT polymerization in the presence of rigid-chain polyacids and PAMPSA-tere-PASA mixture: the preferential growth of absorption near 600 nm is related to formation of polarons.

The obtained films were examined by cyclic voltammetry, UV-Vis-NIR spectroscopy and spectroelectrochemistry, as well as atomic force microscopy. Differences in the influence of chain rigidity of acidic polyelectrolytes on the UV-Vis-NIR spectroelectrochemical behavior of PEDOT complexes were revealed (Fig.2.). In the case of PEDOT complexes with PAMPSA-tere-PASA mixture in acid form the UV-Vis-NIR spectroelectrochemical properties were close to those of PEDOT complex with the rigid-chain polyelectrolyte. Speaking about UV-Vis-NIR spectroelectrochemical behavior of PEDOT complexes with the mixture of Na^+-salts of PAMPSA and tere-PASA one can see similarity with the behavior of PEDOT complexes with flexible-chain polyelectrolytes.

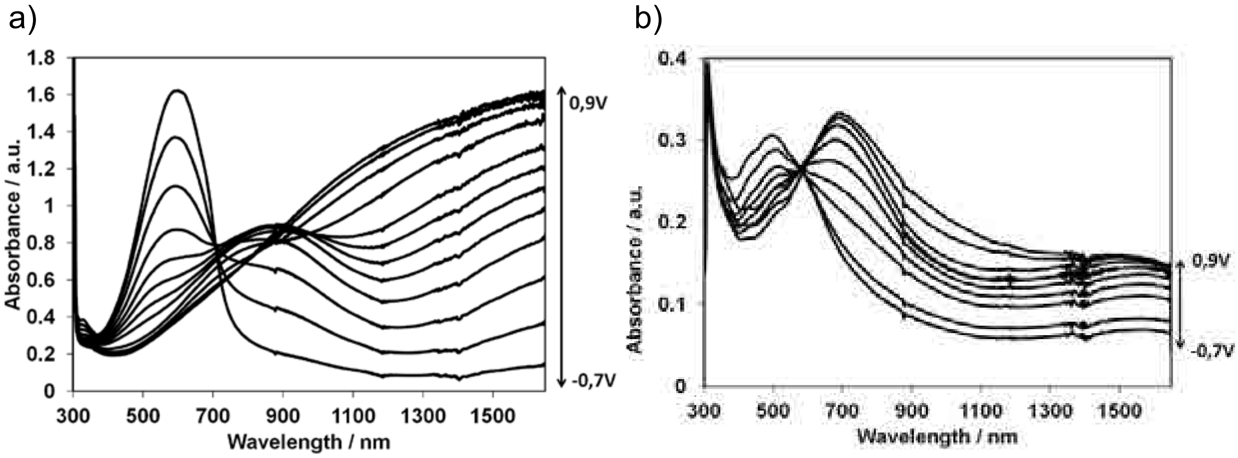

Fig.2. UV-Vis-NIR absorption spectra of PEDOT films prepared by electrochemical polymerization of EDOT in the presence of PAMPSA (a), tere-PASA (PAMPSA-tere-PASA 1:1) (b) measured at different potentials in propylene carbonate solution with 0.5 M $NaClO_4$.

Thin layers of PEDOT complexes with flexible-chain polyelectrolytes were tested as hole transport layers (HTLs) in hybrid solar cells (HSC). $CH_3NH_3PbI_3$ layer of perovskite structure served as photoactive layer. Studies have shown the promise of using the obtained polymer complexes as HTLs in the HSC. It was found that the highest photovoltaic characteristics show devices with PEDOT-PAMPSA complex as hole transport layer (Table 1).

Table 1. Photovoltaic characteristics of HSC with different HTLs, where J_{sc} − short-circuit current density, V_{oc} − open circuit voltage, FF − fill factor, PCE − power conversion efficiency.

PEDOT	**J_{sc}, mA/cm^2**	**V_{oc}, V**	**FF, %**	**PCE, %**
PAMPSA	17.40	0.76	56.70	7.53
PAMPSNa	15.98	0.76	57.62	7.01
PSSA	15.00	0.69	59.49	6.11
PSSNa	14.08	0.71	57.47	5.71

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Electrochemical polymerization of aniline on gold electrodes in the presence of polysulfonic dopants with rigid or flexible backbone.

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Polyaniline (PANI) layers are synthesized in the presence of five types polysulfonic acids with different rigidity of the polymer backbone, poly(4,4'-(2,2'-disulfonic acid)-diphenylene terephtalamide) (tere-PASA, rigid), poly(4,4'-(2,2'-disulfonic acid)-diphenylene isophtalamide) (iso-PASA, rigid), polystyrene sulfonic acid (PSSA, semi-rigid) with molecular weight 70 000 and 1 000 000, and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, flexible). Potentiostatic synthesis and voltammetric redox studies of PANI layers are completed on gold microelectrodes and electrochemical quartz crystal microbalance (EQCM) gold macroelectrodes. It is established that the type of the doping agent has a significant influence on the kinetics of potentiostatic polymerization on both gold micro- and macro-electrodes. PANI/tere-PASA layers show highest redox activity with sharpest and most pronounced redox peaks during potentiodynamic treatment in acidic solution.

EQCM studies indicate significant effect of the type of polysulfonic dopant on the ionic and solvent transport processes in acidic solution. A marked difference is observed in the frequency drift during several consecutive potentiodynamic cycles. Both PANI/tere-PASA and PANI/iso-PASA layers exchange low amount of mass (solvent and ions) during redox transitons and show almost no drift of the resonance frequency during cycling. Based on the obtained results it can be suggested that the “softness” of the five types of layers increases in the sequence t-PASA, i-PASA, PSSA (70000), PSSA (1000000), PAMPSA.

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Ion transport process and mechanical characteristicsof PEDOT layers doped with polysulfonate,dodecylsulfate and perchlorate anions.

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Former studies on PEDOT layers obtainedin the presence of various doping counter ions were focused on ion exchange and mechanical properties of PEDOT in the course of polymerization [1,2].In this investigation polymer layers are synthesized in the presence of one of the four different anionic species – polysterenesulfonate (PSS), poly(2-acrylamido-2-methyl-1-propane-sulfonate) (PAMPS), dodecylsulfate and perchlorate anions. The PEDOT layers are further studied by cyclic voltammetry in hydrochloric and perchloric acids as well as in several buffer electrolytes containing sodium phosphate, cesium phosphate or tris(hydroxymethyl)aminomethane chloride. Simultaneous electrochemical and acoustic admittance measurements are carried out by electrochemical quartz microgravimetry.Based on a theoretical.model the data from the acoustic spectra are further processed to obtain values for the mechanicalshearmoduli for every type of PEDOT layers. The type of the anionic species incorporated in the polymer layers affects the surface morphology, ion exchange and most markedly the viscoelastic properties of the four types of layers. Dodecylsulfate imparts significant stiffness to the PEDOT layers that is preserved during potentiodynamic treatment in all electrolytes. Depending on the doping ions the “softness” of the three other types of layers increases in the sequence perchlorate, PSS and PAMPS.PEDOT-PAMPS coatings present high viscoelasticityand well pronounced changes also in the course of potentiodynamic cycling.

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Electroless deposition of palladium on poly(3,4-ethylenedioxythiophene) - coated graphite electrodes

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Electroless deposition of Pd in the absence of solute reducing species is studied on pre-reduced poly(3,4-ethylenedioxythiophene)(PEDOT)-coated graphite electrodes. PEDOT coatings doped with either dodecyl sulfate (SDS) or polysterene sulfonate (PSS) ions are used in the studies. Two largely differing potentials for deep and mild pre-reduction of PEDOT are chosen and correspond to initial low (deep pre-reduction) and high (mild pre-reduction) conductive states of the polymer material. The role of organic doping ions (PSS or SDS) used in the course of PEDOT synthesis for the electroless deposition of Pd is investigated at constant polymer amount. PEDOT-supported Pd catalysts with homogeneously distributed, high-density Pd nanoparticles (NPs) with sizes ranging between 4 and 12 nm are obtained. It is established that the amount of deposited metal depends significantly on the pre-reduction potential of PEDOT whereas the surface density of the metal NPs is largely influenced by the doping ions used to obtain the PEDOT material. SEM, UV-vis and Raman investigations are used to study possible structural changes of PEDOT provoked by the deep reductive treatment. The data give evidence for irreversible structural changes in the PEDOT/SDS case resulting in a dense morphology that inhibits ionic transport and supports Pd electroless deposition at the polymer/solution interface.

Large amounts of deposited Pd, significantly exceeding the quantity that is expected to be reduced at the expense of PEDOT re-oxidation alone, are found to deposit irrespective of the polymer coating's thickness. Pd particles are observed to deposit also at bare pre-reduced graphite electrode. By means of computed tomography it is found that the graphite substrate has a large open porosity amounting to 23%. The deep reductive pre-treatment occurs at negative enough potential to initiate hydrogen reduction in this porous structure. Comparative XPS and Raman studies of pre-treated and non-treated bare graphite electrodes do not show any effect of the reductive pre-treatment on the chemical state of the substrate. It is suggested that molecular hydrogen entrapped during the reductive treatment plays the role of additional reductant for the electroless Pd deposition and assists the formation of high density Pd nanocatalysts.

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Pd-modified PEDOT layers obtained through electroless metal deposition — electrooxidation of glycerol

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In the recent years glycerol was investigated intensively for its possible application in direct alcohol fuel cells, converting the free energy of the alcohol into electrical energy. The anode catalyst and the corresponding matrix for the deposition of the catalyst are crucial for the efficiency of the fuel cell.

In the present investigation composite layers of catalytically active Pd nanoparticles (NPs) deposited on pre-synthesized layers of the conductive polymer poly-3,4 ethylenedioxythiophene (PEDOT) are used as an anode material for electrocatalytic oxidation of glycerol.

The polymer layers are synthesized in the presence of sodium polystyrene sulfonate (PSS) or sodium dodecylsulfate (SDS) ions on spectral graphite substrate. The Pd particles are obtained by electroless deposition occurring at the expense of the oxidation of the PEDOT layers that are reduced in a former step of the experiment. The polymer matrix is not electroactive for electrooxidation of glycerol and serves only as support for dispersing the catalytic metal phase. The oxidation of glycerol is studied by cyclic voltammetry in alkaline electrolyte. It was found that both types of coatings Pd/PEDOT-PSS and Pd/PEDOT-SDS show high electrocatalytic activity and stability for oxidation of glycerol. At the same time, the Pd/PEDOT-PSS composite layers have three times higher oxidation currents than the Pd/PEDOT-SDS ones. This result is attributed to the different distribution of metallic NPs that depends on the morphology and porosity of the coatings the latter strongly influenced by the doping ions (PSS or SDS) used for synthesis of PEDOT. Homogeneous distribution of individual (non-overlapping) palladium NPs on the polymer surface and inside the polymer layer found in the case of PEDOT-PSS is more advantageous than the dense population of overlapping NPs observed at the polymer/solution interface for PEDOT-SDS.

The effect of the PEDOT polymerization charge on the electrocatalytic activity of Pd/PEDOT layers was also investigated. It is established that in the case of

PEDOT-PSS with increasing polymerization charge both the mass of deposited Pd and the electroactive surface area of Pd NPs increase. Nevertheless the mass electroactivity for glycerol oxidation decreases very probably due to the more difficult access of glycerol molecules deposited inside the polymer structure. For the case of PEDOT-SDS, with increasing Pd amount, accumulation and overlap of Pd particles on the polymer/solution interface takes place and results in decreased electroactive surface area. Data on mass electroactivity (MEA) for glycerol oxidation obtained for both types of PEDOT show three times higher value for the Pd/PEDOT-PSS in comparison to Pd/PEDOT-SDS. For thin PEDOT-PSS-coated graphite electrodes the obtained MEA is comparable to the best results found in the literature for palladium catalysts.

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Composites based on PEDOT and Ag and AgPt nanoparticles for the electrochemical sensing of ascorbic acid

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Ascorbic acid is a chemical compound that plays a key role in several biological processes (free radical scavenging, collagen synthesis, iron absorption and neurotransmitters synthesis). The oxidation of this chemical compound occurs at relative high positive potentials at unmodified electrodes. Therefore; its oxidation peak can be overlapped by other compounds. In addition, ascorbic acid oxidation products can deposit over the electrode surface and block it [1]. In order to avoid that, electrodes have been modified with nanostructures and conducting polymers [2]. In this study composites of silver nanoparticles and silver platinum nanoparticles and poly-3,4-ethylendioxythiophen (PEDOT) were used for the analysis of ascorbic acid.

Ag nanoparticles were synthesized by chemical reduction using citrate as reducing agent and characterized by UV- visible spectroscopy and TEM. AgPt nanoparticles were prepared by a galvanic replacement reaction and were analyzed by SEM/TEM and EDX. PEDOT films were electrodeposited under potentiostatic conditions from a solution of EDOT, SDS (sodium dodecyl sulfate) and $LiClO_4$. Ag and AgPt nanoparticles were incorporated into PEDOT films by codeposition at a constant potential and drop casting. The electrochemical performance of the composites toward ascorbic acid was evaluated by differential potential voltammetry in a phosphate buffer solution (ascorbic acid concentration range: 200 to 1200µM). The sensitivity of the sensors was determined and a shift of the ascorbic acid oxidation potential to less positive values was observed for all the composites.

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Versatile electrochemical immunosensing interfaces based on poly(catecholamines) films

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Sensitive and selective detection of bioanalytes represents an important tool for clinical diagnosis, food quality control and environmental monitoring [1]. Antibodies can provide the necessary high affinity and specificity towards toxins or pathogens detection, usually requiring sandwich-based configurations to enhance the bio-recognition signal. Nanoparticles are often used to label antibodies to achieve low detection limits. When constructing biosensors, one of the crucial steps concerns the robust immobilization of biomolecules, remaining biologically active at the surface [2]. Polydopamine films exhibit the required biocompatibility to be used as support matrix in biosensing interfaces [3].

In this work, we will use electrochemical control to improve the immobilization of proteins over poly(catecholamine) films, through the increase of the anchoring quinone groups available within the polymeric coatings. The assays will be conducted by real-time Surface Plasmon Resonance. The electrochemical detection of the antigen-antibody specific interaction will be achieved by immobilizing the antigen in the polymeric sensing layer and detecting it using nanoparticles functionalized with antibody and an electroactive compound. In addition, the developed poly(catecholamine) interfaces, with ability to inhibit protein non-specific interactions, can be tailored to any target analyte.

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Ternary composites based on electroactive polymer, functionalised carbon nanotubes and reduced graphene oxide – influence of carbon content on electrodeposition process

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In this work electrodeposition of ternary composites based on poly(3,4-ethylenedioxythiophene), functionalised carbon nanotubes (oxidised ox-CNTs or nitrogen plasma treated (p)N-CNTs) and reduced graphene oxide (rGOx) is investigated. The thickness, morphology, porosity and structure of thin nanocomposite films depend strongly on the chemical composition of the synthesis solution, especially on the content of functionalised CNTs. Graphene oxide, present in the synthesis solution, plays a role of counter-ion for forming polymer chains and ensures smooth, layered morphology of the composite films (see Fig. 1).

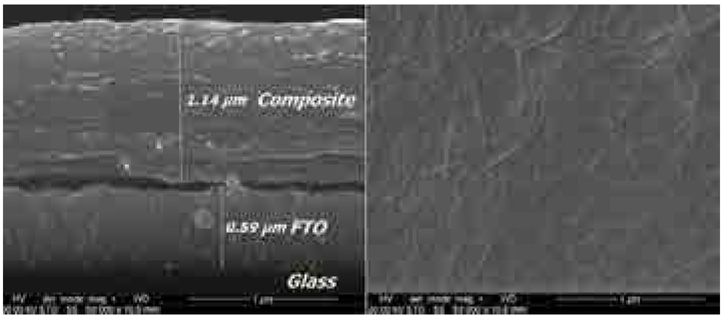

Fig. 1. SEM images of pEDOT/rGOx/ox-CNTs composite.

On the other hand, functionalised CNTs play a role of spacer preventing graphene sheets from re-stacking and increase the porosity of the material, improving ion diffusion through the composite layer. However, too high amount of CNTs in the composite causes its brittleness and lowers adhesion to the electrode substrate. The investigated ternary nanocomposites exhibit increased capacitance values (approx. 320 F cm^{-3}) compared to analogous binary composites based on pEDOT and CNTs (160 F cm^{-3}) [1] or pEDOT and GOx (220 F cm^{-3}) [2].

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Polarization phenomena in electromembrane system with composites based on perfluorinated membrane and polyaniline

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Ion-exchange membranes modified by polyaniline (PANI) are perspective for using in electromembrane process as separation diaphragms by electrodialysis concentration of solutions [1, 2]. The properties of these composites essentially depend on conditions of polyaniline synthesis: concentration of polymerization solutions, potential of redox systems for electron acceptors during the oxidative polymerization of aniline; duration of synthesis and etc. The present work is devoted to the study of polarization phenomena in electromembrane system with composites based on Nafion type sulfocationic perfluorinated membrane and PANI.

The object of the research was perfluorinated MF-4SK membrane obtained at JSC «Plastpolymer» (Saint Petersburg, Russia). The oxidative polymerization of aniline in bulk or on the surface of the perfluorinated membrane were carried out under static conditions in monomer and oxidant solutions, in concentration field by method of successive diffusion of polymerization solutions through the membrane in water, and in an external electrical field [3]. Using Fe^{3+} ions as the oxidants leads to formation of composites with bulk distribution of PANI while using $S_2O_8^{2-}$ or $Cr_2O_7^{2-}$ leads to formation of composites with a primarily surface distribution of PANI. The scheme of polyaniline layer formation on the surface of the MF-4SK membrane under the conditions of an external electric field is shown in Figure 1.

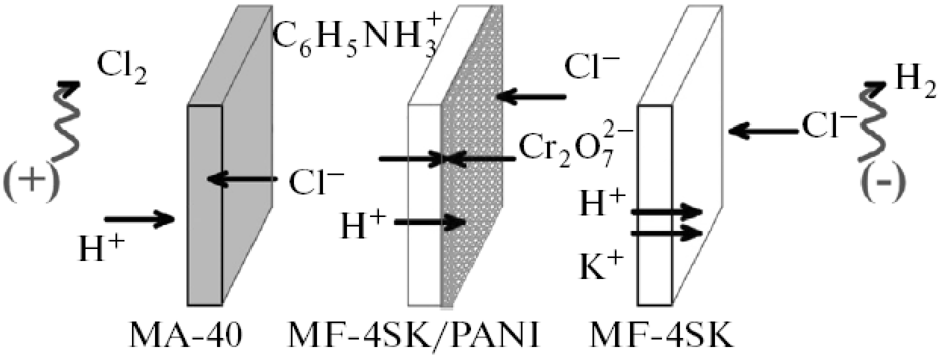

Figure 1. Scheme of the formation of a polyaniline layer on the surface of the MF-4SK membrane under the conditions of an external electric field.

The current-voltage curves (CVC) of membrane in the “free standing” state were measured in a cell equipped with two platinum polarizing and two silver/silver chloride measuring electrodes in HCl solution. Direct current was applied at a specified scan rate to the polarizing electrodes using an Autolab PGSTAT302N potentiostat/galvanostat. The potential drop on the membrane (ΔE) was measured using Luggin–Haber capillaries and the silver/silver chloride electrodes. The experimental Δ*E* value was real time recording by a computer. The slope of the ohmic region of CVC, the limiting current density, the limiting current plateau lengths and potential of system transition in an overlimiting state were determined from CVCs by tangent method using the Microsoft Excel program.

Some peculiarities of polarization behavior of the composites were found. The most essential effect in change of the current-voltage curves of the bulk modified samples is the increase of a limiting current plateau lengths and potential of system transition in an overlimiting state [3, 4]. Curves 1 and 2 in the Figure 2 show the CVCs of the initial and composite membrane which was prepared under static conditions with Fe^{3+} ions as the oxidants.

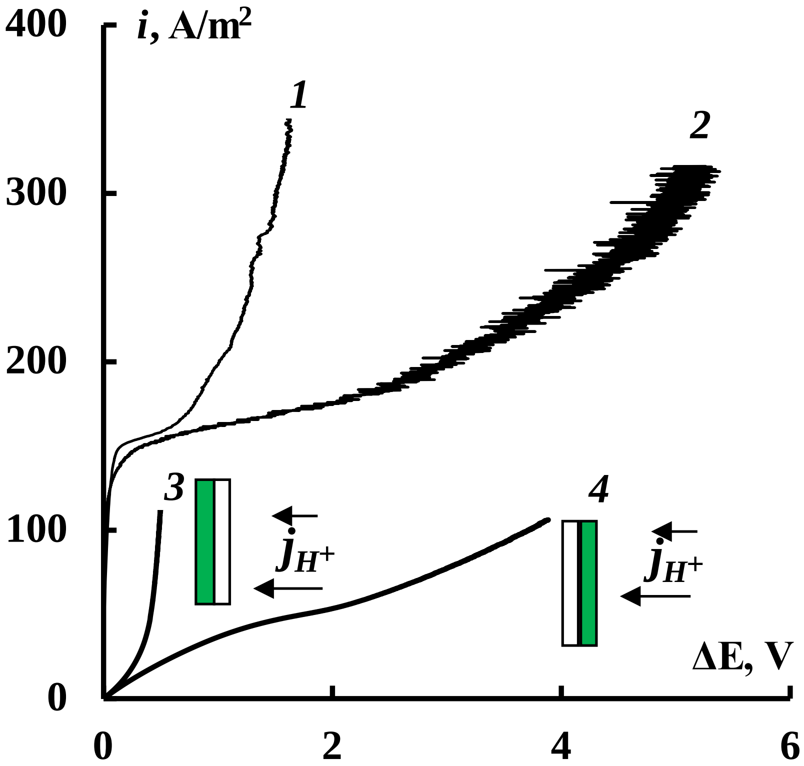

Figure 2. Current-voltage curves measured in 0.05 M HCl: 1 – initial membrane MF-4SK, 2 – MF-4SK/PANI (bulk modified); 3, 4 – different orientation of anisotropic MF-4SK/PANI: 3 – unmodified surface faces the counterion flow, 4 – PANI layer faces the counterion flow.

As can be seen from the Figure 2, the slope of the ohmic part of the curve, which characterizes the conductivity of electromembrane system, is practically the same for these samples. It is consistent with the independent determination of samples electrical conductivity by mercury-contact method [3 – 5]. The length of the limiting current plateau increases 4 times. The same effect is always observed for the composites MF-4SK/PANI [3, 4]. The asymmetry of current-voltage curve is absent by the reversal of the current. It confirms the bulk character of the modification of membrane MF-4SC by polyaniline in an external electric field if Fe^{3+} ions were used as the oxidants.

The asymmetry effect of CVC for anisotropic composites depend on the polyaniline layer orientation towards counter ion flow is usually observed [4, 6]. Curves 3 and 4 in the Figure 2 show the current-voltage curves of the composite membrane which was prepared in external electric field with $Cr_2O_7^{2-}$ ions as the oxidants. An analysis of the CVC parameters of the anisotropic composites shows its asymmetry. The pseudo-limiting current appears due to the formation of an internal bipolar boundary between cation-exchange membrane and PANI layer which have anion-exchange properties [6].

Based on the analysis of the polarization behavior of the samples, we can determine their effective applications in various electrochemical devices. Materials with moderate asymmetry of the current-voltage curve and sufficiently high density of the limiting current are promising for use in electrodialysis because, as is known, modification of perfluorinated membranes with polyaniline increases their selectivity and reduces the diffusion and electroosmotic permeability [7]. Anisotropic composite membranes with a diode-like effect may be used as membrane switches or relays.

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Electroosmotic properties of ion-exchange membranes modified by polyaniline

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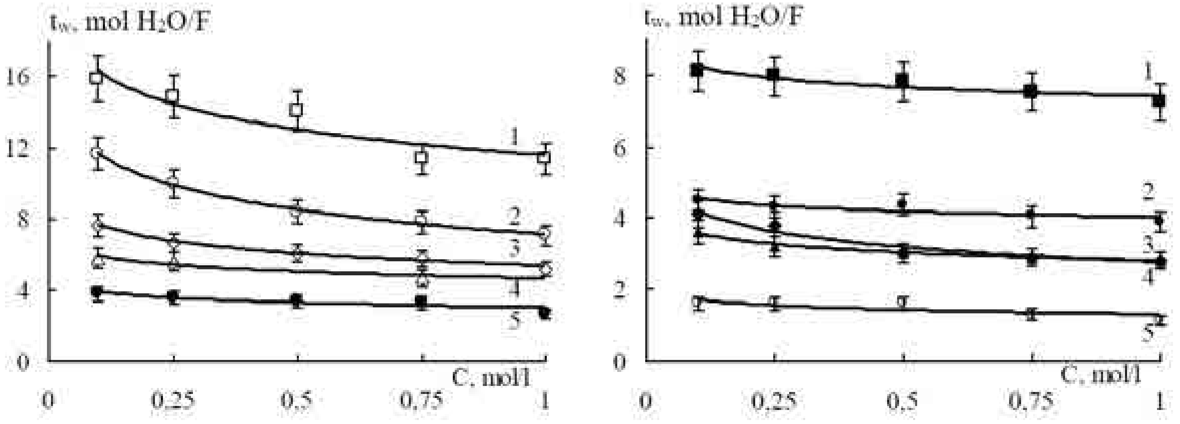
This work is devoted to investigation of electroosmotic permeability, water content and conductivity of the modified ion-exchange membrane by polyaniline (PAn). The influence of method of polyaniline synthesis, structural types of membrane polymer matrixes and electrolyte type solutions on electroosmotic permeability of composites with polyaniline were studied [1, 2]. The electroosmotic permeability of the membranes and water transport number were measured by the volumetric method in a two-chamber cell with reversible silver chloride electrodes. Experimental data on measuring ion-exchange capacity (*Q*) and water content (*W*) were used to calculate specific water content of membranes (n_m, mol H_2O/mol SO_3^-).

Difference between electroosmotic properties of bulk and surface modified membranes was revealed. It was shown that the polyaniline layer on the surface of the perfluorinated membranes significantly reduces water content, water transport number and conductivity in wide range concentrations of the HCl, LiCl, NaCl, KCl and CsCl solutions. Figure 1 demonstrates the concentration dependences of the water transport numbers (t_w) in the wide range of electrolyte solutions. The comparison of the data for composite and initial membranes has shown the effect of essential decrease of the water electrotransport across the polyaniline layer which is equal 50% for all electrolyte solutions. The other interesting result is the set of water transport numbers in the concentrate electrolyte solution for the composite samples (Fig. 1) which have t_w values $7 \rightarrow 4 \rightarrow 3 \rightarrow 3 \rightarrow 1$ mol H_2O/F for $Li^+ \rightarrow Na^+ \rightarrow K^+ \rightarrow Cs^+ \rightarrow H_3O^+$ accordingly. These values are close to the hydration numbers of the same ions in the electrolyte solutions, which dependence on the ion radii. It is interesting to note that the surface polyaniline layer reduces the water electrotransport in the all concentration region (Fig. 1 b). So, blocking properties of surface polyaniline layers can be used for the determination of close hydration numbers of transported ions.

Modification of heterogeneous membrane MK-40 under the same conditions does not lead to such an effect. The decrease in the electroosmotic permeability of modified polystyrene-based membranes does not exceed 10% (Fig. 2). It can be explained by different structure of membranes MF-4SK and MK-40. It leads to different localization of polyaniline in the composites based on them [2].



a) b)

Figure 1. Concentration dependences of the water transport numbers for membranes MF-4SK (a) and MF-4SK/PAn (b) in dependence on the counter-ions type: 1 – Li^+, 2 – Na^+, 3 – Cs^+, 4 – K^+, 5 – H^+

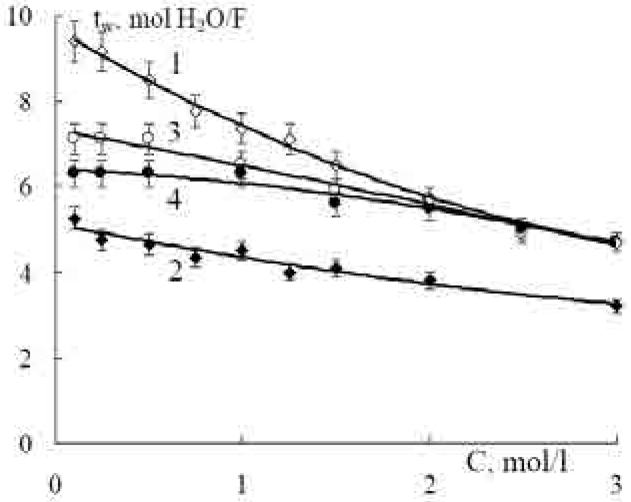


Figure 2. Concentration dependencies of water transport numbers in NaCl solutions: 1 – MF-4SK; 2 – MF-4SK/PAn; 3 – МК-40; 4 – МК-40/PAn

The obtained values of water transport numbers for all of the samples were compared with the specific water content (n_m) of membranes to reveal differences in the amount of water distributed in the membrane structure under equilibrium conditions and the amount of water transferred through the membrane under the electric field. The transition the MF-4SK membrane to the composite MF-4SK/PAn is accompanied by the decrising of both static (n_m) and dynamic (t_w) characteristics. This is explained by the morphological changes in the initial membranes associated with the appearance of organic components and changing of water state in samples.

To note the influence of the nature of polymeric matrix on the electroosmotic transference it was calculated the relation of t_w/n_m. This relation means that only a part of the whole amount of water is transported in the electric field. Values of t_w/n_m ratio characterizing the fraction of water transferred with Na^+ ions upon the imposition of electric field compared to the content of water in membrane are shown in figure 3. It is clear that approximately half the water does not participate in electrotransport for both initial membranes MF-4SK and MK-40. Intercalation of PAn in structure of sulphocationic membranes with different polymer matrixes have different influence on changing values of t_w/n_m ratio (Fig. 3). This opposite changes might be due to the different level of heterogeneity of MF-4SK and MK-40 membranes. It leads to blocking effect of polyaniline on MF-4SK transport channels.

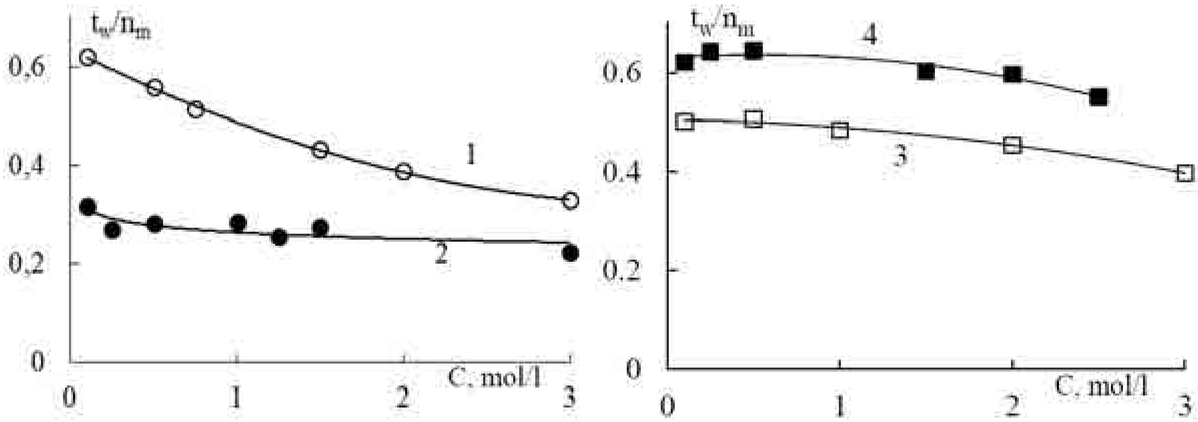


Figure 3. Concentration dependencies of t_w/n_m in NaCl solutions:
1 – MF-4SK; 2 – MF-4SK/PAn; 3 – MK-40; 4 – MK-40/PAn

Such investigations are useful to solve the problem concentrating the sodium chloride solution by electrodialysis processes. It was established that the composites based ion-exchange membrane MF-4SK and polyaniline are perspective to application in electromembrane processes of obtaining concentrate electrolyte solutions [3].

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Electromagnetic shielding behavior of composite films prepared with carbon materials and conducting polymers

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Electromagnetic (EM) radiation is becoming more and more serious problem with increasing use of electrical and electronic devices in our daily lives. The human body is daily exposed to EM radiation of different intensity, frequency and duration. It may causes the serious problems for health.

Conducting polymers (CPs) are interesting materials for EM shielding (EMS) due to their good electrical conductivity. Also, the CPs could be used to minimize the problems with EMS and reduces the pollution of the environment as well due to reducing the amount of metal which usually used for the EMS materials. In addition metal can't be used as EM absorbers due to the surface reflection.

Three CPs, like polyaniline (PAni), polypyrrole (PPy) and Poly3,4-ethylenedioxythiophene (PEDOT) were investigated in this work. The CPs coated carbon materials (like graphite and carbon black) were prepared by chemical polymerization of monomers on the surface of carbon particles in order to develop the novel EMS materials. The advantages of using both CPs and carbon materials as conducting fillers EMS materials were investigated. The idea was that the carbon provides long and continuous electrical conducting pathways. Besides, the small contact surfaces between the carbon particles could be increased by using CP as an interface layer at the contact points between the carbon particles. This would provide a good conductivity for EMS materials.

The research focuses on the microwave frequency in the range up to 4.0 GHz. A radiated shielding effectiveness testing was performed in a reverberation homemade chamber. Shielding effectiveness of EMS composite film with a thickness about 100 mcm was defined as the difference between the received power with and without the shielding parts assembled. The shielding effectiveness of CP/carbon materials ranged between -15 dB and -35 dB. It was observed that an increase of shielding effectiveness of CPs/carbon materials is obtained for higher surface conductivity composite due to CPs. A better conductivity of material produces a better reflection of EM waves. Also, it was observed that the shielding effectiveness of CP/carbon materials increased with frequency.

Current-voltage curves of anisotropic composites based on the cation-exchange membranes and polyaniline in the different electrolyte solutions

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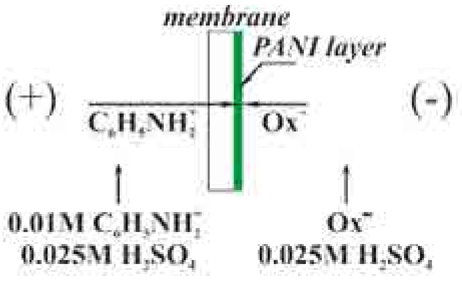
The various phenomena were found during the study of electrochemical properties of the anisotropic composites based on Nafion type membrane MF-4SK and polyaniline. Asymmetry of the diffusion permeability and the current-voltage curve, barrier effect of a polyaniline layer for electroosmotic flow and blocking effect for the transport of protons in an electrical field were observed [1-3]. The aim of this work is the investigation of polarization behavior of composites containing polyaniline on one of their surfaces.

Two types of membranes were used as the initial. They were the homogeneous membrane MF-4CK and the heterogeneous electrodialysis membrane MK-40, which is a polymer blend composed of a synthetic highly basic sulfonated cation-exchange resin KU-2 and polyethylene and reinforced with a Kapron mesh to impart necessary mechanical strength. Composites were obtained *in situ* by aniline oxidizing polymerization under direct current conditions [2]. A 0.01 M aniline solution in 0.025 M H_2SO_4 was fed into the cell chamber on the anode side and $(NH_4)_2S_2O_8$ or $K_2Cr_2O_7$ solution in 0.025 M H_2SO_4 was introduced on the cathode side. A 0.025 M H_2SO_4 solution was fed in the electrode chambers. The synthesis was carried out at 100 A/m^2 densities during 60 min for MF-4SK membrane and 120 min for the MK-40 membrane. The anilinium cations were transferred, in accordance with the direction of electric current, across the cation-exchange membrane into the concentration chamber (Fig. 1). The oxidizer anions, in turn, migrated to the membrane surface, where the oxidative polymerization of aniline was occurred. Thus, a polyaniline (PANI) layer formed on the membrane surface on the cathode side.

The membrane voltammetry method permits to characterize membranes during the polarization processes. The current voltage curves (CVC) of these materials in different electrolyte solutions were measured. The main characteristics of CVC are the slope of the ohmic region to the axis of potential, the value of limiting current density and the plateau length were estimated for the each of membrane orientations in relation to counter ions flow. The asymmetry of CVCs were observed for all composites (fig. 2). The analysis shows that the asymmetry effect of the CVC is more pronounced for the composites based on MF-4SK membrane.



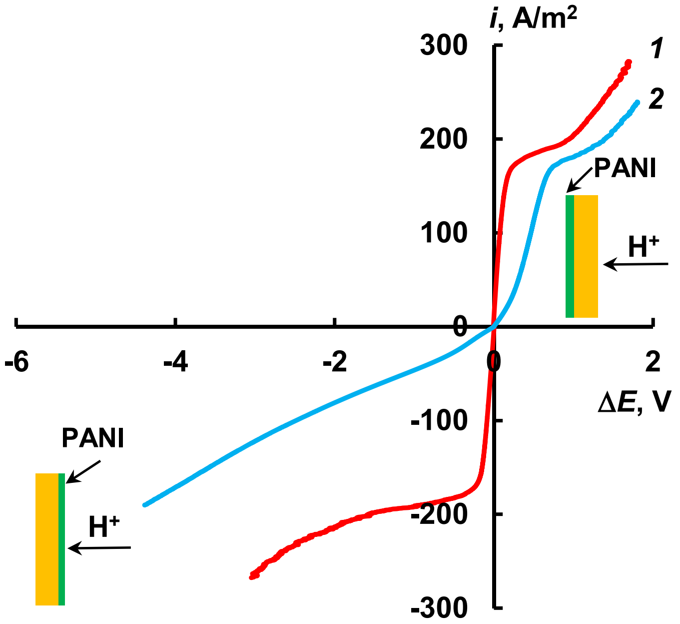


Fig. 1. Scheme of polyaniline synthesis on the membrane surface under the action of the electric field.

Fig. 2. CVCs of MK-40/PANI (1) and MF-4SK/PANI (2) measured in 0.025 M H_2SO_4 solution.

The influence of the electrolytes nature on the asymmetry of current voltage curves was studied. It was found that the asymmetry effect of the CVC is more pronounced in acid solutions, as compared to salt solutions, for composites based on MF-4SK membrane.

Acknowledgments: This work was supported by the Russian foundation for the basic research (project № 18-38-20069).

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Application of composites based on ion-exchange membranes and polyaniline for separation of singly and multiply charged cations

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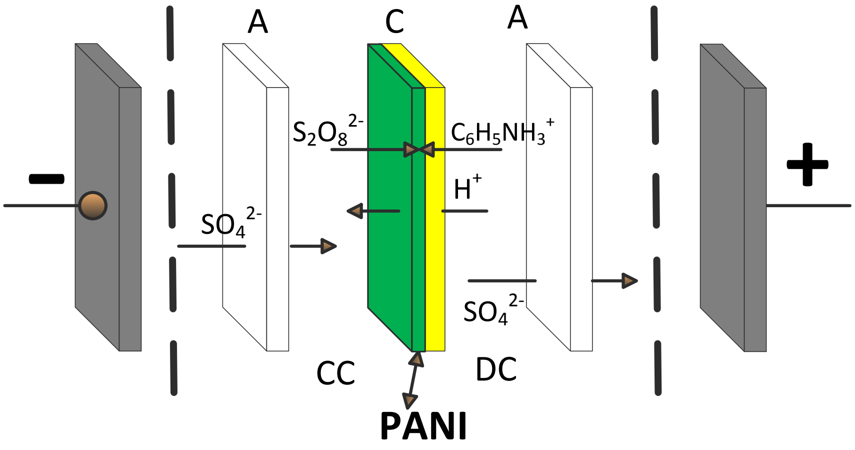
Electromembrane technologies are being widely used at present time to solve a variety of problems associated with the separation and concentration of electrolyte solutions, as they are cost effective and environmental friendly.

An urgent task is to modify ion-exchange membranes in order to impart charge selectivity to them for efficient separation of a mixture of single- and multiply charged ions. One of the promising modifiers for imparting charge selectivity to cation-exchange membranes is polyaniline (PANI) [1, 2]. The purpose of this work is to study the competitive transfer of sodium and calcium cations, as well as hydrogen and calcium ions through ion exchange membranes modified with polyaniline.

In this work, the competitive transfer of single- and multiple charged cations across the base membranes MK-40, as well as anisotropic composites MK-40/PANI was investigated. The modified membranes were obtained by electrochemical synthesis in an electrodialysis cell, according to the scheme shown in Figure 1.



A – anion-exchange membrane; C – cation-exchange membrane;
DC – desalting chamber; CC – concentration chamber;
EC – electrode chamber; PANI –polyaniline layer
Figure 2. Scheme of formation of a polyaniline layer on the surface of the membrane MK-40

The working size of the membranes was 5x20 cm^2, the number of chambers was 5. A mixture of 0.1 M NaCl and 0.05 M $CaCl_2$, as well as 0.1 M HCl and 0.05 M $CaCl_2$ was used as working solutions. The value of the voltage drop on the pair chamber was 1-5V. The kinetic dependences of the change in the concentration of ions in the desalting and concentration chambers were obtained and the main mass transfer characteristics of electrodialyzers were calculated. It was found that the flux of calcium ions exceeds the flux of sodium ions for all investigated voltage drops on the pair chamber. In this case, at first, an increase in the fluxes for both ions is observed with increasing voltage, but at higher voltages, the growth slows down sharply, which is possibly due to the transition of the system to the limiting state. The use of modified MK-40/PANI composite membranes allows reducing the transfer of a double charged ion (Ca^{2+}) through the membrane. Thus, the obtained modified membranes can be successfully used to separate mixtures of single- and multiply charged ions.

Acknowledgments: This work was supported by the Russian foundation for the basic research (project № 18-38-20069).

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Redox Active Coordination Polymers Based on Ferrocene as Efficient Electrocatalysts for Hydrogen Evolution Reaction

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The coordination polymers (CP) are attractive objects for constructions of various materials for molecular electronics, adsorbtion, catalysis, sorption, luminescence, biomedicine etc From a broad variety of organic functional groups employed as ligand in CPs synthesis, the incorporation of ferrocene units into CP arrays could be attractive due to the electronic donating ability, reversible redox chemistry, steric properties and effortless functionalization of this stable fragment. A large number of ferrocene-based ligands have been exploited in the field of coordination chemistry to produce multimetal-containing complexes. Nevertheless, the reports on CPs containing ferrocenyl groups are limited mainly to the ferrocenyl coordination polymers, based on ferrocenyl-substituted carboxylates and pyridine-containing ferrocene.

We focus on the design and synthesis of coordination polymer based on ferrocenylphosphinic acids, because the first examples on their basis have shown interesting properties.1,1′-Ferrocenediphosphinate is an excellent candidate, due to stable ferrocene moiety and two phosphinate coordination sites. Moreover, its conformational lability can provide many interesting structures and allows the ligand to adopt conformation most suitable for metal coordination. Furthermore, the combination of the rotational freedom of the ferrocene core together with tetrahedral geometry of incorporated phosphinate groups could initiate an axial chirality of resulted CPs, if combined with define inorganic node.

Herein we report on the synthesis, crystal structure, spectroscopic and electrocatalytic properties of transition metal-based CPs with ferrocene-containing diphosphinate ligand.

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New Coordination Polymers Based on Transition Metals for Preparation of Energy Storage

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In recent years, a lot of effort has been devoted to the development of various rechargeable and reversible energy storage devices and energy converters, such as supercapacitors, fuel cells and ion batteries. Designing devices with high energy density and power requires the use of high-performance electrode materials in combination with suitable electrolytes. Coordination polymers (including metal–organic frameworks), a developing class of porous materials. The main advantage of MOFs is their controlled structure and tunable porosity at the molecular level by selecting metal nodes and organic linkers. As a result, they are widely used in various branches of science.

Herein we report on the synthesis, crystal structure, spectroscopic and electrochemical properties of transition metal-based CPs with ferrocene-containing diphosphinate ligand. Flexible metal-organic frameworks has been synthesized using ferrocene-based ligand bearing phosphinic groups ($Fc(PHOOH)_2$ = 1,1'-ferrocenediyl-bis(*H*-phosphinic acid)). In this compound metal (Co or Mn) are bound by phosphinate fragments to give infinite chains and the latter are interconnected by ferrocene groups to form a 2D coordination polymer ($[M(Li_2S_2)_2(Fc(PHOO)_2)]_n$).

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Stable isoporphyrin/porphyrin copolymer: mechanism of the electrochemical routes and photovoltaic properties

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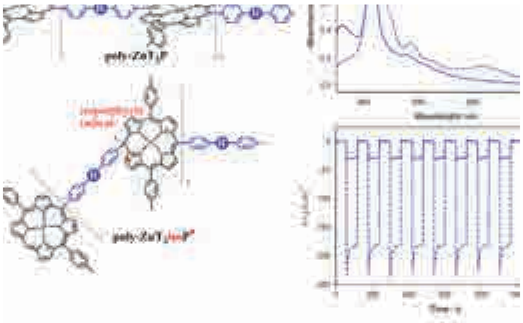
Isoporphyrin are mainly described in the literature as a intermediate of the reaction (biosynthesis of chlorophyll molecules as well as heme oxidation). The formation of isoporphyrins can be obtained upon nucleophilic attack on oxidized porphyrin. Optical spectrum of isoporphyrin present a typical strong absorption at the near-IR region but also remarkable redox behavior [1]. Most of the isoporphyrin reported show a high tendency to decompose either by ring opening or by rearomatization to give the starting porphyrin [2]. But, different procedures have developed to synthesize stable isoporphyrins [3].

In this presentation, new strategy to obtain stable isoporphyrin integrated in the polymers we will presented and will be compared with "classical" porphyrin copolymer with viologen spacers developed radical cation as well as dication porphyrin using porphyrin such as zinc 5,15-ditolyl-porphyrin (**ZnT$_2$P**) are powerful electrophiles which can rapidly react with nucleophiles such as dipyridyl ligand (py-R-py) to form copolymers containing stable isoporphyrins (**poly-ZnT$_2$isoP$^\bullet$**) or porphyrin (**poly-ZnT$_2$P**) depending of the applied potential chosen. Mechanisms of electrochemical routes to these electroactive copolymers will be presented as well as the optical and amazing redox properties of **poly-ZnT$_2$P** and **poly-ZnT$_2$isoP$^\bullet$** (Fig. 1). Forma been monitored by EQCM. The impedance properties as well as the photovoltaic performances have been investigated where **poly-ZnT$_2$isoP$^\bullet$** present considerably better performance in comparison of **poly-ZnT$_2$P**.



gure 1. Left: structures of copolymers **poly-** d **poly-ZnT$_2$isoP$^\bullet$**. Right: optical and otocurrent characteristics of **poly-ZnT$_2$P** **ly-ZnT$_2$isoP$^\bullet$** copolymers.

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Stainless-assisted synthesis of metal nanoparticles: can the electrolytic approach boost the potentialities of this green and scalable method?

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Metal nanoparticles (NPs) are receiving increasing attention in several fields. Among the methods for NPs preparation, the chemical reduction of metal ions is widely applied, based on the use of precursor and reducing/stabilizing agents. In these cases, byproducts and adsorbates that may affect negatively the quality of the colloid are often present. Recently, few research groups have proposed steel corrosion to assist the synthesis of NPs starting from a precursor salt, such as $HAuCl_4$ [1,2]. In this approach, stainless steel can be used as removable reducing substrate in the aqueous preparation of gold nanocolloids. This innovative method is very easy, quick and cost-effective, allowing the synthesis of highly stable NPs without additional capping agents. However, the mechanisms behind this reaction are not yet fully understood. Based on this protocol, we have evaluated the role of several parameters (e.g. reaction time, precursor concentration, effect of Cl^-, stainless steel composition, etc.). Moreover, we have systematically measured the stainless steel open circuit potential under the different experimental conditions, which allowed for a better correlation between the behavior of different substrates towards corrosion and the resulting NP reaction yield. We have also started investigating how the application of an external potential to the stainless steel, driving the system towards an electrolytic process, influences the whole process in terms of NPs composition and properties (as per detailed spectroscopic and morphological analyses). In this communication, we will provide an overview of the solid-mediated reduction process and we will critically comment on its tuneability by an external bias.

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A New Type of Cyclic Silicone Additive for Improving Energy Density and Power Density of Li-O_2 Batteries

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Capacities and power density of Li-O_2 batteries are closed contacted with physical properties of electrolyte. In this work, we research the electrochemical performance of the mixed electrolyte between dimethylsulfoxide (DMSO) and N, N-dimethylacetamide (DMA), firstly. The cell with 70% of DMA mixed electrolyte exhibited high discharge rate capability and low over-potential that the charge platform is below 3.6V at a current density of 0.2 mA cm^{-2}. The titration result showed that DMA is more stable than DMSO in Li-O_2 batteries. It is because that the stability of high donor number (DN) solvent is less than that of the low DN solvent in Li-O_2 batteries, even though high DN solvent has a high discharge capacities. [1, 2]

Based on this, we proposed a new strategy; namely, by combining a relative stable solvent with low DN and a stable additive as the cell electrolyte, the relationship between high capacity and high stability could be balanced. A novel type electrolyte additive, octamethylcyclotetrasiloxane (OMTS), is applied to Li-O_2 batteries with TEGDME-based electrolyte with low DN. The electrochemical tests show that, With an optimal OMTS content (10% OMTS), the cell displayed a discharge capacity of 6778 mAh g^{-1} at 0.05 mA cm^{-2}, and its discharge capacity still has an acceptable capacity of 1823mAh g^{-1} at an ultra-high current density of 1 mA cm^{-2}. Specially, the capacity retention of the cell with optimal OMTS content is more than double that of the cell with no OMTS additive at large current density of 1 mA cm^{-2}. The further NMR and Li_2O_2 yield measurements during discharge indicate that OMTS additive does not alter the discharge product and compromise the stability of electrolyte.

Acknowledgments: Funding support from 973 program (2014CB932301)

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POSTERS II

Effect of changing chalcogen atom on electron delocalization on benzochalcogendiazoles radical anions.

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Benzochalcogendiazoles (BChDA) are strong electron acceptor compounds that are widely investigate in the field of organic photovoltaics (OPV) and organic field effect transistors (OFET) [1,2]. In combination with electron donor unit BChDA are part of a lot of low and high molecular weight ambipolar compound, that can be reversibly both p- and n-doped.

Subject of our research was group of three model donor-acceptor-donor molecules that differing in chalcogen atom in central benzochalcogendiazole unit. Experimentally have been determined electrochemical and spectral properties and examine quantitatively delocalisation of unpaired electron on electrochemically generated radical anions of investigated compounds series.

Both experimental and computational results show that the heavier chalcogen atom, the spin density localize more at moleule center.

Acknowledgments:
This work was funded by Narodowe Centrum Nauki (NCN) grant OPUS no. 2016/23/B/ST5/03103.
This research was supported in part by PLGrid Infrastructure.

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Size, ligand and solvent effects in electrochemistry of electroactive CdSe QD - Cd^{2+}/Cd_{ad} system

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Quantum dot (QD) films are widely studied by electrochemical means, due to variability of their physical properties under charge injection and subsequent processes which are of interest for electrochromic and photovoltaic devices development [1,2]. Although significant knowledge of size-effects in QD electrochemistry has been accumulated over the last decades, there is a lack of information, especially concerning QD surface influence on electrochemical response.

We showed earlier [3] that interfacial charge transfer in CdS QD/Cd^{2+}(aq) and CdSe QD/Cd^{2+}(aq) systems leads to Cd underpotential deposition (upd) with the upd potential dependent on the QD size. In this work we present recent results of a systematic study of size and capping ligand effects on cadmium underpotential deposition onto film electrodes which were electrophoretically formed of well-characterized nearly monodisperse CdSe QDs as described in [4].

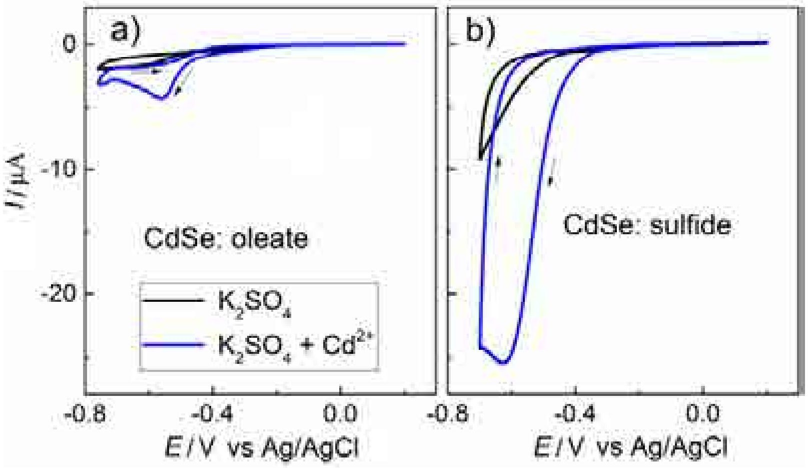

Figure 1. Cathodic reduction of Cd^{2+} on (a) oleate-capped and (b) sulfide-capped CdSe QD films. QD diameter: 4.5 nm, d*E*/d*t*: 5 mV s^{-1}. Electrolyte: 0.5 M K_2SO_4 + 10 mM $CdSO_4$. Geometric surface area: 0.13 cm^2.

Oleate-capped CdSe QDs were electrophoretically deposited onto FTO substrate from colloidal solution in nitrobenzene giving films with high adhesion and good electrical contact with the substrate. Electrochemical behavior of the films was first examined with cyclic voltammetry in nitrogen-purged aqueous electrolyte containing K_2SO_4 and $CdSO_4$ (Figure 1). A well-defined cathodic peak attributed to Cd upd appeared upon $CdSO_4$ addition to the blank electrolyte solution. The electrochemical response of oleate-capped QDs in Cd upd was weak (Figure 1a), and increased strongly with the oleate substitution by sulfide (Figure 1b).

Cd upd on electrodes composed of CdSe QDs of different size has revealed a well-pronounced size-dependent behavior (Figure 2). The upd onset and peak potentials shifted positively with the QD diameter increase.

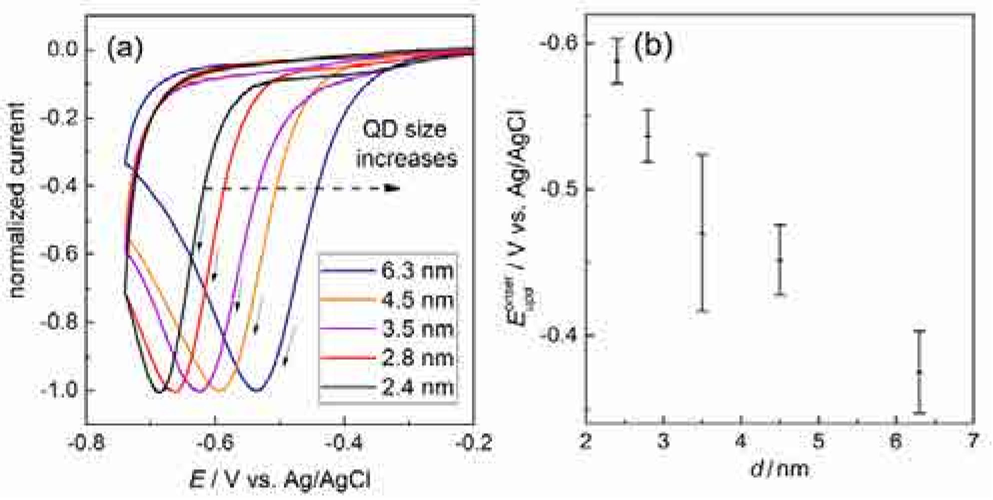

Figure 2. (a) Cathodic reduction of Cd^{2+} on sulfide-capped CdSe QD films at variable QD diameter. (b) The upd onset potential dependence on QD diameter

The observed dependence of the upd potential on QD size is similar to that of the potential of electron injection into conduction band edge (LUMO). Hence, we can conclude that Cd upd onset is governed by LUMO position. Cd upd proceeds irreversibly and therefore is observed only in the first cycle of cyclic voltammogram.

The discovered size effect is of interest for studying QD redox behavior and QD surface modification thus promoting electrochemical methods into physics of nanostructures.

Acknowledgments: This research has received funding from Horizon 2020 research and innovation programme under MSCA-RISE-2017 grant agreement No 778357.

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The effect of trap states on the optoelectronic properties of semiconductor photoelectrodes

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Detailed mechanistic understanding of the optoelectronic features is a key factor in designing efficient and stable photoelectrodes. *In situ* spectroelectrochemical methods and electrochemical impedance spectroscopy provides an opportunity to scrutinize the effect of trap states on the optical and electronic properties of different semiconductors, and to assess their stability against (photo)electrochemical corrosion. Different metal oxides and halides were studied, and results gathered for TiO_2, NiO and CuI will be presented in this talk. The absorption bands in the UV-visible spectrum and the Raman spectral features were directly influenced by the applied bias potential. These spectral changes exhibit a good correlation with the alterations observed in the charge transfer resistance. Interestingly, the population/depopulation of the trap states, that are responsible for both the changes in the optical and electronic properties, occur in a different potential/energy regime. These insights are also important for solar cell research where different semiconductors are often employed as charge carrier-transporting materials.

IrO2/TiO2 nano-catalysts applicable as anode materials in electrolyzers

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A facile, alternative method was developed to combine the properties of TiO2 with the electrocatalytic activity of IrO2 for oxygen evolution reaction. Ir was depositied on the surface of TiO2 powder by UV photodeposition from appropriate Ir salt aqueous solutions.

The resulting of Ir/TiO2 composites have been characterized by transmission electron microscopy (TEM), energy-dispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS). The XPS results showed that Ir was deposited in an oxide form (IrO2) during the preparation.

The electrochemical characterization of the resulting IrO2/TiO2 material was carried out by cyclic voltammetry (to identify the surface electrochemistry of the catalyst) and linear sweep voltammetry to test oxygen evolution/water splitting activity.

Acknowledgments: Financial support of CEST, Austria in the frame of the COMET program is gratefully acknowledged. Bilateral joint research project “Preparation of efficient catalysts for fuel cell, electolyzers and photo-fuel cells by galvanic replacement” 2016-2018 between Bulgarian Academy of Sciences (BAS) and Aristotle University of Thessaloniki, Greece is also acknowledged.

Characterization of $PtIrO_2/TiO_2$ as Bifunctional Electrodes for Unitized Regenerative Fuel Cells

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Unitized Regenerative Fuel Cells (URFCs) is an attractive and efficient method for producing hydrogen and clean energy. Nevertheless, to combine a polymer electrolyte water electrolyzer (PEMWE) and a polymer electrolyte fuel cell (PEMFC) is still a big challenge. It is still necessary to overcome several practical and structural features. The oxygen reduction (ORR) and the oxygen evolution (OER) are the limiting reaction steps at the oxygen electrode for PEMFC or PEMWE, respectively [1,2]. Therefore, its high-efficiency depends on the type of electrocatalysts. As a consequence, a broad research is focused on developing a new design for the oxygen electrode in URFCs. In this work, a bifunctional electrode for OER and ORR were obtained by photodeposition of Pt and IrO_2 on TiO_2 support. The resulting $PtIrO_2/TiO_2$ composites have been characterized by transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS) and X- ray photoelectron spectroscopy (XPS). Electrochemical characterization by CV and LSV in aqueous 0.1 M $HClO_4$ reveals that $PtIrO_2$ catalyst exhibits electrocatalytic properties for ORR and OER showing up a possible use in URFCs.

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Composition, electrical and optical properties of nanoporous TiO_2 doped with copper and molybdenum oxides

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Nanoporous titanium oxides are synthesized using a galvanostatic-tensiostatic method in electrolytes based on ethylene glycol solvent with water and ammonium fluoride additions. The porosity of the oxides is estimated by re-anodization in a suitable non-dissolving electrolyte, their optical properties are assessed using diffuse reflectance spectroscopy. Modification of the titanium oxides is created via electrodeposition of copper and molybdenum oxides in potentiodynamic conditions. X-ray photoelectron spectroscopic data point to a non-stoichiometric copper oxide with a composition close to Cu_2O. The results for molybdenum oxide indicate that it contains mainly Mo(V), substantial amounts of Mo(VI) and lesser quantities of Mo(IV). The conduction mechanism in such doped titanium oxides was studied by electrochemical impedance spectroscopy. Diffuse reflectance measurements indicate a greatly improved absorption of visible light in comparison with pristine nanoporous TiO_2 which points to prospective photocatalytic abilities of the modified oxides as photoanodes (with Mo-oxide) and photocathodes (with Cu-oxide).

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A Concerted Electrochemical and Theoretical Investigation of the Ag/TiO_2 nano-heterojunction

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Suitably designed nano-heterojunctions are able to enhance synergistic functionalities of different materials yielding to "brave new systems" with innovative and sometimes unexpected physicochemical properties [1]. However, the complete understanding of these devices has to be deeply studied. In this work, a concerted theoretical and electrochemical investigation is proposed to gain insights into a metal-semiconductor interface, namely that created by the silver/anatase hybrid nanocomposite, a promising material for advanced sensing applications [2]. In particular, it provided the first photorenewable and anti-fouling sensor device, enhancing the analytical limits in terms of accuracy, sensitivity, detection limits, and photoactivity [3]. Furthermore, the hybrid material is proven to be extremely robust against aging, showing complete regeneration, also after one-year storage.

The electrochemical/electroanalytical virtues of the Ag/TiO_2 junction were evaluated in terms of current densities and reproducibility, providing their explanation at the atomic-scale level and demonstrating how and why the final device can act as silver-cation positive electrode [4]. Moreover, Cyclic Voltammetry and Electrochemical Impedance Spectroscopy were used in combination with periodic plane-wave DFT calculations, giving comparable qualitative but also quantitative results. In particular, we theoretically estimated the overall amount of electron transfer toward the semiconductor side of the interface at equilibrium and suitably designed electrochemical experiments, which strictly agree with the theoretical charge transfer estimates. Moreover, photoelectrochemical measurements and theoretical predictions show the unique permanent charge separation occurring in the device [4].

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Influence of surface layers onto lithium intercalation into the nanotubes of titanium dioxide

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The electrochemical behavior of nanotubular titanium dioxide in the electrolyte containing lithium salts were investigated by means of the method of a cyclic volt amperometry and galvanostatic discharge. The titanium dioxide nanotubes received on a titanic foil by method of anode oxidation in ethylene glycol solution represent the self-organized formations with a diameter of tubes of 30-50 nanometers and with height of 20 microns. From cyclic volt amperogrammes the dependences characterizing diffusive kinetics of the process were received. On the basis of these data the coefficients of lithium diffusion in titanium dioxide were calculated. Modification of a surface of the massif nanotubes with use of various options of sedimentation of the ion-conducting layer was carried out and change of characteristics of diffusive transfer at forming the ion-conducting layer on a surface was shown. The obtained data demonstrate that the ion-conducting layer created on a surface begins to define electrochemical intercalation of lithium in titanium dioxide and changes a boundary condition for its further diffusion into the depth of phase.

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Effect of Structure of Polymeric Nickel Complexes with Salen-Type Ligands on The Stability in Solutions of Water-Containing Electrolytes and The Charge Transfer Parameters

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Polymeric transition metal complexes with salen-type Schiff base ligands are considered as promising materials for modification of electrical double layer capacitor electrodes. Among the applied conductive polymers, complexes of transition metals with the derivatives of salen (N,N'-ethylenebissalicylimine) ligand exhibit a set of important features like reversible electrochemical oxidation over a wide range of the potential [1] and specific capacity up to 300 F/g [2]. The results of supercapacitor electrode modification by polymer films of nickel complexes with salen-type ligands have been reported [3], however the influence of the ligand structure on the electrochemical properties and stability of these polymers that define their performance in the energy storage applications have not been systematically investigated. However, the properties of these polymers, such as their capacity, charge transfer rate and stability are mainly influenced by the ligand structure. This report describes results of systematic investigation of capacitance, charge transfer rate and stability of polymeric nickel complexes with different salen-type ligands. Analysis of results obtained by different electroanalytical techniques shows that introduction of electron donating substituents into the phenyl rings and diamine bridge of the salen ligand causes noticeable changes in electrochemical properties of corresponding polymeric nickel complexes, leading to formation of more stable films with good energy storage properties.

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NiO-based hybrid material for CO_2 reduction catalysis

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The development of efficient, stable, ecofriendly and cheap electrode materials is of paramount importance to insure global sustainable development, through the use of solar energy conversion devices such as Dye-sensitized Solar Cells (DSCs, for photovoltaic conversion) and Dye-sensitized PhotoElectrosynthesis Cells (DSPECs, for photocatalytic conversion to “Solar Fuels”). In this regard, achieving an efficient photo-induced charge separation at the molecular level, at interfaces and in bulk materials, is crucial.[1] Investigation of hybrid materials has already brought appreciable knowledge and improvements to the field.[2]

We focus our interest on the elaboration of NiO-based p-type photocathodes for solar energy conversion by photocatalysis (CO_2 reduction into Solar Fuels), using DSPECs prototypes (with a photoactive working electrode). The layer-by-layer preparation of functional photoelectrodes requires the control of the arrangement of the various components for optimal charge transfers and transport. For example, we use controlled-deposition electrochemical techniques such as *in situ* electro-assisted PhotoElectroPolymerization (*PEP*) for the preparation of the Hole-Transporting Material (HTM, used as a charge carrier within the device) on the photosensitized mesoporous semi-conductor of the electrode. Recent progress based on electrocatalytic and photoelectrocatalytic approaches for CO_2 reduction will be presented.

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Electrochemical Reduction of CO_2 Using Supported Au Nanoparticles.

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Abstract

Since the tide of industrialization begun, there has been a rapid increase in the concentration of anthropogenic CO_2 in the atmosphere. This has become a matter of global concern because of the environmental implications it brings, such as global warming, sea level rise and soil infertility [1]. There is however, the need to stabilize CO_2 emissions by reducing or recycling CO_2 into value-added products; either at its nascent stage or after its storage. Electrocatalytic reduction of CO_2 is an environmentally clean technology capable of converting CO_2 with high rate and selectivity to gas phase products (CO, CH_4) and liquid phase products (HCOOH, CH_3OH) [2]. Here, we report a one pot synthesis of Au nanoparticles supported on carbon based materials. These materials were then deposited on a glassy carbon electrode (GCE) surface and were used for CO_2 electro-reduction in 0.1M TBAPF6 electrolyte and acetonitrile solvent. Results showed that the reduction of CO_2 took place at -1.4 V vs Ag/AgCl. The material properties and catalytic activity were interpreted using Microscopy, Raman and Fourier transform Infra-red (FTIR) spectroscopy.

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Electrochemical CO_2 reduction on functionalized metal porphyrins

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The past few years has witnessed arousing interest in electrochemical reduction of CO_2 in alleviating anthropogenic CO_2 into valuable chemical feedstocks or fuels. However this fascinating research area remains a scholarly endeavor in terms of selectivity, stability and efficiency of the catalytic systems. Among the available resources, Macrocylic metal complexes with versatile molecular structures can be tailored to enhance its selectivity and electrocatalytic efficiency towards CO_2 and holds the promise of closing the CO_2 cycle. Here we report facile one pot electropolymerization of keto functionalized Zinc and Nickel octaethylporphyrin using 4, 4'-bipyridine as a bridging nucleophile on the electrode surface. These polymeric film formation at the meso position of the electrogenerated macrocylic radical cation were corroborated by cyclic voltammetry, Ultraviolet-visible (UV-Vis) and Fourier transform Infra-red (FTIR) spectroscopy. The uniform and homogeneous film formed at the electrode surface was evaluated for their potential in the electroreduction of CO_2.

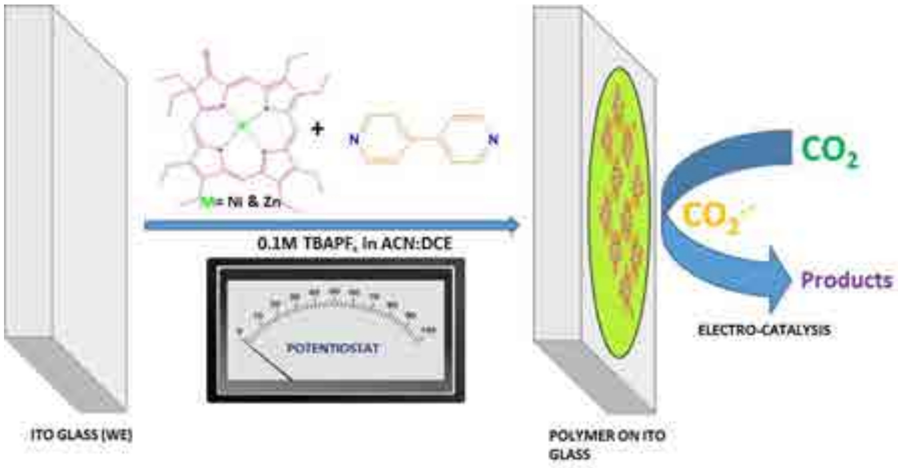

Figure1: Schematic of elctropolymerization and catalytic electroreduction of CO_2.

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Au-Ag Bimetallic Catalysts with Different Composition for CO_2 Reduction

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Developing highly efficient and selective catalysts with long-term stability is a crucial step toward the sustainable electrochemical conversion of CO_2 to valuable chemicals[1–3] In this work, the electrocatalytic reduction of CO_2 on Au-Ag bimetallic alloyed nanoparticles with different compositions was evaluated. This system provides an ideal model for understanding the correlation between the catalytic activity and the bimetallic composition of the electrocatalysts. It was found that the CO Faradaic efficiency (the syngas ratio ($CO:H_2$)) can be tuned by controlling the composition of the catalyst particles. This trend was attributed to changes in the electronic properties, which in turn results in different binding strength of COOH and CO intermediates. Notably, a gradual shift of Fermi level (E_F) away from the vacuum level (E_{VAC}) was observed with increasing Au content. This shift correspondingly reduces the binding energy of the intermediate on the Au-Ag bimetallic surfaces, resulting in the gradually changing catalytic activity.

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Comparative study of the electrochemical performance of ’’self-deposited’’ electrocatalysts on 3D Ni-foam in alkaline media

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Electrochemical water splitting has been considered as promising strategy for renewable clean energy. The OER and ORR reactions (involve the two-electron or four-electron transfer reactions) are hindered by significant overpotentials and slow kinetics and presents a bottleneck, restricting the efficient development of water splitting technology. In order to overcome these limitations, the OER and ORR reactions should employ an active catalyst to accelerate the reactions. Platinum group metal elements (Pt, Ir, and Ru) are known as the best catalysts for these reactions but their availability, stability, and cost are prohibitive to commercialize on a broader scale.

To address this problem, extensive effort has been focused on earth-abundant and economical catalysts for enabling OER reaction efficiently, such as transition metal oxides, chalcogenides, nitrides and carbides.

Herein, we report recent developments in nanostructured materials ‘’self-deposited’’ on 3D nickel foam by ,,Deep and Drying method’’ (DDM) as potential electrode candidates for partial electrode reaction during electrochemical water electrolysis.

The ,,Deep and Drying method’’ provide good opportunity for production of earth abundant, cost effective, non-precious self-made electrodes with low overpotential, good electrocatalytic activity and high stability.

The catalytic efficiency of the prepared electrocatalysts is evaluated in 1M KOH using the conventional electrochemical methods of cyclic voltammetry and steady state polarization curves.

It is found that the type of the anions (Cl^-, NO_3^-, SO_4^-) in the solution during DDM affect the electrocatalytic properties of the Ni-foam. Results also show that the direct synthesis of nanostructured catalysts via DDM on a conducting substrate improve the performance of the resultant electrocatalysts due to their surface areas and the synergistic effect between the electrocatalyst and the conductive substrate.

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Photoelectrochemical studies on alloyed PbI_2/CuI electrodes

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Metal halide semiconductors have drawn wide attention in semiconductor research due to their remarkable optoelectronic properties, ease of preparation, and abundant constituent elements and their position is now indispensable after the perovskite wave.[1,2] Still, most of the research works are focussed on lead halides (PbI_2), combining another suitable metal halide with PbI_2 is an opportunity to study the impact of mixed halides on performance and stability.

Copper iodide (CuI) is another trending halide semiconductor with p-type wide bandgap and high hole mobility.[3] Expecting that the combinations of these two p-type materials perform better than the individual components, CuI and PbI_2 with different molar compositions were prepared. The photoelectrical properties and stability were checked carefully. The hybrid with equal molar ratio of PbI_2 and CuI produced highest photocurrent. The band emission of CuI is completely quenched in the presence of PbI_2, elucidating efficient charge transfer from CuI to PbI_2, and consequently improving the photocurrent. Theoretical studies on PbI_2-CuI were done to understand the possible interactions between CuI and PbI_2 in the alloy. Here, we identify a promising alloyed photocatalyst with high activity for photoelectrochemical applications.

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Graphene based fibre shaped flexible supercapacitor for wearable electronics

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Graphene has revealed a spacious range of encouraging applications with its strong mechanical strength, superior flexibility, high intrinsic carrier mobility and large surface area [1]. Graphene based electrodes have been using for flexible supercapacitors which are suitable for many applications such as wearable electronics, because of their special character like facile synthesis, electronic properties, etc. [2].

In this study, different types of yarn, based on graphene, were used as flexible supercapacitor electrodes. Wet spinning method was used to prepare the graphene based yarn, which displays special morphologies and mechanical properties. The produced yarns were characterized by cyclic voltammetry and electrochemical impedance spectroscopy (CV and EIS), SEM, FTIR and Raman spectroscopy. Capacitor behaviors were studied with different techniques.

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2D Metal Oxide Based Photoelectrochemical Biosensor for Glucose Detection

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Over the past years, semiconductor materials had gain popularity due to their physical and chemical properties, especially perovskite materials were subjected to many researches as a topic. Perovskite is a common name for compounds which have ABO_3 or A_2BO_4 structural formula and $CaTiO_3$ like properties.[1,2] Perovskites can be in various structures and can be separated to the thin sheets. 2D array provides high surface area and thinness, easy tailoring and increased functionality.[3] These features have been a major factor for choosing to use them in different applications and areas like in solar fuel cells, as catalyst, dielectric material, capacitor, sensing material, etc.[4] Photoelectrochemical sensor was selected in this work since PEC is very promising due to using visible light as a excitation source which provide high sensitivity and accuracy. Also, low cost and small devices can be prepared compared to florescence and electrochemical sensor.[5]

In the present work, the sensing properties of $KTiNbO_5$ and N-doped $KTiNbO_5$ perovskites, which were prepared with solid state method, were investigated. $KTiNbO_5$ was preferred for the work because of particular features like 2D structure, charge transfer nature, easy modifiability.[6] Moreover, N-doping altered the geometry of molecule that resulted in new functionalities such display good band-to-band excitation, increased the photoactivity and increased the absorption intensity.[7,8] The prepared powders were treated with acid to form proton exchanged powders. They were used at the exfoliation step to form nanosheets and the obtained nanosheets were coated with layer-by-layer to form multilayer thin film. In the next step, films were exposed to UV light to get organic-free material. Characterizations of films done by UV-Vis spectra, X ray diffraction and scanning electron microscopy. For photoelectrochemical detection of glucose, cyclic voltammetry and chronoamperometry measurements were done under different conditions. Photocurrent values were determined at both dark and light ambient.

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Influence of structure of Lix$FePO_4$ onto Nernst response of the potentiometric sensor

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Lithium ferrophosphate demonstrates good reversibility in charge-discharge cycles despite the existence of several consecutive stages of process, including phase transition.

This property of high reversibility and speed of electrode process was applied for use of this material as an electrometric sensor.

As a sensitive element the composite layer applied on an inert metal substrate, containing electro conductive additive and iron lithium phosphate were used. Calibration curves for this electrode in solutions of lithium carbonate of different concentration were obtained. Influence of degree of lithium de-intercalation in the electrode onto its Nernst characteristics was investigated.

Natural increase in an inclination in Nernst's equation in approximating experimental dependence with reduction of degree of de intercalation of lithium was found. Such behavior is connected with change of electro-conductivity of a sample. High currents of exchange for a lithium cation on a board of the section do not allow to be polarized considerably the border in corrosion process, causing Nernst behavior of the electrode.

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Transparent boron-doped diamond electrodes for (EPR) UV-VIS-NIR spectroelectrochemistry

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Transparent boron-doped diamond electrodes exhibit an interesting option for spectroelectrochemical measurements. Basic requirement for any working electrode in spectroelectrochemistry is its compatibility with the used spectral technique itself. This means the transparence in the case of transmission techniques like UV-VIS-NIR, as well as its sufficiently small interaction with microwave radiation in the case of EPR spectroscopy. Very general and important attribute of the spectroelectrochemical electrode must be its spectral background independent on the polarization within the available potential window[1,3].

Presented electrodes cover the doping level from semiconducting materials with high transparence to the metallic, very dark looking material. However, for spectroelectrochemistry, the optimal option is to use the doping level from 250 ppm to 750 ppm, according to their transparency. Electrodes are transparent from 300 to 2000 nm. For EPR spectroelectrochemistry, the only usable electrode is one with the lowest doping level (250 ppm). All electrodes exhibit very wide electrochemical window and conditioning upon cycling in one (anodic or cathodic) region. All studied electrodes exhibit stable spectral background, which is the very important aspect for spectroelectrochemistry.

Its stability is associated with low sp2 contaminant content as the result of preparation technique used[2]. The usability of electrodes was confirmed on a real samples and compared with conventional electrodes in spectroelectrochemistry.

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Methodological development of square-wave voltammetry

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1. Introduction

Square-wave voltammetry (SWV) is well-known and versatile voltammetric technique for analytical application, mechanistic studies and kinetic measurements of electrochemical processes [1]. In a quest for further methodological development several modifications have been recently proposed, such as multisampling SWV [2], SW chronoamperometry (or electrochemical faradaic spectroscopy) [3], and some novel concepts presented in the current communication, i.e., cumulative SWV and a hybrid technique between differential pulse and square-wave voltammetry.

2. Multisampling procedure in SWV

Understanding SWV as a repetitive double-step chronoamperometric technique, a novel methodology has been recently proposed based on the multisampling current procedure (Fig. 1). Single current measurement is replaced with multisampling, enabling construction of a series of so called *multi-sampled SW voltammograms*, which reflect the chronoamperometric behaviour of the electrode reaction. Proposed procedure is useful when the experiment is conducted at low frequency, i.e., long duration of the potential pulses, allowing sampling the current at the last portion of each pulse without sacrificing the large ratio of the faradaic-to-charging current.

Figure 1B illustrates the difference between multi-sampled and conventional SW voltammograms. The red line corresponds to the net voltammogram simulated at f = 10 Hz (duration of a single pulse t_p = 50 ms) but sampling the current at t_s = 40 ms, whereas the blue dashed line refers to the conventional voltammogram simulated at f = 12.5 Hz (t_p = t_s = 40 ms). Even though in the two cases the current is sampled at equal time (40 ms), the outcome of the two assumed experiments is not identical, revealing the difference in the multisampling and conventional SWV. With multisampling SWV one can construct a series of SW voltammograms from a single experiment, the analysis of which might enable full characterisation of the electrochemical reaction.

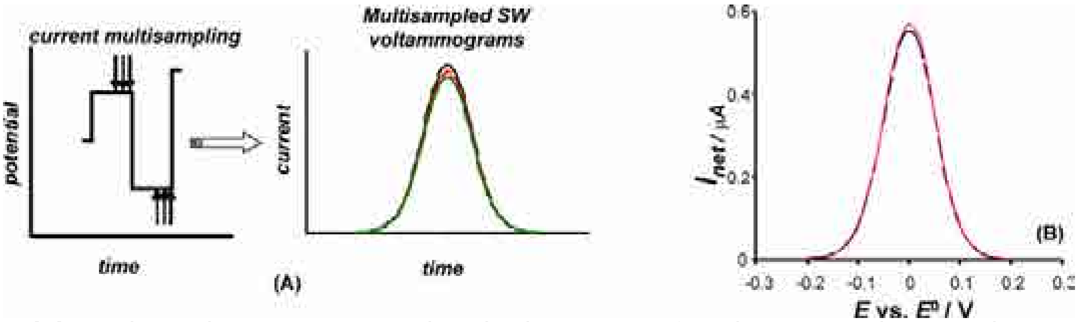

Fig. 1. (A) Multisampling current procedure in the course of a single potential cycle in SWV and corresponding multisampled net SW voltammograms. **(B)** Comparison of net voltammetric components of a reversible electrode reaction of a dissolved redox couple simulated at f = 10 Hz (t_p = 50 ms) by sampling the current at t_s = 40 ms (red line) with the conventional voltammogram (blue dashed line) simulated for f = 12.5 Hz (t_p = t_s = 40 ms).

3. Simplified form of square-wave voltammetry: square-wave chronoamperometry

Square-wave chronoamperometry, is simplified form of conventional SWV. It is a pulse-form chronoamperometric experiment, the excitation signal being obtained by combining a constant potential (mid-potential, E_{mid}) with a short-duration, small potential pulses (Fig. 2A). The main tool in hand for electrokinetic purposes is the frequency (f), the height of potential pulses (E_{sw}), and the mid potential (E_{mid}).

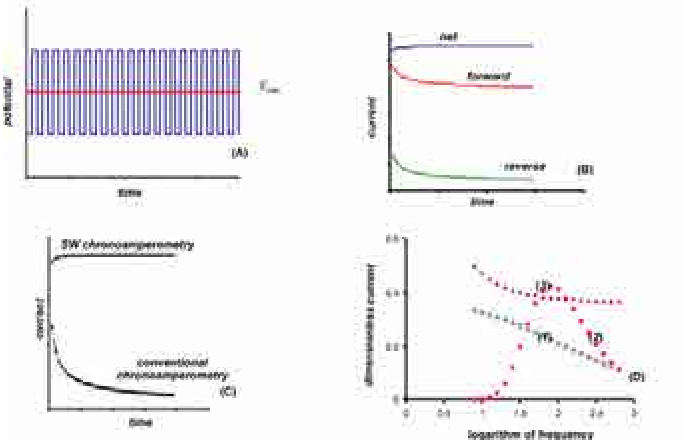

Fig. 2. (A) Potential modulation in electrochemical faradaic spectroscopy; **(B)** typical response presented in a form of SW chronoamperogram; **(C)** Comparison of the net response in EFS and conventional chronoamperometry; **(D)** Typical frequency spectrum of (***1***) a quasireversible electrode reaction of a solution resident redox, (***2***) quasireversible surface confined electrode reaction and (***3***) reversible catalytic electrode mechanism.

Current sampling and presentation of chronoamperometric data is analogous to SWV, consisting of forward, reverse, and net (differential) chronoamperometric curve (Fig. 2B). Surprisingly, the net chronoamperometric component does not depend on time of the experiment (Fig. 2C). Additionally, for electrokinetic purposes, the typical way of presenting the data is in the form of a “spectrum” of net currents as a function of the frequency (Fig. 2D), thus alternative name *electrochemical faradaic spectroscopy* (EFS) is coined. Figure 2D illustrates that the frequency spectrum is sensitive to both electrode kinetics and mechanism. Generally, the proposed simple technique unifies the advantages of both conventional SWV and chronoamperometry.

3 Towards enhanced sensitivity of square-wave voltammetry

Finally, in order to improve analytical performances of SWV two new ideas are presented. The first one is an attempt to increase the sensitivity of SWV by simple processing of conventional net voltammograms, leading to the methodology termed as *cumulative square-wave voltammetry*. In cumulative voltammetry the current at a given potential (I_{cum}) is calculated as a sum of all previous current values of the conventional voltammogram (*I*) i.e., $I_{cum} = \sum_j I_j$. The cumulative voltammogram is a sigmoid curve with a limiting current (I_{lim}) that is an order of magnitude higher than the net peak-current. The first, preliminary experimental verification has been done with the experiments with H_2O_2 measurement at macroscopic Pt electrode.

Finally, in order to improve the ability of SWV to suppress the residual background current, a hybrid technique is proposed between differential pulse voltammetry an SWV. The potential modulation is a combination of steps and pulses, where each step of the staircase ramp is modified with two opposite pulses imposed at the end of each step. The proposed technique keeps the ability typical for SWV to access the kinetics of very fast charge transfer processes and to provide an insight into the mechanism of the electrochemical reaction. On the other hand, as in differential pulse voltammetry, discrimination against the background current, as well as accession to the kinetics of sluggish electrode reactions can be achieved by adjusting the ratio between the step-to-pulse duration ratio.

Acknowledgments: Financial support through the NATO SPS G5550 project (Gas sensors for preventing terrorist attacks) is gratefully acknowledged.

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Square – wave voltammetry of whole blood serum

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Bilirubin is yellow-orange pigment derived from degradation of blood cells. Bilirubin biotransformation mainly occurs in liver and is excreted in bile and urine. Its tetrapyrrole-structure is very important in understanding the solubility of bilirubin in water and a variety of nonpolar solvents. According to several X–ray analysis, bilirubin structure was found to be stabilized by six intramolecular hydrogen bonds. Despite having a number of polar chains, hydrogen bonds formed between propionic acid – carboxylic group and nitrogen atoms in pyrrole rings make this molecule tightly ridged and prevent interactions with polar solvents.

Bilirubin is marker molecule for some common diseases, such as Gilbert syndrome, jaundice, hemolytic disease, idiopathic neonatal hepatitis, etc. For example, jaundice is a condition characterized by hyperbilirubinemia and deposition of bile pigment in skin, mucous membranes and sclera, resulting with yellowish appearance of the patient. Also, serums isolated from patients diagnosed with hepatitis are proven to contain significantly elevated bilirubin level.

In blood bilirubin is bonded to albumin in a stable complex ($K_d \approx 10^{-8}$) and in this form bilirubin is transported to the liver. Inside the hepatocytes, bilirubin is rapidly conjugated with glucuronic acid to produce bilirubin monoglucuronide and bilirubin diglucuronide, which then are excreted into bile, where bilirubin diglucuronide is the major fraction ($\approx$ 90%) and the minority of bilirubin is found as monoglucuronide.

The main idea of the present study is to develop a sensor for rapid and sensitive determination of bilirubin in whole blood serum, meaning that no chemical pretreatment of serum is needed, as it is the case with spectrophotometric methods used for quantitative determination of bilirubin in serum (e.g. diazo method). The present study was made using square–wave voltammetry (SWV) in a phosphate buffer at pH 7,3 using edge plane pyrolytic graphite electrode (PPGE). Although blood serum is a very complex mixture of biomolecules, voltammetric profiles obtained are simple, with intensive and well–defined two net-SW peaks. The net-peak current revealed a clear difference between hyperbilirubinemia and normal level of blood serum bilirubin. Typical net SW voltammogram is depicted in Fig. 1, consisting of two peaks, located at about 180 mV and 730 mV vs. Ag/AgCl (3 M KCl) reference electrode, respectively. The intensity and morphology of the voltammetric response seems to be superior to all corresponding literature data [1].

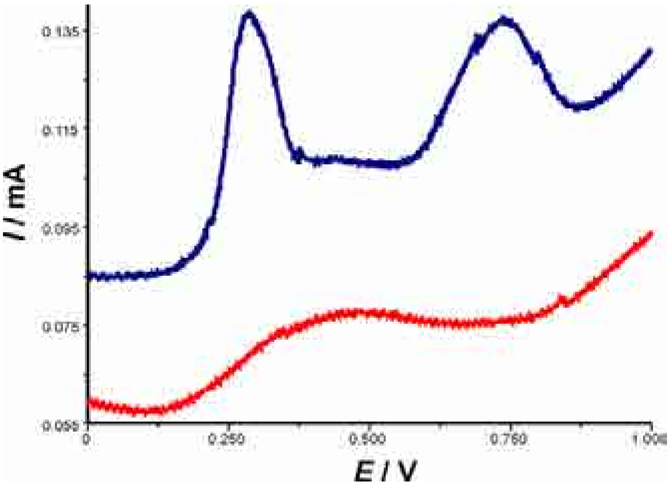

Fig. 1. Typical net SW voltammogram of human blood serum (blue) recorded in a 10 mL phosphate buffet at pH 7.3 containing 200 μL of blood serum and the blank voltammogram of the buffer (red). SWV parameters are: frequency *f* = 50 Hz, amplitude E_{sw} = 50 mV, and step potential ΔE = 1 mV.

A detail analysis of the voltammetric features by altering the accumulation time, SW frequency and SW amplitude (pulse height) revealed that the first voltammetric response is a consequence of a rapid, quasireversible surface confined electrode reaction, while the behavior of the second peak is more complex. The first response exhibits typical SW voltammetric features of a surface confined electrode mechanism, such as quasireversible maximum and net-peak splitting by increasing the SW amplitude [2].

The voltammetry of blood serum has been compared to the voltammetry of pure bilirubin. Optimization of the system for quantitative bilirubin determination in the whole blood serum is in progress.

Acknowledgments: The support through the NATO Science for Peace and Security Programme under grant SPS G5550 is acknowledged with gratitude.

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Electrochemistry of Mercaptosuccinic Acid on Hanging Mercury Drop Electrode

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Mercaptosuccinic acid or thiomalic acid (MSA) is a thiocarboxylic acid that forms stable complexes with heavy metal ions as Hg^{2+}, Cd^{2+} and Pb^{2+} among others [1] and it has been used as a therapeutic agent against the poisoning with different metal ions.

When cyclic voltammetry (CV) experiments are performed by using a hanging mercury drop electrode (HMDE) as the working electrode in presence of MSA, it is possible to distinguish an electrochemical “quasi-reversible” behavior that seems to be due to the catalytic oxidation of Hg^0 in presence of the MSA to Hg_2^{2+} followed by the disproportionation of Hg_2^{2+} to Hg^{2+} and Hg^0 and then the reduction of Hg^{2+} to Hg^0, as indicate the following proposed mechanism:

$$2\,Hg^0 + 2\,MSA \rightleftarrows Hg_2(MSA)_2 + 2\,e^- \quad (1)$$

$$Hg_2(MSA)_2 \rightleftarrows Hg^0 + Hg(MSA)_2 \quad (2)$$

$$Hg(MSA)_2 + 2\,e^- \rightleftarrows Hg^0 + 2\,MSA \quad (3)$$

Also, a Hg^{2+} - MSA complex was synthesized by mixing a solution of $HgCl_2$ and a solution of MSA in a ratio of 1:2 in acidic medium. After isolating the complex from the solution, it was electrochemically evaluated by using CV and it shows the same electrochemical behavior of HDME in presence of MSA.

The mechanism above has been simulated by using the DigiElch V8 software and further experiments should be done to achieve a deeper understanding on the electrochemistry of MSA on HMDE.

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Electrochemical faradaic spectroscopy: concept, mechanistic approach and analytical application

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1. Introduction

Chronoamperometry (CA) is one of the simplest electrochemical techniques. As well known, the contribution of the nonfaradaic, charging current is negligible after a short time period, which besides simplicity, is the main advantage of the technique. Modern pulse voltammetric techniques can be understood as repetitive, short time chronoamperometric experiments conducted at consecutive different potential steps or pulses [1]. In the family of pulse voltammetry square-wave voltammetry (SWV) is the most useful and advanced technique [2]. Its potential modulation is composed of equal, opposite potential pulses, imposed on a staircase potential platform. SWV is superior technique regarding kinetic measurements, mechanistic study and analytical sensitivity. Despite all advantages, understanding of the response is not straightforward, which limits accessibility and application in different scientific fields.

In order to keep both simplicity of CA and advantages of SWV, recently, a new modified form of pulse chronoamperometric technique was proposed, termed as SW chronoamperometry or electrochemical faradaic spectroscopy (EFS) [3]. The excitation signal consists of short repetitive potential pulses imposed on a constant potential (Fig. 1A). Similar to SWV one samples the current at the end of each potential pulse (Fig. 1B) and the resulting SW chronoamperogram consists of three components: forward, backward and differential, net component (Fig. 1C).

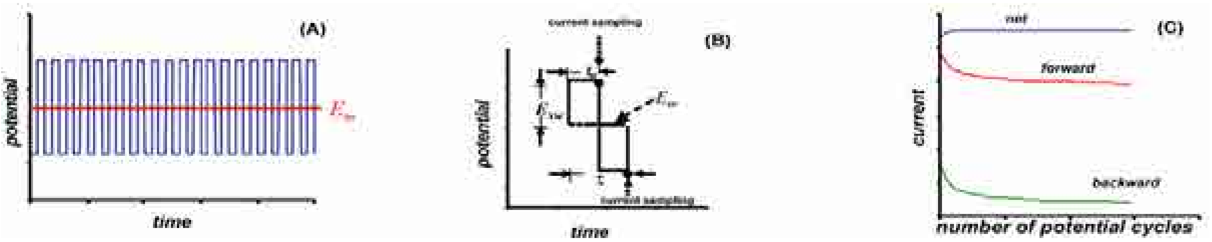

Figure 1. Potential modulation **(A)**, one potential cycle **(B)**, and typical response **(C)** in EFS.

Critical parameters of the technique are pulse height (i.e., SW amplitude E_{sw}), mid-potential (E_m), frequency of pulses ($f = 1/(2t_p)$, cf. Fig. 1B), and number of potential cycles (Fig. 1C). Two adjacent, oppositely oriented potential pulses compose one potential cycle in EFS (Fig. 1B).

In this work we test analytical performances of the new technique considering analysis of a simple, fast, quasireversible electrode reaction of a dissolved redox couple at a conventional solid electrode. Experimental data are compared to conventional SWV and CA.

2. Experimental

The analyte was $K_4[Fe(CN)_6]$ in an KCl (0.1 mol L^{-1}) aq. solution used as a supporting electrolyte. Deionized water was used, and experiments were conducted at room temperature. Voltammograms and chronoamperograms were recorded with Autolab potentiostat. Basal plane pyrolytic graphite electrode (BPPGE), Ag/AgCl/(3 mol L^{-1} KCl), and a platinum wire were used as a working, reference and counter electrode, respectively. The BPPGE surface was renewed by cleaning with Al_2O_3 water slurry and rinsed with water.

3. Results and discussion

As in chronoamperometry, the response of EFS is primarily affected by the number of SW potential cycles and the mid-potential (E_m). For a quasireversible electrode reaction of a dissolved redox couple (Red/Ox) the most important feature of the response at $E_m = E^{\phi'}$ (Red/Ox) is the constant net current component (cf. Fig. 1C). The relative difference between the net currents measured at 9th and 59th potential cycles is 0.3% only, for a pulse frequency of about 10 Hz; for comparison, the corresponding difference in conventional chronoamperometry is 8%. Hence, in EFS constant net current response is obtained at a macroscopic electrode after a few SW cycles, resembling the steady-state response typical for microelectrodes, which is very promising for analytical application.

In order to check analytical performances of the proposed techniques, an experimental analysis with $[Fe(CN)_6]^{4-}$ have been conducted with CA, SWV and EFS under identical experimental conditions and corresponding parameters of the potential modulation. The formal potential of the studied redox couple, as measured with cyclic votammetry, is $E^{\phi'} = 215$ mV. This value was used in conventional CA and as mid-potential in EFS. The pulse height for both SWV and EFS is $E_{sw} = 50$ mV, as the most useful value for analytical application [2]. In addition, the frequency (f) was 10 Hz ($f = 1/(2t_p)$). To reassure a steady current in EFS and effectively discrimination against the charging current in CA, the total time was 50 s.

In order to determine and compare the limit of detection (LOD) only the net currents of both pulse-techniques (SWV and EFS) have been utilized. The reported currents in EFS and CA for a given concentration is an average from the last 5 seconds of the experiment (i.e., last 50 potential cycles in EFS). Limit of detection was obtained from the linear regression line over the concentration interval from 0.5 to 5 μmol L^{-1}. Two sets of experiments have been conducted, i.e., by renewing the electrode surface between each measurement and without cleaning, to avoid differences in the surface morphology of the electrode, assuming that the adsorption of the redox species is negligible.

From the data summarized in Table 1 is obvious that CA cannot be applied at submicromolar level, regardless whether experiments are conducted at single electrode or by surface cleaning. The analytical data with SWV and EFS depends significantly on the conditions of the electrode surface, which is a general problem with permanently variable surface morphology of solid electrodes and residual background current. Nevertheless, the best results have been obtained with EFS without cleaning of the electrode, the LOD being well below the submicromolar concentration level (0.28 μmol L^{-1}).

Table 1. LOD data obtained with the three techniques with and without cleaning of the BPPGE

LOD / μmol L^{-1}	With cleaning	Without cleaning
CA	1.252	1.361
SWV	1.105	0.668
EFS	2.245	0.28

4. Conclusion and further work

From the presented data it follows that EFS is highly promising chronoamperometric technique, unifying the advantages of simple CA and sophisticated pulse voltammetric techniques. It enables differential, constant net current to be measured over time, which is a unique feature of the technique. The variation of the potential in a form of short, small potential pulses over a constant potential contributes in better discrimination of the background, residual current compared to SWV, which is the main reason for an improved limit of detection. These features of EFS are meaningful in future application with electrochemical sensors.

Acknowledgments: The support through the NATO Science for Peace and Security Programme under grant SPS G5550 is acknowledged with gratitude.

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Studying the evolution in time of bimetallic nanoparticles morphology by Cyclic Voltammetry

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Over the last decades, bimetallic nanosized systems have attracted more and more interest thanks to their novel optical, catalytic, magnetic, and sensing properties, often different from the ones of their monometallic counterparts. Studies directed towards the size, shape, composition, and functionalization of the bimetallic nanoparticles are optimized to design sophisticated materials for the intended applications. Considering these facts, it is important to evaluate not only the type and the quantity of the two metals involved, but also their morphological distribution (e.g. alloy or core-shell). Characterization techniques normally used to investigate bimetallic systems are HR-TEM and EXAFS, very expensive and not so easily accessible. Recently, electrochemistry has been employed as alternative or complementary, low-cost, efficient technique with very promising results [1-3], allowing the discrimination between alloyed and perfect or defective core-shell systems after their synthesis. A further achievement is the possibility to follow step by step the formation morphology of these nanomaterials during their synthetic procedure. In the present work, we present a study on Au-Pt bimetallic nanoparticles, in form of alloy or core-shell. Cyclovoltammetry (CV) is used as a fast, low-cost and simple screening technique to distinguish the general composition of the sample and to understand the evolution in time of the systems morphology during their synthesis. An additional advantage is the possibility to conduct the study of the material simply in liquid form, without the need of using solid supports, as normally required by other characterization techniques. Interesting results are obtained for Au-based bimetallic samples, gaining information in accordance with TEM images and EXAFS spectra. This fact moves the interest towards the study of other bimetallic systems, to be used in catalytic, electrocatalytic and electroanalytical applications.

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Enhanced performances of RGO-AuNPs hybrids towards electroanalytical applications

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In recent years, lot of attention has been devoted to understanding the properties of hybrid nanocomposites, “brave new materials” made of two or more organic and inorganic components. These systems show enhanced or novel physico-chemical properties with respect to the single components, resulting not only from the sum of the precursors’ ones, but also from interactions occurring at their interface, the so-called “heterojunction”. However, a remaining challenge is to understand in depth the phenomena here originating. In the present work, to start fulfilling this gap, a deep electrochemical study of hybrids made of Reduced Graphene Oxide (RGO) and Au nanoparticles (NPs) is performed, analysing carefully the role played by each single component of the material on the electrochemical properties. In more details, RGO platforms are surface functionalized with 1-aminopyrene or 1-pyrene carboxylic acid that act as heteronucleation and growing sites of the amine- or thiol-coated Au NPs of different dimensions (from 3 to 20 nm). At first, Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements are carried out in order to characterize the different hybrids. Then, the materials are applied as electroanalytical sensors for both organic and inorganic molecules (dopamine and As, respectively) with very promising results, comparable or even better than analogous systems reported in literature [1-2]. Moreover, preliminary tests on H_2O_2 detection open the venue to the application of these materials in biosensor applications. The properties of the hybrid nanocomposite, enhanced with respect to those of the single components, are ascribed to charge transfer occurring at the heterojunction from the Au NPs to the RGO, assisted and channelled by the pyrene linker.

Acknowledgments: The authors acknowledge the MIUR National Project PRIN 2012 (prot. 20128ZZS2H).

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Electrochemistry of homemade peroxide-based explosives

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Triacetone triperoxide (TATP) is immensely powerful and easy to prepare explosive used in many terrorist attacks in recent years. The absence of nitro groups, no fluorescence, and weak UV absorption makes this explosive very challenging for detection. Using MS or IR spectroscopy is not suitable for on-site testing. Therefore, there is high interest in designing field deployable sensors for detection of TATP that are highly sensitive, small and easy to use. Research on electrochemistry of TATP can provide foundation for building such sensors.

One reported method for detection of TATP is first to irradiate the sample with strong UV radiation after which TATP decomposes to H_2O_2 that is later detected using Prussian blue modified electrodes. [1] The principal idea in our study is to combine the decomposition of the TATP (on the gold nanoparticles) and the detection of H_2O_2 (on the Prussian blue particles) at the surface on the electrode. Therefore, a glassy carbon electrode was modified with gold-prussian blue nanocomposite according to the method by Phani et al. [2]. The modification was performed by continuous cycling between 1 V and 0 V (vs reference electrode Ag/AgCl/ 3 mol/L KCl) in a solution containing 1 mmol/L $K[AuCl_4]$, 1 mmol/L $K_3[Fe(CN)_6]$ and 0.1 mol/L KCl as supporting electrolyte. (Figure 1)

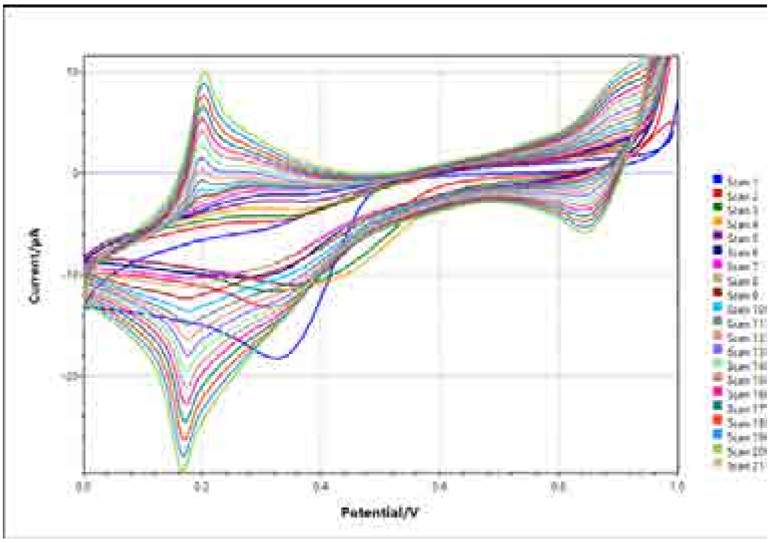

Fig.1 Modification of glassy-carbon working electrode with gold-prussian blue nano-composite by continuous cycling between 1 V and 0 V. The solution contains 1 mmol/L $K[AuCl_4]$,
1 mmol/L $K_3[Fe(CN)_6]$ and 0.1 mol/L KCl as supporting electrolyte. After scan 7 the characteristic peaks of prussian blue can be noticed.

For the study TATP was synthesized, purified and characterized with IR spectroscopy. The sample was then dissolved in 1-propanol. Amperometric measurements were performed at room temperature using a stirred 5 mL solution containing HCl and 0.1 M KCl and added certain amount of 1-propanol. (Figure 2) Working potential of 0.0 V vs Ag/AgCl/ 3 mol/L KCl was applied allowing the transient current to decay to a steady-state value, before spiking a given aliquot explosive solution. Presence of acidic media is necessary for the decomposition step of TATP [3]. Moreover, the same experiments were performed with electrode modified with only Prussian blue according to Karyakin et al. [4]. The performance of both electrodes is compared.

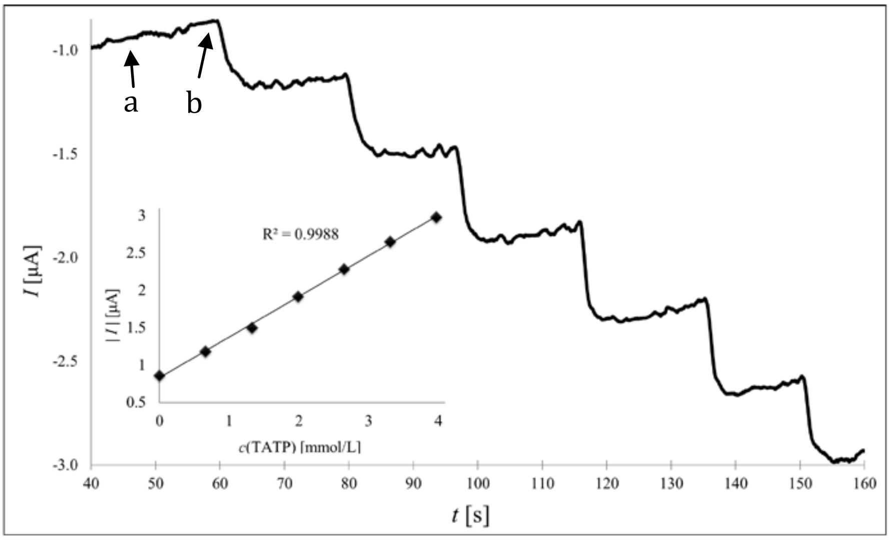

Fig. 2 Current-time recording for addition of acid treated a) blank (1-propanol) b) TATP solution in 1-propanol. The sample was prepared by dissolving 10 mg of TATP in 1 mL of 1-propanol. The solution was then treated with 1 mL HCl (2 mol/L) for 2 minutes. Signals were recorded for 0.1 mL addition of the treated solution into the stirred 5 mL electrolyte solution (0.1 mol/L KCl and 0.1 mol/L HCl with 2 mL of 1-propnol). Presence of acid hydrolyses the TATP to hydrogen peroxide that is detected at the gold-prussian blue modified glassy-carbon electrode held at 0.0 V [vs. Ag/AgCl (3 mol/L KCl)]. Inset shows the current response with the concentration of TATP. Smoothing was performed using the Savitzky-Golay algorithm.

In these experiments the detection of TATP is done indirectly through the liberated hydrogen peroxide. To the best of our knowledge there is no electrochemical method for direct detection of TATP. There are some theoretical studies of TATP with its complexes with ions. [5, 6] This was a principal idea to do series of experiments where electrochemistry can be utilized for the detection of these complexes. It was found that copper ions have most promising results. The cyclic voltammogram of a solution of 2 mmol/L copper(II) chloride in dry methanol and 0.1 mol/L tetrabutylammonium chloride recorded on a platinum working electrode shows a reversible electrochemical reaction $Cu^{2+} \rightleftharpoons Cu^{+}$. The addition of TATP solution in methanol, alters the voltammogram of the Cu^{2+}/Cu^{+} redox couple.

Further experiments are needed to conclude if the interaction of TATP and copper ion is trough complex formation of other reactions.

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Asymmetry of the limiting currents of two-layer and modified single-layer ion-exchange membranes

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The work studies the current-voltage characteristics(CVC) of bilayer step-charged [1] and single-layer gradient-charged [2] ion-exchange membranes under changing the direction of the external electric field. The consideration is carried out within the framework of the Nernst-Planck approach accounting for both diffusive layers. The asymmetry of both the totalCVC and the limiting currents in such systems is established. The reason is non-uniform distribution of fixed charges in the membrane matrix, leading to the asymmetrical dependence of the electric potential and electrolyte concentration on the coordinate normal to the membrane surface. In case of a two-layer membrane with one neutral layer, a sharp increase in the limiting current was established when the charged layer was oriented towards the electric field compared with the opposite orientation. In the last case, the limiting state occurs not on the surface of the membrane, but at the interface between the neutral and charged layers.

Theory

The limiting current density of a uniformly charged single-layer membrane in 1:1 electrolyte solution is usually calculated by the well-known Peers equation[4]:

$$I_{\lim} = \frac{FDC_0}{\delta\left(T_+ - t_+\right)}, \tag{1}$$

where t_+–the cation transfer number in the solution(closeto 0.5), T_+–integral or effective number of cation transport, δ– thickness of diffusive layers, F– Faraday constant, D – diffusivity of the electrolyte molecule in a bulk solution, C_0 – electrolyte concentration.For a perfectly selective (permselective) cation exchange membrane, we have $T_+ - t_+ \approx 0.5$ and therefore

$$I_{\lim}^{ideal} = \frac{2FDC_0}{\delta}. \tag{2}$$

The limiting current densities of a step-charged two-layer membrane in 1:1 electrolyte solution were firstly derived in [1] in implicit form and they are different. When one layer of the membrane is uncharged (neutral) and oriented towards the counter-ion flux then for positive limiting current density we can get the approximate formula:

$$I_{\mathrm{lim}}^{+}=\frac{2FDD_{\mathrm{m1}}C_0}{\left(\delta D_{\mathrm{m1}}+\gamma_1 h_1 D\right)}+\frac{FD_{\mathrm{m2}}}{h_2}\left(\sqrt{\rho_2^2+4\frac{C_0^2}{\gamma_2^2}\left(1+1\Big/\left(1+\frac{h_1}{\delta}\frac{D}{D_{\mathrm{m1}}}\right)\right)^2}-\rho_2\right), \qquad (3)$$

where indexes 1 and 2 are responsible for the neutral and negatively charged layers having thicknesses h_1 and h_2 respectively, D_{m} is diffusivity of electrolyte molecule inside the membrane, γ is distribution coefficient depending on the surface interactions, ρ is the charge density. For the opposite orientation of applied electric field we also derived the approximate expression for negative limiting current density:

$$-I_{\mathrm{lim}}^{-}=\frac{2FDC_0}{\delta}+\frac{FD_{\mathrm{m2}}}{h_2}\left(\sqrt{\rho_2^2+4\frac{C_0^2}{\gamma_2^2}\left(2+\gamma_1\frac{h_1}{\delta}\frac{D}{D_{\mathrm{m1}}}\right)^2}-\rho_2\right). \qquad (4)$$

If one of the membrane layers is neutral, then it acts as a kind of additional diffusion layer for the charged part of the membrane, because limiting state occurs at the interface between layers. In this case, as it follows from (3) and (4), the asymmetry coefficient of the limiting current density $\eta=I_{\mathrm{lim}}^{+}\Big/\left(-I_{\mathrm{lim}}^{-}\right)$ is always less than unity, which means that the value of the positive limiting current, when the neutral layer is oriented towards the flow of counter-ions, is always less than the absolute value of the negative limiting current with the opposite orientation of the applied electric field.

When the neutral layer is absent (h_1=0) and the membrane becomes one-layer object, from (3) and (4) it is easily to get the formula for the absolute value of limiting current density:

$$I_{\mathrm{lim}}=\frac{2FDC_0}{\delta}+\frac{FD_{\mathrm{m}}}{h}\left(\sqrt{\rho^2+16\frac{C_0^2}{\gamma^2}}-\rho\right). \qquad (5)$$

Comparing (2) and (5) we conclude that Peers' formula (2) does not consider physicochemical and geometrical characteristics of the membrane while new formula (5) takes them into account.

Conclusion

The theoretical results were applied to perfluorinated MF-4SC (the Russian equivalent of Nafion®-117) bilayer membranes modified using halloysite nanotubes and platinum nanoparticles.It is theoretically proved that the limit current is practically unattainable in the experiment in case of a cation-exchange linearly charged membrane with a neutral surface oriented towards external electric field, that is confirmed experimentally for MF-4SC membranes modified with polyaniline on the one side [5].The studies carried out allow one to control the degree of asymmetry of the limiting currents of ion-exchange membranes that are non-uniform in a fixed chargedistribution and can potentially lead to the creation of membrane sensors and diodes.

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Cell model for electrical conductivity and electroosmotic permeabilityof ion-exchange membrane

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Electroosmotic permeability of ion-exchange membranes (IEMs) significantly limits their use in fuel cells (FCs). Excessive water loss by such membranes leads to their overheating and possible destruction of the fuel cell. Hence, for efficient operation of IEMs in the FCs, it is necessary to know how their electroosmotic permeability (EOP) will change when the moisture content and the background electrolyte concentration as well as the geometric and physicochemical characteristics of the ionite grains are varied. The existing approaches for calculations of electroosmotic permeability do not fully answer the abovementioned questions. So, we developed a closed cell model of an ion-exchange membrane [1], considering the transfer of water or another solvent in the hydrated/solvate ion shells.

Basing on the thermodynamics of non-equilibrium processes (the Onsager approach), we have set up and solved the boundary value problem (BVP) for the system of Stokes, Brinkman, Nernst-Planck-Poisson equations governing the flow of a binary non-symmetric electrolyte through a liquid cell in the center of which there is a porous spherical particle, having a constant exchange capacity. At the boundary of the liquid shell, we used the Kuwabara (absence of vorticity) condition, and at the interface between the porous particle and the electrolyte solution, we used the continuity conditions for velocity vector, normal components of ion fluxes and the total stress tensor. The results of the BVP solution were applied to obtainexact and approximate formulas for the electroosmotic permeability $L_{12}$and specific electrical conductivity(SEC) $L_{22}$of a charged membrane as a function of the fraction of the solid conducting phase (or moisture content), geometric and physicochemical characteristics of an ion-exchange grain and concentration of electrolyte [2].

In this work, we applied the developed cell model to the characterization of MF-4SC cation-exchange membranes previously made in the pristine state, as well as MF-4SC modified with halloysitenanotubes, functionalized with Pt or Fe nanoparticles [3] and placed in solutions of different concentrations of HCl. Electroosmotic permeability of the membrane at a constant current density, $D_I = L_{12}/L_{22}$ (m^3/C), was determined by the volumetric method in a two-chamber cell with polarizing silver chloride electrodes. The conductivity L_{22} (S/m) of the membranewas calculated based on the measurement of its active resistance.

Theoretical Part

The formulas for L_{12} and L_{22}, obtained in the general case of a non-ideal membrane in [2], are rather cumbersome ones. Therefore, we present here only the formulas for L_{22} and $D_\mathrm{I} = L_{12}/L_{22}$ in the limiting case of an ideally selective cation-exchange membrane (case of excluded co-ions) and 1:1 electrolyte:

$$L_{22} = C_0 D_+ \frac{F^2}{RT}\left(\frac{2m_0}{3-m_0}\left(1+\frac{D_-}{D_+}\right) + \frac{9(1-m_0)}{3-m_0} \frac{\left(\frac{D_{\mathrm{m+}}}{D_+}+\frac{\bar\rho}{\bar\rho_0}\right)\bar\rho}{m_0\bar\rho\left(\frac{D_{\mathrm{m+}}}{D_+}+\frac{\bar\rho}{\bar\rho_0}\right)+\left(3-m_0\left(1+\frac{\bar\rho}{\bar\rho_0}\right)\right)C_0} \right), \qquad (1)$$

$$D_\mathrm{I} = \frac{3}{F\bar\rho_0} \frac{3-m_0\left(1-\frac{D_{\mathrm{m+}}}{D_+}\right)}{\left(\frac{D_{\mathrm{m+}}}{D_+}+\frac{\bar\rho}{\bar\rho_0}\right)\left(9(1-m_0)+2m_0^2\left(1+\frac{D_-}{D_+}\right)\right)+2m_0\left(1+\frac{D_-}{D_+}\right)\left(\frac{3-m_0}{\bar\rho}-\frac{m_0}{\bar\rho_0}\right)C_0}. \qquad (2)$$

Here m_0– macroscopic porosity of the membrane, $D_\pm$– diffusion coefficients of electrolyte ions in a dilute solution, $D_{\mathrm{m+}}$ – diffusion coefficient of the counterion (cation) in the membrane, $\bar\rho = \rho_\mathrm{V}/F$ – membrane exchange capacity (ρ_V – fixed charge volume density), $\bar\rho_0 = \mu^\mathrm{o} D_+/(k_\mathrm{D}RT)$– characteristic exchange capacity of the system (estimates show that $\bar\rho_0 >> \bar\rho$), k_D – specific (Darcy) hydrodynamic permeability of the ionite grain (gel), μ^o – dynamic viscosity of the solution, R – the universal gas constant, T – the absolute temperature, C_0 – equivalent concentration of the electrolyte solution in equilibrium with the membrane. By virtue of ideality, formulas (1) – (2) do not include the diffusion coefficient of a co-ion $D_{\mathrm{m-}}$ in the membrane and the coefficient of equilibrium distribution γ_m of electrolyte molecules in the pores of the membrane [1, 2].

Despite the approximate formulas (1) – (2), they work well for real membranes. It is seen that the dependence (2) of electroosmotic permeability D_I at constant current density on the concentration C_0 of a 1:1 electrolyte solution is hyperbolic one and decreases monotonically to zero with increasing C_0.

Comparison Between Theory and Experiment

The magnitudes of the model physicochemical parameters $(D_{\mathrm{m+}}, m_0, \bar\rho_0)$, obtained from optimization procedure written for Mathematica software, are listed in the Table. The values of exchange capacity $\bar\rho$ were measured in independent experiments for all membranes used. Specific hydrodynamic permeability of a cationite grain (gel) was evaluated using relation $k_{\mathrm{D}} = \mu^{0} D_{+} / \left(\bar{\rho}_0 RT \right)$ (last column of the Table). It is seen from the Table that k_{D} decreases from pristine to modified membranes. It may mean compaction of the ionite grains (gel) due to their modification by halloysite nanotubes with metal nanoparticles. It should be noted that the macroporositym_0 is within the limits of the values obtained by the standard contact porosimetry method [4] and proton diffusivity in tested membranes is less approximately from 10 to 15 times than in a dilute electrolyte solution.

Table. Physicochemical Parameters Obtained by Simultaneous Optimization Using Approximate Formulas (1)-(2) for Ideal Cation-Exchange Membrane

Membrane	D_{m+}, **μm^2/s**	m_0, **%**	$\bar{\rho}$, **mol/dm^3**	$\bar{\rho}_0$, **mol/dm^3**	$k_{\mathrm{D}}, \left(\overset{\circ}{\mathrm{A}}\right)^2$
MF-4SCpristine	586	9.6	1.08	106	3.64
MF-4SC/Hall+Pt	838	10.1	1.22	158	2.45
MF-4SC/Hall+Fe	674	8.9	1.16	167	2.32

Conclusion

In this work, within the framework of the thermodynamics of nonequilibrium processes based on the cell model of the ion-exchange membrane (porous charged layer), two electrokinetic coefficients of the Onsager matrix are determined: electroosmotic permeability and electrical conductivity. The membrane is considered as an ordered assemblage of porous charged particles of spherical shape, placed in spherical shells filled with a solution of a binary electrolyte. Based on the results obtained by the least squares method and specially developed optimization procedure, the physicochemical parameters of the cell model were found, which allowed acceptably describing the available experimental results for the pristinecation-exchange membrane MF-4SC and this membrane modified by halloysite nanotubes which are functionalized with platinum or iron nanoparticles.

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Formation of phosphorus oxide complexes during electrochemical treatment of liquid-phase exfoliated few-layered phosphorene films: kinetic studies in aqueous and non-aqueous solutions

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Phosphorene (BP), which represents the family of 2D nanomaterials, has attracted an exponential amount of interest since its discovery in 2014. Phosphorene is a single, puckered layer of black phosphorus consists of P_6 rings in a chair conformation. BP shows many desirable properties like: anisotropy, high carrier mobility and direct and tunable bandgap. Thus, this material exhibits high potential for practical applications in the field of electronics, infrastructure, and energy. However, the broader application of this material is limited by its surface deterioration caused by ambient atmosphere [1,2].

In this study, we present the electrochemical performance of few-layered phosphorene drop-casted on the boron-doped diamond substrate. The BP film was obtained from black phosphorus by ultrasonic assisted liquid-phase exfoliation in N-methyl-2-pyrrolidone. The efficient exfoliation of BP flakes was revealed by scanning electron microscopy and Raman spectroscopy. The cyclic voltammetry measurements were conducted in aqueous (0.5 M Na_2SO_4) and non-aqueous (acetonitrile with 0.1 M $TEABF_4$) electrolytes in the wide potential window (-2.0 to 2.5 V and -3.0 to 1.0 V vs. Ag|AgCl|3M KCl, respectively) thanks to the boron-doped diamond substrate application. The results revealed a formation of polyphosphoric quasi-oxide layers during the anodic polarization. The electrochemical impedance spectra, recorded in 0.5 M Na_2SO_4 at rest potential, confirms $P_xO_y(OH)_z$ formation through the appearance of additional time-constant as can be seen on Bode plots.

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The Acidity Constants (pK_{a1} and pK_{a2}) of Menatetrenone (MK-4) in a DMPC Monolayer on Mercury

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Adhesion-spreading [1] of 1, 2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) liposomes containing menatetrenone (MK-4, a vitamin K_2 constituent) was used to prepare a monolayer on a hanging mercury drop electrode. The redox properties of menatetrenone in the monolayer were studied using aqueous buffers over the pH range 4 to 14 by cyclic voltammetry. Menatetrenone exhibits an electrochemically reversible system in cyclic voltammetry (Figure 1). From a plot of the mid-peak potentials [E_{mp}] vs. pH, the 1st and 2nd pK_a values were found indistinguishable close to each, both being 13.0 ± 0.2 (see Figure 2). The approach to transfer water insoluble quinoide compounds to lipid monolayers on mercury for the determination of acidity constants will be extended to other biochemically important quinoide compounds. The effect of the chemical nature of the lipids on the acidity constants will also be studied.

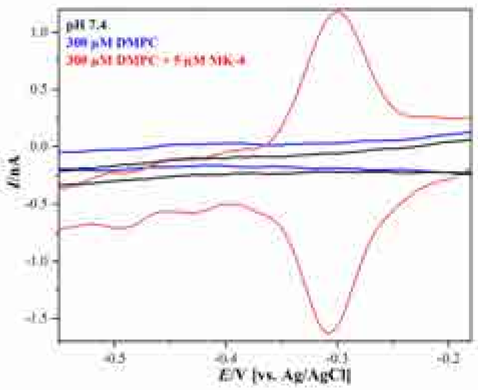

Figure 1. Cyclic voltammogram of DMPC + MK-4 compared to DMPC lipids and buffer at pH 7.4, scan rate =25 mV s^{-1}.

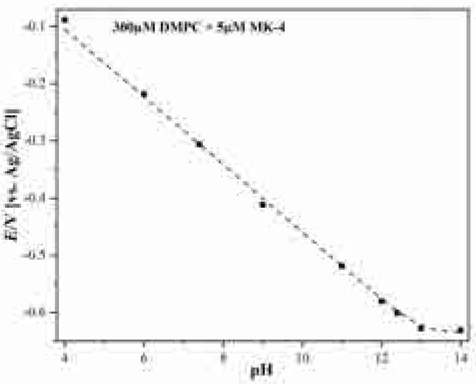

Figure 2. Dependence of E_{mp} on pH for DMPC + MK-4, scan rate = 25 mV s^{-1}.

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Electrochemical synthesis of Ni-Re catalyst for Hydrogen Evolution Reaction possessing superior catalytic activity

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Ni–Re cathodes catalytic activity towards hydrogen evolution reaction (HER) in the solution of sodium hydroxide was studied. Ni–Re coatings were deposited onto the surface of a copper substrate from ammonium-citrate solutions in the galvanostatic regime. The obtained deposits were examined by modern physical methods, namely: XPS, XRD, and SEM with X-ray microanalyzer. It was established that the full reduction of nickel species occurs during electrodeposition, while rhenium species electroreduction is incomplete. Large amounts of Re(IV) oxide were detected in the electrode deposits.

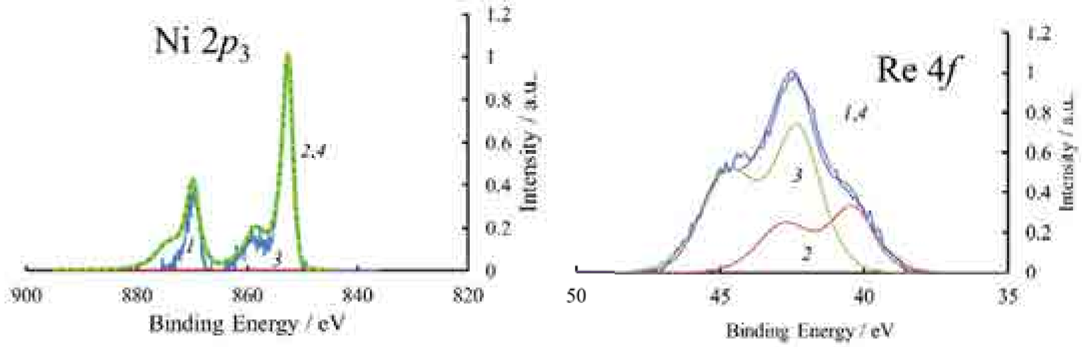

Fig. 1 High-resolution Ni 2p_3 (1 – experimental curve, 2 – Ni(0), 3 – Ni(+2), 4 – approximated curve) and Re 4*f* (1 – experimental curve, 2 – Re(0), 3 – Re(+4), 4 – approximated curve) XPS spectra.

Ni–Re coatings immediately after electrodeposition were X-ray amorphous. Heat treatment at 450 °C in vacuum resulted in the change in their crystal structure. After heat treatment, they were the solid solution of nickel in hexagonal rhenium lattice. It should be noted that the heat treatment under an argon atmosphere did not lead to crystallization of Ni–Re deposits. This fact can be associated with a high content of hydrogen sorbed by the deposits during their electrodeposition.

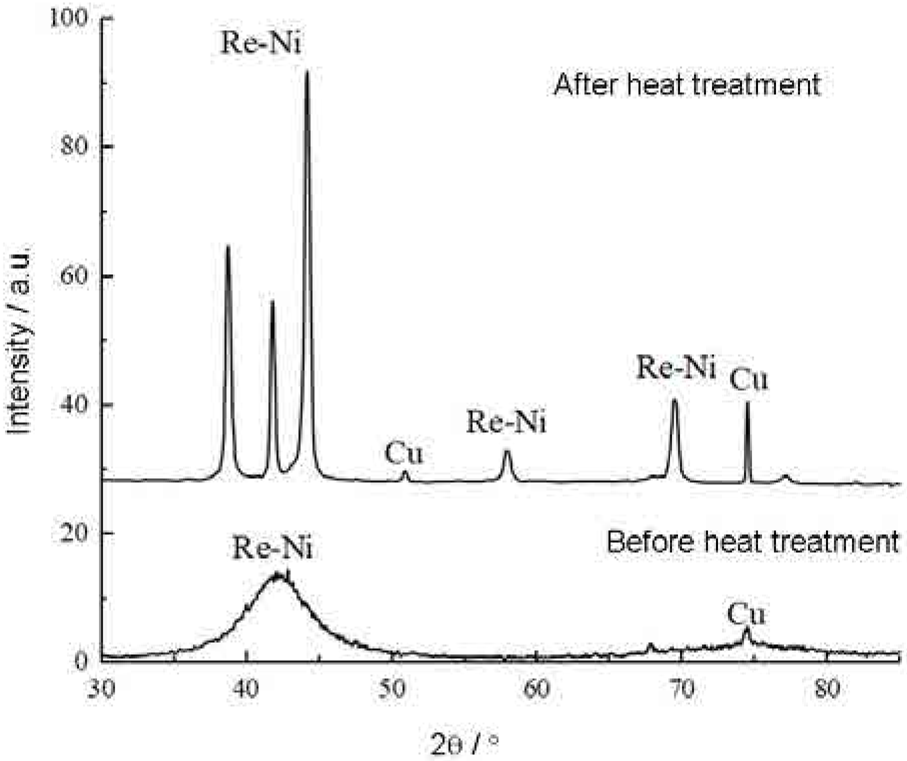

Fig. 2 Ni–Re deposits diffractograms before and after heat treatment. CuK_α radiation. The coatings were deposited onto a copper substrate

The increase in rhenium content in Ni–Re deposits caused the increase in their catalytic activity towards HER that is accompanied by Tafel slope decreasing. This is due to high surface coverage by adsorbed hydrogen atoms (θ_H) and its dependence from electrode potential. Heat treatment at 450 °C vacuum resulted in the decrease in catalytic activity towards HER.

The latter seems unexpected and interesting. Based on literature data [1] one can assume that namely rhenium oxides such as ReO_2 catalyze hydrogen evolution reaction. The reduction of these oxides by hydrogen atoms accumulated by the Ni–Re deposits in the course of their electodeposition occurs during heat treatment. This reaction can be expressed by the following equation:

$$ReO_2 + 4\ H_{abs} \rightarrow Re + 2\ H_2O.$$

Reduction of rhenium oxides during heat treatment is proved by XPS spectra. The quantity of Re(0) increases after heat treatment of Ni–Re deposits. On the other hand, the amount of oxygen fixed on the spectra decreases.

Ni–Re alloys themselves do not possess so high catalytic activity as materials containing nickel and rhenium oxides. Therefore, the reduction of rhenium oxides results in decrease in the catalytic activity towards hydrogen evolution reaction.

Table. HER kinetic parameters on Ni–Re alloys.

No	*x*(Re), %	lg i_o [A cm^{-2}]	*b*, mV dec^{-1}
1	55	–5,1	134
2	68	–4,1	115
3	72	–4,0	114
4	76	–4,3	93
5	76 (after heat treatment)	–5	88
6	80	–3,6	81
7	88	–3,4	88

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57.	**Lucero,Gisella**	**Germany**
58.	**Lušpai,Karol**	**Slovak Republic**
59.	**Lyutov, Vladimir**	**Bulgaria**
60.	**Magdesieva,Tatiana**	**Russia**
61.	**Mandler, Daniel**	**Israel**
62.	**Mirceski, Valentin**	**North Macedonia**
63.	**Mirsky, Vladimir**	**Germany**
64.	**Morin,Sylvie**	**Canada**
65.	**Mussini, Patrizia**	**Italy**
66.	**Najkov, Kosta**	**North Macedonia**
67.	**Nakova, Aneliya**	**Bulgaria**
68.	**Nekrasov, Alexander**	**Russia**
69.	**Ozturk, Turan**	**Turkey**
70.	**Pailleret, Alain**	**France**
71.	**Petkucheva,Elitsa**	**Bulgaria**

72.	**Pickup,Peter**	**Canada**
73.	**Pron, Adam**	**Poland**
74.	**Ragoisha, Genady**	**Belarus**
75.	**Rapta, Peter**	**Slovak Republic**
76.	**Román Silva, Javier Ignacio**	**Germany**
77.	**Ruhlmann, Laurent**	**France**
78.	**Rutkowska, Iwona**	**Poland**
79.	**Santoni, Marie-Pierre**	**France**
80.	**Schoetz, Theresa**	**United Kingdom**
81.	**Scholz, Fritz**	**Germany**
82.	**Sezer, Esma**	**Turkey**
83.	**Shkirskaya, Svetlana**	**Russia**
84.	**Šimková, Ludmila**	**Czech Republic**
85.	**Sjödin, Martin**	**Sweden**
86.	**Skompska, Magdalena**	**Poland**
87.	**Stejskal, Jaroslav**	**Czech Republic**
88.	**Stojanov, Leon**	**North Macedonia**
89.	**Stoyanova, Radostina**	**Bulgaria**
90.	**Testolin, Anna**	**Italy**
91.	**Todorov, Jovica**	**North Macedonia**
92.	**Topal, Sebahat**	**Turkey**
93.	**Topal,Sema**	**Turkey**
94.	**Trchová, Miroslava**	**Czech Republic**
95.	**Tsakova, Vessela**	**Bulgaria**
96.	**Ustamehmetoglu, Belkıs**	**Turkey**
97.	**Viana, Ana**	**Portugal**
98.	**Vorotyntsev, Mikhail**	**Russia**
99.	**Wilamowska-Zawłocka, Monika**	**Poland**
100.	**Xia, Yongyao**	**China**
101.	**Yu, Aishui**	**China**
102.	**Zagorska, Malgorzata**	**Poland**
103.	**Zanardi, Chiara**	**Italy**
104.	**Zhang, Xiaogang**	**China**
105.	**Zhecheva, Ekaterina**	**Bulgaria**
106.	**Zolotukhina, Ekaterina**	**Russia**