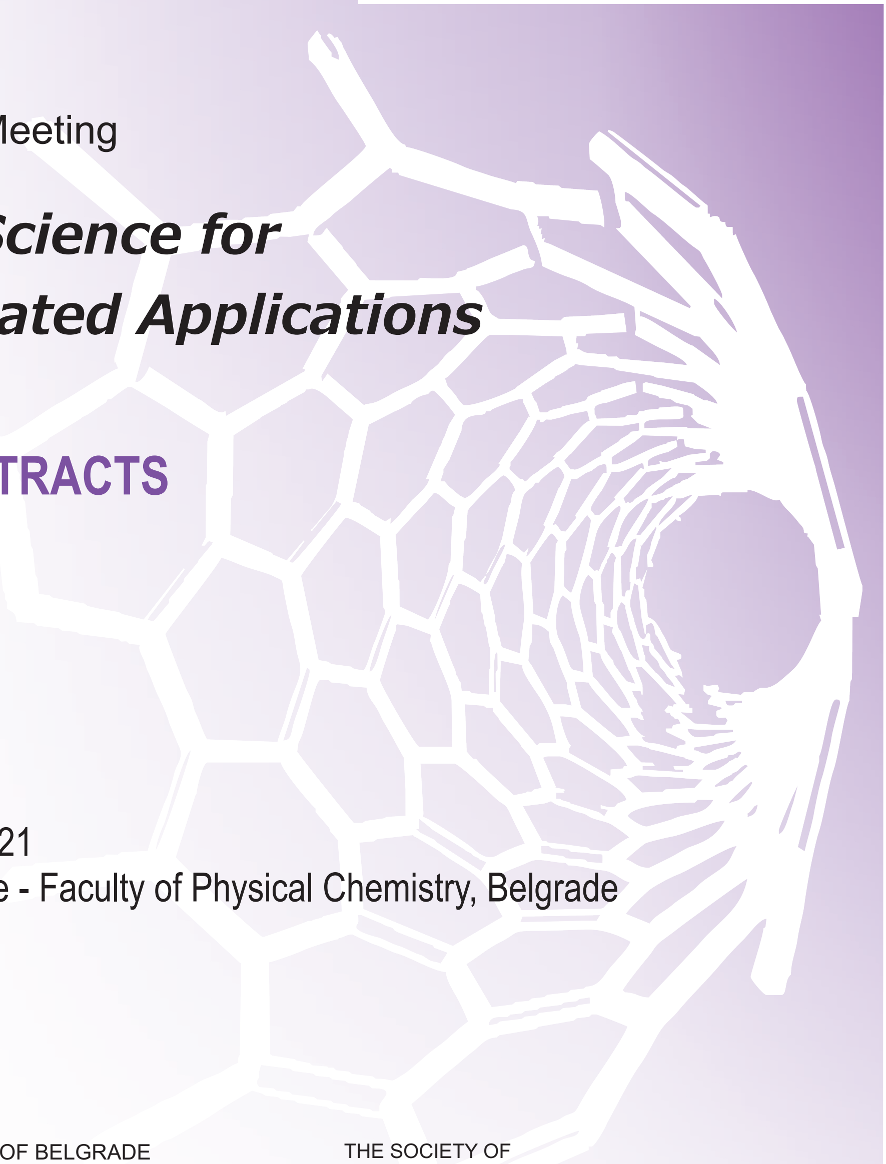
PHYSICAL CHEMISTRY 2021

4th International Meeting
on

Materials Science for Energy Related Applications

BOOK OF ABSTRACTS



September 22-23, 2021
University of Belgrade - Faculty of Physical Chemistry, Belgrade

UNIVERSITY OF BELGRADE
FACULTY OF PHYSICAL CHEMISTRY
Belgrade, Serbia

THE SOCIETY OF
PHYSICAL CHEMISTS OF SERBIA
Belgrade, Serbia

4th International Meeting

on

Materials Science for Energy Related Applications

held on September 22-23, 2021 at the
University of Belgrade, Faculty of Physical Chemistry,
Belgrade, Serbia
(online meeting)

is a satellite event of

PHYSICAL CHEMISTRY 2021

15th International Conference on Fundamental
and Applied Aspects of Physical Chemistry

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Editors
Prof. Dr. Igor A. Pašti
Assist. Prof. Dr. Ana S. Dobrota

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Preface

International Meeting on Materials Science for Energy-Related Application (IMMSERA) was launched in 2014 as a satellite event of the Physical Chemistry conference series. It is a biannual event, but Covid-19 pandemics resulted in a three-year gap as the last meeting took place in 2018.

For that reason, 4IMMSERA is a completely online event. We are happy that IMMSERA is taking place but aware that an online event cannot replace real on-site knowledge sharing as discussion. Therefore, we present two plenary lectures (Prof. Coy and Dr. Smiljanic) and 35 oral presentations divided into six sessions this year. We hope that the exchange of knowledge and new findings and discussion will be productive in this difficult situation.

Looking back at the development of IMMSERA, we believe that the meeting has reached a critical mass and that it requires rebranding. The next meeting, 5IMMSERA, will grow to a stand-alone event with a pre-tailored programme covering state-of-the-art developments in the field of energy-related materials, with approximately 50% of invited lectures. We shall retain a small format of the meeting – within 2 days we aim to approximately 40 oral presentations, without any overlap between conference sessions, allowing every participant to participate in the discussion of presented results. We strive for scientific excellence and the formation of a hotspot to exchange scientific ideas and top-level scientific results.

We thank all the participants of 4IMMSERA and hope that the dissemination of their research will bring new ideas and collaborations.

Editors
Prof. Dr. Igor Pašti,
University of Belgrade – Faculty of Physical Chemistry
Dr. Ana S. Dobrota, assistant professor,
University of Belgrade – Faculty of Physical Chemistry

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Materials for electrochemical power sources

CARBONIZED POLYPYRROLE-GELATIN CRYOGELS FOR ELECTROCHEMICAL STORAGE APPLICATIONS

Konstantin A. Milakin[a], Sonal Gupta[a], Ognen Pop-Georgievski[a], Zuzana Morávková[a], Udit Acharya[a], Stefan Breitenbach[b], Christoph Unterweger[b], Patrycja Bober[a]

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Designing novel electrode materials is an important direction of the development of energy storage technology, such as supercapacitors, contributing to solving the modern challenge of switching to green and renewable sources of energy. Carbons with high surface area and optimized targeted morphology are considered to be the most promising for the purpose due to having a fast charge-discharge rate and high cycling stability [1]. One of the approaches for the preparation of such materials is the carbonization of conducting polymers and their composites, which are known to keep their morphology and have increased surface area after the conversion to carbon [2,3].

The present work is focused on the preparation of nitrogen-enriched carbon materials by carbonization of macroporous polypyrrole-gelatin cryogels, where both gelatin and the conducting polymer are the sources of nitrogen. The cryogel precursors were carbonized at various temperatures, and the influence of the carbonization temperature on molecular structure, morphology, and physicochemical properties of the resulting carbonaceous materials was studied regarding potential electrochemical storage application.

It was found that at all carbonization temperatures in the range 100–700 °C the resulting carbon materials maintained their integrity and macroporous morphology (pore size 4–16 μm). The presence of nitrogen in the carbonized cryogels was confirmed by elemental analysis. Raman spectroscopy showed that disordered carbon peaks started emerging at 300 °C, and with increasing the carbonization temperature, they dominated the spectra with a simultaneous increase of the ratio of D and G bands corresponding to higher structural order and degree of carbonization. The conductivity of the carbonized cryogels was found to go through a minimum depending on the carbonization temperature: at first, it decreased from 5×10^{-2} S cm^{-1} (initial cryogel) to 4×10^{-10} S cm^{-1} (300 °C) and starting from 400 °C increased to 2×10^{-5} S cm^{-1} (700 °C). The specific surface area was shown to follow a similar trend reaching 441.7 m^2 g^{-1} (600 °C), which is one order of magnitude higher than the value for the initial cryogel (23.3 m^2 g^{-1}). The increase of carbonization degree at higher carbonization temperatures was also found to result in enhanced electrochemical performance of the carbonized materials, which manifested in higher gravimetric capacitance (up to 209 F g^{-1} at 700 °C). The capacitance stability was demonstrated for at least 1000 cycles.

Acknowledgments: The authors wish to thank the Czech Science Foundation (21-01401S) for the financial support.

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MODIFICATION OF SURFACE OXYGEN GROUPS OF GRAPHENE OXIDE BY ION BEAM IRRADIATION FOR SUPERCAPACITOR APPLICATIONS

Marko Gloginjić[1], Željko Mravik[1,*], Danica Bajuk-Bogdanović[2], Andrzej Olejniczak[3,4], Vladimir A. Skuratov[3], Igor Pašti[2], Zoran Jovanović[1]

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Surface oxygen groups may have a significant impact on the electrochemical charge storage properties of graphene oxide (GO). The presence of these groups on GO should be properly balanced so that electronic conductivity is optimized, while only the groups that are beneficial to capacitance are preserved. Ion beam irradiation can be identified as a technique where a controllable change of surface chemistry and structure of GO is possible through varying the energy and the fluence of an ion beam. In the present study, the influence of proton-beam irradiation on the surface chemistry and structural properties of GO paper was investigated. GO paper was irradiated with 15 keV proton-beam to fluences from 5×10^{16} to 2×10^{17} ions cm^{-2}, while Fourier-transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy (RS) were used for the analysis of the surface chemistry and structural properties. Results indicate increasing reduction of surface oxygen groups and the preferential removal of the alkoxy and epoxy groups as fluence increased. Desorption of these basal plane groups was outlined in our previous work as important for charge storage capacity, probably due to conductivity increase [1]. When oxygen content was compared to: 1) relative areas of specific functional groups from FTIR and XPS and 2) parameters of Raman peaks, an interesting correlation was found that suggest optimal fluences for tuning the surface chemistry and structural properties of GO. Modification of surface chemistry originates from the physical and chemical effects of ion beam irradiation which were also investigated theoretically. The interaction of functional groups with H-atom was investigated using DFT and semi-empirical (SE) approach. SE calculations revealed that the chemical reduction of the epoxy group appears at H-atom energies below 1.5 eV. Results indicate that ion-beam irradiation can be used for controllable modification of surface chemistry of GO where the applied fluence can be used for tuning the degree of change, which may have implications to electrochemical charge storage properties.

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RESIDUAL MANGANESE AND INERT ELECTROLYTE – EFFECTS ON THE ORR ACTIVITY OF ELECTROCHEMICALLY REDUCED GRAPHENE OXIDES

Dalibor Karačić[1,2], **Igor A. Pašti**[2], **Sanjin J. Gutić**[1]

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Graphene-based materials are amongst the most promising materials for application as a stable support for different electrocatalytically active particles. Affordable large-scale preparation of these materials is usually based on the chemical oxidation of graphite to graphite-oxide or graphene oxide. In some cases, this step uses a significant quantity of manganese(VII), which remains in the reaction mixture in the form of Mn(II). If thus prepared material is to be used as a support for the investigation of electrocatalytic properties of other materials, manganese must be removed as effectively as possible by thorough purification.

Here we present results of ORR electrocatalytic activity testings at different degrees of post-synthetic rinsing of electrochemically reduced graphene oxide films, prepared by drop-casting of graphene oxide obtained by modified Hummers method, in order to quantify the impact of manganese residues on the ORR activity of the material. The electrochemical reduction was performed and monitored by cyclic voltammetry in KOH and Na_2SO_4 aqueous solutions, while ORR activity was measured in aqueous KOH at glassy carbon RDE. Manganese content was determined by the AAS technique. In both cases, electrocatalytic activity decreased with the manganese content. However, electrocatalytic activity for the same GO sample reduced in KOH was lower compared to the one reduced in neutral Na_2SO_4, which suggests that the choice of the inert electrolyte also affects the activity of the final material. In fact, a graphene oxide film with low (but still measurable) content of Mn, reduced in aqueous KOH, has activity as low as bare glassy carbon electrode, at least for the mass loadings used in the experiments presented here.

ON THE USE OF IONIC LIQUIDS AS ELECTROLYTE ADDITIVES TO ENHANCE THE PERFORMANCE OF ALKALINE WATER ELECTROLYSIS

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Alkaline electrolysis is a mature technology for producing hydrogen without consuming fossil fuels. The use of electricity from renewable energy sources creates the opportunity to prepare hydrogen gas as a green energy carrier, helping the economy to switch from carbon-based to green and sustainable energy sources. Nowadays, most of the global hydrogen production is still based on the steam reforming of fossil fuels [1]. To make electrolysis competitive towards steam reforming, enhancing the efficiency of hydrogen and oxygen evolution reactions (HER and OER) is essential. Extensive research has been done to improve the efficiency of the electrode reactions, mainly by developing suitable electrocatalytic materials. However, other approaches can also decrease the electrode reactions activation overpotential, namely the use of electrolyte additives, such as room temperature ionic liquids (RTILs). Improved HER kinetics in the presence of RTILs has been previously confirmed in both acidic and alkaline solutions [2,3]. RTILs can be tailor-made to increase their beneficial effect on the HER and OER kinetics. The present work examines four new tailored RTILs having the same chloride anion and where the methylimidazolium cation contains different alkyl chains. These include 3-ethyl-1-methylimidazolium chloride (C2), 3-butyl-1-methylimidazolium chloride (C4), 3-(2-methoxyethyl)-1-methylimidazolium chloride (C1OC2), and 3-(2-ethoxyethyl)-1-methylimidazolium chloride (C2OC2). The effect of the addition of small amounts (1 vol.%) of the listed RTILs on HER and OER kinetics in alkaline solution (8 M KOH) is analysed using Pt electrodes. Cyclic voltammetry, linear scan voltammetry, and chronoamperometry are carried out at different temperatures between 25 ºC and 80 ºC. The most relevant kinetic parameters were calculated and compared with previously reported data. Furthermore, gas volume measurements were done in a small-scale alkaline electrolyser to compare the gas production in pure 8 M KOH solution and after the addition of the chosen RTILs.

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COMPARISON OF DIFFERENT ACTIVATION METHODS FOR THE PREPARATION OF VISCOSE-BASED ACTIVATED CARBON FIBERS FOR USE AS SUPERCAPACITOR ELECTRODES

Stefan Breitenbach[1,2*], **Christoph Unterweger**[1], **Christian Fürst**[1], **Achim Walter Hassel**[2]
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Energy storage systems represent a key technology for the use of renewable energies. Supercapacitors are highly regarded energy storage devices due to their ability to store and release large amounts of energy very quickly. A key role in this technology is played by the electrode materials.

In this study, activated carbon fibers were prepared from viscose fibers. Different activation methods (activation via potassium hydroxide, carbon dioxide, and water vapor) were examined and compared in terms of morphology, porosity, and heteroatoms of the produced activated carbon fiber and the electrochemical properties of the electrodes fabricated from it.

The activated carbon fibers produced by water activation showed the highest specific capacitance of 180 F g^{-1} (Figure 1). In addition, this sample showed the lowest internal resistance in the supercapacitor, which can be attributed to the high purity due to the lack of heteroatoms. Activation using CO_2 followed by water activation finally produced samples reaching specific capacities up to 240 F g^{-1} and specific energy up to 42.4 W h kg^{-1}.

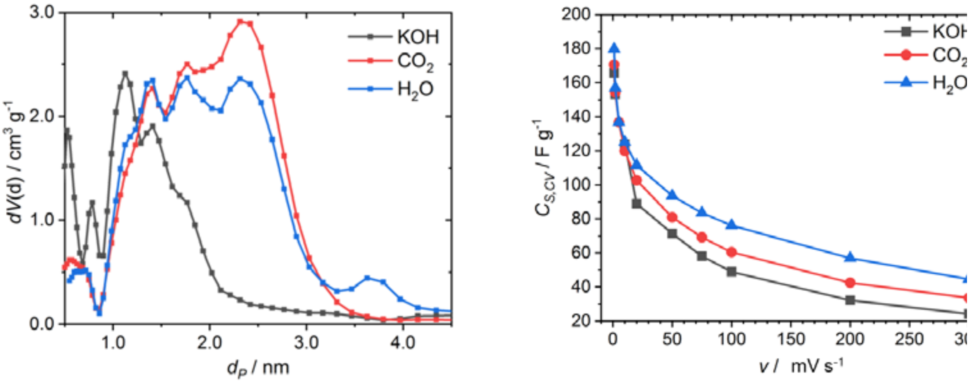

Figure 1. Pore size distribution (left; derived from adsorption isotherms using N_2 at 77K, NLDFT, slit-pore model) and specific capacitance $C_{S,CV}$ (right; derived from cyclic voltammetry at different scan rates v) of the fabricated activated carbon fibers.

Acknowledgments: The work was supported by the European Regional Development Fund (EFRE) and the province of Upper Austria through the program IWB 2014-2020 (project BioCarb-K).

ULTRATHIN Pt FILMS ELECTRODEPOSITED ON MAX PHASE SUBSTRATE AS CATHODIC CATALYSTS IN PEM FUEL CELLS

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MAX phase materials, such as Ti_2AlC have demonstrated their superior properties in a variety of applications[1]. Not only mechanically and chemically stable, heat, wear and corrosion-resistant, they have also shown excellent stability in a wide potential range when used in electrochemical systems with acidic electrolytes. This stability, as well as fair chemical inertness, makes them a promising alternative for catalyst supports in proton exchange membrane fuel cells, compared to state-of-the-art carbon-based materials.

Platinum is known for its catalytic properties in both anodic and cathodic reactions taking place in proton exchange membrane fuel cells (PEMFC). Considering the high cost of Pt, obtaining ultrathin films of Pt that would still cover the electrode surface is of great importance for practical use. To understand the Pt electrodeposition process from the initial stages, Pt has been electrodeposited usually on other metals, such as Au[2,3] or Ru[4], at a constant potential or current. Considering these results and having in mind the practical use of MAX phases as catalyst supports, as well as our previous research of Ru[5], Pd[6], Ir[7,8] thin films deposition on MAX phase substrates, in this research, we report a method for successful electrodeposition of ultrathin Pt films (10-100 monolayers-ML) onto Ti_2AlC substrate. This method relies on the use of the LSV technique, under optimised conditions, where we took into account the hydrogen evolution occurring at negative potentials, as well as the MAX phase passivation, that was eliminated with the use of a pretreatment. Pt was deposited from 3mM K_2PtCl_4 in 0.5M NaCl (pH=4), at a Ti_2AlC disc, using a rotating disc electrode (RDE), and its presence on the whole surface was confirmed by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), and also by X-ray photoelectron spectroscopy (XPS) for the 10ML sample.

Oxygen reduction reaction (ORR) was investigated at such prepared electrodes (10-100ML Pt@Ti_2AlC), using an RDE at rotation speeds in a range of 600-3400 rpm. The results show a good activity, compared to commercial catalysts, and exceptional stability in terms of a very low decrease in electrochemically active surface area of the samples under prolonged operation.

Acknowledgments: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451- 03-68/2020-14/200053 and Contract No.451-03- 68/2020-14/200135). The authors wish to thank Prof. M. Radovic from the Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843, USA, for preparation of Ti_2AlC substrates.

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BOOSTING SUPERCAPACITOR PERFORMANCES IN ACIDIC ELECTROLYTE USING DIFFERENT CHLORINE SALTS

Milena Pijović, Ivana Perović, Snežana Brković, Gvozden Tasić, Bojan Janković, Nikola Zdolšek

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Electrochemical supercapacitors are high-power energy storage devices with unlimited cycle life (compared to a high-energy battery). In order to improve the electrochemical behaviour of supercapacitors there are two possible ways: development of new (highly porous) electrode materials and new formulations of electrolytes.

In this research, we proposed a new formulation of electrolytes, opposite to acidic (H_2SO_4) or basic (KOH) electrolytes which are usually used for supercapacitors. Herein, we investigated the effects of different chlorine-based salts in 1M H_2SO_4 electrolyte. For this purpose, different carbon materials were prepared by carbonization of biomass. All these carbon materials were activated by physical and chemical activations. Pure 1M H_2SO_4 electrolyte showed very low specific capacitances. But, adding chlorine salts in 1M H_2SO_4 electrolyte specific capacitance increase almost three to four times.

VISCOSE FIBERS-DERIVED CARBONS FOR ELECTROCHEMICAL CAPACITORS AND SELECTIVE OXYGEN REDUCTION TO PEROXIDE IN ALKALINE MEDIA

Stefan Breitenbach[1,2], Nemanja Gavrilov[3,*], Igor A. Pašti[3], Christoph Unterweger[1], Jiri Duchoslav[4], David Stifter[4], Achim Walter Hassel[2], Christian Fürst[1]

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Biomass-derived carbons have numerous attractive properties, including low price, possibility to scale up production, and great variability of their properties, allowing their applications in different technologies. The latter point is specifically related to various pore sizes, which can be tuned using synthesis conditions, good conductivity, and the presence of heteroatoms which are naturally present in precursor and remain in carbon upon carbonization. Here we describe several biomass-derived activated carbons prepared from viscose fibers and their application as capacitive electrodes and catalysts for oxygen reduction reaction (ORR) in alkaline media. Capacitance measurements were done in both aqueous and non-aqueous solutions, and we find that capacitance up to 200 F g^{-1} is reached (Figure 1). However, this holds only for the material with a very high specific surface area (SSA, reaching 2245 m^2 g^{-1}). Materials with lower SSA show lower capacitances but not proportionally to the SSA. This finding is likely due to the relatively large contribution of pseudocapacitance, which can be up to almost 80%, depending on the surface chemistry of specific carbonaceous material. When it comes to ORR, we find that SSA does not determine the onset potential. Also, the selectivity of ORR is not determined by SSA (Figure 1), as all the studied materials follow a $2e^-$ reduction mechanism, converting O_2 to peroxide. However, as the ORR overpotential increases, the SSA takes the dominant role and determines ORR kinetic current. For the material with the highest SSA, ORR kinetic currents reached values of 250 A g^{-1} at −0.259 V vs. Standard Hydrogen Electrode. In conclusion, our results show that activated carbon fibers derived from viscose fibers can find different applications in energy conversion and storage if the properties of the materials are properly tuned.

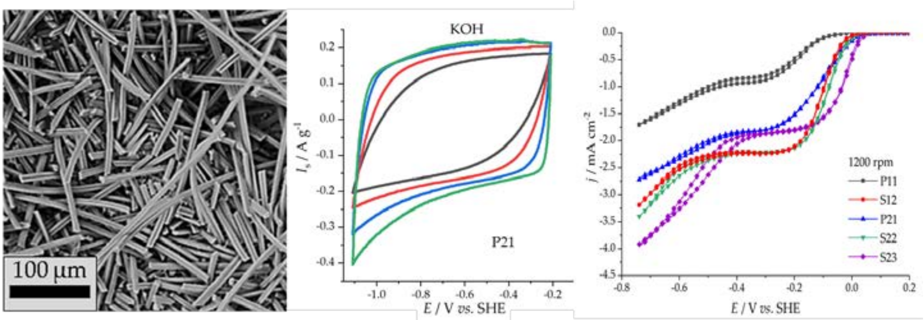

Figure 1. SEM micrographs of viscose fibers-derived activated carbons, capacitive response, and ORR polarization curves in alkaline solution (0.1 mol dm^{-3} KOH).

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ZnO/CARBON FROM BIOPOLYMER CROSSLINKING AS A SUPERCAPACITOR MATERIAL

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Carbon-based materials, obtained by carbonization of biomass or biopolymer precursors, can have highly developed surfaces with different pore structures, large pore volumes, good electrical conductivity, and thermochemical stability, which are all beneficial for use in supercapacitors. Further capacitance enhancement is sought through composites with metal oxides, including graphene/Co_3O_4, porous carbon/manganese dioxide, carbon nanotubes/zinc oxide, among others [1,2]. Herein we describe the electrochemical preparation of ZnO/C composite via alginate crosslinking directly at the zinc electrode surface. Obtained gels are dried and carbonized at 650 °C and 800 °C for 2 hours with a heating rate of 10 °C min^{-1}. Capacitance measurements, done in 6M KOH aqueous solution, reveal capacitances of up to 235 F g^{-1} (Figure 1) for ZnO/C composite carbonized at 800 °C. Carbon material obtained by washing out the zinc with HCl prior to drying/carbonization, provides only around 89 F g^{-1}. The presence of Zn during different temperature treatment led to an increase in values of measured capacitances, i.e., 111 F g^{-1} (650 °C) and 235 F g^{-1} (800 °C). The increase is in part due to the increase in specific surface area (from 540 m^2 g^{-1} (C – no Zn) to 1056 m^2 g^{-1} (ZnO/C 800)) and pore volume of the composite materials, and partly due to pseudocapacitance. Homogeneous dispersion of zinc ions between alginate chains is beneficial for carbon activation. At elevated temperatures, zinc ion reduction by surrounding carbon starts which evolves carbon dioxide and develops composites surface area. Evidently, this process is more favourable at 800 °C than at 650 °C. Using Dunn analysis, it is estimated that the remaining Zn/ZnO and oxygen groups account for around 12% capacitance, i.e., pseudocapacitance, while the other 88% comes from electric double layer charging on the highly developed surface. Briefly, the results presented here show that zinc ions can be used as crosslinkers and later as an activating agent for the preparation of composite materials with applications in energy storage.

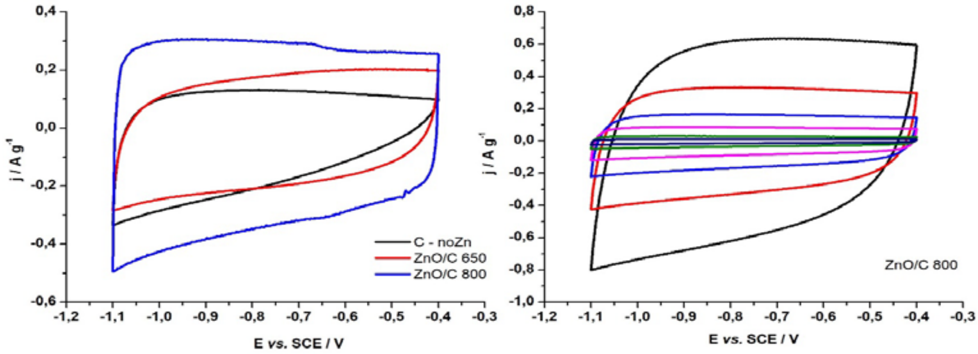

Figure 1. Capacitive response between composites (left) and CVs at the different sweep rates in alkaline solution (6M KOH) for ZnO/C treated at 800 °C.

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PREPARATION OF AuNiMo/Ti CATALYSTS AND INVESTIGATION OF THEIR CATALYTIC PROPERTIES FOR BOROHYDRIDE OXIDATION

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Here we present a simple approach to prepare low gold/nickel-molybdenum/titanium (AuNiMo/Ti) based catalysts by electrochemical and chemical methods. At first, NiMo foams were electroplated on the Ti surface from a bath containing 1 M HCl, 1.5 M H_2SO_4, 0.01 M Na_2MoO_4, and 0.01 - 0.5 M $NiCl_2$. The electrochemical deposition was carried out at the current density of 50 mA cm^{-2} and 500 mA cm^{-2} for 3 min. The Au crystallites were deposited on the prepared NiMo/Ti electrodes by their immersion into 1 mM $HAuCl_4$ + 0.1 M HCl for 10 s. The morphology and composition of the catalysts have been examined using scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and inductively coupled plasma optical emission spectroscopy. The electrocatalytic properties of the prepared AuNiMo/Ti catalysts for sodium borohydride oxidation was investigated by recording cyclic voltammograms in a 1 M NaOH solution containing 0.05 M $NaBH_4$ at a potential scan rate of 10 mV s^{-1} in potential range from -1.2 up to 0.6 V vs. Ag/AgCl/KCl$_{sat}$ at a temperature of 25 ºC. Direct alkaline $NaBH_4$-H_2O_2 single fuel cell tests have been carried out using the prepared AuNiMo/Ti with a geometric area of 2 cm^2 as the anode and a Pt sheet as the cathode. The anolyte was composed of an alkaline mixture of 1 M $NaBH_4$ + 4 M NaOH, and the catholyte contained 5 M H_2O_2 + 1.5 M HCl. The performance of the fuel cell was evaluated by recording the cell polarization and obtaining the corresponding power density curves.

It was found that the prepared AuNiMo/Ti catalysts with Au loadings in the range of 1.8 up to 3.9 μg$_{Au}$ cm^{-2} have a higher activity towards the oxidation of sodium borohydride as compared to that of NiMo/Ti. The higher catalytic activity of the prepared AuNiMo/Ti catalysts under various conditions may be related to the production of smaller gold nanoparticles and their fine and uniform dispersion on the surface. The AuNiMo/Ti catalysts seem to be promising anodic materials for direct borohydride fuel cells.

Acknowledgments: This project has received funding from European Social Fund (project No 09.3.3-LMT-K-712-19-0138) under grant agreement with the Research Council of Lithuania (LMTLT).

Hydrogen energy and hydrogen storage materials

INTERACTION OF LIGHT ALKALI METALS WITH AMMONIA BORANE: A THEORETICAL STUDY

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Ammonia borane – AB (formula: NH3-BH3) has been known for its extraordinary gravimetric hydrogen capacity (nearly 20 wt.%) and is therefore considered as promising hydrogen storage material. However, there are several drawbacks to overcome, namely dehydrogenation kinetics is rather poor, and three-step desorption releases contaminated hydrogen with each subsequent step requiring significantly higher temperature. In addition, there are detrimental by-products (e.g., borasine, diborane) that also limit its practical application. Eliminating at least borasine release is possible through the reaction of alkali metal (M=Li, Na) with AB and producing monometallic amidoborane salts MAB.

In this paper, electronic structure calculations and the analysis of charge density topology of pure AB, lithium, and sodium amidoboranes were performed in order to investigate cohesion and bonding nature. The influence of the specific alkali metal substitution will be assessed using calculated IR and Raman spectra and analysis of vibrational bands in comparison to pure AB.

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DATA SCIENCE AND DEEP LEARNING FOR THE DEVELOPMENT OF NEW HYDROGEN STORAGE MATERIALS

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Prediction of metal hydride formation enthalpy is one of the key requirements for a rapid design of new hydrogen storage materials. In the last decades, DFT (density functional theory) approach showed good predictive potential for the ground state properties and accurate energies of hydride formation. However, calculating ZPE contribution and temperature effects in addition to formation energy at 0K is computationally and time-consuming and therefore often avoided, resulting in discrepancy to experiment.

The development of machine learning and, in particular, deep learning, opens a new perspective for predictive modeling of materials properties. Data collected through DFT calculations can be combined with experimental results in a predictive model, aiming to exploit unexplored compositional space. In this work, we consider the application of MatErials Graph Network (MEGNet) [1] to the prediction of hydrogen formation behavior, and screening of potential dopants in reversible metal hydride materials. Various approaches, relying on transfer learning and both experimental data and computational repositories (MP [2], NOMAD [3]) are proposed as a route to accurate prediction of a structure-property relation for hydrogen storage materials. Domains of applicability of these models are addressed.

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LOWERING THE ENERGY CONSUMPTION FOR HYDROGEN PRODUCTION BY USING NON NOBLE CATALYST IN FORM OF IONIC ACTIVATORS

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In order for renewables to become the future basis of sustainable development and energy supply, it is necessary to find the most suitable way for storing and transporting energy from these intermittent sources. Hydrogen is currently the best candidate as an energy medium, which meets all the requirements for such energy manipulation and fits into future energy concepts. With the objective to the hydrogen-based economy have a realistic and sustainable perspective in the future, hydrogen production has to be cheap, efficient, and sufficiently rapid to meet the needs of a growing market. The best way to achieve these goals is to increase the energy efficiency of the hydrogen generation process from alkaline water electrolysis, which is environmentally friendly and satisfies all the prerequisites for sustainable development.

The aim of this work was to investigate the possibility of increasing the energy efficiency of the alkaline electrolysis process through a technologically simplified process of in situ activation, i.e., by dissolving a combination of the d-metal complexes directly into the electrolyte during an electrolytic process. The catalytic activities of in situ added cobalt, molybdenum, and tungsten ionic activators were investigated, the mechanism of the hydrogen electrode reaction under different experimental conditions was studied, as well as the influence of the concentration of ionic activators, operating temperature, and current density on energy consumption. Experimental results have shown that the use of an appropriate combination of d-metal as ionic activators can significantly affect the reduction of energy consumption in the alkaline electrolysis process, even up to 15% in individual cases. The origin of this effect was determined using quasi-potentiostatic, galvanostatic, and impedance spectroscopy techniques during the in situ electrodeposition in an alkaline electrolyzer. The synergetic effect is observed, with its maximum at industrial conditions (high temperature and current density). Obtained results could have a significant impact on the industrial process for alkaline hydrogen production and suggest good catalytic performance not only by the increase of the real surface area of the electrodes but also from the true catalytic effect.

SOLID STATE MECHANOCHEMICAL SYNTHESIS OF NOVEL BIMETALLIC AMIDOBORANES

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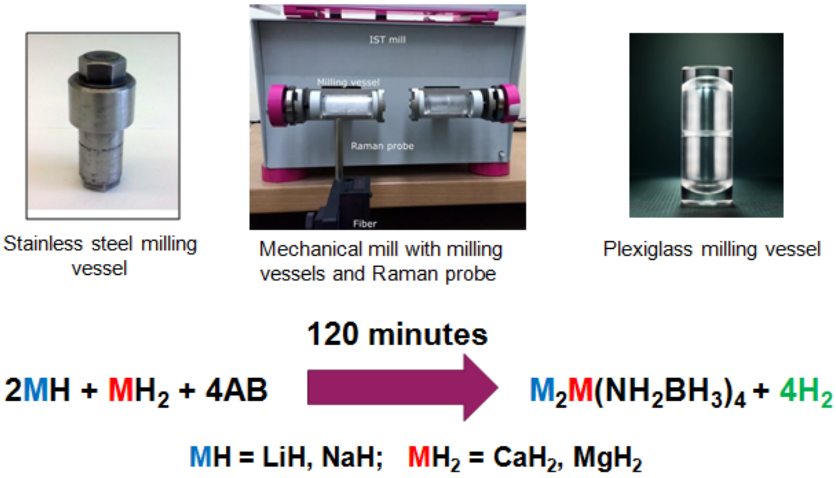
Solid-state mechanochemistry can be a very useful technique for the synthesis of bimetallic amidoboranes - very prominent materials for hydrogen storage. By using the mechanical ball milling, a solventless solid-state reaction between ammonia borane (NH_3BH_3, AB), alkali metal hydrides (NaH, LiH), and alkaline earth metal hydrides (CaH_2 and MgH_2) is absolutely possible [1-3]. Exclusively hydrogen and bimetallic amidoboranes are obtained as final products. Herewe report several examples of successful synthesis - $Na_2Mg(NH_2BH_3)_4$, $Li_2Mg(NH_2BH_3)_4$, $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$.



Stainless steel milling vessel

Mechanical mill with milling vessels and Raman probe

Plexiglass milling vessel

Figure 1. Up: milling equipment for solid-state synthesis experiments; Down: chemical reaction during the milling process.

Using the Raman spectroscopy for solid-state in-situ monitoring of reaction between ammonia borane and hydrides, we firstly synthesized two mixed metal Mg-containing amidoboranes - $M_2Mg(NH_2BH_3)_4$ (M=Li, Na). As milling equipment, we used PMMA (plexiglass) jars and stainless steel balls. The mentioned approach allowed real-time observation of key intermediate phases and a straightforward follow-up of the reaction course. Detailed analysis of time-dependent spectra revealed a two-step mechanism through $MNH_2BH_3 \cdot NH_3BH_3$ adducts as key intermediate phases which further reacted with MgH_2, giving $M_2Mg(NH_2BH_3)_4$ as final products.

After the success with Mg-containing amidoboranes we have also developed a new green and rapid mechanochemical procedure for the synthesis of Ca-containing alkaline metal amidoboranes, $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$, using a similar approach – solid-state reaction between metal hydrides and ammonia borane. The tandem technique - in-situ X-Ray diffraction with temperature profile measurement was used for monitoring of mechanochemical syntheses. In such a way, we revealed how the course of the reactions and their thermal profiles strongly depend on the starting alkali metal hydride. For instance, NaH induced a sudden and dramatic increase in temperature of the reaction mixture, which induced a partial decomposition of thermally labile AB and influenced the yield and composition of reaction products. The changing of milling reactor material from insulating plastics (PMMA) to thermally conductive stainless steel readily amended this issue, most likely through more effective heat dissipation.

In summary, solid-state chemical reaction for bimetallic amidoborane synthesis is shown in Figure 1. In all four cases, as products, only mixed metal amidoborane and hydrogen gas are obtained, without the usage of any solvent. This means that such kind of synthesis is fulfilling all aspects of green synthesis.

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INTERACTION OF HYDROGEN WITH PHTHALOCYANINE MACROCYCLES FOR REVERSIBLE STORAGE

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Hydrogen is often considered the fuel of the future that will play an important role in the reduction of fossil fuel dependency. Hydrogen is considered a green energy source because it can be generated from renewable sources and emits no harmful products during combustion. Hydrogen storage represents the biggest setback that hinders its wider use, and significant effort is placed in overcoming this impediment. Albeit compelling progress has been made, most of the solutions lack reversibility of the hydrogen adsorption/desorption processes and require high hydrogen pressure or cryogenic temperatures for it. [1–3] In this contribution, we investigated the interaction of hydrogen with metal-containing phthalocyanine macrocycles supported on Au(111) substrates using mass spectroscopy techniques such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Temperature Programmed Desorption Spectroscopy (TPDS) for use as reversible storage. Different surface supported metal-containing phthalocyanine molecules demonstrated contrasting behaviour upon exposure to hydrogen at room temperature.

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Application of polymeric materials in the energy conversion and storage

2D-LIKE POLYDOPAMINE MEMBRANES FROM THE AIR/WATER INTERPHASE: TOWARDS THE IMPROVEMENT OF THEIR MORPHOLOGICAL PROPERTIES AND SUCCESSFUL TRANSFER ON MULTIFUNCTIONAL SUBSTRATES

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Polydopamine (PDA) is a relatively new biomimetic polymer that has made a sizable impact in various fields, e.g., preparation of the Li-ions batteries, synthesis of antibacterial materials, biosensors engineering, molecular imprinting, tissue engineering, bioimaging, and finally-photocatalysis [1,2]. PDA can be synthesized by an oxidative polymerization of dopamine hydrochloride induced by alkaline pH, most often achieved by the use of the Tris buffer solution [3–5]. During this process, three types of PDA can be formed and distinguished, and they are namely: nanoparticles embedded in the solution, thin coating on virtually any type of substrate that is immersed in the solution, and the membrane at the air/water (a/w) interphase [6]. When appropriate soft-stirring conditions and constant oxygen inflow are applied, these a/w membranes can be synthesized, showing the different structural and chemical character from the PDA generated in the bulk solution. Therefore, they became an object of interest for the materials science society in recent years. More importantly, in our previous study, we have shown as the first an unknown laminar 2D-like structural arrangement of these membranes [7]. That was of great importance, especially while taking into account their potential applications, e.g., construction of the new type of van der Waals heterostructures [8]. Unfortunately, to this date, there is no systematic and comprehensive study towards efficient production of these materials, towards homogenous and continuous large surface area membranes of a high quality. However, our group managed to obtain ultrathin "optimized" membranes of a great homogeneity and wettability, using a novel spectroscopic reflectometry setup to observe their growth in situ, and standard “scooping” technique to transfer them onto desired substrate. Therefore, in this study, several attempts were made to further optimize the procedure, by refining a scooping technique and polymerization conditions i.e. time of oxidation and reagents concentration among others. Morphological properties of the final membranes (thickness, roughness) were investigated by Atomic Force Microscopy **(Figure 1a)**. Moreover, structural studies have been carried out, namely Raman spectroscopy **(Figure 1b)** and X-ray diffraction **(Figure 1c)**. This research made it possible to optimize the morphological and structural properties of the obtained membranes, which present great quality of the surface without cracks and visible discontinuities **(Figure 1d)**.

Finally, further optimized ultrathin 2D-like PDA membranes were obtained, which can be easily transfer onto desired substrate resulting in laminar PDA/semiconductor nanocomposite

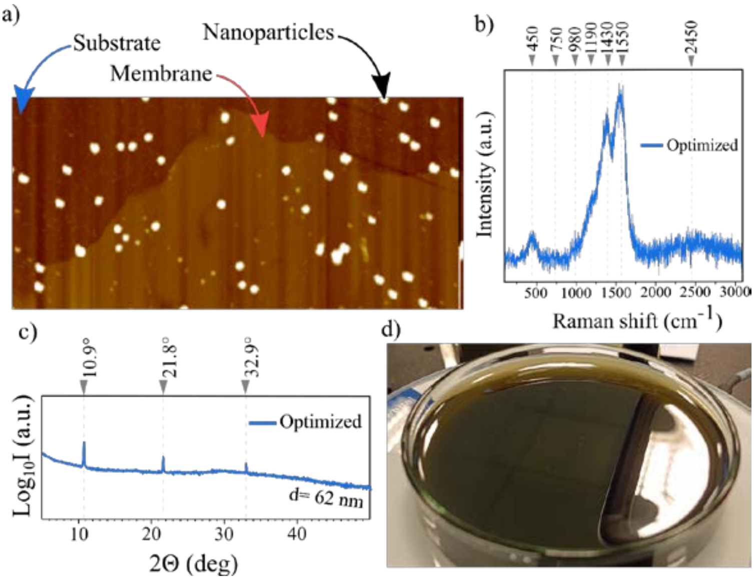

Figure 1. a) AFM image of the membrane transferred onto Si (100) substrate. **b)** Raman spectra of the optimized membrane. **c)** Diffractogram of the optimized membrane revealed by the XRD. **d)** Surface of the PDA ultrathin membrane from the air/water interface.

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ELECTRICAL ENERGY STORAGE CAPABILITIES OF P(VDF-TrFE-CFE) RELAXOR POLYMERS

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Different dielectric polymers such as polypropylene, polycarbonate, and polyethylene tetra phthalate have been commercially used in thin or thick film capacitors for decades. The performance of various copolymers of polyvinylidene fluoride P (VDF) and their nanocomposites for capacitor applications has also been intensively studied.

In the present work, we report on the energy storage properties of relaxor terpolymers, P (VDF-TrFE-CFE). The compositions of P (VDF_x-$TrFE_{1-x}$-CFE_y, x/1-x/y) with 51.3/48.7/6.2, 63.8/36.2/7.2, 59.8/40.2/7.3, 70/30/8.1, 64.8/35.2/7.8, and 68/32/8.5 have been studied. The polymer nanocomposites of few compositions with zirconium doped barium titanate nanoparticles are also investigated. The barium doped zirconium titanate particles were prepared via the hydrothermal method. The free-standing polymer and its nanocomposite films were prepared through the solution casting method. The discharged energy density was evaluated through the polarization-based method. A few compositions showed double hysteresis loops indicating the field-induced phase transition to the ferroelectric state. This causes an increase in hysteresis losses and thus decreases the charge-discharge efficiency. The 59.8/40.2/7.3 sample shows the highest energy density (~ 5 J/cm^3 at E = 200 MV/m) among all compositions while retaining an efficiency above 60%. The polymer nanocomposites show an increase in the polarization, and therefore the discharged-energy density also increases.

MODIFICATION OF PROPERTIES OF PLA NANOCOMPOSITES

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Polylactic acid (PLA) is a polymer that has had a huge impact on the evolution of the bioplastics industry during the last 30 years. It is linear thermoplastic polyester derived from renewable sources that displays properties such as bio-compatibility, bio-degradability as well as the ability to be molded into different shapes. The latest endeavours are moving toward durable bioplastics, which is desired for long-term multiuse application in automotive, electronics, and other industries.

The main goal of this work was to show a simple method of preparation of polylactide nanocomposites using a synthesized hybrid filler *n*SiO_2@Fe. Hybrid filler was used to possibly, in any way, affect electric properties of produced PLA nanocomposites.

Hybrid filler was synthesized using a method of reducing an iron salt ($FeCl_3$) to elemental iron, also known as zero-valent nano iron (*n*ZVI, Fe^0), with $NaBH_4$ as a reducing agent of the chemical reaction.[1] Nanosilica was used as a carrier for the reduced *n*ZVI particles. Nanocomposite material was produced using the melt-mixing method. PLA was used as a composite matrix, to which commercial silica nanoparticles (*n*SiO_2) and new synthesized hybrid nanoparticles of silica and iron nanoparticles (*n*SiO2@Fe) were mixed as filler with different mass ratios (1 % nanosilica, 1 % nanosilica +0.05 % hybrid filler, 0.5 % nanosilica +0.5 % hybrid filler and 0.5 % hybrid filler).

Synthesized hybrid nanoparticles were analysed using UV-VIS spectroscopy and scanning electron microscope (SEM). The size of particles was determined using the dynamic light scattering method (DLS). Results of SEM and DLS showed that synthesized nanoparticle filler *n*SiO_2@Fe were still in range of nanometre-scale (178 ± 118,85 nm), and with the UV-VIS spectra of the filler, we could confirm the existence of both *n*SiO_2 and Fe^0 in the hybrid particles.

Structural and thermal properties of pressed nanocomposites were analysed; SEM micrographics showed that mainly a homogeneous dispersion of both nanofillers was achieved. Only one of the samples showed a nonuniform dispersion and formation of large agglomerates of fillers in the matrix (0.5 % nanosilica + 0.5 % hybrid filler). Performed measurements of thermal conductivity and electric resistivity reveal that the thermal conductivity of the PLA nanocomposites was not affected by the addition of nanosilica or hybrid nanofillers. As expected, *n*SiO2@Fe hybrid filler had an impact on the electric properties of the nanocomposite. The properties improved because hybrid filler had lowered the values of measured electric resistance of the PLA nanocomposites. Electric properties of nanocomposites were highly conditioned by the dispersion of the *n*SiO2@Fe hybrid filler in the PLA matrix, which is consistent with the SEM results.

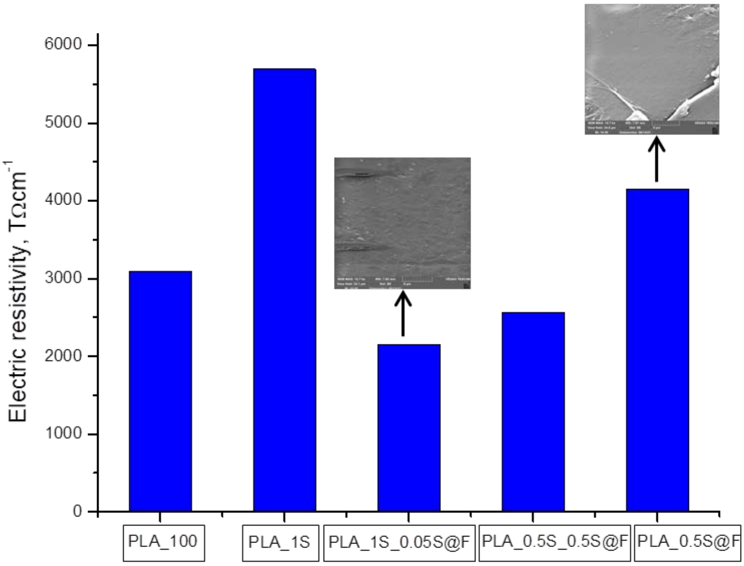

Figure 1. Change of electric resistivity of PLA polymer in nanocomposites corroborated with SEM micrographics (samples PLA_1S_0,05S@F and PLA0,5S@F)

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Catalysis, electrocatalysis and photocatalysis in energy conversion and storage

PHOTOCATALYTIC APPLICATIONS OF POLYDOPAMINE BASED NANOCOMPOSITES

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Light-driven photocatalysis is at the core of global energy concerns, and this is because of the crucial implications that light-driven hydrogen production has on the reduction of our fossil fuel dependency. Polydopamine (PDA) is a popular mussel-inspired material with large applicability in biomedical and drug delivery fields, which recently has been gathering attention in the fields of catalysis and photocatalysis. PDA is highly biocompatible and can be easily polymerized on many surfaces by a variety of methods. PDA has been long debated to show similar semiconducting and electron-conducting properties as Eumaline and Melanine, advocating its use in sensing and electronics. Moreover, PDA has been shown to be an ideal photocatalyst when combined with semiconductor interfaces. This is because it seems to play an unexpected role in enhancing hydrogen production and tuning optical bandgaps of coated semiconductors**[1,2]**. In this talk, we will show the recent advances towards understanding the role of PDA on the enhanced photocatalytic properties of several semiconductors (ZnO and ZnS), and we will discuss further strategies and developments in order to optimize coating processes of PDA**[3,4]**. Finally, we will outline some of the prospects and opportunities for PDA/semiconductor research in the next few years.

Acknowledgments: Authors acknowledge the financial support from the National Science Centre (NCN) of Poland by the OPUS grant 2019/35/B/ST5/00248

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Pt NANOPARTICLES SUPPORTED ON ORGANIC MATRIX TRIS(AZA)PENTACENE AS SELECTIVELY ACTIVE ELECTROCATALYST FOR HYDROGEN OXIDATION/EVOLUTION AND SUPPRESSIVE FOR OXYGEN REDUCTION

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Hydrogen-fed fuel cells are recognized as the next-generation power supply devices for both stationary and mobile applications. Pt or Pt-based alloys finely dispersed on high area carbon supports are state-of-the-art catalysts for electrochemical reactions taking place in PEMFCs, namely hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR) at the cathode [1]. Major degradation of the Pt-catalyst layer occurs during shut-down/start-up events when air backfills anodic fuel cell compartment and thus unwanted ORR enrolls at the Pt-anode. This causes counter-reactions ongoing on Pt-cathode and its degradation due to the rise of the local potentials up to 1.5 V – 2 V [2]. Developing a Pt-based electrocatalytic material able to selectively catalyze HOR while suppressing ORR is therefore beneficial for the durability of the fuel cells.

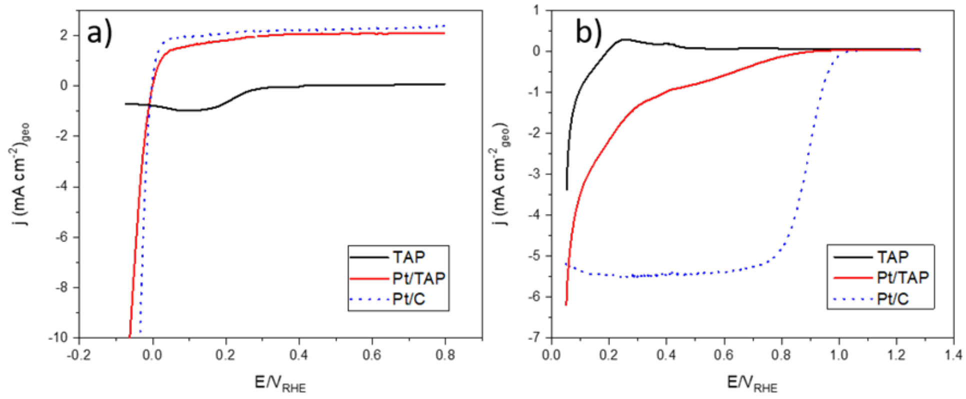

Figure 1. (a) Polarization curves for HOR/HER recorded for TAP, Pt/TAP and Pt/C samples (scan rate 10 mV/s); (b) Polarization curves for ORR recorded for TAP, Pt/TAP and Pt/C samples (scan rate 20 mV/s). In both cases, curves were recorded in 0.1 M $HClO_4$ electrolyte at 1600 rpm [3].

We present here an organic matrix tris(aza)pentacene (TAP), a member of π-functional materials with ladder-like conjugated nitrogen-containing units, as the support for Pt nanoparticles to form a "smart" fuel cell anode able to selectively run HOR and to effectively suppress ORR [3], as shown in Figure 1. "Switching-on/off" of the composite material activity is provided by the chemistry of TAP support that undergoes reversible reduction/oxidation in the low potential region (< 0.45 V_{RHE}), which provokes TAP - H_xTAP transition. The conductivity of the reduced H_xTAP enables supported Pt particles to effectively run HOR (and also HER), Figure 1a. In contrast, restricted conductivity of oxidized TAP analog leads to a substantial drop in the ORR activity with respect to benchmark Pt/C catalyst, Figure 1b.

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Pt NANOPARTICLES SUPPORTED ON TITANIUM OXYNITRIDE AS AN ADVANCED ELECTROCATALYTIC MATERIAL FOR HYDROGEN EVOLUTION REACTION

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The transition from fossil fuels to hydrogen as the main energy carrier is a highly desirable scenario that would be beneficial from several aspects, including environmental, social, and economic. A sustainable way to produce high purity hydrogen is water electrolysis, in which hydrogen evolution reaction (HER) occurs as the cathodic process. Pt nanoparticles supported on high area carbon materials are state-of-the-art catalysts for this reaction and ensure fast HER kinetics in acid media, while the stability of Pt/C catalysts during HER is satisfactory. One possible way to additionally improve both activity and stability of Pt-based catalysts is to develop an alternative support material capable of inducing strong metal-support interaction (SMSI). One interesting candidate is titanium oxynitride ($TiON_x$), which was already reported by our group as advanced support for Ir nanoparticles that exhibited excellent oxygen evolution performance [1-3]. In a recent publication, enhanced stability and activity of Ir supported on $TiON_x$ were indeed connected with SMSI induced between $TiON_x$ and Ir [2].

In this contribution, Pt/$TiON_x$ composite was prepared by supporting Pt nanoparticles over $TiON_x$, which was finely distributed over reduced graphene oxide support. In comparison with a commercial Pt/C catalyst, higher HER activity in acid media was obtained, as can be seen in Figure 1a.

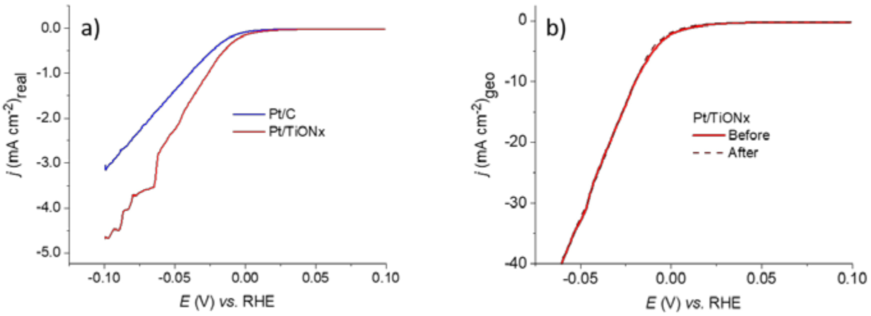

Figure 1. (a) Polarization curves for HER on Pt/C and Pt/$TiON_x$ recorded in Ar-saturated 0.1 M $HClO_4$ at a scan rate of 10 mV/s. Current densities are given with respect to real Pt electrochemical surface area obtained from CO stripping; (b) Polarization curves for HER on Pt/TiONx recorded before and after stability testing in the same electrolyte (10 mV/s). The stability test included 5000 scans (100 mV/s) between 0.1 V_{RHE} and -0.2 V_{RHE}; current densities are given with respect to geometric area.

In addition, Pt/TiON$_x$ catalysts showed excellent stability during prolonged cycling in the HER potential region, Figure 1b. We believe that SMSI between TiON$_x$ support and Pt particles appropriately tunes the hydrogen adsorption energy on Pt, which is the initial step in the HER mechanism. At the same time, SMSI prevents detachment or agglomeration of Pt particles during HER by stronger interaction with TiON$_x$ support, which enhances the stability of Pt/TiON$_x$.

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INVESTIGATION OF ATOMIC DISSOLUTION AND REDEPOSITION ON Pt-Co/C NANOPARTICLES AT RELEVANT CURRENTS FOR LOW-TEMPERATURE PROTON EXCHANGE MEMBRANE FUEL CELLS

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In the path of achieving performance and durability goals set for the low-temperature proton exchange membrane fuel cells (PEMFC), it is important to critically investigate mechanisms of degradation of current state-of-the-art cathodic materials. Some of the bimetallic nanoparticulate carbon-supported platinum alloys have shown better performance compared to the carbon-supported platinum nanoparticles when tested with conventional electrochemical screening techniques such as thin-film rotating disk electrode (TF-RDE). [1] When tested with the membrane electrode assembly setup, those same materials show the worst performance at the high current densities. [2] Due to this, catalyst development should include testing with methodologies that can investigate the properties of the material at relevant current densities. We explored the mechanisms of structural changes of Pt-Co/C nanoparticles using identical location transmission electron microscopy (IL-TEM) coupled with the recently introduced modified floating electrode (MFE) [3]. We employed careful analysis of the micrographs taken before and after the exposure of nanoparticles to the electrochemical activation protocol. In this fashion, we were able to track the structural changes made on the same nanoparticle on the atomic scale caused by the electrochemical perturbation with real-life device relative currents. Different mechanisms, such as etching and redeposition, were analysed and discussed in terms of the stability of the nanoparticle surface. This demonstrates the importance of the bottom-up approach in the analysis of structure-stability properties of electrocatalytic nanoparticles in contrast to the state-of-the-art *ex-situ* techniques, where the history of the observed nanoparticle is unknown. [4]

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PHOTOCATALYTIC OXIDATION OF AMMONIA ON TiO_2 IMMOBILIZED ON RUBBER PADS UNDER ARTIFICIAL SOLAR IRRADIATION

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Industrial development affects air quality, but it also encourages the advancement of technology and the interest of scientists. Increased emissions of ammonia (NH_3) caused by agricultural activities have been impacting environmental issues, such as species composition through soil acidification, direct toxic damage to leaves, and by altering the susceptibility of plants to drought, pathogens, and frost, sensitive habitats. Furthermore, due to NH_3 contribution to the formation of secondary particulate matter (PM), it significantly affects human health[1]. In regard to the application of heterogeneous photocatalysis for air, purification has been developed over the last decades [2]. Photocatalysis is a promising method for removing air pollutants using ultraviolet radiation, which stimulates reactions between a photocatalyst, compounds, and contaminants in the air. Therefore, this paper presents the experimental results of photocatalytic degradation of ammonia on rubber pads with immobilized titanium dioxide (TiO_2) by the modified sol-gel method[3].

Experiments were performed in a semi-pilot photocatalytic wind tunnel under simulated solar irradiation with different portions of UV light. Rubber pads were made of recycled rubber granulates. The aim of the experiments was to remove ammonia from the air stream. The kinetic study resulted in intrinsic reaction rate constants calculated using the axial dispersion model, including mass transfer considerations and first-order reaction rate kinetics with photon absorption effects. The results confirmed photocatalytic oxidation of ammonia towards molecular nitrogen (N_2) in the photocatalytic wind tunnel. Therefore, the preliminary results obtained in this work represent a good basis for sizing reactors on a pilot level to prevent further environmental pollution.

Acknowledgments: This work has been supported by the following project „Recycling rubber & solar photocatalysis: ecological innovation for passive air and health protection", supported by European Regional Development Fund, KK.01.1.1.07.0058.

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IMMOBILIZATION OF TITANIUM DIOXIDE ON A RUBBER PADS FOR PASSIVE AIR AND HUMAN HEALTH

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Over the past few years, people's awareness of environmental pollution and its negative consequences has been increasingly awakened. Air quality declines with time, but it also encourages the new accomplishment in technology. The synergistic action of solar radiation and photocatalysts (semiconductors) triggers redox reactions on the surface of photocatalysts which successfully remove volatile organic compounds, unpleasant odours, sulphur dioxide, and nitrogen oxides, ammonia, etc. [1]. The advantage of photocatalysis is sustainable, cheap, and environmentally friendly technology that achieves complete or partial decomposition of pollutants. One of the solutions to achieve passive protection of air and human health is to immobilize titanium dioxide (TiO_2) on the surface of rubber pads which can be seen on children's playgrounds and various sports fields. Waste tire management involves environmental, social, and economic problems, which have been a major challenge for scientists and industry for decades.

Therefore, this paper presents experimental results of one of the possible methods of titanium dioxide immobilization on a recycled rubber pad. Rubber pads were obtained from the industry that incorporates recycled rubber granulates in its productions. Commercially available TiO_2 P25, which is one of the best photocatalysts, has been immobilized by the modified sol-gel method [2]. Characterization of the immobilized layer in terms of crystal structure and morphology was investigated by Scanning Electron Microscopy (SEM). Advantages and disadvantages were compared so that further research on this topic could be performed. By applying TiO_2 on rubber substrates and placing them in the environment in which we live, we come to the possibility that the air we breathe every day is purified and less harmful.

Acknowledgments: This work has been supported by the following project „Recycling rubber & solar photocatalysis: ecological innovation for passive air and health protection", supported by European Regional Development Fund, KK.01.1.1.07.0058.

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PRELIMINARY CHARACTERIZATION INVESTIGATION OF TiO_2-SnS_2/GO-RGO NANOCOMPOSITES FOR HYDROGEN GENERATION

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The development of the future energetic sector requires the higher promotion of the use of alternative fuels, such as hydrogen, specifically ones produced from renewable sources. One of the ambitious ways for such production is photocatalytic water splitting under solar light irradiation. The main means of carrying out the reaction are photocatalytic nanomaterials. The most used photocatalyst is TiO_2, which is characterized by UV-light response and high rates of charge recombination. Therefore, it is necessary to combine such material with other semiconducting materials that have high visible-light response and that decrease charge carrier recombination rate.

In this work, hydrothermally synthesized TiO_2-SnS_2/GO-RGO nanomaterial with different ratios of GO-RGO (graphene oxide – reduced graphene oxide) within the samples was subjected to detailed characterization analysis prior to photocatalytic H_2 production investigation. The pure components were also examined with the purpose of comparing newly designed and synthetized TiO_2-SnS_2/GO-RGO. Analyses include the determination of material's thermal stability, morphology, optical and semiconducting properties.

SEM analysis showed the presence of GO/RGO layers on a TiO_2 surface decorated with SnS_2 hexagonal nanoparticles, while UV/Vis diffuse reflectance spectroscopy (DRS) enabled calculation of the material's bandgap (E_g) energy. Results of the FTIR analysis confirmed the presence of the expected functional groups within investigated samples, while high purity and an approximate portion of individual components were determined through TGA measurements. Semiconducting properties were analysed with photoelectrochemical tests that include EIS, CV-LSV, Mott-Schottky, and Open Circuit Potential (OCP) measurements. The results indicate a positive effect of GO-RGO presence on decreasing charge recombination rate and the electron lifetime. All summarized results indicate a promising application of the as-synthesized materials in photocatalytic hydrogen generation processes.

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LIFECYCLE OF H_3PO_4 DOPANT DURING HIGH-TEMPERATURE PEM FUEL CELL OPERATION

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High-temperature fuel cells with a proton-conductive membrane (HT PEM FC), using H_2 as fuel and O_2 from the air as an oxidant, represent a viable compromise between low-temperature systems and solid oxide fuel cells. HT PEM FC comprises reasonable resistance against poisoning by impurities in H_2 fuel, especially CO, and feasible heat recuperation. These traits make it a good candidate for stationary and mobile applications.

The basis of HT PEM FC technology is the membrane, composed of polymeric matrix based on polybenzimidazole or polypyridine doped with H_3PO_4. Such a system offers excellent proton conductivity within the temperature range of 120 to 180 °C. However, the presence of concentrated acid at elevated temperatures creates an extremely corrosive environment [1, 2]. Consequently, degradation Pt catalyst on the electrodes is one of the major issues during optimisation of HT PEM FC [3, 4]. To counter this problem, a relatively high loading of Pt on electrodes is currently used.

Degradation of Pt catalyst is closely tied to dopant, which is not entirely stable during HT PEM FC operation. H_3PO_4 can be reduced on the anode electrochemically at potentials corresponding to H adsorption and chemically by gaseous H_2 [5, 6]. This leads to the production of phosphorus oxoacids and other compounds such as Pt-P. One of the proven reduction products is H_3PO_3, an acid strongly adsorbing on Pt surface [5], able to reduce Pt oxides chemically [6] and being incorporated into the membrane as a part of ion-conductive media. The exact effect of H_3PO_3 on the performance of HT PEM FC and degradation of its catalyst is still not fully understood.

The focus of the presented study is to provide an overview of H_3PO_3 formation and electrochemical behaviour on Pt and the effect of H_3PO_3 on HT PEM FC performance. The electrochemical behaviour was studied in three consequent stages, the first being experiments on a bulk Pt electrode in a concentrated H_3PO_4 electrolyte at temperatures above 120°C. The electrochemical behaviour of H_3PO_3 was investigated by the addition of acid to the electrolyte with subsequent voltammetric measurements, providing information about the mechanism of H_3PO_3 oxidation kinetics on Pt and its adsorption properties. In the next step, H_3PO_4 was (electro)chemically reduced, and oxidation of reduction products on a Pt was studied by voltammetric methods. These experiments confirmed H_3PO_3 as one but not the only product of H_3PO_4 reduction. Within the second stage, a half-cell composed of endplate with flow field, gas-diffusion electrode, and membrane on one side and concentrated H_3PO_4 electrolyte with counter and a reference electrode on the other. In comparison with bulk Pt, electrochemical oxidation of H_3PO_3 on nanoparticles proceeds via a much more complex mechanism that also includes decomposition of H_3PO_3 on a Pt nanoparticle surface. This phenomenon was investigated in parallel at ambient conditions with ion-exchange chromatography, confirming that the decomposition process indeed takes place even without the presence of O_2. To verify the intake of H_3PO_3 by the membrane, the conductivity of membranes doped with different ratios of H_3PO_3: H_3PO_4 using both the in-plane and the through-plane techniques. In the last stage, all previously gained knowledge was utilised for the evaluation of HT PEM FC single cell tests, during which H_3PO_3 was introduced into the cell after start-up.

In summary, the reduction of H_3PO_4 dopant is an important part of HT PEM FC technology, with a potential impact not only on its performance but also on the degradation of catalysts on the electrodes. This work provides an insight into the very complex problematics of H_3PO_4 lifecycle, which investigation is demanding in terms of both the experimental arrangements and analytical methods. However, without the full understanding of dopant behaviour, one cannot expect a significant breakthrough in improving catalyst stability during HT PEM FC operation.

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SIMULTANEOUSLY DEPOSITED PtM (M = Ni, Fe, Cu) ON GRAPHENE NANOPLATELET AS BIFUNCTIONAL OXYGEN ELECTRODE CATALYSTS

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In this work, Pt-M (M = Ni, Fe, Cu) nanoparticles were supported on graphene nanoplatelets (GNPs) and tested as electrocatalysts for the positive electrode of unitized regenerative fuel cells (URFCs), i.e., for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Catalysts were synthesized via simultaneous supercritical carbon dioxide ($scCO_2$) deposition technique, where the primary metal (Pt) and secondary metal (Ni, Fe, Cu) were deposited onto GNPs by $scCO_2$ in the same step. This resulted in ca. 20 wt.% Pt loading and M loading in the 1.4 - 3.4 wt.% range. Adsorption isotherms of the precursors onto the GNPs[1] were used to determine the desired amount of the corresponding precursors.

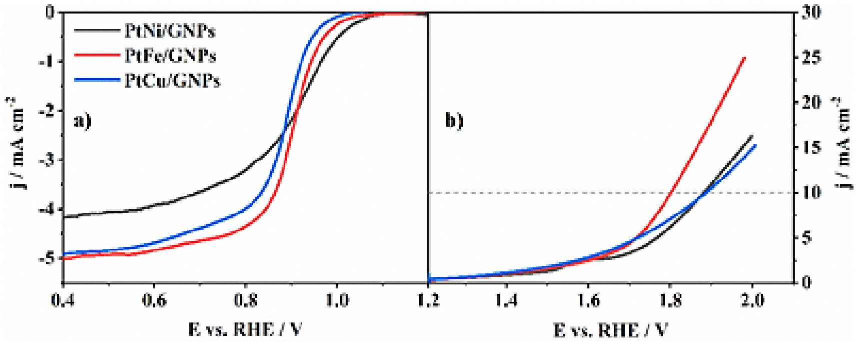

Figure 2. LSVs for all tested catalysts in a) ORR potential region at 1800 rpm and b) in OER potential region at 1200 rpm.

Electrocatalytic activity toward ORR was investigated in 0.1 M KOH by performing a series of linear scan voltammetry (LSV) experiments at different rotation rates to calculate the number of exchanged electrons, n, and the Tafel slope, b, two key parameters in electrocatalyst benchmarking. Use of Fe as secondary metal resulted in the highest diffusion-limited current density, j_d, of -4.65 mA cm^{-2}, followed by PtCu/GNPs (-4.37 mA cm^{-2}) and PtNi/GNPs (-3.65 mA cm^{-2}), **Figure 1a**. Commercial Pt/C (40 wt.% Pt) catalyst reached a j_d value of -6.44 mA cm^{-2} [2]. PtFe/GNPs sample also showed the lowest values of the Tafel slope (81 and 66 mV dec^{-1}) and the number of exchanged electrons value of 3.66, indicating 4e- ORR mechanism.

OER investigation was performed at 1200 rpm, **Figure 1b**. Once again, the catalyst with Fe as secondary metal showed superior performance in terms of the lowest OER onset potential, the highest achieved current densities, and the lowest value of the Tafel slope. Furthermore, ΔE, the difference between the potential at which OER achieves 10 mA cm^{-2} current density and half-wave potential of ORR, $E_{1/2}$, has the lowest value for PtFe/GNPs sample (≈0.89 V). Preliminary results showed the great potential of the synthesized PtFe/GNPs catalyst. Further investigations will be focused on testing its long-term stability.

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BREAKING DOWN THE ACTIVITY LOSS DURING O_2-EVOLUTION STABILITY TESTS ON COMMERCIAL IrO_2-BASED CATALYSTS

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In order to meet the atmospheric CO_2-concentration targets set at the COP21 in Paris [1], the use of green hydrogen produced via electrolysis as a clean energy sector is of great importance. Over the past few years, the interest in polymer electrolyte membrane water electrolyzers (PEMWEs) to produce such green H_2 has steadily increased [2], mainly due to these devices' ability to run dynamically and give a fast response, the high purity of the produced H_2 that can additionally be delivered pressurized, as well as the high current densities at which PEMWEs operate [3]. However, the need for Ir-based materials to catalyze the sluggish oxygen evolution reaction (OER) in PEMWE anodes might hamper their large-scale application since the cost of Ir represents a significant fraction of the overall capital costs [3], and its supply becomes utmost challenging [4]. Therefore, reducing PEMWEs' Ir content is essential, and one way to do so is by using support materials that enhance the dispersion of Ir active sites.

With this motivation, in this study, we investigated several IrO_2-based catalysts provided by Umicore®. Besides their OER activity, the catalysts' stability is also a key factor since PEMWEs are expected to operate for up to 20 years [4]. In order to evaluate OER stability, we used an accelerated stress test (AST) to promote catalyst degradation and to imitate the dynamic operational conditions encountered when an electrolyzer is coupled with intermittent, renewable energy sources. Interestingly, the supported catalysts exhibited higher stability than pure IrO_2, even if the impact of the support on the initial OER activity was not significant. Changing the catalysts' synthesis route led to an increase in OER-activity, but concomitantly a decrease in stability was observed. To understand these differences in stability, the relative impact of different degradation mechanisms on the overall performance loss of these supported and unsupported materials was systematically evaluated. Namely, the intrinsic deactivation of the catalysts caused by alterations in their oxidation state and/or crystalline structure, morphology changes and/or dissolution were investigated. Additionally, artifacts related to the use of rotating disk electrode (RDE) voltammetry for such measurements [5] were also examined and will be discussed.

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APPLICATION OF GENERALIZED COORDINATION NUMBER AS PLATINUM DISSOLUTION DESCRIPTOR

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Platinum and similar noble metals are materials with excellent adsorption and catalytic properties, and they are the first choice materials for processes like oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). Due to high prices, there is a high demand to discover cheaper materials with similar properties or to limit the consumption of platinum-like materials by predicting their properties and behaviour in various (electro)catalytic systems and increasing their stability. In this work, Pt (111) slabs with two, three, and five platinum layers were modelled. Different values for biaxial lateral strain from -6 % to +2 % were applied, and DFT calculations were employed to calculate dissolution energies. For particular atoms in all slabs, generalised coordination numbers were calculated using the procedure described by Calle-Vallejo [1]. The centers of the d-band for all systems were also calculated. All these calculations were combined in order to describe energetically favourable sites for dissolution processes. Moreover, Pt_{43} nanoparticle was also modelled and theoretically described in terms of the dissolution of particular atoms depending on generalized coordination numbers. Presented results can be used for engineering novel Pt-based (electro)catalysts with enhanced stability.

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AFFORDABLE DENSITY FUNCTIONAL THEORY SIMULATION METHODS FOR ELECTROCATALYSIS

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Performing first-principles density functional theory (DFT) simulations within the generalized gradient approximation (GGA) can be challenging in the field of electrocatalysis. GGA-DFT itself has limitations predicting the energetics of gas-phase molecules leading to substantial errors in their formation energies, hybrid functionals could be used for gas-phase molecules, but these are not accurate for metals. A way to address this problem is to apply ad-hoc energy corrections to the gas-phase molecules of interest to minimize the errors when calculating adsorption processes in electrocatalysis.[1] Besides those intrinsic errors, another interesting challenge in electrocatalysis is the description of the solvated species- protons and charged species in the bulk solution phase and the description of these same species at the metal-electrode interface. Solvation effects can be captured by different types of solvation models and can be applied to both adsorbed species (electrode-adsorbate-electrolyte interface) or species that are in the bulk solution. These models are explicit solvation, [2–5] where solvent molecules are added in the simulation cell, implicit solvation,[6–8] where the solvent is modeled as a dielectric continuum by applying certain dielectric constant of the solvent of interest or a combination of the two. For the particular case at the metal-electrode interface, a simple and practical model that can be used instead of the more expensive models is the near-surface solvation model, where only the necessary explicit solvent molecules are added to the simulation cell to simulate the first solvation shell to stabilize the adsorbed species. However, simple methods to address the solvation energies of ions in bulk solution still remain challenging. Thermodynamic cycles can provide a practical and simple approach by relating the exact free energy of a solution-phase ion to that of a neutral gas-phase or solid-state species, for instance, by using experimental redox potentials, in this way, there is no need to model solvation for the bulk solution-phase species with DFT.

Here, I plan to briefly show some insights related to affordable methods for first-principles DFT in computational electrocatalysis. I will specifically focus on the effect of GGA-functionals, including and not including long-range interactions on the near-surface solvation of *OH, important when considering using pre-calculated solvation energies, on discussing a method to obtain free energies of charged species in bulk solution based on thermodynamic cycles, important for electrochemical adsorption processes and finally to show a systematic workflow to determine errors associated to organic functional groups, important to improve the accuracy of calculated onset potentials of electrocatalytic reactions.

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First Steps in Materials Science - Student‘s Pitch presentation section

ELECTROSYNTHESIZED POLYPYRROLE FILMS IN THE PRESENCE OF ORGANIC DYES

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Polypyrrole (PPy) is one of the most studied conducting polymers due to its unique electronic properties and ease of synthesis. It can be easily synthesized through chemical or electrochemical oxidative polymerization in various organic and aqueous solutions. PPy and its composites for energy storage devices have been extensively studied due to their promising conductivity and electrochemical performance. Up to now, the improvement in PPy's electrochemical and energy performance to deliver an impressive energy storage system is still a challenge for many researchers. Recently, studies have been made where the incorporation of organic dyes such as safranin [1,2] and acid blue 25 [3,4] to PPy have resulted in the formation of PPy nanostructures with improved conductivity. Organic dyes, either cationic or anionic, are reported to act as the structure guiding agent when integrated into PPy during chemical polymerization [1,4]. However, the electrosynthesis of PPy with the presence of organic dyes is not yet well established, and the electrochemical and capacitive behaviour of PPy with the presence of safranin and acid blue 25 are not yet fully explored.

Herein, PPy, PPy-safranin, and PPy-acid blue 25 films were electrosynthesized on glassy carbon electrode by cyclic voltammetry in 0.2 M HCl aqueous solution with a potential window of –0.30 – 0.75 V versus Ag/AgCl reference electrode for 25 cycles at a scan rate of 20 mV/s. Morphological, electrochemical activity and stability, and capacitive performance of the produced films were elucidated using scanning electron microscopy (SEM), cyclic voltammetry, and Raman spectroscopy. With the presence of organic dyes, the formation of cauliflower-like structures is obtained for PPy-safranin films, while fibrillar morphological formation is observed for PPy-acid blue 25. For PPy film, typical globular morphology was formed. Raman spectra of the PPy-safranin and PPy-acid blue 25 films showed an increase of bipolaron to polaron ratio, indicating better order of chain organization as compared to pristine PPy. The incorporation of safranin and acid blue 25 resulted in an increase in the electroactivity of the films. The areal capacitance of PPy-safranin and PPy-acid blue 25 was higher compared to PPy film. Specifically, PPy-acid blue 25 has the highest areal capacitance, which was approximately 10 times higher than PPy's capacitance. Similarly, the electrochemical stability of PPy has improved from 84% cycling stability performance to 89% and 99% with the presence of acid blue 25 and safranin, respectively. Therefore, the incorporation of organic dyes like safranin and acid blue 25 to PPy results in the promising electrochemical performance of such films, which can be highly beneficial for applications in energy storage devices.

Acknowledgments: The authors wish to thank the Czech Science Foundation (19-04859S) for the financial support.

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FINISHING OF POLYAMIDE FABRIC WITH SOME BORON COMPOUNDS

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This paper described finding the most suitable methods of pretreatment polyamide fabric with some boron compounds. It is about the finishing processes of polyamide fabric in order to improve capillarity, water absorption, flammability, and wetting time. Huge amounts of water, chemicals, dyes, and auxiliaries are used in textile finishing processes, which can cause danger to the environment and have a toxic effect on workers in the industry. Therefore, the possibilities to replace harmful chemicals with less aggressive and biodegradable ones have been intensively researched for many years. Depending on the applied more suitable means and their ability to react with the fiber, different properties of the fabric are achieved and aesthetic, and exploitation values are increased. The functionality of boron compounds, such as boric acid and its alkyl or aryl substituents (boric acid), borax and sodium tetraborate as antibacterial agents, has been extensively studied in various industries. The research determined that after treatment with boric acid and sodium tetraborate, the hydrophilicity of the fabric increased. Also, there is an increase in water absorption, i.e., capillarity and water absorption, as well as much faster wetting. When testing the flammability of the fabric, it is noticeable that the raw fabric is difficult to burn and burn, given the presence of auxiliary substances that are applied to the textile during production. By washing and removing these substances, polyamide fabrics become more combustible, i.e., constantly burning until complete combustion of whole samples. Polyamide fabric treated with boron compounds begins to burn with self-extinguishing after a few seconds. The obtained results suggest the possibility of using boric acid and sodium tetraborate in the finishing processes of polyamide fabric, all in favor of better effects, savings, and environmental protection.

ELECTROCHROMIC PROPERTIES OF IRON (II) METALLO-SUPRAMOLECULAR POLYMERS BASED ON THIENO[3,2-*B*] THIOPHENE

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Electrochromic (EC) materials have recently gained enormous attention due to a wide range of applications in optical displays, smart windows, optical switching devices, camouflage objects, robotics, flexible electronics, smart textiles, etc. [1]. Various types of materials are known to show electrochromic phenomenon, such as transition metal oxides, polyoxometalates, coordination compounds, and conjugated polymers [2,3]. Currently, metallo-supramolecular polymers (MSPs) have gained significant attention as EC materials due to easy processability and reversible switching between different oxidation states.

Herein, new MSPs derived from unimers with thieno[3,2-b]thiophene central unit, bis(tpy) end groups and various linkers (none, ethynediyl, 1,4-phenylene, and 2,20-bithophene-5,50-diyl) were synthesized [4]. Fe-MSP films prepared by spin-casting on Indium Tin Oxide (ITO) glass were characterized by atomic force microscopy, cyclic voltammetry, and UV/vis spectroscopy, and the relation between the unimers structures and their electrochromic performance was investigated. Of the studied MSPs, Fe-2,5-bis(2,2′:6′,2′′-terpyridine-4′-yl)thieno[3,2-b]thiophene showed the highest optical contrast and coloration efficiency (CE = 641 $cm^2\ C^{-1}$) as well as the fastest optical response (Fig. 1).

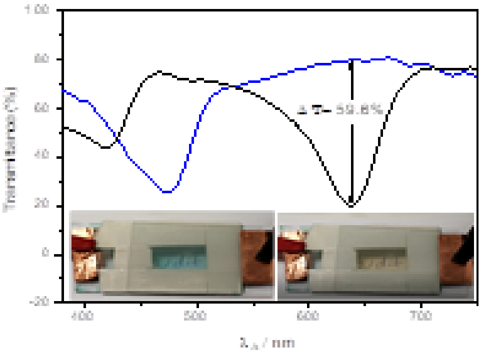

Figure 1. Photographs and UV/vis transmittance spectra of Fe-MSP EC device in the reduced colored state (black curve, 0 V) and oxidized bleached state (blue curve, 1.4 V).

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DFT ANALYSIS OF HER ON TITANIUM OXYNITRIDE AND GRAPHENE SUPPORTED Pt NANOPARTICLES

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Due to the growing demand for renewable energy, water splitting reaction and hydrogen evolution reaction (HER) are of great interest. Pt nanoparticles are very efficient catalysts for HER, but different supports can influence their performance. Hence, the comparison between the graphene and titanium oxynitride (TiON) supports was made with the aid of density functional theory (DFT) calculations to evaluate the effect of the support on the dissociative adsorption of hydrogen on Pt nanoparticles (note that hydrogen chemisorption energy is believed to be an important descriptor of the catalyst's HER performance).

Pt nanoparticles with the (111) and (100) facets of different sizes were investigated. Both standalone and supported nanoparticles were considered, where graphene and TiON were used as supports. DFT calculations showed that the TiON surface binds Pt nanoparticles considerably stronger than the graphene layer. Strong interaction between Pt and TiON also induces some structural deformation of nanoparticles, whereas, on graphene, there is a minimal effect on the Pt−Pt bond lengths inside the nanoparticle.

Different coverages of chemisorbed H on Pt nanoparticles were considered, ranging from a single H atom per nanoparticle to high coverages, the latter being more relevant for experimental conditions. Results at low coverage indicate that TiON support weakens the interaction between Pt and H, whereas the graphene layer has a small effect on the H bonding, which is to be expected due to the weak nanoparticle−support interaction. The Pt−H bond strength also varies with respect to the position of H relative to the support. Results for higher coverage showed a similar trend, i.e., TiON support, in general, weakens the bonding of H to Pt nanoparticle, whereas the effect of graphene is minute. Calculations also showed that Pt nanoparticles can adsorb a significant amount of hydrogen; more than 1 H atom per surface Pt.

From the comparison between the two supports, we can deduce that TiON support interacts strongly with Pt nanoparticles and weakens the Pt−H bond. It is worth noting that weaker Pt−H interaction suggests a faster HER reaction because, according to the volcano-plot analysis of HER, Pt binds H too strongly. Stronger nanoparticle−support interaction can also be correlated with a lower tendency toward sintering. Out results, therefore, agree with the experimental study, which shows that Pt nanoparticles supported on TiON are superior for HER than the widely used Pt nanoparticles supported on graphite.

Acknowledgments: This research is being performed in collaboration with N. Hodnik, M. Smiljanić, M. Bele, and M. Gaberšček from the National Institute of Chemistry, Slovenia.

A RHODIUM–EXCHANGED NICKEL ELECTRODE AS AN ALTERNATIVE ELECTROCATALYST FOR THE HYDROGEN EVOLUTION REACTION IN ALKALINE MEDIA

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In an effort to create an alternative electrocatalyst for the hydrogen evolution reaction (HER) by combining different materials to form composites, alloys, or heterostructured electrodes, nickel has gained much attention. Recently, there has been progress in the synthesis of nickel-based catalysts for HER in alkaline media [1]. It is important to note that HER in alkaline media, compared to that in acidic, results in less environmental pollution and equipment corrosion [2]. The electrocatalytic performance of rhodium–exchanged nickel electrode for HER was studied in a 1 M KOH solution. A Ni disc electrode doped with various concentrations of Rh was used as a working electrode. The different Rh concentrations were obtained by spontaneous galvanic exchange of Ni by Rh, in a concentrated $RhCl_3$ solution, for different time intervals. The cyclic voltammograms acquired after 0, 10, 20, and 30 s of Ni/Rh spontaneous exchange are shown in Figure 1a. It may be observed that the maximum current (measured at –1.45 V vs. SCE) of HER is substantially increased after 10 s, confirming that Rh improves the electrocatalytic activity. The Ni/Rh ratio of the electrode was measured using energy dispersive X-ray microanalysis (EDX). The results showed, although a slightly uneven distribution of Rh on the electrode surface, a steady increase in Rh concentration with longer exchange intervals. This is in agreement with the results obtained by electrochemical measurements, which showed that the measured current is increased with prolonged galvanic exchange times. The electrode surface morphology and the 3D reconstruction of the surfaces for different Rh concentrations were obtained using scanning electron microscopy (SEM). It was observed that the roughness of the surface remained nearly unchanged regardless of the Rh concentration. A typical SEM micrograph and the corresponding 3D reconstruction of the electrode obtained after 20 s of Ni/Rh exchange is shown in Figure 1b and c. In addition, a density functional theory (DFT) calculation of hydrogen adsorption on the (111) and (100) surfaces of Ni and Rh–exchanged Ni was used to determine the adsorption energies. The absolute value of the adsorption energy calculated for the Ni(100) surface was higher than that for the Ni(111) surfaces, both for clean Ni and Rh–exchanged Ni. In addition, the calculated absolute value of the adsorption energy of hydrogen on Rh–exchanged Ni was lower than that on clean Ni for both surfaces. This work shows that the Rh–exchanged Ni electrode shows the potential to be used as an alternative electrocatalyst for HER in alkaline media.

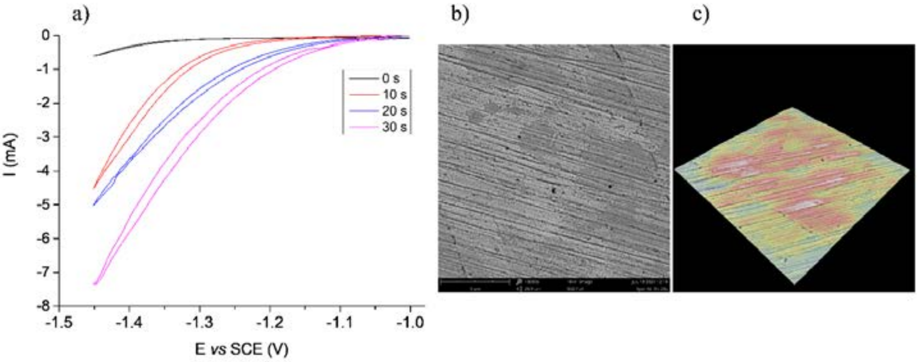

Figure 1. a) The cyclic voltammograms of Rh–exchanged Ni electrode obtained after 0, 10, 20, and 30 s of Ni/Rh galvanic exchange in $RhCl_3$; b) the SEM micrograph and c) the corresponding 3D reconstruction of the surface of the electrode obtained after 20 s of Ni/Rh exchange.

Acknowledgments: This research was supported by the Serbian Ministry of Education, Science and Technological Development (Contract number: 451-03-68/2020-14/200146) and the Science Fund of the Republic of Serbia (PROMIS programme, RatioCAT, no. 606224). This research was sponsored in part by the NATO Science for Peace and Security Programme under grant no. G5729.

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General

ENGINEERING THE MEMBRANE SEPARATOR OF LOW-TEMPERATURE LIQUID FUEL CELLS

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This work intends to develop a theoretical model for membranes for application in low-temperature liquid fuel cells, referring, particularly, to the direct borohydride-peroxide fuel cell (DBPFC), as a first step to create a numerical model. The DBPFC is based on the anodic oxidation of sodium borohydride ($NaBH_4$) in alkaline solution with the simultaneous cathodic reduction of hydrogen peroxide (H_2O_2) in acid media. As the DBPFC uses both fuel and oxidant solutions that are liquid at room temperature, it is a promising device for power generation in space and underwater applications, where O_2 gas is not easily available.

Crossover through the membrane that separates the anodic and cathodic compartments, specifically in the case of high pH-gradient between the solutions involved, is a crucial point to improve the performance of these fuel cells. Understanding the mechanism behind the behavior of cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs) will lead to an improvement also for the recently proposed pH-gradient-enabled microscale bipolar interface (PMBI) [1].

The model is mainly based on the Nernst-Planck equations, where all components of the system are considered to explain the passage of the ions through the membrane used. The latter is split into one section where there is a constant electric field due to the potential difference between the electrodes and another section without it, but where there is a local difference of electric potential between the two sides of the membrane, i.e., the membrane potential. This effect is created by the different diffusivity of the ions inside the membrane. To keep the electroneutrality in the fuel cell compartments, the system uses a mechanism where the faster ions are slowed down, and the slower ions are accelerated to allow both oppositely charged ions to pass. The passage of the ions is considered individually for each species involved. Each sub-system is considered to work independently based on the different concentrations on each side of the membrane and the specific membrane potential created. The total membrane potential (of the whole DBPFC system) is, consequently, the overlayed effect of all sub-systems, according to the superposition principle. This model is an upgrade to the generally accepted approach where specific kinds of ions are blocked/hindered by the ion-selective membrane [2]. To validate the proposed model, we have taken as an example a sub-system of the DBPFC to show experimentally that the ions from a 4 M NaOH solution will pass through a Nafion membrane, increasing the pH of the second compartment containing only distilled water. Therefore, not only Na^+ will be transferred inside the Nafion CEM, but also OH^- will pass to maintain the electroneutrality of the solutions. As the Na^+ ions will pass at the same velocity of OH^-, there will be a delayed Na^+ passage through the membrane due to the OH^- hindering.

These experiments allow investigating the mechanisms inside the membrane and finding the diffusivity of the components passing through it. This will lead to a better understanding of the processes occurring inside the DBPFC membrane, which has been used until now as a black box, where the initially selected inputs lead to obtaining the polarization and the power density curves as outputs. So far, numerical models for fuel cells have been mainly used for gaseous flows involved, as in the well-studied PEMFC, but a working numerical model for liquid fuel cells is not available in the literature. This study aims to be a starting point to the creation of a corresponding model where liquid solutions are involved and thus suitable for modeling DBPFCs.

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ELECTROCHEMICAL CHARACTERISATION OF TiO_2/SnS_2 PHOTOELECTRODE IN THE PRESENCE OF PHARMACEUTICALS

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The extensive use of pharmaceuticals has resulted in the release of large quantities of pharmaceuticals in the aquatic environment, and therefore it is necessary to develop various methods and materials suitable for pharmaceutical degradation. The photocatalytic and photoelectrocatalytic degradation of the organic pollutant attracts considerable attention because of its high efficiency, nontoxicity, and low cost. One of the most important photocatalytic candidates is TiO_2. Since it is limited to UV-irradiation, significant efforts have been done to extend its absorption range into the visible light region through TiO_2 doping or TiO_2 composite formation.

In this work, photoelectrochemical properties of TiO_2/SnS_2 composite were examined in the presence of three different pharmaceuticals (amoxicillin, ciprofloxacin, and desvenlafaxine). The interaction of an organic molecule and photocatalyst is an important parameter that influences the efficiency of the photocatalytic and photoelectrocatalytic processes [1]. However, although in literature there is a large number of reports related to photocatalyst characterization by electrochemical methods, there is a scarce number of reports related to the influence of organic compounds on the photoelectrochemical activity of the material. The results obtained in this work have revealed that the electrochemical techniques, as an easy and fast method, can determine the adsorption process. TiO_2/SnS_2 composite was characterized in 0.1 mol dm^{-3} NaCl solution containing the pharmaceuticals by using linear polarization, open circuit potential monitoring, and electrochemical impedance spectroscopy measurements. It was shown that the presence of pharmaceuticals decreases the photocurrent and increases the charge transfer resistance due to the adsorption process.

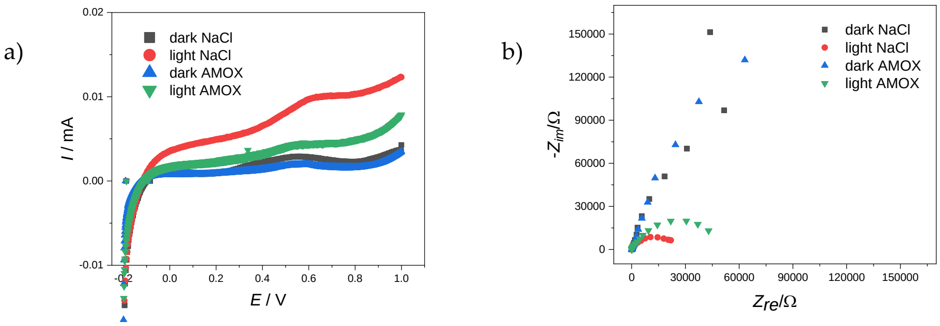

Figure 1. Linear sweep voltammetry responses obtained for light and dark characteristic of TiO_2/SnS_2 electrode in the presence and absence of amoxicillin.

Acknowledgments: This study has been fully supported by the Croatian Science Foundation under the project Nano-sized Solar-active Catalysts for Environmental Technologies, NaSCEnT (IP-2018-01-1982).

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ULTRASOUND AND GRAPHENE OXIDE – SOMETHING GOOD AND SOMETHING BAD

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Ultrasound is used in materials chemistry labs for synthesis, homogenization, cleaning, and other purposes. Also, it is an inevitable step in the preparation of electrode materials consisting of powders, especially when the thin-film technique is used. Besides, for graphene oxide (GO), it is known that it can be used to fragment GO under extended treatments. However, we show that using graphene oxide to prepare catalytic inks for short periods of time (5-30 min) also induces irreversible effects that can be related to the alteration of the GO properties induced by ultrasound. These effects are seen not only in the results of electrochemical testing but also in the photoluminescent properties, while oxidation debris can be detected using ultrahigh performance liquid chromatography. To explain these effects, we performed molecular mechanics study of graphene oxide under lateral strain, assuming that ultrasonic cavitations cause mechanical deformations of GO sheets. Our results suggest that under lateral strain, GO sheets break at points weakened by line and point defects, producing debris of different sizes. Our results suggest that it is necessary to take special care when using ultrasound to homogenize GO dispersions, as it can cause undesirable artifacts and alter the measured properties.

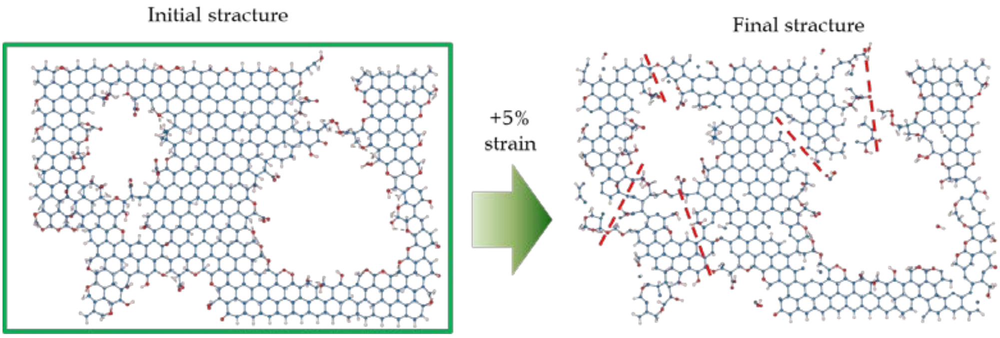

Figure 1. Breaking of GO sheet under mechanical strain – molecular mechanics view

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