NATIONAL INSTITUTE OF CHEMISTRY

9th ISE Satellite Student Regional Symposium on Electrochemistry

BOOK OF ABSTRACTS

Zagreb, Croatia, June 14th, 2019

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"9th ISE Satellite Regional Symposium on Electrochemistry" (ISE - SRSSE) is organized under the patronage of the International Society of Electrochemistry (ISE).

The professional and grammatical errors of the abstracts are the authors' responsibility.

PREFACE

The organizers are honored to have the opportunity to host a meeting of the graduate and postgraduate students and post-doctoral researchers “9th ISE Satellite Regional Symposium on Electrochemistry” (ISE – SRSSE) at Ruđer Bošković Institute, Zagreb, Croatia on Friday 14th July 2019.

The symposium is particularly encouraging young scientists to present their research in the form of oral presentations. The meeting consists of three sections that cover broad aspects of electrochemistry fields, from analytical chemistry, corrosion, atmospheric electrochemistry, electrochemistry of materials for energy storage/conversion, with in total 20 presentations with participants from Croatia, Serbia, Slovenia, and France. Apart from the three sections, a plenary section is included as well, where experienced researchers will introduce their work in the field of electrochemistry.

The aim of the meeting is to create a synergy between young scientists in the region by gathering, creating a network, and expanding knowledge in the field of electrochemistry.

In the end, we would like once again to gratefully acknowledge the ISE sponsorship for the financial support given. The opportunity is provided for students and young researchers to gather and exchange their scientific ideas in various fields of electrochemistry and establish connections.

We hope that the 9^{th} ISE Satellite Regional Symposium on Electrochemistry will meet the expectations of participants to present and discuss their results and create contacts that may result in future collaboration making this meeting a pleasant and rewarding experience.

Kristijan Vidović	Primož Jovanovič	Sarah Mateša
(*NIC*)	(*NIC*)	(*IRB*)

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PLENARY LECTURE

SPOT THE DIFFERENCE AT THE NANOPARTICLES: IDENTICAL LOCATION ELECTRON MICROSCOPY

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Electrocatalysis is a study of relationships between the transformation of electrical energy in chemical bonds and, in the reverse process, the energy stored in chemical bonds back to electrons that can power electrochemical energy storage and conversion systems. It presents one of the cornerstones for future sustainable energy (zero CO_2 emissions) utilization. Therefore if we want to leave the conditions on Earth in reasonable shape, with for instance affordable green energy, for our children, further development and breakthroughs in these directions are needed. Electrochemical nanoparticles catalytic performance is determined by exact and specific structure, composition and morphology of its surface and near-surface area: also referred to as the structure-activity relationship. However, besides activity also stability of electrocatalysts is at least equally important for the application. Can we start talking about a structure-stability relationship? When nanoparticles get exposed to real conditions and prolonged use much is still to be learned.

Identical location electron microscopy (IL-EM) offers a unique opportunity to track the morphological, compositional, and structural changes at the nanoscale. Advancements in the scanning transmission electron microscopy together with groundbreaking identical location approach have made it possible, for the first time, to track the evolution of the same nanocrystal during materials electrochemical biasing down to atomic level (Fig. 1). [1]. However, an IL approach can also be used in the scanning electron microscope and others. Along with the importance of the stability in electrocatalysis a few examples of IL-EM will be presented in the lecture.

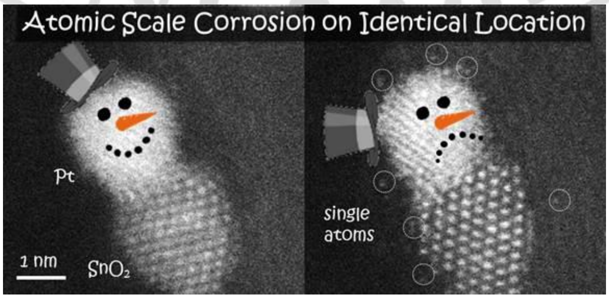

Figure 1: HAADF images of Pt–SnO_2 nanoparticles (ethanol electrooxidation catalyst) with Janus shape in the form of dumbbell or snowman. [2]

REFERENCES:

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ELECTROCATALYSTS STABILITY INVESTIGATION BY ELECTROCHEMICAL FLOW CELL ANALYTICS

Primož Jovanovič[a], Andraž Pavlišič[a], Vid Simon Šelih[b], Martin Šala[b], Samo Hočevar[b], Marjan Bele[a], Francisco Ruiz-Zepeda[a], Goran Dražić[a], Nejc Hodnik[c], Miran Gaberšček[a,d]

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Electrocatalysts play an important role in sustainable energy-related fields. As these catalysts still need improvement on activity and especially stability, a lot of effort is invested in developing new materials. However, their application is hindered due to the complex interplay of different parameters. A more rapid development of electrocatalysts can be achieved with the help of advanced experimental tools [1]. To tackle this, an electrochemical flow cell (EFC) linked to inductively coupled plasma mass spectrometer (ICP-MS) has been utilized for catalyst stability research. The applicability of the method will be demonstrated on a few dissolution studies of nanoparticulate electrocatalysts for proton exchange membrane fuel cells and electrolysers.

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ELECTROCHEMISTRY IN ATMOSPHERIC CHEMISTRY

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Besides the predominant gaseous phase, in the troposphere there is also the minor aqueous-phase compartment, which is closely connected with the atmospheric particulate matter (PM). Nevertheless, it is believed that the yet unexplained deviation of global atmospheric models from field observations could arise from the inappropriately described atmospheric aqueous-phase chemistry. We have recently identified electrochemistry to be a promising tool for the advanced investigations of the atmospheric aqueous phase.

The composition of the organic fraction of atmospheric PM is largely unknown. Although electrochemistry is a bulk method with limited selectivity, it can be effectively used in the quantification of important groups of compounds in atmospheric PM, such as surface active substances [1] and nitrophenols [2]. Besides, lack of commercially available standards for the identification of yet unidentified components of atmospheric organic aerosols often requires *de novo* synthesis. By selectively producing large quantities of reference material in short time, electrochemistry can be of great help also in this regard.

In the field of atmospheric chemistry, the biggest challenge that requires the most interdisciplinary research is the study of multiphase processes. It considers atmospheric aqueous-phase chemistry in relation to the atmospheric gas-phase composition. In this sense, electrochemistry can be utilized in two ways. Product studies in a simplified natural environment can be performed (i) by applying a distinct potential to the investigated reaction mixture, the potential being representative of particular atmospheric oxidant, or (ii) by studying in detail cyclic voltammograms of relevant reaction mixtures to be able to attribute a particular redox process or an ECE mechanism to every observed peak. By this, novel reaction mechanisms occurring in the atmospheric aqueous-phase can be identified [2].

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POTENTIAL OF MASS SPECTROMETRY IN ELECTROCHEMISTRY

Martin Šala

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Hyphenation of analytical techniques has become a common practice over the recent decades, because of the paradigm 1+1=3, meaning that with the combination of two techniques one benefits more than just a sum of the individual techniques is in most cases true. Most of the hyphenations are limited to combinations of sample sampling and the analysis for example laser techniques and mass spectrometry (MS) detection (MALDI, LA-ICPMS...). But in the case of hyphenation of electrochemistry and mass spectrometry the potential of preparation of compounds in electrochemical way and subsequent analysis in MS gives many possibilities in studying the reaction mechanisms, both electrochemical, or other that can be also alternatively mimic with electrochemical setup.

The lecture will cover the general instrument setups, parts of the MS instruments and the differences in particular types. Specifics and advantages/drawbacks of different ionization sources and mass analyzers will be discussed. Furthermore, the sample introduction possibilities and their applications will be explained.

Finally, a few examples for online and offline, organic and inorganic analysis will be given.

ORAL PRESENTATIONS

ELECTROCHEMISTRY AS A POWERFUL TOOL FOR MECHANISTIC STUDIES IN CONDENSED-PHASE REACTIONS

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There is more and more evidence that chemical processes in the atmospheric aqueous phase (i.e., clouds, fog, and aerosol water) efficiently contribute to aging of organic components and secondary organic aerosol (SOA) formation (Ervens *et al.*, 2011). Atmospheric aqueous-phase chemistry can also contribute to the formation of chromophores. Such SOA are known as atmospheric brown carbon (BrC), which absorbs light of the near-ultraviolet and blue wavelengths and so influences the climate by radiative forcing. However, little is known about the mechanism of BrC formation.

One of the major precursors to BrC are aromatic compounds. Methylnitrocatechols (MNCs) are known BrC constituents (Frka *et al.*, 2016) and their formation mechanism has been recently proposed (Vidović *et al.*, 2018). Three possible pathways of dark 3-methyl-5-nitrocatechol (3M5NC) and 3-methyl-4-nitrocatechol (3M4NC) formation, markedly dependent on reaction conditions, were considered. In the dominant pathway, nitrous acid (HNO_2) is directly involved in the transformation of 3-methylcatechol (3MC) *via* consecutive oxidation and conjugated addition reaction.

By studying the nitration of 3MC as a case example, we present a powerful experimental platform for the investigation of homogeneous reaction mechanisms in a condensed phase. To confirm the proposed reaction mechanism by Vidović *et al.* (2018), each individual step of the complex mechanism (oxidation and nitration) had to be isolated and separately studied. For this purpose, electrochemistry was used for the generation of reactive intermediate.

The dominant two-step reaction pathway, oxidation of 3MC and nitration of 3-methyl-*o*-quinon, was studied by means of electrochemistry. All reactions were carried out in 0.1 M phosphate buffer, pH 6.5, as a carrying electrolyte. An Ag/AgCl reference electrode and platinum wire as a counter electrode were used. As working electrodes, glassy carbon (GC) disk electrode (analytical) and GC rod electrode (preparative) were used. Electrochemical reaction products were confirmed also by HPLC-UV/VIS. Every ten minutes a sample was taken from the electrochemical cell and analysed in terms of electrochemistry (Figure 1) and HPLC-UV/VIS.

The present study introduces a novel experimental platform for studying the mechanisms of complex condensed-phase reactions involving redox processes. A multidisciplinary approach was applied to completely describe the reaction mechanism of dark catechol nitration under mild atmospheric conditions. Moreover, a new dark hydroxylation route was found.

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IMPEDANCE SPECTROSCOPY: A POWERFUL METHOD FOR ANALYSIS OF ELECTRICAL PROCESSES IN LITHIUM TUNGSTEN PHOSPHATE GLASS-CERAMICS

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Impedance spectroscopy (IS) – a popular tool for analysis of electrical properties allows detailed investigation of composite materials like glass-ceramics. Notably, it enables the analysis of electrical response of every component within the composite. In this work IS is used for detailed analysis of complex mixed ion-polaron glass-ceramics.

Glass-ceramics, Li50W@600 and Li50W@800, were prepared by heat-treatment of the starting bulk $5Li_2O$-$5ZnO$-$40P_2O_5$-$50WO_3$ (in mol%) glass at 600 ˚C and 800 ˚C for 6 hours.

Analysis of IS results provided a detailed insight into changes of DC conductivity and relaxation processes based on the of $Z''(\omega)$ and $M''(\omega)$ spectra in a wide frequency (0.01 Hz – 10^6 Hz) and temperature (303 K – 513 K) range. Structure and morphology of prepared materials were studied by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM).

PXRD diffractograms showed that after heat-treatment of starting glass, Li50W@600 remained amorphous, while Li50W@800 contained two polymorphs of $W_2O_3(PO_4)_2$, orthorhombic and monoclinic. This was in accord with SEM analysis which showed sporadically distributed dendritic crystallization on the surface of Li50W@600, while SEM of Li50W@800 confirmed massive crystallization with some residual amorphous phase.

IS measurements revealed that DC conductivity values of prepared glass-ceramics and the parent glass are within the same order of magnitude which indicates that the formation of $W_2O_3(PO_4)_2$ polymorphs does not impede predominantly polaronic electrical transport.

Further, $Z''(\omega)$ and $M''(\omega)$ spectra of Li50W@600 show practically overlapped peaks suggesting a single bulk response. On the other hand, Li50W@800 spectra show three distinct maxima in $Z''(\omega)$ and one slightly broadened peak in $M''(\omega)$ spectrum. This indicates four distinct processes contributing to the total electrical conductivity which are related to the glass matrix, both crystallized polymorphs and grain boundary.

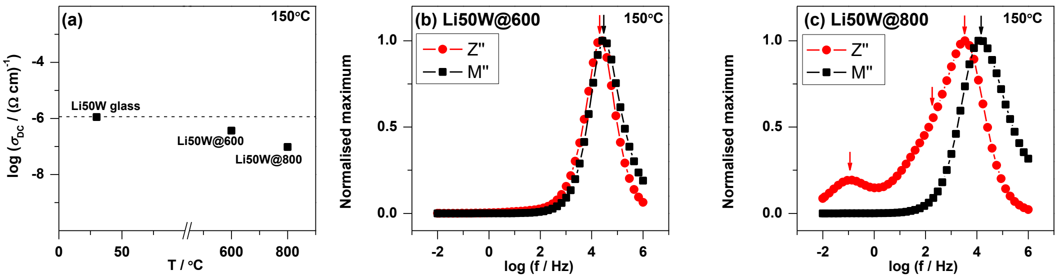

Figure 1. (a) DC conductivity, (b) and (c) normalised imaginary impedance, *Z''(ω)*, and electrical modulus, *M''(ω)*, at 150 ˚C of investigated materials.

APPLICATION OF Cu(II) ION-SELECTIVE ELECTRODE (Cu-ISE) FOR Cu SPECIATION IN COASTAL WATERS

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Copper (Cu) is a micronutrient required in a number of cellular processes that are key for phytoplankton growth. However, at physiologically high concentrations, copper is toxic and may affects both planktonic abundance and diversity in coastal waters. Range of copper concentrations between these two extremes is relatively narrow [1]. In natural waters Cu is mostly found as inorganic and organic complexes. A classical model for estimation of the bioavailability/toxicity assumes free Cu (Cu^{2+}) as an indicator for potential Cu toxicity. Due to very low concentration of Cu in natural waters, the measurement of Cu is very challenging. The most used analytical techniques are electrochemical ones, mainly anodic and adsorptive cathodic stripping voltammetry (ASV and AdCSV, respectively [2]). Potentiometry based on Cu(II) ion-selective electrode was also found promising (measurements down to pM levels), despite a common opinion that it is not sufficiently sensitive to measure Cu concentrations below 1 µM, especially in marine waters due to the chloride influence [3,4].

In this work we examined the applicability of Cu-ISE (based on jalpaite membrane) for the measurement of free Cu in model solution (0.5 M NaCl) and seawater. The calibrations of Cu-ISE were performed at different levels of total Cu (0.3 mM - 0.01 µM) and ethylenediamine (EN: 1 mM - 5 µM) concentrations. At high total Cu, calibrations were linear down to pM/fM level of free Cu (Fig. 1), with the obtained slopes very close to theoretical Nernstian one (29.6 mV per decade). However, the decrease of the slope was observed by lowering the total Cu concentration, so that as low as ~10 mV per decade was found at 10 nM Cu concentration. Calibrations performed only with additions of Cu showed "super-Nernstian" response with linear range down to 10 nM of Cu in 0.5 M NaCl and 100 nM Cu in seawater. Several aspects of the practical use of Cu-ISE will be discussed, along with the examples of Cu-ISE application in real seawater samples.

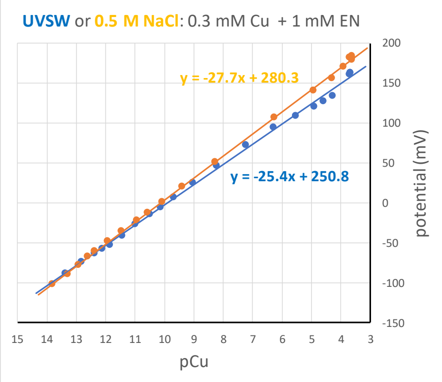

Fig. 1. Calibration curves of Cu-ISE

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ELECTROCHEMICAL SENSORS FOR SECURITY AND ENVIRONMENTAL APPLICATIONS

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Concerns related to global security have given rise to increased research in the field of explosive detection, aimed at developing analytical methods for fast, sensitive, and simple determination of explosives in trace amounts [1]. Particular attention has been given to the peroxo-based explosives due to their increasing usage [2], the issue being that the standard chemical identification techniques are not suitable for peroxo explosives. Hydrogen peroxide, which is both precursor and degradation product of peroxo explosives, is a redox active compound prone to both oxidation and reduction. This implies that electrochemical techniques offer themselves as a prime choice in detection of peroxide-based explosives [3].

In designing gas electrochemical sensors the electrode surface has to be modified to achieve high electrocatalytic properties. There are several possible ways how to achieve this, for examples modification of the electrode surface with the insoluble redox active complex such as iron(III) hexacyanoferrate(II), known as Prussian-blue or its mixed metal analogues [4]. They could be considered as an artificial peroxidase and redox mediator for efficient shuttling of electrons between the electrode surface and the H_2O_2 molecule, obtained by degradation of the peroxo explosive [5]. Furthemore, besides electrocatalytic properties of the surface modified electrode, the overall performances of H_2O_2 electrochemical gas sensors depends on the electrochemical technique applied, i.e. the excitation protocol in the course of the operation of the sensor. In this context, better outcomes can be achieved with advanced voltammetric techniques such as fast scan cyclic voltammetry and square-wave voltammetry [6].

Our current investigation has been focusing on the development of semi-solid electrolytes comprising several functions: i) accumulation of the analyte from the gaseous phase thus considerably improving sensitivity, ii) derivatization of the gas analyte facilitating more accessible electrochemical detection or even chemical derivatization of electrochemically inactive compounds into electrochemically active ones and finally, iii) semi-solid ionic electrolyte offering rapid diffusion of the analyte to the electrode surface. Recent results in along these lines and in terms of electrochemical detection of gaseous H_2O_2 will be discussed.

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ATOMIC FORCE MICROSCOPY AND ITS USE IN ELECTROCHEMISTRY

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ABSTRACT TEXT: Atomic force microscopy (AFM) is a type of scanning probe microscopy which can be used to characterize a variety of substances with a high resolution of less than a nanometer. Using a very sharp tip the surface can be scanned by repeatedly touching the surface. The technique allows for very accurate mapping of topography, force measurements, and changing the properties of the sample in a controlled way. [1] In order to learn more about electrical properties of a material, techniques such as Kelvin Probe Force Microstopy (KFM) and Electrostatic Force Microscopy (EFM) are available. [2] I will discuss their advantages over more traditional approaches and what I hope to learn about fuel cell catalysts by using the AFM. I will discuss possibilities of using the in situ electrochemical AFM (EC-AFM) for catalyst screenings, where the AFM acts as an observer of changes in the electrode surface morphology during electrochemical reactions and investigates the solid-liquid interface. [3]

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OPTIMIZATION OF THE PROTECTIVE LAYER OF NON-TOXIC CORROSION INHIBITORS

OPTIMIZACIJA ZAŠTITNOG SLOJA NETOKSIČNIH KOROZIJSKIH INHIBITORA

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U ovom radu istraživana su zaštitna svojstva modificiranog sloja hrđe nastalog kombinacijom različitih korozijskih inhibitora na čeliku unutar 24 h u destiliranoj vodi. Korišteni su prirodni, netoksični inhibitori: škrob, polietilen glikol (PEG 400), kestenov tanin, propolis i heksamin. Vizualna inspekcija izgleda nastalih slojeva odabrana je kao početni evaluacijski parametar kvalitete sloja s ciljem dobivanja optimalne koncentracije i vrste inhibitora: tanin 300 ppm u sinergizmu s propolisom 80 ppm formira sloj najboljeg izgleda. Uz vizualno praćenje, kvaliteta prevlaka potvrđena je i SEM analizom, dok su krajnji odabrani slojevi podvrgnuti elektrokemijskim mjerenjima: elektrokemijskoj impedancijskoj spektroskopiji (EIS) i linearnoj polarizaciji (LP). Rezultati EIS-a ukazuju na dobra zaštitna svojstva optimiziranog sloja dok je pretpostavka da polarizacijom pri povećanoj brzini miješanja dolazi do pomaka korozijskog potencijala u pozitivnom smjeru, upućujući na katodno i/ili mješovito djelovanje inhibitorskog sloja. Time bi bila pronađena primjena dobivenih svojstava – u protočnim sustavima vodovodne/slane vode gdje je pretpostavka da će visoka otpornost na hidrodinamički tlak biti posljedica barijernog djelovanja modificiranog sloja hrđe povećanom dotoku kisika do metalne površine [1].

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ELEKTROANALITIČKE METODE U KARAKTERIZACIJI VODENOG OKOLIŠA

ELECTROANALYTICAL METHODS IN CHARACTERIZATION OF AQUEOUS ENVIRONMENT

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Elektroanalitičke metode (EM) su skupina analitičkih postupaka kod kojih se pomoću analognih električnih veličina tj. napona električne struje ili električnog naboja dobiva informacija o koncentraciji i aktivitetu određivane molekulske vrste. EM zbog svoje brzine i jednostavnosti, visoke osjetljivosti, mogućnosti istovremenog i direktnog određivanja više različitih analita, bez prethodne obrade uzorka imaju široku primjenu u analizi organskih i anorganskih tvari. Snažna interakcija između Hg i sumpora (S) čini ih prikladnima za praćenje/procjenu kakvoće voda s obzirom na prisutnost različitih S vrsta [1]. Elektroanalitičko određivanje otopljenih reduciranih S specija (RSS) na Hg elektrodi temelji se na njihovoj interakciji sa Hg elektrodom, pri čemu dolazi do elektrooksidacije Hg i stvaranja netopivog živinog sulfida (HgS), čija je struja redukcije na potencijalu od -0,68 V /vs. Ag/AgCl) direktno proporcionalna koncentraciji RSS u otopini [1].

U ovom radu, primjenom voltametrijskih metoda (fazno osjetljive voltametrije izmjeničnom strujom, a.c. voltametrija - mjerenja van faze, cikličke voltametrije–CV, i diferencijalno pulsne voltametrije-DPV) na Hg elektrodi preliminarno su istraživana dva prirodna vodena sustava, okarakterizirana prisutnošću S vrsta. Prvi sustav je Rogozničko jezero u kojemu je praćena specijacija S vrsta u vodenom stupcu na različitim granicama faza unutar kojih se mijenjaju redoks uvjeti, odnosno oksidacijska stanja i S vrste. Posebno je istraživano područje kemokline te oksični i anoksični vodeni sloj. DPV metodom, prema uvjetima iz dostupne literature [2], na dubinama ispod 9 m (kemokline) potvrđena je prisutnost polisulfida. U oksičnom sloju detektirani su hlapivi organosumporni spojevi čija je prisutnost potvrđena i u uzorku kiše koja je padala neposredno prije uzorkovanje vodenog sloja Rogozničkog jezera.

Drugi istraživani sustav je podzemna voda s poljoprivrednog područja rijeke Neretve, u kojem je pored RSS određivana i prisutnost površinski aktivnih tvari (PAT) [3]. Primjenom a.c. voltametrije izmjeničnom strujom, detektirani su valovi na vrlo negativnim potencijalima (< -1,65 V), koji se prema dostupnoj literaturi mogu pripisati organskim biomakromolekulama [4] koje u našem slučaju sadrže S.

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ELEKTROKEMIJSKA SINTEZA GRAFENSKOG PAPIRA ZA PRIMJENU U NAPREDNOJ ELEKTRONICI

ELECTROCHEMICAL SYNTHESIS OF GRAPHENE PAPER FOR ADVANCED ELECTRONIC APPLICATIONS

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Grafen je monosloj ugljika koji posjeduje delokalizirane π elektrone, dobru električnu provodnost i veliku specifičnu površinu. Zbog njegovih izvanrednih svojstava, područje primjene grafena je vrlo široko. O načinu sinteze ovise njegova fizikalna svojstva, kemijska svojstva i dimenzije. U ovom radu grafen je sintetiziran elektrokemijskim putem. Cilj rada je bio elektrokemijska sinteza grafenskog papira (ErGO) uz grafenov oksid (GO) kao prekursor, ispitivanje elektrokemijskih i strukturnih svojstva ErGO te sastavljanje samostojećeg savitljivog superkondenzatora s ErGO aktivnim materijalom. Grafenov oksid (GO) je vakuumskom filtracijom ili metodom nakapavanja nanesen na podlogu od filter papira. Elektrokemijska redukcija GO je provedena u troelektrodnom sustavu tehnikom kronoamperometrije. Da je doista dobiven ErGO papir potvrđeno je na temelju porasta električne provodnosti dobivenog materijala. Grafenski papiri okarakterizirani su metodom infracrvene spektroskopije s Fourierovim transformacijama signala (FTIR), Ramanovom spektroskopijom, rendgenskom difrakcijskom analizom (XRD) i pretražnim elektronskim mikroskopom (SEM) pri čemu je dokazano da je redukcija uspješno provedena. U ovom radu je pokazano da je elektrokemijskim putem moguće jednostavno prirediti različite forme grafenskog papira, što će ovisiti o odabiru predloška na koji se nanosi GO. Dobiveni grafenski papiri korišteni su za izradu superkondenzatora kod kojeg je grafenski papir nanesen na strujni kolektor od nikla (*klasični superkondenzator*) i superkondenzatora sa savitljivim samostojećim grafenskim papirom (*FKIT superkondenzator*). Pripravljeni superkondenzatori ispitani su metodom cikličke voltametrije (CV) i metodom elektrokemijske impedancijske spektroskopije (EIS), a njihova stabilnost testirana je punjenjem/pražnjenjem superkondenzatora kod konstantne struje. Oba superkondenzatora su pokazala dobra kapacitivna svojstva. Kod *klasičnog superkondenzatora* zabilježene su veće vrijednosti specifičnih kapaciteta (44 F g^{-1}) u odnosu na *FKIT superkondenzator* (13 F g^{-1}). Međutim, prednosti *FKIT superkondenzatora* su činjenica da u izvedbi nije korišten strujni kolektor te njegova savitljivost, što mu omogućava primjenu u naprednoj elektronici.

Ključne riječi: grafenov oksid, grafen, grafenski papir, elektrokemijska redukcija, superkondenzator

ISPITIVANJE ZAŠTITNIH FILMOVA FOSFONSKE KISELINE NA RAZLIČITIM METALNIM PODLOGAMA PRIMJENOM ELEKTROKEMIJSKE KVARC-KRISTALNE MIKROVAGE

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Korozija je prirodni fenomen koji svake godine uzrokuje velike ekonomske i ekološke gubitke. Iako su na tržištu prisutni brojni sustavi zaštite od korozije, i dalje postoji potreba za novim ekološki i ekonomski prihvatljivim rješenjima. Jedno od mogućih rješenja su samoorganizirajući monoslojevi (engl. Self-Assembled Monolayers, SAMs), tanki, uređeni filmovi dugolančanih organskih kiselina.

Samoorganizirajući monoslojevi sve više nalaze primjenu u mikroelektronici, senzorici i elektrokatalizi, ali također imaju i veliki potencijal u korozijskog zaštiti zbog svojih specifičnih svojstava. Organske molekule koje mogu formirati SAM-ove sastoje se od tri dijela - dvije funkcionalne skupine i alkilnog lanca koji ih povezuje. Jedna funkcionalna skupina služi za adsorpciju na metalnu površinu i naziva se glava molekule, a druga skupina je završna i određuje svojstva sloja. Dugi alkilni lanac predstavlja barijeru difuziji agresivnih iona do metalne površine. Neke od prednosti samoorganizirajućih monoslojeva su jednostavnost primjene, ekonomska isplativost i mogućnost prekrivanja velikih površina malom količinom materijala.

Cilj ovog rada je dobiti bolji uvid u svojstva SAM-ova praćenjem procesa formiranja zaštitnih filmova oktadecilfosfonske kiseline (engl. octadecylphosphonic acid, ODPA) na različitim metalnim podlogama (zlato, bakar i nehrđajući čelik). U tu svrhu je korištena elektrokemijska kvarc-kristalna mikrovaga (engl. electrochemical quartz crystal microbalance, EQCM). Mjerenja su provedena u 3%-tnoj otopini NaCl-a kao korozivnom mediju simultanim korištenjem EQCM-a i elektrokemijske impedancijske spektroskopije.

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NOVA GENERACIJA ANODA ZA LITIJ-IONSKE BATERIJE

NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES

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The success of Li-ion batteries in the early 1960s took years of research and contribution of many scientists and engineers. Since then there are several electronic revolutions and still lithium-ion (Li-ion) cells are the most widely used as rechargeable battery system for portable electronic devices and electrical vehicles. It has many advantages like high energy density, long storage life, small volume, light weight, low self-discharge efficiency and non-memory effect. The most widely used anode is graphite whose lithiated compounds have stable phases up to the LiC_6 stoichiometry corresponding to a theoretical specific capacity of 372 mAh / g[1]. In contrast, silicon possesses a very high theoretical capacity of 4200 mAh / g and can intercalate 4.4 Li into Si at high temperature to form $Li_{15}Si_4$[2]. Silicon also features a working potential around 0.4 V vs. Li^+/Li which is safer than operating potential of graphite (0.05 V vs. Li^+/Li). Although silicon possesses all of these advantages, silicon based anodes suffer from huge volume expansion upon cycling (≈400%) causing electrode fracture and electrical isolation during repeated cycling [3]. Continuous volume changes cause the breaking-reformation of the solid electrolyte interphase (SEI) film which leads to consumption of lithium-ions and electrolyte. Exhaustion of the electrolyte causes the degradation of conductivity and induces fast capacity loss [4]. The porous structure can provide a large space to accommodate volume expansion and provide a large surface area for lithium-ion transport from electrolyte to silicon [5]. In this work we present silicon microparticles as anode material for lithium-ion battery. Anode was based on powder silicon mixed with polyvinylidene fluoride (PVDF) and conductive carbon black (CB) in N-Methyl-2-pyrrolidone (*NMP*). The structural properties of the anode was characterized by *scanning electron microscope* (SEM). Silicon particles were also characterized with gas adsorption measurements to obtain pore size distributions and size of particles. Capacitive properties and stability were determined by using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic measurements.

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IONSKA PROVODNOST U ALUMINOFOSFATNIM STAKLIMA S „MIJEŠANIM“ ALKALIJSKIM OKSIDIMA

IONIC CONDUCTIVITY IN MIXED-ALKALI ALUMINOPHOSPHATE GLASSES

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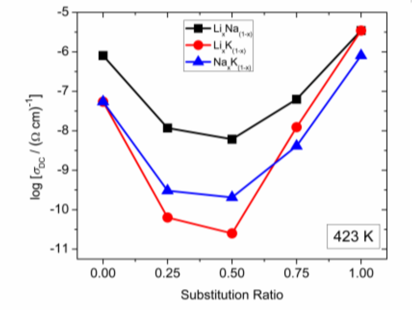
The mixed-alkali effect (MAE) is nonlinear deviation of the ionic conductivity observed when one type of alkali cation is replaced by another at their constant total cation content. Various models[1,2] try to describe this effect but a comprehensive understanding is still lacking. In this work, three series of mixed-alkali aluminophosphate glasses, [xLi$_2$O-(40-x)Na$_2$O-10Al$_2$O$_3$-50P$_2$O$_5$, xLi$_2$O-(40-x)K$_2$O-10Al$_2$O$_3$-50P$_2$O$_5$ and xNa$_2$O-(40-x)K$_2$O-10Al$_2$O$_3$-50P$_2$O$_5$, x=0-40 mol%] are examined to clarify the influence of cation size mismatches on the extent of MAE. Electrical properties of glasses are studied by impedance spectroscopy (IS) in a wide frequency (0.01 Hz – 10^6 Hz) and temperature (303 K – 523 K) range, whereas Raman spectroscopy is used to obtain information about glass network and different cation environment.

Raman spectra show two most intensive bands corresponding to ν_s(P-O-P) and ν_s(P-O$_2$) stretching vibrations of bridging and non-bridging oxygen atom in metaphosphate glasses, respectively. Both of the vibrational frequencies are sensitive to the cation environment and are shifted to the lowest frequency with addition of smaller cations. In all three series of glasses the results of IS measurements revealed strong MAE with DC conductivity minimum at 0.5 of cation substitution. The change in extent of MAE corresponds to the difference in cation size mismatches; that is a deepest minimum obtained for the Li-K series (Figure 1). A possible explanation of the effect assumes that ion hopping probability is reduced because of the mismatched energy sites adopted for more dissimilar cations.



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LEAD(II) OXIDE ELECTRODEPOSITION BASED ELECTROCHROMIC CELL THAT CAN BE USED IN A SMART WINDOW APPLICATION

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Electrochromic devices have capability to change colour reversibly when electric power is applied and can sustain selected colour after disconnection.[1] As such, they present an interesting alternative to liquid crystal displays and light emitting diodes, which require constant supply of electricity for their operation. A new type of electrochromic device, that uses electrodeposition of lead (II) oxide in combination with hydrogel stabilised water-based electrolyte has been assembled and investigated. Device operation was investigated using a series of electrochemical techniques, along with UV-Vis transmittance spectroscopy. Presented devices uses electrodeposition of PbO from electrolyte-hydrogel solution, with response time of less than 15 s. High difference between bleached and tinted state was recorder and low potentials (+1.7 V) was required for tinting along with selective self-bleaching effect when short-circuited. Hydrogel P-DMAM-NIPAM with ratio 85:15 in combination with water based Pb^{2+}/Ni^{2+} electrolyte in combination with PbO electrode and NiO counter electrode showed excellent characteristics, achieving good repeatability, high transmittance in bleached state and good coloration in tinted state, along with good stability. This type of electrochromic cells could be used an alternative to existing intercalation-type electrochromic devices.

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ELEKTROKEMIJSKO ODREĐIVANJE ASKORBATNE KISELINE POMOĆU GRAFITNE ELEKTRODE MODIFICIRANE KOMPOZITOM SILIKATNIH NANOSFERA I GRAFENA

ELECTROCHEMICAL DETERMINATION OF ASCORBIC ACID ON A SILICA NANOSPHERE/GRAPHENE COMPOSITE MODIFIED GRAPHITe ELECTRODE

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A large number of scientific papers have demonstrated the health benefits of consuming healthy food that contains significant amount of antioxidants. Fruits like oranges, lemons or kiwi are an important source of water-soluble antioxidants in a diet, but their content may change during storage [1], this is why the determination of water-soluble antioxidants like vitamin C has great practical importance.

In this work, we present the influence of surface modification of the working electrode with composite materials on analytical performance in the determination of ascorbic acid by cyclic voltammetry. We have tested the analytical performance of the graphite electrode modified with commercially available Carbon graphene ink (Gwent group, UK). The Carbon graphene ink (CGI) was mixed with monodisperse solid nonporous silica nanospheres with the attempt to increase the active surface area and to provide homogenous porous structure for controlled diffusion of electroactive species.

The surface modification of supporting graphite electrode (d=0.5 mm), was performed by drop casting of the CGI. After drying, the electrode was polished on lint-free paper. Spherical nonporous silica nanoparticles (SNPs) were synthesized by a modified method established by Stöber, Fink and Bohn [2]. The composite material was made by mixing SNPs with carbon graphene ink, where the mass ratio of graphene and SNPs was 1:1.

The comparison was made between working electrodes modified with CGI ink and CGI/SNPs composite material. Addition of SNPs remarkably enhanced the peak currents of ascorbic acid. Graphene is already known for improving analytical performance and direct electron transfer at the graphene/electrolyte interface when used as a component of electroanalytical devices but with the addition of SNPs, we enhanced the active surface, because of SNPs large specific surface area. The composite material has promising analytical properties and can be used for the production of low-cost screen-printed electrodes for direct determination of ascorbic acid in the food products.

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UMREŽAVANJE SAMOORGANIZIRANIH PREVLAKA PRIMJENOM IONIZIRAJUĆEG ZRAČENJA

CROSSLINKING OF SELFASSEMBLED COATINGS USING IONISING IRRADIATION

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Cilj rada bio je razviti polimerne nano prevlake primjenom ionizirajućeg zračenja te ispitati njihovo djelovanje u svrhu zaštite metalnih implantata od korozije. Korozija je proces nenamjernog trošenja konstrukcijskog materijala pod kemijskim, fizikalnim i biološkim djelovanjem okoliša. Procesom korozije smanjuje se masa i upotrebna vrijednost materijala te skraćuje vijek trajanja proizvoda [1]. Nanošenje prevlaka na površinu čeličnih predmeta najraširenija je metoda zaštite od korozije. Prevlakama se odvaja agresivni okoliš od zaštićenog predmeta. Materijal prevlake mora biti što postojaniji prema mediju kojem je izložen [2].

Tehnologija nanošenja polimernih prevlaka dostupna je od 50-ih godina prošlog stoljeća, a uporaba polimernih prevlaka za zaštitu materijala značajno je zaživjela u posljednja dva desetljeća, s cijelim nizom posve novih područja primjene koja se gotovo svakodnevno proširuju. To se može protumačiti ekološkim prednostima, stalnim razvojem novih polimernih materijala i opreme te postupaka njihova nanošenja [3].

Radijacijsko umrežavanje odnosi se na postupak u kojem se ionizirajuće zračenje koristi za poticanje brzih kemijskih reakcija koje rezultiraju stvaranjem polimera. Umrežavanje učvršćuje prevlake, smanjuje prodor vanjskih molekula, poboljšava mehaničku čvrstoću i kemijsku otpornost, kao i druga funkcionalna svojstva, čineći takve prevlake otpornijima i značajno produžujući njihov vijek trajanja.

U ovom radu ispitivali smo mogućnost umrežavanja samoorganizirane prevlake elaidinske kiseline (*EA*), nano debljine, primjenom različitih doza zračenja gama zrakama ^{60}Co. *EA* je trans-masna kiselina, $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, s jednom dvostrukom vezom koja je ključna za umrežavanje. Ispitivanja su provedena na medicinskom čeliku, odnosno 316L leguri. Za elektrokemijska ispitivanja korištena je 3%-tna otopina natrijevog klorida. *EA* se nanosila samoorganiziranjem iz otopine etanola na površinu uzoraka. Primijenjene su sljedeće metode ispitivanja prevlaka:

- Elektrokemijske metode (potenciostatska polarizacijska tehnika i elektrokemijska impedancijska spektroskopija) i
- Infracrvena spektroskopija s Fourierovom transformacijom (FTIR).

Ispitivanja su pokazala da se primjenom ionizirajućeg zračenja mogu umrežiti samoorganizirane prevlake *EA* te da je doza zračenja od 200 kGy potrebna za dobivanje prevlake s najboljim zaštitnim svojstvima.

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Vitamin C ili askorbinska kiselina je vitamin topljiv u vodi, prvi sintetizirani vitamin, koji posjeduje značajna antiradikalna svojstva. Najčešće se sadržaj vitamina C u hrani određuje primjenom titracijskih tehnika, međutim zbog brze i lake oksidacije na površini elektrode od staklastog ugljika ukazuje da su voltametrijske tehnike dobar izbor za određivanje njegovog sadržaja u hrani. Oksidacija vitamina C na površini elektrode od staklastog ugljika je ireverzibilan proces. U ovom radu ispitana su elektrokemijska svojstva vitamina C primjenom cikličke (CV), diferencijalna pulsne (DPV) i pravokutnovalne voltametrije (SWV) te protočne kronopotenciometrije (FTC). CV, DPV i SWV mjerenja potvrdila su da je elektrokemijska oksidacija na elektrodi od staklastog ugljika (GCE) ireverzibilni proces. Nadalje, ispitana je linearnost, limit detekcije i limit kvantifikacije za sve četiri primijenjene elektrokemijske tehnike koje su se pokazale kao osjetljive i selektivne metode za određivanje sadržaja vitamina C u realnim uzorcima hrane.

SUPERKONDENZATORI TEMELJENI NA KOMPOZITNIM MATERIJALIMA VODLJIVI POLIMER/GRAFEN

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Poli(3,4-etilendiokstiofen) (PEDOT) je π-konjugirani vodljivi polimer koji se već duže vrijeme koristi kao aktivni materijal u superkondenzatorima. Razlog tome je njegova niska cijena, dobra električna provodnost i pseudokapacitivna svojstva. Dodatno poboljšanje pseudokapacitivnih svojstava moguće je postići ako se koristi kompozitni materijala vodljivi polimer/grafen. Naime, u dosadašnjim istraživanjima pokazano je da prisustvo grafena u strukturi vodljivog polimera povećava elektronsku vodljivost i njegovu poroznost, čime je olakšana izmjena iona tijekom odvijanja redoks reakcije [1].

Cilj ovog rada je bila ugradnja grafenova oksida (GO) u strukturu PEDOT sloja elektrokemijskim putem u prisustvo površinski aktivne tvari poli(4-stiren sulfonata)(PSS). PSS poboljšava topivost EDOT monomera, smanjuje oksidacijski potencijal monomera te može poboljšati fizikalno-kemijska svojstva sintetiziranog sloja. Morfološka i strukturna svojstva slojeva priređenih u prisustvu i bez prisustva grafena određena su korištenjem pretražne elektronske mikroskopije i UV/Vis spektroskopije. Elektrokemijska svojstva slojeva određena su metodama cikličke voltametrije (CV) i elektrokemijske impedancijske spektroskopije (EIS). Od pripremljenih materijala sastavljeni su simetrični superkondenzatori koji su ispitani CV i EIS metodama. Stabilnost superkondenzatora određena je nabijanjem/izbijanjem superkondenzatora kod konstantne vrijednosti struje tijekom 1000 ciklusa.

1] A. Österholm, T. Lindfors, J. Kauppila, P. Damlin, C. Kvarnström, Electrochim. Acta 83 (2012) 463-470.