12th ISE Satellite Student Regional Symposium on Electrochemistry

June 30th 2023

Faculty of Chemical Engineering and Technology
Zagreb, Croatia

BOOK OF ABSTRACTS

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July 30th 2023
Faculty of Chemical Engineering and Technology
Zagreb, Croatia

12th ISE Satellite Student Regional Symposium on Electrochemistry

Book of abstracts

Croatian Society of Chemical Engineers

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Preface

The "12th ISE Satellite Student Regional Symposium on Electrochemistry" (12th ISE-SRSSE) held on June 30th, 2023. It was an honor and pleasure for us to host it. A hybrid form was used for the symposium, on-site participation at the Faculty of Chemical Engineering and Technology, Zagreb, and online. The International Society of Electrochemistry (ISE) sponsored the meeting to encourage young scientists, postgraduate and graduate students to share their research and results in a friendly atmosphere.

With the exception of 2020 owing to the COVID-19 pandemic, the 12th ISE-SSRSE was successfully arranged for the twelfth year. The symposium's goal was to inspire young researches in the fields of electrochemistry and electrochemical engineering to present their work in the form of oral presentations. 22 young scientists from Croatia, Serbia, Slovenia and the Czech Republic participated in the conference, which featured of 19 oral presentations in total. Oral presentations included a wide range of electrochemical topics, including electrochemistry of materials for various purposes, hydrogen evolution, corrosion, environmental and analytical chemistry.

The organizing committee would like to express its gratitude to all participants and its appreciation to the International Society of Electrochemistry for its support in enabling young scientists to share their various areas of electrochemistry and establish contacts that could lead to future collaboration.

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Contents

ORAL
PRESENTATIONS

Voltammetry of atmospherically important Cu(II)-catechol complexes in aqueous phase

Saranda Bakija Alempijević[1, *], Slađana Strmečki Kos[1]

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Atmospheric Cu(II)-binding ligands can be of different origin (natural or anthropogenic) and represent different organic molecules. Poorly characterised humic-like substances (HULIS), a range of polycarboxylic acids and hydroxyl forms, various pollutants, form with Cu(II) ions complexes of different stability. Thus, the enrichment of Cu(II) ions in the aerosol is governed by the ability of their complex formation. Cu(II) complexation in the atmospheric aqueous phase can alter redox reactions, the formation of radicals, or the cycling of other metal ions [1,2]. Therefore, it is important to examine the redox properties of Cu(II) - organic complexes at various conditions in the atmospheric water phase.

We used square wave voltammetry (SWV) on the mercury drop working electrode to study the electrochemical properties of Cu(II) complexes with substituted catechols: 4-nitrocatechol (4NC), 3-methyl-4-nitrocatechol (3M4NC), 3-methyl-5-nitrocatechol (3M5NC), and 4-methyl-5-nitrocatechol (4M5NC) in aqueous electrolyte. By changing the ligand or Cu concentration, we followed the formation of the complexes. The stability or degradation of the complexes was studied over time at one pH and by lowering the pH. The order of relative stability of the complexes, the influence of substituted groups in the catechol structure and the mechanism of electrode processes are discussed based on the obtained voltametric results.

ACKNOWLEDGMENTS

We acknowledge HrZZ project BiREADI (IP-2018-01-3105) for financial support.

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The Role of Surface-Active Substances in Urban New Particle Formation

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New particle formation (NPF) plays a significant role in generating atmospheric aerosol particles [1][2]. However, the mechanisms underlying urban NPF events are poorly understood [1]. This study presents evidence of frequent NPF events occurring in Ljubljana, Slovenia, making it the first report of such events in this region. Our research aims to enhance the understanding of NPF's nucleation and growth mechanisms by employing a comprehensive approach that combines online measurements and offline particle collection, followed by thorough electrochemical analysis.

By harnessing the capabilities of electrochemistry as a powerful tool to measure surface activity, we have discovered a significant relationship between the growth of atmospheric particles and the presence of surface-active substances. Our research aims to illuminate the complex processes that drive NPF in urban regions. Through the application of these methods, we hope to gain a deeper understanding of the intricate mechanisms involved in NPF and its connection to surface-active substances.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Slovenian Research Agency (research program P1-0034) and the Croatian Science Foundation (IP-2018–01-1717 MARR.

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Fast detection of the marine organic matter properties

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Surface active substances (SAS) as a reactive fraction of dissolved organic carbon (DOC) are a key component of many marine biogeochemical processes with different physicochemical properties due to their origin and composition [1-3]. The presence of SAS in natural waters can be detected by adsorption on the hydrophobic surface of a mercury electrode (Hg) using the electrochemical method of phase-sensitive alternating current voltammetry (PSACV) [2 and references therein]. PSACV can selectively measure faradic (in-phase) or capacitive current (out-of-phase) as a function of electrode potential. Out-of-phase measurements reflect the adsorption of SAS that adsorb competitively to Hg, expressed as the equivalent adsorption effect of a given amount (mg dm^{-3}) of model SAS, usually the nonionic Triton-X-100 [1-3]. A valuable parameter of DOC normalized surface activity (NSA=SAS/DOC) appears to be a practical tool for detecting fine changes in DOC reactivity-hydrophobicity. Additional insight into the nature of DOC can be gained by analyzing PSACV curves with or without characteristic sharp desorption peaks compared to various selected model SAS expected in the marine environment [2,3]. In this study, we present the NSA of different natural marine samples using a graphical and numerical approach, paying special attention to the analysis of PSACV curves of the studied samples. We typify NSA for several phenomena along the coastal zone of the Adriatic Sea (Croatia) that contribute to organic carbon accumulation: (1) invasive ctenophora swarms (*Mnemiopsis leidyi*) in summer 2020 and red tide blooms in spring 2021 in the Northern Adriatic, (2) formation of gel-like aggregates in the coastal waters of the Central Adriatic in summer 2021, and (3) the water column of the marine lake (Rogoznica Lake, Central Adriatic), with NSA ranging from 0.010 to 0.543.

ACKNOWLEDGMENTS

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First application of electrochemistry in assessment of metal exposure in storks

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Biochemical changes in organisms rapidly reflect environmental conditions and can therefore serve as biomarkers of pollution effects. For persistent pollutants such as metals, apex predators are particularly suitable bioindicators because they accumulate pollutants that are taken up by all organisms at lower levels of the food chain [1]. Common biomarkers of metal exposure are metallothioneins (MT), proteins responsible for metal homeostasis and detoxification. In the present study, metal exposure was estimated by measuring MT concentrations in the blood plasma of white storks (*Ciconia ciconia* Linnaeus, 1758). Samples (n=71) were collected in June and July 2021 at seven sites under different anthropogenic influences: Nature park Lonjsko polje as the reference site, Jakuševec landfill, agriculturally impacted Crnac polje and Jelas polje, industrially impacted Slavonski Brod, Donje Podunavlje known for high As levels, and Podunavlje known for As and Hg contamination. MT concentrations were quantified by differential pulse voltammetry, using the modified Brdička procedure. Although differences between sampling sites were not significant, the highest MT levels were measured at sites Donje Podunavlje and Jakuševec, influenced by metal and pesticide exposure, and waste disposal. Baseline MT concentrations in blood plasma of white storks (68% of the total data) ranged from 0.38 to 0.54 mg mL^{-1} and represent the first data in Croatia, which may facilitate future risk assessments using these organisms.

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Interaction of lectin Sambucus Nigra with trisaccharides in the osmolyte presence

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Protein-carbohydrate interactions are involved in numerous biochemical/biological pathways and play an essential role in various biological processes such as development, infection, immunology, and carcinogenesis [1,2]. However, these interactions are relatively weak, which makes their detection challenging. In this work, we use constant current chronopotentiometric stripping (CPS) to detect and study complexes of lectin Sambucus Nigra with trisialyllactoses. CPS is a structure–sensitive and label-free analysis that can be used to study structural changes not only of free proteins but also of those in complexes with binding ligands [3]. We also show that the presence of an osmolyte excess, in our case mannose, can significantly improve the reproducibility of experiments and the ability to distinguish between individual complexes.

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Development and characterisation of Zn-ion battery based on V_2O_5

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Rechargeable batteries are one of the most important issues in the present time, especially due to its application in portable electronic devices and electrical vehicles. Lithium-ion battery has made a significant influence to our society due to high available energy density. However, it does not meet today's needs of modern society. One of the disadvantages of this battery is usage of organic electrolyte and its flammability, high cost, toxicity and need to provide perfectly dry environment during manufacturing process. All aforementioned properties encourage development of more safe, less expensive and green battery devices. Zinc-ion aqueous battery meets all the requirements for the green battery and therefore it is getting more interesting and significant efforts are being made continuously to develop this battery [1].

The aim of this work was to prepare flexible free-standing reduced graphene oxide (rGO) decorated with V_2O_5 and rGO decorated with carbon nanotubes (CNT), as well as to apply prepared materials in a zinc-ion battery. In the first step, a modified GO paper was prepared from a dispersion containing graphene oxide (GO) and V_2O_5 or CNT by vacuum filtration. GO was transformed into a rGO by electrochemical reduction. This procedure enabled formation of a flexible free-standing material suitable for zinc-ion battery application. rGO paper decorated with V_2O_5 was used as the cathode material, and rGO decorated with Zn was used as the anode material. The zinc-ion battery characterisation was carried out in 2 mol dm^{-3} $ZnSO_4$ by mean of cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charging/discharging process.

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Novel electrolytes based on calcium salts for next- generation electrochemical supercapacitors

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Supercapacitors are emerging electrochemical energy storage devices with wide potential applications in the transportation sector and renewable energy sources. Their unique properties, such as long cycle life, high power density, fast charge & discharge, and high specific surface area, open many possible applications in science and engineering.[1] However, low energy density still limits their commercial applications. One of the ways to increase energy density is the right selection of electrolytes. Herein, we present new electrolytes based on calcium salts in organic solvents. To prove our concept, we conducted electrochemical measurements on symmetrical cells with activated carbon as an active material with cyclic voltammetry, galvanostatic charge and discharge, and electrochemical impedance spectroscopy. The measurements aimed to establish the influence of solvent, cation, and anion of the salt, and the concentration as parameters influencing supercapacitor performance. It was shown that calcium exceeds all other candidates in terms of capacitance and cyclability. Calcium-based electrolytes showed an increase in capacity at higher voltages. Besides, the type of solvent and concentration significantly affect supercapacitor performance. Finally, the optimal performing electrolyte was compared with the commercial one to highlight the difference in capacitance and potential application. Results indicate that chosen electrolyte is a suitable replacement for the current commercial electrolyte.

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This research has been supported by NATO Science for Peace Multi-Year Project ″High Energy Calcium - Oxygen Batteries″, NATO SPS G5910.

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The effect of cobalt and copper on carbon-based nickel catalysts for hydrogen and oxygen evolution reactions

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Due to the environmental problems brought on by rapid industrialization and climate change, the production of sustainable energy without the release of CO_2 has become essential. Green hydrogen, which emits no greenhouse gases or fine dust, is regarded as the ideal clean energy source that will contribute to global energy security [1]. In this study different carbon-supported nickel-based catalysts were used to gain an understanding on the effects of cobalt and copper addition on the water splitting half-reactions in the alkaline environment. As part of the evaluation, the powder catalysts were mixed into inks and spray coated on a gas diffusion layer. The measurements were conducted in a gas diffusion electrode (GDE) half-cell setup with the reference electrode being a reversible hydrogen electrode (RHE) and the counter electrode being a platinum mesh. We can see the different polarization curves for both half-reactions in Figure 1.

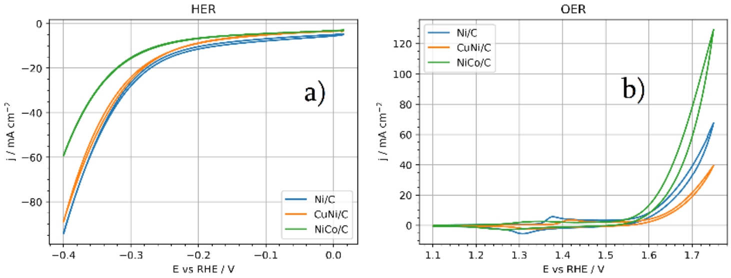

Figure 1: *polarization curves for a) hydrogen evolution reaction and b) oxygen evolution reaction of three different Ni catalysts*

As can be seen from Figure 1, the addition of Co impedes the activity while the addition of Cu does not have a significant effect on the hydrogen evolution reaction (Fig. 1a). On the other hand, we can observe that the addition of Co promotes the oxygen evolution reaction while the addition of Cu impedes it (Fig. 1b).

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Impact of the experimental conditions on the performance of polycrystalline Ni for hydrogen evolution reaction

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The electrochemical production of hydrogen plays a crucial role in advancing renewable energy, facilitating energy storage, fuel cells, and enabling clean and sustainable alternatives for various industrial applications. [1]

This study analyzed the effect of mechanical and electrochemical preparation methods on the activity of a polycrystalline Ni electrode for hydrogen evolution reaction (HER). Mechanical preparation involved annealing to remove surface oxides, while electrochemical preparation focused on generating oxides and hydroxides, particularly a combination of β-$Ni(OH)_2$ and NiOOH. The study aimed to understand the influence of these protocols on HER activity.

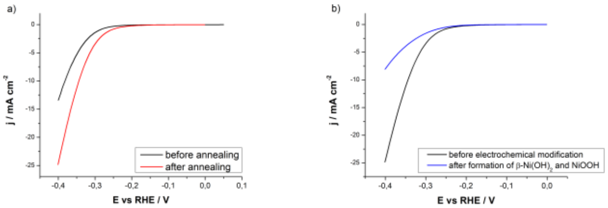

Figure 1. *LSV curves of hydrogen evolution reaction with mechanical preparation (a) and electrochemical preparation (b).*

The polarization curves show that different preparation protocols have a significant impact on the material's catalytic activity. Annealing greatly enhances the hydrogen evolution reaction (Fig. 1a), while electrochemical production of β-$Ni(OH)_2$ and NiOOH greatly diminishes the overall activity (Fig. 1b).

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Electrochemical CO_2 Reduction on Boron-doped Carbon Wrapped Copper nanostructures

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CO_2, a greenhouse gas, has become the main problem of modern world [1]. Decarbonization, carbon sequestration and carbon recycling are of the most important strategies to lower net carbon emissions. (Photo)electrochemical technologies offer promising solution for conversion of CO_2 to more reduced and valuable species. Copper-based materials have shown to be the most promising, due to their unique ability of C-C coupling and formation of products such as ethylene and propan-1-ol, which other materials fail to achieve. There are variety of factors that impact activity and selectivity of the reaction, including the catalyst surface structure, morphology, composition, the choice of electrolyte ions and pH, and the electrochemical cell design [2].

In this study, we have designed unique nanostructures of boron-doped carbon wrapped copper interfaces to test for the electrochemical conversion of CO_2 to value-added products. The electrocatalyst has been fully characterized with advanced multi-analytical techniques. This electrocatalyst was coated on a glassy carbon plate and assembled into a sandwich type cell, that was constantly bubbled with CO_2. We varied applied potentials from -0,9 V to -1,3 V and performed electrolysis for an hour. Gaseous products that formed were analyzed on-line with gas chromatography and after the experiment, liquid products were collected and analyzed with NMR spectroscopy. Faradaic efficiency calculations show that material coverts CO_2 very effectively to formate/formic acid on all potentials and that the amount of ethylene produced increases with increasing potential.

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High proton conductivity in 2D oxalate-bridged [Mn^{II}Cr^{III}] coordination polymers with alkyl-ammonium cations

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Oxalate anion, $C_2O_4^{2-}$, play the important role due to its different options of coordination to metal centres and its potential to arbitrate in the electronic effects between paramagnetic metal ions. Through the "building block chemistry" approach, in which a molecular anionic ligand such as the tris(oxalato)metalate anion, $[M^{III}(C_2O_4)_3]^{3-}$, is used as ligand in reaction with other metal cations, many (hetero)polynuclear species exhibiting different magnetic ordering, have been obtained. By combining the intrinsic properties of the host, especially the magnetic ones, with additional functionalities derived from the selected guest molecules, very interesting multifunctional properties can be obtained. The simplest method to introduce proton carriers is to incorporate a counterion such as hydronium (H_3O^+) or ammonium [NH_4^+, $(CH_3)_2NH_2^+$,...] ions during synthesis, resulting in the charged compounds [1]. They have been extensively studied as proton conductive materials. By slow evaporation of an aqueous solution containing $[A]_3[Cr(C_2O_4)_3]$ [A = $(CH_3)_2(C_2H_5)NH^+$ or $(CH_3)(C_2H_5)_2NH^+$] as a building block and $MnCl_2{\cdot}2H_2O$, two novel oxalate-bridged [Mn^{II}Cr^{III}] coordination polymers, $\{[NH(CH_3)_2(C_2H_5)]_8[Mn_4Cl_4Cr_4(C_2O_4)_{12}]\}_n$ (**1**), $\{[NH(CH_3)(C_2H_5)_2]_8[Mn_4Cl_4Cr_4(C_2O_4)_{12}]\}_n$ (**2**), were obtained. Compounds **1** and **2**, comprising an irregular 2D anionic layers $[Mn_4Cl_4Cr_4(C_2O_4)_{12}]_n^{8n-}$ interleaved by the hydrogen-bonded templating cations, exhibit remarkable humidity-sensing properties and very high proton conductivity at room temperature. In addition to powder and single crystal X-ray diffraction, the obtained compounds were characterized by thermal analysis, IR and impedance spectroscopy.

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Electrochemical synthesis and characterization of WO_3 photoactive material

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WO_3 has been one of the most researched photocatalysts in the last 20-30 years, along with TiO_2 and Fe_2O_3, with applications ranging from photocatalysis to electrochromic and photochromic devices. Stability in aqueous solutions under acidic conditions, resistance to photocorrosion, band gap of 2.5 (2.7) eV, non-toxicity, biocompatibility, low cost and a potential of the valence band edge located near 2.9 V vs. reversible hydrogen electrode make this metal oxide semiconductor a promising photocatalytic material for organic contaminant degradation.

In this work WO_3 was electrodeposited onto FTO (fluorine tin oxide) glass substrate from an acidic aqueous solution using a procedure adapted from Yourey and Bartlett [1]. Photoelectrochemical activity was evaluated under UV and visible light irradiation. The obtained electrodes were characterized using various electrochemical methods including linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), open circuit potential measurement (OCP) and Mott-Schottky analysis as well as chronoamperometry (CA) method. Electrodes with the most promising responses were tested for photoelectrochemical amoxicillin degradation.

ACKNOWLEDGMENTS

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Surface modification of dental materials

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Nowadays, the major challenge for engineers is to produce dental implant surfaces that closely mimic the characteristics of natural bone to allow patients to achieve healthy bone conditions and oral rehabilitation [1]. Most dental implants are made of titanium and its alloys. Parameters such as geometry and surface topography are crucial for a successful early clinical outcome. Since a rough topography favours both bone anchorage and biomechanical stability, it is of great importance that dental implants have a rough surface [2]. In addition to the surface properties, the chemical composition also contributes to the biological processes during osseointegration.

The main aim of this study was to modify the titanium surface with a protective and at the same time osteoconductive coating by the electrospinning method. The coating consists of polyvinylpyrrolidone (PVP) fibres as a carrier of calcium ions. It is known that calcium is very important for bone health and metabolism. Therefore, it should be actively involved in the osseointegration process and accelerate and promote the formation of new bone surrounding the implant. The surface morphology of the modified titanium was carried out by scanning electron microscopy (SEM) and the chemical elemental analysis of the coating by energy dispersive X-ray spectroscopy (EDS). The corrosion properties of unmodified and modified titanium were investigated in an artificial saliva solution under real application conditions by electrochemical impedance spectroscopy (EIS). The results indicate improved corrosion protection behaviour of the coated titanium compared to unmodified titanium.

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Functional calcium phosphate coatings on biomedical Co-Cr based implant material

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The increasing proportion of the elderly population combined with rising number of bone degenerative diseases and defects have led to the need for further development of bone repair and orthopaedic implant technology. Calcium phosphate-based (CaP) bioceramic materials are widely used in the field of bone regeneration, both in orthopaedics and in dentistry, due to their good biocompatibility, osseointegration and osteoconduction [1]. However, in spite of these desirable properties, CaP materials are brittle and have low impact resistance limiting their suitability for load-bearing conditions [2]. Hence, the formation of CaP coatings on high-strength implant materials such as Co-Cr based alloys combines the superior mechanical properties of metals with the osteoconductive properties of CaP materials.

The main goal of this study was to examine the effect of calcium phosphate coating (CaP coating) on the corrosion resistance of Co-Cr based alloy, commercially used as an orthopaedic implant material. The CaP coating was deposited to the CoCrMo alloy by the electrochemical cathodic deposition method (electrodeposition conditions determined by cyclic voltammetry (CV) method). The successful formation of CaP coating was confirmed by optical microscopy (OM) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). The comparison of electrochemical behaviour of unmodified and CaP modified CoCrMo alloy was performed using *ac* and dc electrochemical methods, including linear polarization resistance (LPR), Tafel extrapolation method and electrochemical impedance spectroscopy (EIS) in simulated body fluid, Hank's solution under *in vitro* conditions. Electrodeposition of the CaP coatings on CoCrMo alloy results in formation of functional biocompatible corrosion resistant coatings.

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Solid-contact ion-selective electrodes on printed substrates

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Adaptation of ion-selective electrodes into an all-solid-state configuration offers a path towards miniaturized, flexible and cost-effective electrochemical sensors and facilitates their use in biomedical, agricultural, environmental, and industrial analyses. Integration of a solid ion-to-electron transducer layer as a replacement for the inner filling solution led to their improved stability and reproducibility and enabled the use of modern and scalable manufacturing technologies such as screen-printing and inkjet printing [1]. Low sensitivity of the potentiometric method based on the logarithmic dependence between potential and activity limits its use for precise measurement of small changes in the activity of the primary ion. A novel coulometric transduction method was introduced to allow such detection by amplifying the analytical signal via increasing the capacitance of the solid contact [2]. In this study, all-solid-state ion-selective electrodes with different solid contact materials were prepared on printed substrates. Electrodes with electropolymerized PEDOT:PSS solid contact were prepared on screen-printed substrates, while electrodes with an inkjet-printed graphene solid contact were prepared on inkjet-printed substrates. The potassium ion-selective membrane was drop-cast on top of the solid contact. Prepared ion-selective electrodes were characterized by potentiometric, coulometric and impedance measurements.

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Influence of surface treatments of stainless steel investigated by EIS paste electrolyte measuring cell

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The corrosion resistance of stainless steels depends, among other things, on the surface finish. In order to increase corrosion resistance, various types of surface treatments have been developed for stainless steels. These treatments mainly include polishing, pickling, and passivation by chemical dissolution, usually by treatment with an acidic solution that removes surface impurities, especially after welding.

In this study, the effects of the most common passivation treatments (according to ASTM A967) on AISI304 stainless steel were compared. One of these treatments was selected and applied to welded AISI304 stainless steel. The effect of the passivation treatment was also compared with the effect of mechanical cleaning performed after MIG welding.

A portable EIS cell based on the use of paste electrolyte was used to study the effects of these treatments and different roughness on the formation of the passive layer. The open circuit potential (OCP) was monitored for 1000 seconds prior to the EIS measurements. With the objective of contributing to the corrosion monitoring of welded and passivated stainless steel components, the present work investigated the suitability of a paste electrolyte cell for characterizing the passive layer. The successful application of this cell has the advantage that it can be used on non-flat and complex surfaces, which still makes electrochemical tests difficult.

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The influence of electrolytes on the results of electrochemical tests

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In the modern world, the use of electrochemical tests and electrochemical methods has become necessary. Whether it is the construction of buildings, bridges, installations, oil pipelines or the restoration of cultural monuments, it is necessary to carry out electrochemical tests before the actual performance in order to evaluate the quality and corrosion resistance of the construction materials or protective coatings that will be used. Electrochemical impedance spectroscopy (EIS) and linear polarization, which are used to calculate the polarization resistance (R_p), have found a special role in such tests. After choosing the test method, the main question that arises is what kind of electrochemical cell and what kind of electrolyte will be used in that test. This is a particularly important issue if the electrochemical test must be performed on an irregular or inclined surface, as is usually the case in practice. In such cases, it will certainly not be possible to use a classic electrochemical cell, a three-electrode system with a liquid electrolyte, because the liquid electrolyte can easily spill. For this practical reason, there was a need for cells with an electrolyte in a solid state: the gel-electrolyte or hydrogel.[1] Hydrogels consist of a network of hydrophilic polymer chains and a liquid constituent, water. Today, the most commonly used hydrogels are sodium polyacrylate, poly(acrylamide) copolymer, poly(ethylene oxide) copolymer, cross-linked carboxymethyl cellulose, and poly(vinyl alcohol) copolymer (PVA).[2] In recent years, some natural polymers, such as gelatin, chitosan and agar, have been used as gel-electrolytes.[1] In this work electrochemical studies by EIS and linear polarization were conducted on different substrates by using three types of three electrode electrochemical cells. The first one is classical cell with liquid electrolyte, the second one with PVA hydrogel and the third with agar hydrogel. Obtained result of electrochemical studies are compared with the respect to the substrate.

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Phosphonic acids as adhesion promoters of water-based coatings

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Corrosion of metals is a significant problem in industries which often results in major economical losses and safety hazards. Nowadays, different strategies are applied to protect metals from corrosion, including surface coating technology, manufacturing new alloys, cathodic protection and others. Surface coating technology is the most convenient and effective method among them, so it has been used extensively in industry for improving corrosion resistance of metals. In the past, commonly used anti-corrosion coatings were organic coatings. However, it was discovered that these coatings contain a large amount of volatile organic compounds, which are harmful to environment and human health. Therefore, water-based coatings have attracted increasing attention in recent years [1]. Unfortunately, water-based coatings contain hydrophilic groups and surfactants, so corrosive ions and water molecules can easily pass through the coating, leading to poor barrier properties. Incorporation of protective fillers into these coatings was proven as a viable way to address this issue. An example of compounds commonly used as fillers are phosphonic acids, which were proven to be good corrosion inhibitors and adhesion promoters [2].

In this work, two types of phosphonic acids are investigated, 12-aminododecylphosphonic acid and (12-phosphonododecyl)phosphonic hydrochloride acid. As tested electrodes CuSn12 bronze is used whose surface was previously polished and oxidized. For two groups of electrodes, phosphonic acids were applied by immersing into acid solutions, while for the other two groups, phosphonic acids were applied with a brush. For the investigation of protection level and adhesion electrodes was left without acid and coated only with a water-based coating using a brush. The electrochemical measurements, linear polarization (LP) and electrochemical impedance spectroscopy (EIS) are conducted in a solution of acid rain (pH = 5) during 30 days. Pull-off test was performed for all types of prepared samples in order to test coating adhesion.

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Electrochemical Impedance Spectroscopy to Determine Protective Properties of Polymer Nanocoatings

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Electrochemical impedance spectroscopy (EIS) is a relatively new and powerful method for electrochemical characterization of electrochemical systems [1]. It is widely used to study corrosion processes, semiconductors, batteries, electroplating, and electroorganic synthesis [2]. EIS can also be used to characterize films or coatings covering metal surfaces exposed to an electrolyte. Fatty acids spontaneously adsorb on the surface of metals and form a protective film known as self-assembled molecular layers (SAMs). Crosslinking of SAMs by ionizing radiation results in the formation of polymer nanocoatings (PNPs). PNPs have all the advantages of SAMs, but the additional crosslinking of SAMs significantly improves their other properties, such as durability and stability. However, the efficiency of the protective nanocoatings depends on the preparation procedure.

The aim of this work is to determine the influence of different SAM application methods and the influence of the dose rate of applied radiation required to obtain polymer nanocoatings with the best protective properties. Elaidic acid (EA), $C_{18}H_{34}O_2$, an unsaturated trans fatty acid, was used to form SAMs on the surface of copper by different application methods: dipping, brush application and spraying. To effectively crosslink SAMs, a suitable dose rate should be applied. For this purpose, dose rates of 22.00 kGy/h, 1.76 kGy/h, and 0.17 kGy/h were investigated. The protective properties of the PNPs were investigated under simulated atmospheric conditions using EIS. The results showed that PNPs prepared by the dipping method and crosslinked at the highest dose rate (22.00 kGy) exhibited the most effective protective properties.

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