

# 10<sup>th</sup> ISE Satellite Student Regional Symposium on Electrochemistry

*2<sup>nd</sup> July 2021, online event*

## BOOK OF ABSTRACTS



Croatian Society of Chemical Engineers

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## Preface

It was our great pleasure and honour to welcome all participants of "10<sup>th</sup> ISE Satellite Regional Symposium on Electrochemistry" (10<sup>th</sup> ISE-SRSSE) held on July 2<sup>nd</sup>, 2021, via Microsoft Teams platform. The meeting was held under the support of the International Society of Electrochemistry (ISE) to encourage young scientists, the postgraduate and graduate students, to present their research in a friendly atmosphere.

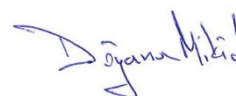
10<sup>th</sup> ISE-SSRSE took place successfully for the tenth year in a row, with exception of year 2020 due to COVID-19 pandemic. The aim of the symposium is to encourage a cooperation of young scientists from different institutions and industry. The symposium included six sections with in total 21 presentations held by participants Croatia, Serbia, Germany, and Austria. Sections covered broad aspects of electrochemistry fields: electrochemistry of materials for energy storage/conversion, corrosion, environmental and analytical chemistry.

We would like to thank all participants once again for their presentations and gratefully acknowledge the International Society of Electrochemistry for the given support, providing the opportunity for young researchers to exchange their working experience in various fields of electrochemistry and make connections that may result in future collaboration. We hope this was pleasant and rewarding experience for them.

Saša Marcinek



Dajana Mikić



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# Oral Presentations

## MEMBRANE CHARACTERIZATION FOR THE USE IN AEM ELECTROLYSERS

Ema Kovačević<sup>1</sup>, Rory Bagacki<sup>2</sup>, Iris Dorbandt<sup>2</sup>, Erno Kemppainen<sup>2</sup>, Rutger Schlatmann<sup>2</sup>,  
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The need for clean and efficient energy transfer nowadays is growing and one of the most encouraging possibilities is hydrogen. To make that possible, a low-cost and high efficiency water electrolyzer is vital. One of the most promising options is an anion exchange membrane electrolyser (AEMEL). Their main component is the anion exchange membrane, which is used to transport OH<sup>-</sup> ions from the cathode to the anode. The AEM uses a diluted KOH solution which allows the use of non-PGM (platinum group metals) catalysts. However, more research on AEMEL is needed to match the performance of proton exchange membrane electrolyser (PEMEL).

Research into the work of an AEM electrolyzer was done at the Helmholtz Zentrum Berlin with emphasis on comparing the effect of the type of anion exchange membrane used. With a zero-gap electrolyzer setup, diffusion losses were minimized. The activation losses which come from the OER (oxygen evolution reaction) and HER (hydrogen evolution reaction) were minimalized with catalysts, electrodeposited NiMo at cathode and electrodeposited NiFe at anode, both on Ni-foam. The study focused on the ohmic losses, which come mostly from the resistance of the AEM. To identify this losses Electrochemical impedance spectroscopy was used. An AEM electrolyser using the Dioxide Materials® 5 cm<sup>2</sup> electrolyzer cell was re-used for this purpose. The tested membranes were Fumasep® FAA-3-50, Fumasep® FAA-3-PK-130 and Sustainion®X37-50. The electrolyte used was 1.0 M KOH at ambient temperature. Running the cell at 2.0 V with the membranes Fumasep® FAA-3-PK-130, Fumasep® FAA-3-50, and Sustainion® X37-50 gave 575 mA, 1043 mA and 691 mA respectively. The area resistances of the membranes in that order were 5.461  $\Omega\text{cm}^2$ , 2.367  $\Omega\text{cm}^2$  and 3.864  $\Omega\text{cm}^2$ . Thus, Fumasep® FAA-3-50 which caused the lowest AEM related energy losses would be the first choice for implementation in the electrolysis cell, followed by Sustainion® X37-50 and Fumasep® FAA-3-PK-130.

# PHOTOELECTROCHEMICAL PROPERTIES OF $\text{BiVO}_4$ AND $\text{rGO-BiVO}_4$ AS VISIBLE LIGHT PHOTOELECTRODES

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Recently, the utilization of materials based on  $\text{BiVO}_4$  for solar energy harvesting has gotten attention as a narrow band gap semiconductor in different applications [1,2]. In this work, an iso-type heterojunction  $\text{BiVO}_4$  was synthesized by co-precipitation method and by preparing bilayer of  $\text{rGO-BiVO}_4$ , the role of reduced graphene oxide (rGO) in the enhancement photoelectrochemical water splitting (PEC-WS) of  $\text{BiVO}_4$  was analyzed. It was found that rGO possesses an excellent photo-generated electron/hole separation and transport properties and remarkably enhanced the photoelectrochemical (PEC) water splitting of  $\text{BiVO}_4$ . The photocurrent response of  $236.59 \mu\text{A cm}^{-2}$  for  $\text{rGO-BiVO}_4$  was obtained which was 53 times more than that of  $\text{BiVO}_4$ . In addition, the impact of a series of organic components with an aromatic ring, used as hole scavengers, on PEC activities was investigated for both photoelectrodes. The component with electron donating substituent group in the aromatic ring improved the PEC activities more than that of the component with electron withdrawing substituent group. However, it was shown that the optimum concentration should be used in order to obtain hole scavenger effect.

- [1] A. Martinez-de La Cruz, U.G. Perez, Materials Research Bulletin 45 (2010) 135-141.
- [2] T.-G. Vo, H.-M. Liu, C.-Y. Chiang, Catalysis Science & Technology 9 (2019) 4588-4597.

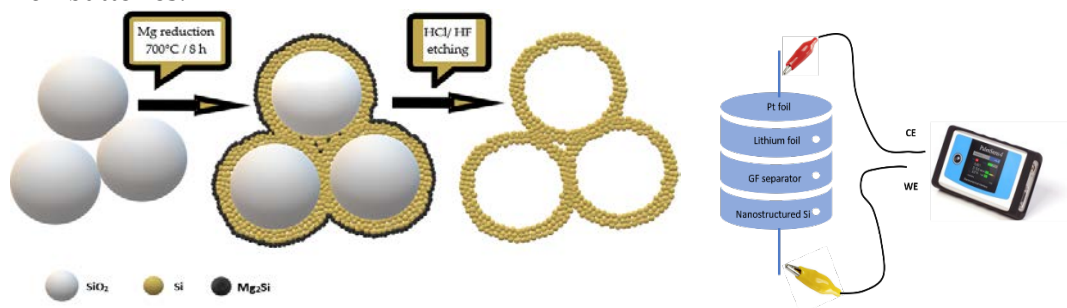
# NOVEL HONEYCOMB SILICON STRUCTURE AS POTENTIAL ANODE MATERIAL FOR Li-ION CELLS

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Silicon stands out as next generation anode material due to its superior theoretical specific capacity of 4200 mAh / g which is a result of intercalation 4.4 Li into Si at high temperature to form  $\text{Li}_{15}\text{Si}_4$ [1]. 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. Porous silicon with high surface can improve accessibility of the electrolyte to silicon and increase lithium diffusion length which increase capacity[2]. Magnesiothermic reduction (MRR) of silica ( $\text{SiO}_2$ ) is a facile method for the synthesis of porous silicon spheres at lower temperatures than conventional silica reduction methods[2]. In this work, honeycomb Si nanostructure was prepared by MRR method and treated with silver ions ( $\text{Ag}^+$ ) which are reduced to form Ag nanoparticles. The Ag nanoparticles were placed within the pores thus being directly connected to both the silicon structure as well as the current collector, which results in improved electrochemical performance of the honeycomb structure[3]. The aim of this work is to investigate the mechanism and kinetics of  $\text{Li}^+$  ions intercalation in the porous structure of newly prepared materials as potential anodes for Li-ion batteries.



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- [2] J. Entwistle, A. Rennie, S. Patwardhan, A review of magnesiothermic reduction of silica to porous silicon for lithium-ion battery applications and beyond, *J. Mater. Chem. A* 6 (2018)
- [3] D. Chen, X. Mei, G. Ji, M. Lu, J. Xie, J. Lu, J.Y. Lee, Reversible Lithium-Ion Storage in Silver-Treated Nanoscale Hollow Porous Silicon Particles, *Angew. Chemie* 124 (2012) 2459–2463.

# SUPERCAPACITOR PERFORMANCE OF ACTIVATED CARBONS DERIVED FROM SUCROSE

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Electrochemical properties of carbonaceous materials, synthesized from sucrose and afterwards activated using KOH, LiOH and NaOH, were investigated. CV, PEIS and charge/discharge (C/D) techniques were employed and results were correlated to adsorption/desorption data and corresponding microporous structure of examined materials. All the samples showed supercapacitive behavior typical for carbon blacks. Obtained capacitive properties were found responsive and consequential to physicochemical structuration induced by synthesis procedure and subsequent activation. KOH-activated sample exhibited the highest real surface area and capacitance. A 100 C/D cycles were required for this sample to reach the maximal capacitance, which afterwards started to decrease upon further cycling. . On the other hand, NaOH-activated sample is of much better cyclability, although its initial, up to 100<sup>th</sup> cycle, capacitance values, as well as BET surface area, were lower in comparison to KOH-activated sample. However, despite much higher initial capacitance values of KOH-activated sample, its steady-state capacitance was lower than that reached by NaOH-activated carbon. LiOH-activated sample was of low BET surface area and weak capacitive performances as well.

# A NOVEL APPROACH FOR THE STUDY OF THE KINETICS OF SOL-GEL SYNTHESIS OF TITANIUM DIOXIDE NANOPARTICLES AS CATALYST SUPPORT

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Owing to a wide range of application in kinetics (photocatalysis, electrocatalysis, etc.), it is of high importance to define in details correlation between structure and synthesis of TiO<sub>2</sub> particles. The aim is to elucidate the kinetics of TiO<sub>2</sub> solid phase formation by sol-gel approach as newly-structured suitable carrier of batteries/fuel cells electrocatalytic materials.

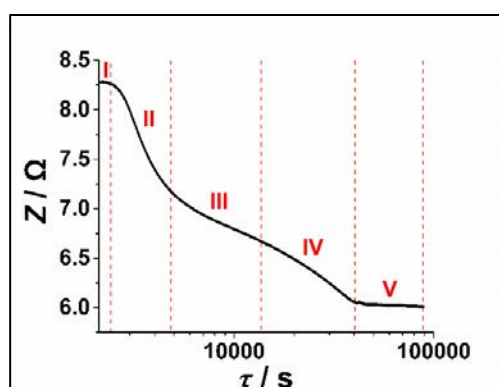


Figure 1. The typical change of high frequency impedance of a synthesis medium during TiO<sub>2</sub> solid phase formation. Conditions:  $c(\text{TiCl}_3) = 0.022 \text{ mol dm}^{-3}$ ,  $c(\text{HCl}) = 0.077 \text{ mol dm}^{-3}$ ,  $t = 50 \text{ }^\circ\text{C}$ .

TiO<sub>2</sub> nanoparticles were synthesized from TiCl<sub>3</sub> precursor under different conditions (concentration, pH) in an aqueous medium. Formation of a new solid phase was continuously monitored by a dynamic conductometric measurements induced by high frequency impedance sinusoidal voltage perturbations of a conductometric cell. The particle size distributions of the obtained TiO<sub>2</sub> sols were characterized by the dynamic light scattering method, while the microstructure data were obtained by the scanning electron microscopy. The typical change of high frequency impedance during TiO<sub>2</sub> synthesis is presented in Figure 1. It was found that the process proceeds through at least five phases (I–V, Figure 1, seen as high frequency impedance decrease) of different rates and durability, which depend on synthesis conditions.

## ELECTROLYTE INCORPORATION IN Hf AND Ta ANODIC MEMRISTORS

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Hafnium, Ta and their oxidized forms are commonly used for metal-insulator-metal (MIM) memristive structures. Memristors are playing a significant role in the next-generation of thin film micro- and nano-electronic devices since the current memory technology, based on conventional Si devices, has reached its limits. Memristors are mainly used in redox-based resistive switching memories (ReRAMs), logic circuits, sensors and artificial neural networks. The switching, mechanism, hence data storage of such devices, is based on the electric field assisted conductive paths formation due to the ionic drift inside of the oxide layer. Therefore, a selection of suitable media is crucial for the fabrication of the insulating layer sandwiched between two metallic electrodes. In this study, memristors with Hf and Ta used as bottom electrodes were anodized in citrate, phosphate and borate buffer. An influence of electrolyte species incorporation in anodic oxides on electrical and memory characteristics of memristors was studied. Conductive filaments were successfully imaged by TEM and electrolyte species incorporation was confirmed by XPS. Both, Hf and Ta anodic memristors have shown high endurance and data retention as well as high resistance states ratio which makes them ideal candidates for industrial implementation.

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- [2] I. Zrinski, C.C. Mardare, L.-I. Jinga, J.P. Kollender, G. Socol, A.W. Hassel, A.I. Mardare, Phosphate incorporation in anodic hafnium oxide memristors, *Appl. Surf. Sci.* 548 (2021) 149093. <https://doi.org/10.1016/j.apsusc.2021.149093>.

# ELECTRONIC CONDUCTIVITY IN VANADIUM PHOSPHATE GLASSES

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Electronic conduction has been detected in various melt-quenched oxide glasses which contain transition-metal oxides (TMO) such as  $V_2O_5$ ,  $Fe_2O_3$ ,  $MoO_3$ , and  $WO_3$ . These materials are of great scientific interest due to their potential application in many fields such as power sources, photonics, gas sensors, etc. The electronic conductivity in these glasses occurs via electron hopping between transition metal ions in different oxidation states and, as a rule, strongly depends on the amount of transition metal oxide and a fraction of transition metal ions in different valence states. Among various TMOs which can be incorporated into oxide glasses, vanadium (V) oxide is especially attractive since it participates in the glass network formation and hence can be added in large amounts. In this study, a series of binary  $xV_2O_5-(100-x)P_2O_5$  glasses with a wide range of composition from  $x = 30$  to  $x = 90$  mol%, were prepared by the melt quenching method. Obtained glass samples were investigated by Raman and impedance spectroscopies. With the increase of  $V_2O_5$  content bands attributed to the stretching vibrations of V–O and V–O–P bonds are observed. The DC conductivity of glasses increases with the increase of  $V_2O_5$  due to an increase in the concentration of vanadium ions reaching the highest conductivity of  $1.03 \times 10^{-4} (\Omega \text{ cm})^{-1}$  at 30 °C for glass with 90 mol%  $V_2O_5$ . All glasses obey Summerfield and Sidebottom scaling procedures of conductivity spectra indicating that the conductivity mechanism does not change with the temperature.

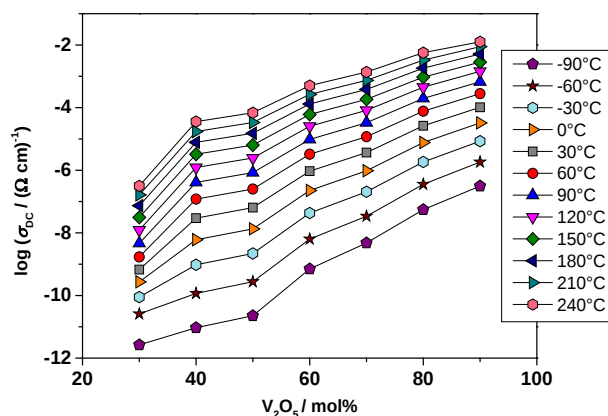


Figure 1. DC conductivity at various temperatures as a function of  $V_2O_5$  content.

## HOW TO IMPROVE THE IONIC CONDUCTIVITY IN SODIUM PHOSPHATE GLASSES?

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Nowadays, sodium phosphate glasses are widely investigated as a cheap and easily accessible material for application in electrochemical devices. However, these glasses usually suffer from low electrical conductivity and a significant research effort has been undertaken to improve this property. In this study we show that the increase in sodium mobility can be achieved in a simple manner, by the addition of WO<sub>3</sub> and MoO<sub>3</sub> which depolymerize condense phosphate glass network and hence facilitate transport of Na<sup>+</sup> ions thus improving overall electrical conductivity.

The research was conducted on two glass series, 40Na<sub>2</sub>O-*x*MoO<sub>3</sub>-(60-*x*)P<sub>2</sub>O<sub>5</sub> and 40Na<sub>2</sub>O-*x*WO<sub>3</sub>-(60-*x*)P<sub>2</sub>O<sub>5</sub>; *x*=0-50 mol% prepared by melt-quenching. The electrical properties were studied by impedance spectroscopy in a wide frequency (0.01 Hz – 1 MHz) and temperature (-90 °C – 250 °C) range. The results showed a significant increase in electrical conductivity with the addition of transition metal ions, being four orders of magnitude in the case of WO<sub>3</sub> and three in the case of MoO<sub>3</sub>. However, the trend in conductivity was not linear, yet exhibited the maximal value at 30 mol% of MoO<sub>3</sub> and 40 mol% of WO<sub>3</sub> (Figure 1). In order to follow structural evolution, <sup>31</sup>P MAS-NMR spectroscopy was used where the compositional dependence of P-O-Mo/W linkages exhibited a similar trend as the electrical conductivity. This led us to conclude that the maximally interconnected phosphate and molybdenum/tungsten units form a favourable environment for fast sodium ion transport in contrast to the predominantly phosphate or molybdenum/tungsten glass network. Furthermore, tungsten oxide was found to be more interconnected with the various P<sub>2</sub>O<sub>5</sub> units inducing therefore a higher electrical conductivity of the Na<sub>2</sub>O-WO<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> glasses.

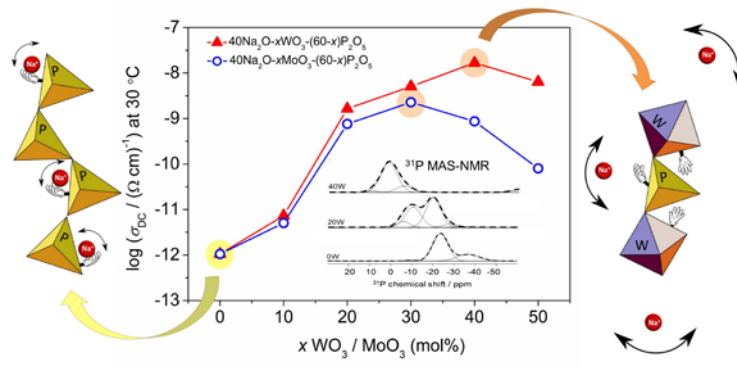


Figure 1. Enhancement of ionic conductivity by addition of  $\text{WO}_3$  and  $\text{MoO}_3$  in sodium phosphate glasses.

## THE EFFECT OF ASCORBIC ACID AS A HOLE SCAVENGER ON ELECTROCHEMICAL RESPONSES OF PHOTOCATALYSTS

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Photoexcitation of the semiconductor yields electron-hole pairs that rapidly recombine. However, this recombination can be prevented by the addition of hole scavengers which increases the survival probability of the electrons. Different organic hole scavengers have been employed to elucidate reaction mechanisms or to improve the reaction efficiency in heterogeneous photocatalysis and electrochemical photocatalysis (PEC) for more than 50 years. Nevertheless, their influence on the electrochemical response of photocatalysts has yet to be thoroughly researched.

This work is focused on the study of ascorbic acid (AA) as a scavenger for photogenerated holes and its effect on the electrochemical response of photocatalysts. Considering that the formal potential of the AA redox couple is  $-0.185$  V (vs SCE) it can be easily oxidized by the photogenerated holes. For the purpose of this investigation photoelectrochemical characterization of  $\text{TiO}_2$  and  $\text{TiO}_2/\text{SnO}_2$  electrodes was carried out in the presence of AA. The electrodes were prepared by the deposition of a commercial  $\text{TiO}_2$  and laboratory prepared  $\text{TiO}_2/\text{SnS}_2$  onto FTO glass plates. All measurements were done in a phosphate buffer solution with or without the addition of AA and by using a three electrode system. Irradiation was carried out by UV or LED lamps. Open circuit potential (OCP) monitoring in chopped light irradiation indicated an increase in photocatalytic activity in the presence of AA. Moreover, linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) responses showed that by the addition of AA higher photocurrents and lower resistances, respectively, are obtained.

## ELECTROCHEMICAL AND SPECTROSCOPIC STUDY OF ARTIFICIALLY OBTAINED SULPHIDE PATINA

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Copper and its alloys exposed to atmospheric conditions form a thin layer of corrosion products called patina. Patina protects the base metal from further corrosion. Color and properties of patina depend on the alloy composition, metallurgical features and type of corrosive environment, i.e. presence of aggressive ions (SO<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>). Patination is slow process that lasts up to 100 years in less corrosive environment. Therefore, artificial patination is used instead. In Croatia, artificial patination using K<sub>2</sub>S<sub>n</sub> is the most familiar method for obtaining black sulphide patina. The application of artificial patina has become a very common method for pretreatment of bronze artefacts exposed to outdoor atmosphere.

In this work artificially obtained sulphide patina on copper and several bronzes (CuSn6, CuSn12, RG7) is exposed to various conditions as accelerated aging in form of continuous immersion in simulated rainwater or alternating wet/dry cycles. Electrochemical properties are examined by using electrochemical impedance spectroscopy (EIS). Composition and morphology of patina are examined by FTIR spectroscopy, SEM/EDX and optical microscopy.

Acknowledgement: This work has been fully supported by Croatian Science Foundation under the project IP-2019-04-5030.

## ELECTROCHEMICAL TEST RESULTS OF BATCH APPLICATION OF OIL-SOLUBLE CORROSION INHIBITORS WITHIN EOR PROJECTS IN THE OIL INDUSTRY

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One of the major problems associated with all EOR projects is that they show a high degree of sensitivity to a natural factor that cannot be changed, and that is corrosion. By injecting carbon dioxide (CO<sub>2</sub>) into the reservoir, in order to increase oil recovery, the production of carbon dioxide in gas and formation water increases in production wells. As carbon dioxide (CO<sub>2</sub>) is extremely corrosive when dissolved in water, it is necessary to inhibit its action by reducing the corrosion rate. In the oil industry, corrosion caused by carbon dioxide dissolved in water is called "sweet corrosion". Dissolved CO<sub>2</sub> in water causes the formation of carboxylic acid, which increases the acidity of the water. The corrosion process occurs in the presence of water, while oil and/or gas themselves are not corrosive. Corrosion rates in non-inhibited systems with high concentrations of dissolved CO<sub>2</sub> in formation water are up to 10 mm/year.

As part of the EOR project, a study was made: *Impacts of CO<sub>2</sub> injection and increase in corrosion rate as a consequence of CO<sub>2</sub> injection*. Due to the impossibility of applying continuous treatment with corrosion inhibitors, most attention was paid to the batch treatment of production wells. For this purpose, laboratory tests of the effectiveness of oil-soluble corrosion inhibitors were performed. All corrosion tests of the effectiveness of corrosion inhibitors were done by attempting to simulate a batch treatment, which would later be used in the field. The principle of all tests is to immerse the test metal coupon in a certain concentration of oil-soluble inhibitor, and then immerse the same metal coupon in the test fluid and monitor the stability of the film on the metal surface over the corrosion rate. Corrosion inhibitors used for batch treatments are generally oil-soluble because, unlike water-soluble corrosion inhibitors, which are more often used for continuous dosing, they create thicker and more stable films on the metal surface, which gives them an advantage in case of inadequate continuous dosing.

Using electrochemical and gravimetric laboratory tests, a very effective oil-soluble corrosion inhibitor was found, which is currently used in the field. Electrochemical tests of the efficiency and stability of the corrosion inhibitor film in the electrochemical cell gave excellent results for all tested systems. The efficacies of the inhibitors were and the presence of pitting corrosion by the cyclic polarization method has not been reported. In the case of electrochemical tests, the stability of the film was not determined by visual inspection after immersion in a solution of copper sulfate but by impedance through the measurement of the capacity of the inhibitor film on the metal surface. According to the measured capacities, the film of corrosion inhibitors on the metal surface showed excellent stability in all cases.

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# CARBON STEEL PROTECTION OF BY VOLATILE CORROSION INHIBITORS

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Low carbon steel is widely used as the main material for atmospheric storage tank floors, and the atmospheric storage tanks play an irreplaceable role in storage and transportation of crude oil and oil derivatives [1,2]. Inhibitors are substances or mixtures that in low concentration and in aggressive environment inhibit, prevent or minimize the corrosion [3].

In order to achieve protection, VCIs (volatile corrosion inhibitors) are increasingly applied in closed systems affected by atmospheric corrosion. VCI is most often applied in quantities, forms and dosages that are mainly based on practical experience rather than scientific research. This research aims to improve the understanding of the impact of VCI inhibitors. The possibility of corrosion protection of carbon steel (S235JR) was investigated by using commercial corrosion inhibitors (Inhibitor A and Inhibitor B). The tests were performed on cleaned steel plates in order to better simulate the real conditions of inhibitor applications. VCI protects the metal in such a way that forms an invisible protective film on the metal surface, thus not affecting the physical properties or functionalities of the metal. The adsorbed monolayer can change the rate of electrochemical reactions such as metal oxidation or oxygen reduction. The tests were performed by electrochemical methods EIS (electrochemical impedance spectroscopy) and Tafel polarization in a cells with aqueous electrolyte (acid rain pH = 6.5; aqueous solution of 1% NaCl) Studied inhibitors were dissolved in corrosive media at different concentrations in order to study their inhibiting efficiency. Additionally, studies were conducted with specially designed electrochemical cell with agar based electrolyte [4], on samples that were exposed to corrosive atmosphere with high humidity and temperature for several days.

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# CORROSION RESISTANCE OF TITANIUM-BASED BIOMEDICAL IMPLANT MATERIALS

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The main goal of this study was to examine the effect of calcium phosphate coating (CaP coating) on the corrosion resistance of titanium alloy, Ti-6Al-7Nb, commercially used as an implant material in orthopedic devices. In addition to enabling osseointegration, the CaP coating forms a kinetic barrier to the electrochemical corrosion reaction, thus protecting the material from corrosion-induced degradation. This further increases the biocompatibility of the implant material.

The CaP coating was deposited to the Ti-6Al-7Nb alloy by the electrochemical cathodic deposition method. Electrodeposition of the calcium phosphate film was performed from an aqueous solution of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  salts and film formation parameters were investigated using cyclic voltammetry (CV).

Electrochemical characterization of the Ti-6Al-7Nb alloy in simulated body fluid, Hank's solution was performed before and after the surface modification. The following electrochemical experimental techniques were used: electrochemical impedance spectroscopy (EIS) and linear polarization (LP) in the narrow ( $\pm 20$  mV vs. open circuit potential) and in the wide ( $\pm 200$  mV vs. open circuit potential) potential range at a scan rate of  $0.1667 \text{ mV s}^{-1}$ . The morphology and microstructure of CaP deposit obtained was characterized by scanning electron microscopy (SEM) and chemical composition was assessed by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR).

# VOLTAMMETRY IN THE STUDY OF UNUSUAL PHENOMENA IN THE SEA. PART I: ORGANIC MATTER CHARACTERIZATION DURING RED TIDE AND GELATINOUS ZOOPLANKTON BLOOMS IN THE NORTHERN ADRIATIC

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Organic carbon (C) is a constituent of many processes in the sea and can be an important indicator of changes in marine system [1]. Due to climate changes, extreme natural weather events (droughts, floods, tropical cyclones, heat waves, intense precipitation i.e. heavy rains, abrupt changes in temperatures, salinity, circulation and mixing, strong winds, Saharan dust transport) are becoming more frequent. Such events lead to unusual phenomena such as mucilaginous algal blooms, red tides, invasive jellyfish blooms, which contribute to eutrophication characterized by anomalous accumulation of organic C in the sea [1-4].

In seawater, organic matter (OM) is a complex of organic compounds (proteins, carbohydrates, lipids, humic and fluvic acids) with different surface active properties [1,2]. Surface active substances (SAS) can be autochthonously produced mainly through primary and secondary production, release or as secondary metabolites under feeding pressure or allochthonously introduced into the marine system from land and atmosphere. An important property of SAS is that it contains hydrophobic (e.g. fatty acid chains, aromatic rings or hydrocarbons) and hydrophilic functional groups (e.g. -NH<sub>2</sub>, -COOH, -OH or -SH) that allow the accumulation of SAS at different phase boundaries (e.g. marine surface-atmosphere, particle-aqueous phase, bottom layer-sediment, pycnocline in a stratified water column). Due to such properties, the presence of SAS in water samples can be monitored by adsorption processes at the hydrophobic surface of the mercury (Hg) as a working electrode, by a simple electrochemical method of phase sensitive alternating current (AC) voltammetry [1-3]. Changes of the Hg electrode double layer reflected on the capacitance current are approximately proportional to all (dissolved and particulate) SAS in the solution. The total SAS can be separated into particulate and dissolved fractions by filtering through a 0.45 µm or 0.7 µm filters. SAS content usually can be expressed in the equivalents of the selected model OM substance of Triton-X-100 (eq. T-X-100) which is considered as a good representative of the most reactive part of the SAS in natural waters [1-3 and references therein]. SAS by normalization to dissolved organic carbon (DOC) content can be expressed as normalized surfactant activity, NSA=[SAS(eq. T-X-100)/DOC] [2,3], comparable to NSA of model substances, as representatives for SAS composition of different natural samples.

This study will present properties of OM compounds, studied based on their reactivity (hydrophobic properties) during unusual phenomena in the northern Adriatic Sea: a) gelatinous zooplankton blooms of the invasive ctenophore *Mnemiopsis leidyi* (Fig.1.A) [4] and b) red tide, mostly composed of *Noctiluca scintillans* bloom (Fig.1.B). These events were

characterized by remarkable increase of organic C content in otherwise oligotrophic area. OM with surface active properties was recorded both in dissolved (SAS 0,081-15,379 mg/L; DOC 0,875-318,100 mg/L) and particulated fractions (SAS 0,113-18,122 mg/L; POC 1,666-18,122 mg/L). The NSA values indicate the presence of more hydrophobic nature of DOC during the gelatinous zooplankton bloom.

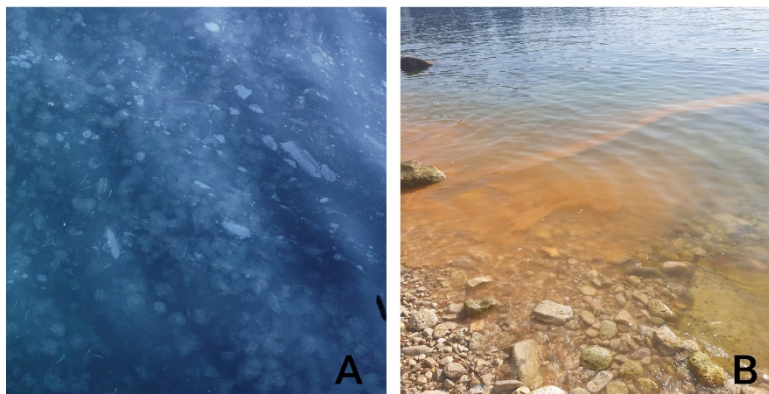


Fig.1. A) invasive ctenophore colony, B) red-tide bloom

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**VOLTAMMETRY IN THE STUDY OF UNUSUAL PHENOMENA IN THE SEA.  
PART II: SULFUR SPECIES CHARACTERIZATION IN THE SEAWATER ANOXIC  
CONDITIONS AND AGGREGATES OF RED TIDE BLOOMS IN THE NORTHERN  
ADRIATIC**

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Sulfur (S), an ubiquitous element in the environment, occurs in different oxidation states from -2 (sulfide,  $S^{2-}$ ) to +6 (sulfate,  $SO_4^{2-}$ ). Reduced forms of S, i.e. reduced sulfur species (RSS:  $S^{2-}$ ,  $HS^-$ ,  $S^0$ ,  $S_x^{2-}$ ,  $RSH$ ), are important forms for processes related to S biogeochemistry and environmental quality [1]. Production of marine S species is mainly related to phytoplankton and microbial activities, as well as eutrophication phenomena and spreading of hypoxic–anoxic dead zones. A significant fraction of natural S emission occurs in the form of organic S, such as dimethylsulfide (DMS), produced by phytoplankton and zooplankton grazing activities. In different natural water systems, electroanalytical methods have been widely used for the characterization and determination of different S species, including dissolved and/or particulate inorganic and organic S forms [2-5]. Electroanalytical determination of dissolved RSS on the Hg electrode is based on their interaction with the Hg, resulting in the Hg oxidation and the formation of insoluble mercury sulfide (HgS) at potentials more positive than -0.60 (vs. Ag / AgCl). The same process occurs during the interaction of Hg with organic and inorganic RSS that deposit HgS, which during the potential scan toward negative values are reduced, and reduction current at -0.68 V is directly proportional to the concentration of RSS in the sample. RSS that are adsorbed on the Hg surface, or form adsorbable RS–Hg complexes (in the case of DMS, DMDS, cysteine, glutathione) are reduced more positively (around - 0.5 vs. Ag/AgCl) [3-5]. By changing deposition potentials from - 0.2 V to - 0.4 V it is possible to make a rough distinction between organic and inorganic RSS that deposit HgS [4, and references therein]. In the presence of organic RSS, by measuring at  $E_d = -0.4$  V, the HgS reduction peak will decrease or completely disappear. Also, in the adopted electrochemical measurements of the RSS in natural samples, the acidification and purging step by  $N_2$  is used to make a distinction between the volatile and non-volatile fraction of the RSS [5].

Unusual phenomena in the sea, such as hypoxia, anoxia or intensive phytoplankton blooms as red tide, can occur as a consequence of environmental, i.e. meteorological conditions, lately highly impacted by climate change.

In this paper, cyclic voltammetry (CV) at the Hg electrode was used for characterization of total RSS ( $RSS_{TOT}$ ); non-volatile RSS ( $RSS_{NV}$ ) and organic S compounds in natural samples collected during the red tide bloom, and in the stratified and holomictic conditions of the unique marine environment on the Adriatic coast (Rogoznica Lake, RL). During stratified conditions in the RL water column, the concentration of  $RSS_{TOT}$  (mainly sulfide/ $S^0$ -like compounds) detected with CV measurements was in the range between 20 nM (oxic layer) to 3 mM (anoxic layer), while concentration of  $RSS_{NV}$  ( $S^0$ -like compounds) ranged between 10

and 100  $\mu\text{M}$ . Additionally, for the first time in the anoxic layer samples differential pulse voltammetry (DPV) was used for determination of polysulfides ( $\text{S}_x^{2-}$ ). The highest concentrations of  $\text{S}_x^{2-}$  (up to 0.1 mM) were determined about 1 m below the oxic/anoxic boundary ( $\sim 10\text{m}$ ) during summer months, when indirectly  $\text{S}_x^{2-}$  formation is proved to be connected by activities of purple phototrophic sulfur bacteria (PSB). In holomictic conditions, when stratification disappeared, concentrations of both  $\text{RSS}_{\text{TOT}}$  ( $\sim 100\text{ }\mu\text{M}$ ) and  $\text{RSS}_{\text{NV}}$  ( $\sim 10\text{ }\mu\text{M}$ ) were decreased and similar throughout the water column. In the same time presence of  $\text{S}_x^{2-}$  and PSB was not detected.

Unlike RL samples, in samples of red tide blooms (mainly composed of *Noctiluca scintillans*), two RSS peaks were detected with CV measurements. First peak, at potential around - 0.5 V, confirms presence of organic S species (RS-Hg type) in the concentration range between 17- 45 nM [3-5]. Second peak at more negative potentials (around -0.68 V), confirms presence of inorganic RSS (sulfide/ $\text{S}_0$ -like compounds) in the concentration range between 7 – 45 nM. Such results support the fact that dinoflagellates among other phytoplankton species contribute the most to the production of sulfur species in the sea [1,3].

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## ELECTROCHEMICAL DETERMINATION OF COPPER COMPLEXING CAPACITY IN THE SURFACE LAYER OF THE COASTAL CENTRAL ADRIATIC SEA

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We studied the effect of atmospheric organic matter deposition on the Cu<sup>2+</sup> complexing capacity (CuCC) in the surface seawater layer of the Middle coastal Adriatic, especially evident in the sea-surface microlayer (SML) during the period of retrieval of the oligotrophic conditions (February-July 2019). We applied differential pulse anodic stripping voltammetry (DPASV) in conjunction with static mercury drop working electrode. The obtained experimental data were fitted into the Langmuir/Gerringa nonlinear mathematical model built in the ProMCC software to determine CuCC parameters (organic ligand class, its concentration and apparent stability constant). We defined the optimal experimental conditions:  $E_a = -0.6$  V,  $t_a = 120$  s,  $E_d = -1.4$  V for 1 s, [Triton-X-100] = 1 mg/L. The presence of L<sub>2</sub> class ligands ([L<sub>2</sub>] = 28 – 392 nM) was determined in all SML samples, while L<sub>1</sub> class ligands were found only in four samples, with concentrations ranging from 41 – 76 nM. The determined concentrations of L<sub>2</sub> class ligands in the underlying water (ULW) ranged from 20 – 70 nM, while no ligands belonging to L<sub>1</sub> class were determined. Values of conditional stability constants for the SML samples were in the range  $\log K_{CuL1} = 10.34 - 11.11$  and  $\log K_{CuL2} = 8.32 - 10.02$ , and for the ULW samples  $\log K_{CuL2} = 9.51 - 10.18$ . The SML showed enrichment with organic ligands by a factor of 0.9 – 9.1 relative to ULW, with the highest concentrations of organic ligands present in SML originating from the specific atmospheric deposition of pollen in April 2019. The deposition of open fires and Saharan dust aerosols in the study period did not have a significant effect on CuCC parameters. The free Cu concentrations (2 – 46 pM) were in the range of the estimated toxic Cu concentration limits.

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# FORMATION OF Co(II)-Phen-PC MIXED LIGAND COMPLEX AT THE MODEL SURFACE OF MERCURY ELECTRODE AND LANGMUIR TROUGH

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Cell membrane represents boundary between the cell and its environment. It consists of phospholipid bilayer in which are embedded functional molecules as membrane proteins, carbohydrates, protein channels, glycolipids which enable various membrane functions from which selective permeability for ions and organic molecules is important for our work [1]. Cell physiology is strongly dependent on the interaction of hydrophobic cell membranes with hydrophilic inorganic ions. The key lipid-type defining membrane bilayers are phospholipids. Among which phosphatidylglycerol, phosphatidylethanolamin and phosphatidylcholine (PC) which are the subject of our investigation, are the most important, especially in algae species [2]. Detailed investigation of Co(II) binding with natural lipid phosphatidylcholine (PC) in aqueous solution was carried out by voltammetric measurements at the mercury drop electrode, complemented by monolayer studies in a Langmuir trough used as model for hydrophobic cell membranes. Penetration of cobalt ions into the PC layer was facilitated by the formation of Co(II)-1,10-Phenanthroline (Phen) complex in the subphase, followed by the hydrophobic mixed ligand Co(II)-1,10-Phen-PC complex formation at the mercury drop interface. Investigation of Co complexation with phosphatidylcholine was performed by cathodic stripping voltammetry in 0.55 mol dm<sup>-3</sup> NaCl solution at static mercury electrode. Complex Co-Phen was registered within pH range 4 to 10 at -1.0 V. Stoichiometry, stability and complex kinetics were determined. Co(II)-Phen-PC complex reduces irreversibly indicating a two-electron transfer chemical reaction at -1.5 V vs Ag/AgCl including reactant adsorption with complex dissociation after reduction takes place. Investigation of Co(II) lipid mixed ligand complex adsorbed at the mercury electrode hydrophobic surface is a significant contribution to the understanding of the processes occurring on the cell membranes hydrophobic surface [3]. Consequently, the surface concentration ( $\gamma$ ) of the adsorbed [Co(II)PhenPC] complex at the mercury drop electrode surface was calculated to be  $1.45 \times 10^{-10}$  mol cm<sup>-2</sup>. Information on the mechanism of Co(II)-lipid complex formation is a significant contribution to the understanding of complex processes at natural cell membranes.

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# SURFACE METHOD APPROACH IN CHARACTERIZATION OF PLASMA MEMBRANE VESICLES DERIVED FROM ALGAL CELLS

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Microalgae are important biological resources that have a wide range of biotechnological applications, especially in terms of pigment and metabolite isolation, while the potential of the plasma membrane vesicles [1] has not been investigated extensively. This study aims to prepare and characterize algal plasma membrane-derived from algal cells by two complementary surface methods. Polarography and chronoamperometry at the dropping mercury electrode enable to examine adhesion behavior of plasma membrane vesicles in respect of applied potential. Results show that fluid vesicles adhere at the wide potential range from -180 mV to -900 mV, which corresponds to the surface charge density from +21  $\mu\text{C cm}^{-2}$  to -13  $\mu\text{C cm}^{-2}$  [2]. The distribution of signal amplitudes of plasma membrane vesicles reflects vesicle size, while signal frequency is related to vesicle concentration in suspension. Atomic force microscopy imaging provides the structural characterization of adhered plasma membrane vesicles on mica surface in air. Results show that the plasma membrane vesicles are in the size range of 5-30  $\mu\text{m}$ , the membranes are spherical, nearly empty, with a membrane height of about 20 nm. In the future expanded knowledge of this unique membrane system could contribute to the design of marine bio-inspired materials for the development of drug delivery systems.

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## APPLICABILITY OF THE PASTE ELECTROLYTE CELL FOR *IN SITU* ELECTROCHEMICAL TESTING THE SURFACE PROTECTION OF BRONZE

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Various electrochemical techniques can be used to obtain information about the condition of a metallic material *in situ*. In particular, electrochemical impedance spectroscopy (EIS) has been shown to be a suitable method to generate valid data. This study, investigates the applicability of the paste electrolyte cell for EIS testing of non-patinated copper and bronze and patinated bronze without and with the protective coating. Comparative measurements were made with three-electrode and two-electrode electrochemical cells and in three different types of electrolytes, an aqueous solution of sodium chloride, tap water and electrolyte paste in the solid state. The aim of this work was to compare the measurements in the two previously mentioned types of electrochemical cells, to evaluate the repeatability and reproducibility of the measurements and to determine the influence of the different electrolytes. The EIS spectra were measured and the numerical values of impedance at 0.1 Hz were taken as an indicator of the level of surface protection by patina or coating. The calculated values of relative standard deviation, repeatability and reproducibility showed satisfactory results, with slightly better repeatability. By comparing the impedance for different electrolytes, it was found that the aqueous solution of sodium chloride did not give a reasonable indication of the degree of surface protection. Electrolyte paste in the solid state proved to be a promising candidate for *in situ* measurements by detecting the impedance ranking in the following order: copper > bronze > patinated bronze > patinated bronze with a protective coating.

# THE ELECTROCHEMICAL STUDY OF GALLIC ACID IN CALCIUM OXALATE SYSTEM

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Gallic acid (3,4,5-trihydroxybenzoic acid) is a secondary polyphenolic metabolite and natural antioxidant mostly found in plants and foodstuff (e.g. strawberry, blueberry, plums, walnut, tea etc.). It shows antioxidative, anticancer and antibacterial activity [1]. Gallic acid is often used in pharmaceutical industry and herbal medicine as well as food supplement [2]. It can also be used as a potential inhibitor of calcium oxalate precipitation [3].

The main goal of our study was to use voltammetric methods for detection of gallic acid in calcium oxalate system. Calcium oxalate was prepared by spontaneous precipitation after mixing calcium solution and oxalate solution in the presence of gallic acid as additive. Calcium oxalate precipitates and calcium oxalate supernatant solution were isolated for electrochemical detection of gallic acid.

Electrochemical measurements were conducted in a three electrode voltammetric cell: working glassy carbon electrode, counter electrode platinum wire and Ag/AgCl reference electrode in a phosphate buffer at three different pH values (pH = 5.8, 6.5 and 7.5). The system was purged with high purity argon before each measurement. Differential pulse voltammetry was used to detect gallic acid in calcium oxalate supernatant solution. Measurements in model systems (only gallic acid solution) revealed linear response in a concentration range from 80  $\mu\text{mol dm}^{-3}$  to 1.75  $\text{mmol dm}^{-3}$ . The obtained results indicated adsorption/incorporation of gallic acid in the calcium oxalate precipitates, regardless of the pH values. Cyclic voltammetry was used to detect interactions between gallic acid and calcium oxalate precipitates.

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## THE INFLUENCE OF AC INTERFERENCE ON ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY MEASUREMENTS ON HIGH IMPEDANCE COATINGS

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The influence of AC interference on electrochemical impedance spectroscopy (EIS) measurements on industrial coating systems was investigated. EIS is an interesting method as it quantifies coating quality by measuring coating impedance. The study first addresses the accuracy, repeatability and reproducibility of measurements made on calibration foils inside and outside the Faraday cage under various intentional AC interferences. The relative standard deviation (RSD) of the impedance of the foils inside the Faraday cage is less than 0.5%. Outside the Faraday cage, a relationship is established between the signal-to-noise ratio, the RSD of the measurements and the relative measurement error. It was found that for the noise amplitude up to 250 mV, both the RSD and the relative error can be kept below 5 % by increasing the DEIS signal amplitude to 250 mV and taking average of ten repeated measurements.