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Faculty of Science



**SPRING ELECTROCHEMICAL
MEETING 2021**
BOOK OF ABSTRACTS

May 20, 2021 On-line meeting

Jana Shepa (ed.)

Košice 2021

Edited by:

RNDr. Jana Shepa

Institute of Chemistry, Faculty of Science of Pavol Jozef Šafárik University in Košice

Reviewed by:

prof. RNDr. Renáta Oriňaková, DrSc.

Institute of Chemistry, Pavol Jozef Šafárik University in Košice

prof. RNDr. Petr Vanýsek, CSc.

Faculty of Electrical Engineering and Communication, Brno University of Technology

Scientific Committee:

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prof. RNDr. Petr Vanýsek, CSc. *BUT Brno*

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RNDr. Radka Gorejová, *UPJŠ Košice*

RNDr. Ivana Šišoláková, PhD. *UPJŠ Košice*

Organisation Committee:

RNDr. Jana Shepa

RNDr. Ivana Šišoláková, PhD.

RNDr. Radka Gorejová

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Czechoslovak Student Chapter

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Preface

The Spring Electrochemical Meeting organized by the Czechoslovak Student Chapter is a response to the need of students to meet each other and share their experience in the field of electrochemistry. This was one of the main reasons why young electrochemists from the Department of Physical Chemistry of UPJŠ in Košice, Palacký University in Olomouc and the Slovak University of Technology in Bratislava joined the worldwide network of student groups operating under the auspices of The Electrochemical Society. The main message of the group is the motto "students for students", which highlights the effort to exchange information and insights in the field of electrochemistry between peers. This approach brings a suitable friendly atmosphere, which is often very important. It offers students the opportunity to gain experience in organizing various workshops and conferences and generally benefits from the integration of students into the scientific community. This is why I am very glad that we managed to organize a competition for young electrochemists under the age of 35 this year. From the selected 10 best entries, one winner was selected. We believe that similar events will continue to take place with increasing participation.

Jana Shepa
Chair of Czechoslovak Student Chapter

Degradable Fe-Zn Material Prepared via Electroless Deposition of Zn on Fe Powder

P. Cipa^{a*}, I. Šišoláková^a, R. Gorejová^a, R. Oriňaková^a

^a Department of Physical Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak Republic
*pavol.cipa@student.upjs.sk

The aim of this work is the preparation of Fe-Zn degradable metallic biomaterials *via* modification of metallic powders. Biomaterials can be used in everyday life, for instance in the form of implants [1-2]. Our aim is to prepare biomaterial characterized by progressive corrosion in organism to eliminate necessity of additional chirurgical intervention at its removal [3].

The practical part of this work is focused on the modification of the commercial iron powder with a zinc layer by wet deposition from a solution of zinc sulphate heptahydrate. It is known that Zn corrodes faster than Fe therefore its addition to the Fe based material should fasten its corrosion rate. The aim of the study is to prepare biomaterial with a desired corrosion rate that will be higher than in the case of pure Fe. Compressed Fe-Zn pellets were prepared from modified powder. Their degradation rate was compared with the degradation rate of pellets from pure Fe and Zn. All measurements were performed in Hanks' solution which simulated the human body environment. Evaluation of the electrochemical measurements showed that the pellets prepared from iron and modified Fe-Zn powder showed a similar degradation behavior. The modified Fe-Zn powder contained 99.8 wt.% Fe and 0.2 wt.% Zn, which was confirmed by composition analysis by energy dispersive spectroscopy (EDX) and atomic absorption spectroscopy (AAS). The results showed that the corrosion speed of pure zinc was the highest among the studied samples (0.523 ± 0.036 mm/year). Pellets prepared from pure iron and Fe-Zn powder corroded at a comparable rate 0.249 ± 0.094 mm/year and 0.178 ± 0.025 mm/year, respectively.

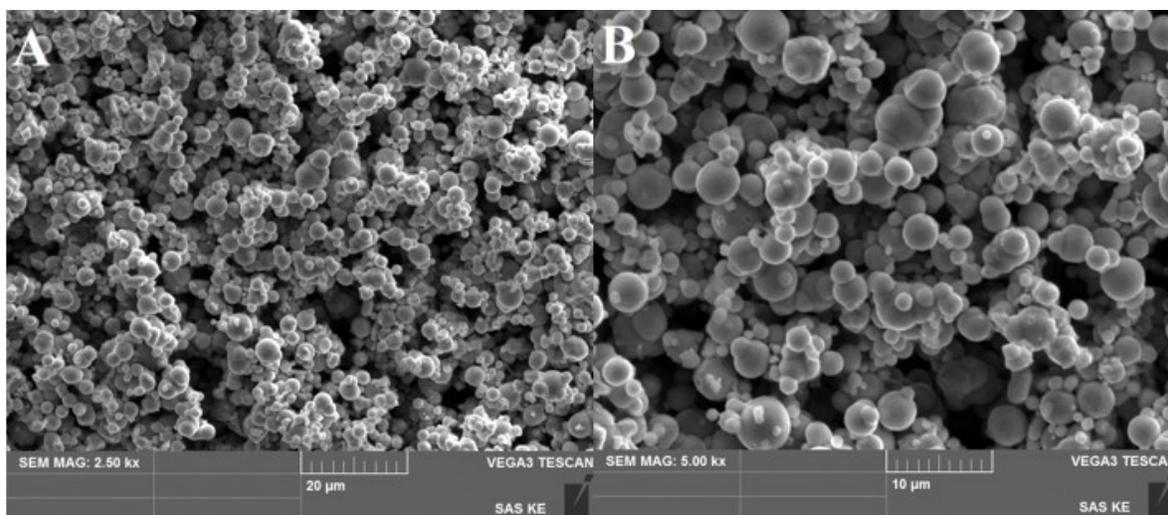


Figure 1 SEM images of Fe-Zn modified powder at 2 500x (A), and 5 000x magnification.

Acknowledgements

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Surface Interaction between Thin Polymer Layer and Metallic Biomaterial and Its Behavior in Protein-Rich Simulated Body Fluids

R. Gorejová^{a*}, J. Shepa^a, K. Sisáková^a, N. Podrojková^a, I. Shepa^b, R. Oriňaková^a, A. Oriňak^a

^a Department of Physical Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak Republic

^b Institute of material research, Slovak academy of sciences, Watsonova 47, 040 01, Košice, Slovak Republic

*radka.gorejova@student.upjs.sk

Knowledge of the behavior of potential biological metallic implants in the simulated body environment is of great importance [1,2]. For this, it is necessary to know the interactions between the implant and its surface layer, which in our case is formed by a polymer film, in detail. In our study, iron-based biodegradable material with a polyethyleneimine (PEI) thin layer was studied. Interaction between the metallic surface and polymeric coating and its nature was studied using density functional theory (DFT) calculations, atomic force microscopy (AFM), scanning electron microscopy (SEM), infrared (IR), and Raman spectroscopy. Electrochemical measurements were employed to study the corrosion behavior of Fe+PEI samples on air and after 60 minutes of immersion in Hank's solution with or without the addition of model protein (bovine serum albumin, BSA). Composition with the protein addition has been selected to approach the real environment of the human body. The computational study revealed a way of bonding of polymeric unit to an iron surface via the -amino group which was also confirmed by the IR measurements. When BSA was adsorbed (Fe-BSA and Fe+PEI-BSA), the increase in resistance after the corrosion process was observed. The decrease in the capacitance was observed for Fe+PEI samples after 60 minutes of immersion. This may be associated with the accelerated creation of corrosion products on the surface of the Fe-PEI samples and indicate its faster degradation rate when compared to the pure iron.

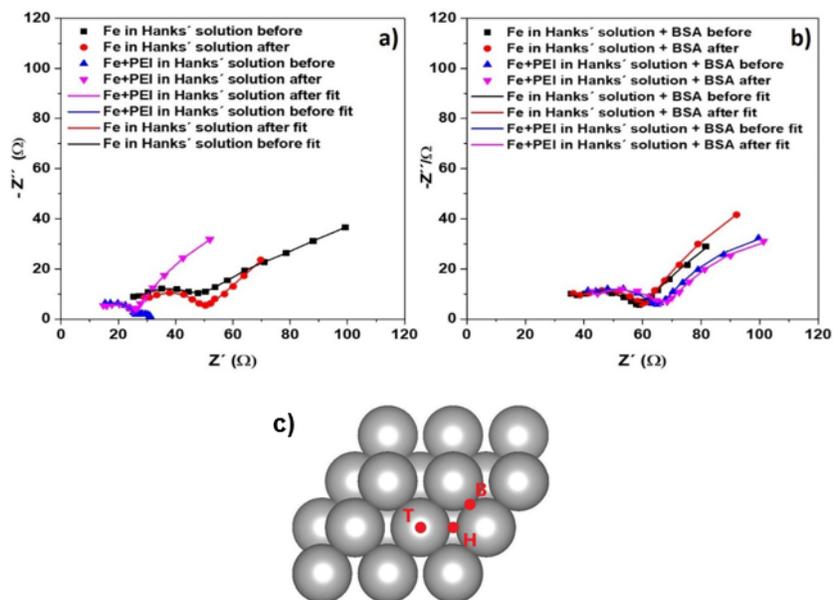


Figure 1 Nyquist plot of Fe samples (Fe, Fe+PEI, Fe-BSA, Fe+PEI-BSA) before and after corrosion (a,b). Locations of the presumed adsorption of the ethylamine molecule on the Fe (110) bcc surface: at the top of the Fe-top atom (T), in the gap between the Fe-hollow (H) atoms, and at the bridge between the Fe-bridge atoms (B) (c).

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Iron and Iron-Nickel Porous Metal Foams as Catalysts for Hydrogen Evolution Reaction

A. Gubóová^{a*}, R. Oriňaková^a, M. Petráková^a, M. Strečková^b

^a Institute of Chemistry, Faculty of Science, P.J. Safarik University, Moyzesova 11, 040 01 Kosice, Slovak Republic

^b Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Kosice, Slovak Republic

*alexandra.guboova@student.upjs.sk

Development of non-noble-metal catalyst for hydrogen evolution is essential for efficient production of hydrogen from water. Despite enormous efforts to replace platinum as the best catalyst for hydrogen evolution, the most high-effective HER catalysts are based on transition metals such as Co, Ni, Fe, Mo and their compounds [1-3], which are prone to corrosion. However, this problem could be overcome by use of alkaline electrolyte instead of acids. Hydrogen production by electrolysis in alkaline environment is the trend of industrial development [4].

Metal foams are perspective catalysts due to their high porosity, strength, durability and catalytic activity. Moreover, they are easily modified, for example via electrodeposition which further increases their activity toward hydrogen evolution.

For this work, iron and iron-nickel metal foams were prepared by dissolving gelatin in distilled water and subsequently mixing in carbonyl iron powder and alternatively also nickel powder. Samples were prepared by impregnating polyurethane foam with metal powder/gelatin suspension and then sintered at 1120 °C to obtain desired structure.

Samples will be used to evaluate their catalytic activity in alkaline environment and will be modified with nanoparticles to improve their catalytic potential even more. Influence of different metal ratio will be also studied in the future.

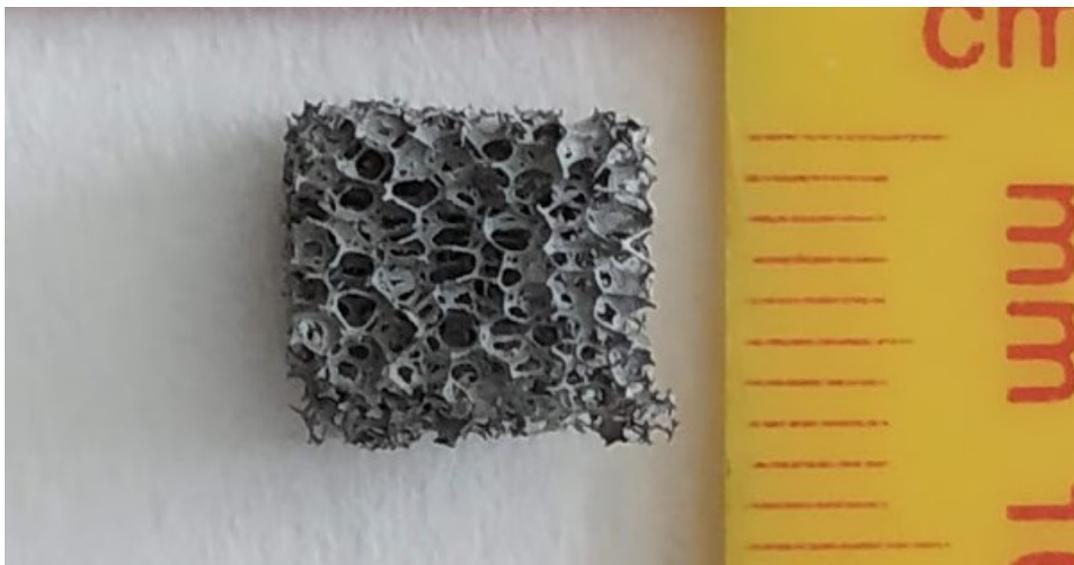


Figure 1 Sample of iron foam prepared from carbonyl iron powder.

Acknowledgements

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Screen Printed Carbon Electrodes Modified by Zinc Nanoparticles as an Electrochemical Sensor for Insulin Detection

F. Chovancová^{a*}, I. Šišoláková^a, J. Shepa^a, R. Oriňaková^a

^a Department of Physical Chemistry, Faculty of Science, Pavol Jozef Šafárik University, Moyzesova 11, 040 11 Košice, Slovak Republic

*frederika.chovancoval@student.upjs.sk

Insulin is an essential hormone which inhibits the excretion of glucose from the liver to the blood [1]. Diabetes mellitus is a progressive disease of chronic hyperglycaemia resulting from insulin resistance or insulin secretion dysfunction [2]. In these times, the worldwide prevalence of diabetes has been rapidly increased [3]. Currently, enzymatic glucose sensors are commercially used to control glucose level in the blood [4]. These sensors confronted diverse problems of stability enzyme (GOx) because of pH or temperature instability [5].

Nowadays, two main groups of analytical assays, immune and non-immune, are used for insulin determination [6]. The significant disadvantages of another methods like capillary electrophoresis and high performance liquid chromatography represent low sensitivity, expensive analysis or arduous [7, 8]. Electrochemical methods could overcome problems of immune and non-immune methods [8]. Electrochemical sensors offer suitable properties like high sensitivity, suitable selectivity, rapid response and low cost [6,9,10,11].

This work deals with the development of electrochemical sensor for the determination of insulin based on screen-printed carbon electrodes (SPCE) modified by multiwalled carbon nanotubes (MWCNTs), chitosan and zinc nanoparticles (ZnNPs). Firstly, the surface morphology of unmodified SPCE was analysed by scanning electron microscopy (SEM) and compared with the surface morphology of ZnNPs/chitosan-MWCNTs/SPCEs at the different deposition times of zinc (15s, 30s, 45s). EDX analysis displays the percentage of elements on the electrodes surface. ZnNPs/chitosan-MWCNTs/SPCEs45s shows the highest amount of Zn 11.4 %, and C 72.83%, with the unbroken structure of MWCNTs. Active surface areas were determined by linear sweep voltammetry and calculated from Randles-Sevcik equation. The active surface area of unmodified SPCE was 0.35 cm². Active surface area of ZnNPs/chitosan-MWCNTs/SPCEs with deposition time of 15s, 30s and 45s was 0.67 cm², 0.82 cm² and 0.97 cm², respectively. Direct oxidation of insulin in the concentration range from 0.5 μM to 5 μM at ZnNPs/chitosan-MWCNTs/SPCEs with different deposition time of Zn (15s, 30s, 45s) was studied via cyclic voltammetry (CV). Thereafter analytical characteristics like the limit of detection (LOD), selectivity and linear range were evaluated. The best electrocatalytic activity displays ZnNPs/chitosan-MWCNTs/SPCE45s. LOD was calculated as 0.28 μM, selectivity was 0.087 mA/μM and linear range was determined as 0.5 μM to 5 μM. Also the stability of ZnNPs/chitosan-MWCNTs/SPCE45s was studied via CV. After the 50 cycles stability of prepared electrodes decreased by only 9.3 %. The influence of

interferences (glucose, sucrose, uric acid, and ascorbic acid) was studied on ZnNPs/chitosan-MWCNTs/SPCEs45s. The interferents were diluted in PBS to simulate physiological concentration of human fluids and contain Cl⁻ ions. Any oxidation peak was observed at potential area characterized for insulin oxidation. Therefore, ZnNPs/chitosan-MWCNTs/SPCE45s can be considered as promising electrochemical sensor for diagnosis of diabetes mellitus.

Acknowledgements

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Electrochemical Sensor for Simultaneous Determination of Reduced and Oxidized Form of Glutathione

V. Jankovský^a, A. Ashrafi^{a,b}, R. Hrdý^b, V. Adam^{a,b}, L. Richtera^{*a,b}

^a Department of Chemistry and Biochemistry, Mendel University in Brno, Zemedelska 1, 613 00 Brno, Czech Republic

^b Central European Institute of Technology, Brno University of Technology, Purkynova 123, 61 200 Brno, Czech Republic

*lukas.richtera@mendelu.cz

Glutathione is the most abundant endogenous non-protein thiol in human body. It is profusely presented in all eukaryotic cells. For glutathione there are two different forms distinguished, reduced glutathione (GSH) and oxidized glutathione (GSSG), which consists of two molecules of GSH linked together with S–S bond [1].

Glutathione plays an important role in many physiological processes. It is involved in detoxification of reactive oxygen species, amino acid metabolism and transport, nucleic acid synthesis, antioxidant regeneration (vitamin E, L-ascorbic acid), cell proliferation, detoxification of xenobiotics, protection against heavy metal ions, and it is also responsible for maintaining redox balance of cells. It also serves as a reservoir and transmitter of cysteine [2].

Physiological ratio of reduced/oxidized glutathione in cells is 100:1. However if any pathological processes take place in cell the ratio can be shifted to 10:1. That transformed ratio can act as an indicator for numerous diseases [3]. The deviation of physiological ratio was demonstrated for patients suffering Alzheimer disease, Parkinson disease, diabetes, epilepsy, or even various types of cancer [4].

Despite the fact that glutathione shows promising potential for involvement in clinical practice, glutathione has been so far determined only experimentally from human blood and plasma samples, mostly using chromatographic techniques [5]. Those techniques are very accurate and specific, but on the other side, the performance of the analysis is quite expensive and requires skilled operator and expensive apparatus. And that is very probably one of the reasons why the glutathione determination has not been implemented into the clinical practice so far. An interesting alternative for the simultaneous determination of GSH/GSSG is the use of electrochemical methods, which are characterized by a favorable cost of instrumentation, speed of analysis and minimization of the need to adjust the sample while maintaining sufficient sensitivity and selectivity. Of course, it is also necessary to take account into the limitations of electrochemical methods that are namely the complicated electrode preparation and maintenance and the influence of the interfering agents that is usually also not negligible. On the bright side in past two decades, two fundamental problems that hampered faster implementation of electrochemical methods into the clinical practice had been solved. The issues were the size of the potentiostat and partially also

electrode maintenance. Potentiostats used to be quite big, heavy and immobile; nowadays there are potentiostats even smaller than a cell phone. The second issue, electrode maintenance, was partially solved by the development of screen printed electrodes (SPE) that are commercially produced and ready to use as delivered. The “partially” is because the electrodes are not always as selective and specific for demanded analyte as reported.

Based on those findings, we have decided to develop electrochemical sensor for simultaneous determination of GSH/GSSH, that could be potentially later transferred to SPE. Simultaneous determination of these compounds is quite challenging, because the GSSG peak appears at potential, where hydrolysis takes place on most of the electrodes.

In the first phase of the experiment, it was necessary to find the proper electrode and its modification material. Due to the easy modifiability, the carbon paste electrode (CPE) had been chosen as working electrode. From the several tested modification materials based on nanoparticles, boron nitride nano powder was identified as the most promising one. In the following phase it was necessary to choose the proper electrolyte with the optimal pH which has to be also as close as possible to the pH of human body fluids, due to the intended purpose of the experiment. Phosphate buffer saline $0,01 \text{ mol}\cdot\text{l}^{-1}$ with pH 7.0 was chosen. We could not use the pH 7.4 that is physiological, because there was a potential thread of autooxidation of GSH that could distort the results. In the following phase there were constructed calibration curves for each form separately and subsequently for both forms together. That verified that the simultaneous determination with our modified CPE is possible. After that the limits of detection (LOD) of and quantification (LOQ) for each for had been calculated. The linear dynamic range and LOD/LOQ showed promising potential for determination in the blood samples.

In a follow-up experiment, which will be focused on the preparation of SPE, the key findings from the CPE experiment will be implemented. At the time, when the electrodes will be tested and stabilized, they will be implemented into microfluidic system, which will be able to determine the GSH/GSSG ratio from a single capillary blood drop. We believe that this system will be suitable for the clinical practice.

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LiNiMnCoO₂ (NMC) as a Cathode Material for Li-ion Battery

V. Niščáková^{a*}, D. Capková^a, A. Straková Fedorková^a, S. Hatokova^b, M. Čigaš^b, Š. Hanigovský^b

^a Pavol Jozef Šafarik University of Košice, Department of Physical Chemistry, Moyzesova 11, 041 54, Košice

^b Fecupral, Jilemnického 3578/2, 080 01, Prešov

* veronika.niscakova@student.upjs.sk

Lithium-ion batteries have many advantages like high energy density, high power density, long cycle life, strong environmental adaptability, and high cell voltage. There are many kinds of lithium-ion batteries, such as LCO; LMO; NCA; NMC; LFP, or LTO [1]. Current commercial Li-ion batteries cover a wide range of specific energy, roughly from 90 to 250 Wh/kg; are light, compact, and work with a voltage of the order of 4 V [2,3]. Due to the high value of the energy content, lithium-ion batteries could be used in many popular devices, such as mobile phones, laptop computers, MP3s, and others. Generally, the performance of any device directly depends on the properties of the materials on which it is formed [2].

The samples that we have used in this work were from recycled Li-ion batteries. We prepared a positive electrode with the following composition 80% NMC; 10% amorphous carbon and 10% PVDF (polyvinylidene fluoride). The surface of prepared electrode was observed with a scanning electron microscope and analyzed in detail by EDX analysis. Subsequently, the electrode was subjected to electrochemical examination by cyclic voltammetry and galvanostatic cycling. The initial capacity at 0.1C was 63 mAh.g⁻¹ and at 0.2C 66 mAh.g⁻¹. Due to the origin and nature of the samples, their results are very good.

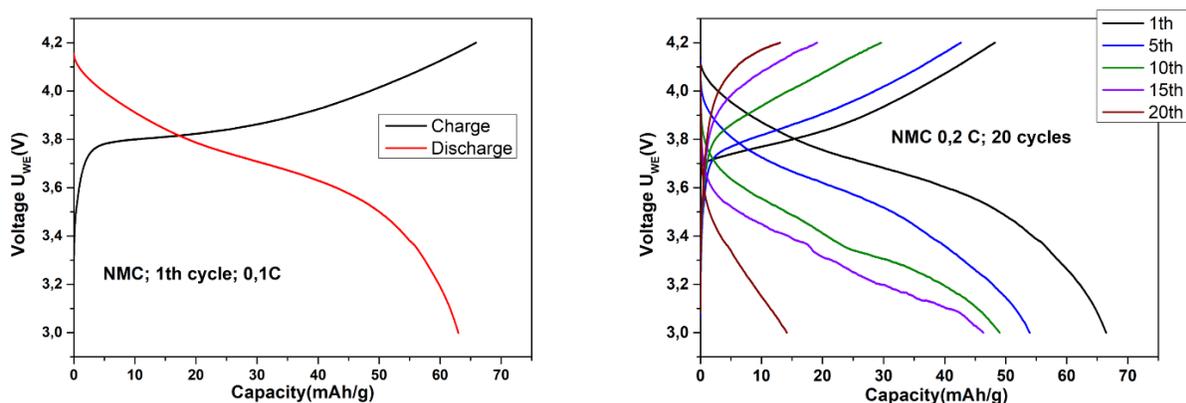


Figure 1 A) Initial charge/discharge curves at 0.1C; B) Charge/discharge curves at 0.2C.

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Simultaneous Determination of Guanine and Adenine in Human whole Saliva with Screen-Printed Electrode Modified with Graphite Nanoparticles Generated by Spark Discharge Process

A. Papavasileiou^{a*}, M. Trachioti^a, J. Hrbac^b, M. Prodromidis^{a,c}

^a Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

^b Department of Chemistry, Masaryk University, 625 00 Brno, Czech Republic

^c Institute of Materials Science and Computing, University Research Center of Ioannina (URCI), Ioannina Greece

* tasospap8@yahoo.gr

Guanine and adenine are two of the most important components of DNA and RNA molecules and abnormal changes in their metabolism suggest deficiency in the immunity system. Their presence in biological fluids in high concentrations is indicative for mutations and oxidative stress associated with various diseases (HIV, cancer etc.). Herein, we developed a screen-printed graphite sensor modified with graphite nanoparticles generated by spark discharge process utilizing pencil leads for determination of G and A in human whole saliva. The modification method [1] is low cost, extremely fast (16 s per electrode) facile and fully automated with the use of 3D positioning device coupled with a power supply, generating graphitic nanoparticles with high electrocatalytic activity in guanine and adenine electrooxidation reaction. Sensor optimization studies indicate that the optimal conditions for G and A determination are in PBS pH 6 as an electrolyte, with anodic voltammetric scan from 0.5 to 1.1 V after a deposition step for 30 s at 0.5 V. The graphite-sparked/SPE is capable of individual and simultaneous determination of guanine and adenine in concentration range from 5-1000 nM and 25-1000 nM while for a signal-to-noise of 3 the limits of detection are 2 nM and 8 nM, respectively. The sensor was successfully applied to saliva samples, after their filtration through 3 kDa MWCO centrifugal tubes to alleviate fouling phenomena of the sensing surface. The method was applied to determine the targets in saliva where the minimum detectable concentrations were 250 nM guanine and 500 nM adenine, while the accuracy of the method was examined by recovery studies in spiked saliva samples. Recovery was 96 – 108%.

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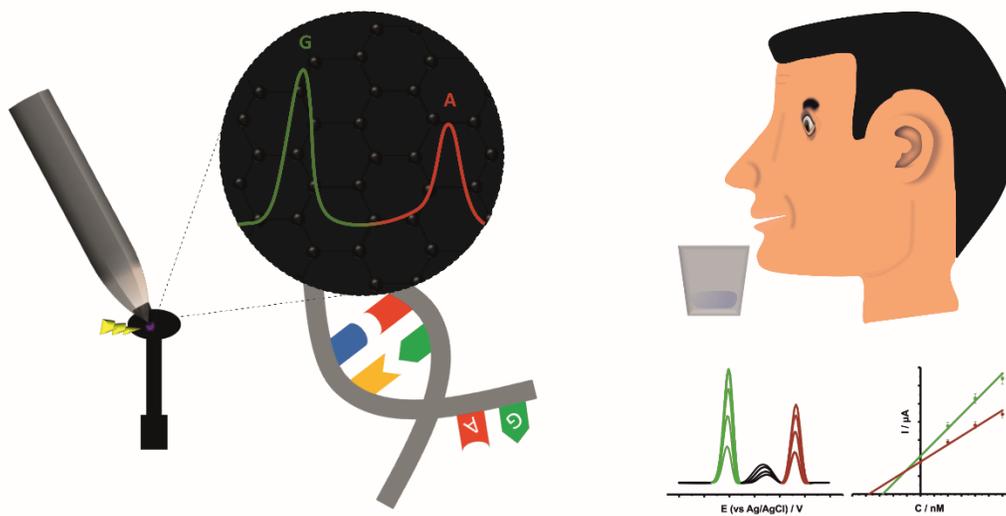


Figure 1 Graphical abstract.

Influence of Bioactive Polymer Coating on Degradation Properties of Fe Biomaterials

M. Petráková^{a*}, R. Oriňaková^a, R. Gorejová^a, A. Oriňak^a

^a Department of Physical Chemistry, Institute of Chemistry, Faculty of Science, P. J. Šafarik University in Košice, Moyzesova 11, 040 01 Košice

*martina.petrakova@student.upjs.sk

Metals as implants play an important role in the human body. Metallic materials are most often used in all bone joint replacements and dental implants. Metal implants have advantages over ceramics and polymers, such as higher tensile strength or fatigue resistance [1]. The aim of surface modification of metals is to improve the bioactivity of biomaterials. It is believed that altering surface morphology may improve the osteoblast adhesion and differentiation [2]. An antiseptic bioactive coating can reduce the risk of infections for implants [3].

In this work the influence of bioactive polymer coating on degradation properties of iron biomaterials was studied. The samples were prepared from carbonyl iron powder (CIP) by cold pressing into pellets with a diameter of 10 mm at 600 MPa. Subsequently, they were sintered at 1120 °C in a reducing atmosphere for 1 hour. The surface of the samples was treated with polymeric polyethylene glycol (PEG). Part of the sample was coated with a polymer layer PEG containing gentamicin. Corrosion properties of coated and uncoated samples were studied using an anodic polarization method in Hanks' solution. In the PEG-coated sample without gentamicin, a shift to a more negative potential value was observed, indicating a higher tendency to corrosion compared to the sample without the polymer coating. The polarization curves shown in Figure 1 indicate an increase in corrosion stability for the gentamicin-coated sample, indicating increased corrosion resistance.

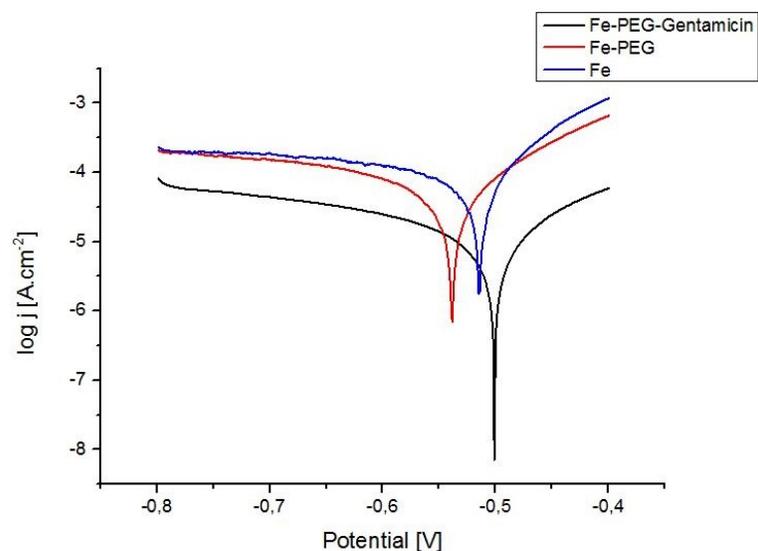


Figure 2 Potentiodynamic polarization curves of Fe, Fe-PEG and Fe-PEG with gentamicin containing measured in Hanks' solution.

Acknowledgements

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Detection of African Swine Fever Virus Using Supermagnetic Nanoparticles

O. Rychly^{a*}, B. Hosnedlova^a, A. A. Parikesit^b, N. V. Hoai^c, M. Kepinska^d, B. Ruttkay-Nedecky^a,
R. Kizek^{a,d,e}

^a CONEM Metallomics Nanomedicine Research Group (CMNRG), Studentska 812/6, 625 00 Brno, Czechia, kizek@sci.muni.cz

^b Department of Bioinformatics, School of Life Sciences, Indonesia International Institute for Life Sciences, Jl. Pulomas Barat Kav. 88, Jakarta Timur 13210, Indonesia

^c Research Center for Environmental Monitoring and Modeling, University of Science, 334 Nguyen Trai street, 100000 Hanoi, Vietnam

^d Department of Biomedical and Environmental Analyses, Faculty of Pharmacy, Wrocław Medical University, Borowska 211, 50-556 Wrocław, Poland

^e Veterinary Research Institute, v.v.i., Hudcova 296/70, 621 00 Brno, Czechia
*rychlono128@gmail.com

Introduction

African swine fever (ASF) is a very serious disease that affects members of the *Suidae* family. ASF first appeared in the sub-Saharan region of Africa [1], and from there the disease spread across the Transcaucasian region to Europe and Asia. There is a growing concern that the disease will spread to other areas as a result of travel and imports of pork products from countries where ASF is present. The causative agent of ASF is an enveloped cytoplasmic double-stranded DNA arbovirus (*Asfavirus*) (genome size 170–193 kbp), which is the only member of the *Asfarviridae* family. The natural cycle of ASF Virus (ASFV) spread occurs only in some parts of Africa and in the Iberian Peninsula. The first case of an outbreak of ASF in China was reported at a suburban pig farm in Shenyang in 2018. The low concentration of viruses in environmental samples makes detection extremely difficult. Therefore, simple, accurate and fast detection methods are urgently needed. Portable detectors based on biological molecules could be very helpful for rapid diagnosis in an outbreak. The aim of this work is to verify the possibilities of direct capture of DNA on magnetic nanoparticles and subsequent detection of DNA using electrochemical methods.

Materials and Methods

All chemicals used in this study were purchased from Sigma-Aldrich (St. Louis, MO, USA), in ACS purity. The resistance of deionised water used for this research was 18 M Ω ·cm⁻¹. Electrochemical measurements were performed with AUTOLAB Analyser connected to VA-Stand 663, using a standard cell with three electrodes. The working electrode was a hanging mercury drop electrode (HMDE) with a drop area of 0.4 mm². The reference electrode was an Ag/AgCl/3M KCl electrode and the auxiliary electrode was a graphite electrode. Gold coated superparamagnetic iron oxide nanoparticles (Au-SPION) were prepared [2]. DNA of ASFV was

selectively captured on Au-SPION, therefore in a sample only DNA of ASFV was present. DNA was detected using electrochemical methods in combination with adsorptive transfer technique (AdT). Two methods were used: differential pulse voltammetry (DPV) – the supporting electrolyte contained 0.2 M acetate buffer (pH 7.0) – and chronopotentiometric stripping analysis (CPSA) – the supporting electrolyte containing 0.2 M McIvaine buffer (pH 5.9) was used. Parameters of CPSA were the following: time of accumulation 120 s, stripping current 20, 10, 5, 1 μA , measurement time 240 s.

Results and Discussion

Electrochemical methods have been used for nucleic acid (NA) analysis for over 50 years. In our work, a strategy for detecting the presence of ASFV using DPV (DNA signal and quantum dots) was proposed [3]. In addition to redox NA signals, NAs also provide catalytic signals. A suitable analytical method for the catalytic signal (peak H) is CPSA. We focused on the description of the basic behavior of the H peak induced by the presence of dsDNA (in McIvaine buffer, pH 7.0). Peak H signal appeared at potential -1.75 V. We verified that the presence of DNA in the sample leads to the catalytic signal of the H peak ($n = 10$). We further studied under which conditions (concentration of DNA in the sample, applied current used for analysis and maximum duration of analysis) different catalytic signals are generated and how the H catalytic peak of DNA changes. The applied current is essential for the subsequently detected dt/dE signal. The applied current suitable for analysis varies according to the amount of dsDNA present in the sample. We tested different applied currents (20, 10, 5 and 1 μA). At a DNA concentration of less than 1 $\mu\text{g/mL}$, we achieved the best-plotted H peaks (dt/dE) at a current of 5 μA . For DNA concentrations of 1, 5 and 10 $\mu\text{g/mL}$, a current of 10 μA was applied and for concentrations of 10, 15 and 20 $\mu\text{g/mL}$, a current of 15 μA was applied. For DNA concentrations above 20 $\mu\text{g/mL}$, the best responses were obtained when applying a current of 20 μA . Sufficient analysis duration (dependence of a potential E on a time t) is required to fully record the signal of the H peak of dsDNA at a given applied current. Extending the DNA analysis time at a given current significantly improved the dt/dE records of the H peak and the reproducibility of the analysis (RSD up to 10%). It was found that the suitable time for which the H peak is reliably plotted is around 240 s.

Conclusion

The combination of Au-SPION and electrochemical detection provides a very useful tool for detecting the presence of NA in very low concentrations. The procedure was validated to detect the presence of ASFV DNA with 100% sensitivity and selectivity.

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Testing of Screen-Printed Electrodes Modified by Streptavidin

J. Shepa^{a*}, I Šišoláková^a, R. Oriňaková^a

^a Department of Physical Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak republic

*jana.shepa@upjs.sk

Electrochemical sensors modified by aptamers attracted much attention due to their favourable properties such as fast response, easy miniaturization, and strong specificity. Currently, the aptamers sensors could be divided into two groups: covalently labeled aptamer and labeled free target detection technology. Another division is into signal-on and signal-off type depending on signal change trends before and after the addition of the target. In general, a variety of sensors with unique detection properties could be constructed due to various oligonucleotide chains and reasonably combined with aptamer [1]. The biotin-streptavidin irreversible complex formation has been often used in commercial immunoassay platforms for clinically important analytes and biomarkers such as viruses and so on [2]. Currently, carbon electrodes modified by streptavidin are a very promising solution for aptamers sensors. The current response of screen-printed electrodes modified by streptavidin was studied in the solution containing potassium ferrocyanide and potassium ferricyanide dissolved in the DPBS (Dulbecco's Phosphate Buffered Saline) solution with concentration 0.1 M. As shown in the Figure 1, the current response increases with an increasing polarization rate, which is an expected phenomenon. Based on this, we could assume that the most advantageous polarization speed for us will be 100 mV/s. Nevertheless, it could be considered a scan rate of 50 mV/s is the most appropriate because the oxidation peak could be most clearly observed. It is essential for us in monitoring the changes caused by the binding of the aptamer or the analyte itself. At a speed of 50 mV/s, the oxidation maximum is clear and at the same time, the current response is higher than that at a lower polarization rate of 20 mV/s. The peak current linearly increasing with the scan rate indicates the diffusion-controlled electrochemical process. Moreover, as shown in the Figure 1 the redox reaction taking place at the modified electrode is an irreversible process.

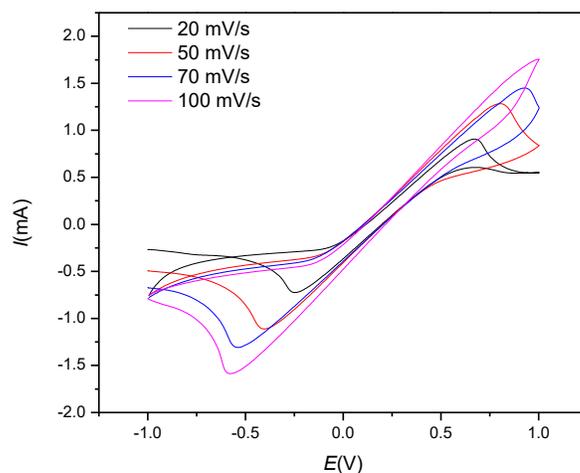


Figure 2 Cyclic voltammograms for carbon electrode modified by streptavidin in DPBS solution with pH 7 at scan rate 20, 50, 70, and 100 mVs^{-1} .

To assess the effect of pH, two molecules of potassium ferrocyanide and potassium ferricyanide were selected as base electrolytes in the same ratio with the final concentration of 0.1 M. These compounds were dissolved in ultrapure water or DPBS solution. At the same time, pH values of 3, 5, 7, and 9 were chosen for these solutions, which were adjusted with dilute hydrochloric acid or sodium hydroxide solution. In the case of an aqueous solution, no significant change in the current response can be observed concerning the pH of the solution. When comparing the current response for aqueous solution and DPBS, no significant difference can be seen, which we attribute to the fact that the current response is provided by a pair of potassium ferro/ferricyanide, which is a strong redox electrolyte. In conclusion, we decided to use a solution with pH 7 in DPBS in further measurements, because this environment is the most advantageous for biological molecules (aptamers and streptavidin) and at the same time it is closest to body fluids to which we should target in real samples.

Acknowledgments

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The Brdička Reaction for the Study of Thermostable Proteins, Especially Metallothionein in Urine

V. Skotak^{a, b}, B. Hosnedlova^{a, b}, B. Ruttkay-Nedecky^{a, c}, T. Para^{d, e}, R. Kizek^{a, b, c, e}

^a CONEM Metallomics Nanomedicine Research Group, Studentska 812/6, 625 00 Brno, Czechia

^b Department of Research and Development, ENVI-ECO-NANOLIFE, s.r.o., Korunni 2569/108, Vinohrady, 101 00 Praha, Czechia

^c Department of Molecular Pharmacy, Faculty of Pharmacy, Masaryk University, Palackeho 1946/1, 612 00 Brno, Czechia;

^d Department of Pharmacology and Toxicology, Faculty of Pharmacy, Masaryk University, Palackeho 1946/1, 612 00 Brno, Czechia

^e Department of Clinical Laboratories. Hospital of Milosrdných bratří, Polní 3, 639 00 Brno, Czechia

*vitsskotak@gmail.com

Introduction

Metallothionein (MT) is a small protein discovered in 1957 by Margoshes and Vallee. MT consists of a single polypeptide chain of 61–62 amino acids containing 20 cysteine residues which contain several bivalent cations (Zn, Cu, Cd, Hg) bound through metal-thiolate linkages. In the Brdička reaction, thiol groups are responsible for the catalytic signals of hydrogen evolution on mercury electrode. New suitable markers are being intensively searched for rapid diagnosis of various cancers. An increase in MT levels can be expected in patients with cancer [1]. One of the most common malignancies is prostate cancer (PCa). Not much information is known about the relationship between MT and urine. A number of studies have been conducted on the electrochemical determination of MT [2]. The aim of this work was the electrochemical determination of MT in urine and its changes in patients with PCa.

Electrochemical measurement

Electrochemical measurements were performed with an AUTOLAB Analyser (Metrohm, Herisau, Switzerland) connected to VA-Stand 663 (Metrohm, Herisau, Switzerland), using a standard cell with three electrodes. The working electrode was a hanging mercury drop electrode (HMDE) with a drop area of 0.4 mm². The reference electrode was an Ag/AgCl/3M KCl electrode, and the auxiliary electrode was a graphite electrode. The supporting electrolyte was prepared by mixing buffer components. The samples analysed by differential pulse voltammetry (DPV) were deoxygenated prior to measurements by purging with argon (99.999%) saturated with water for 20 s. In our studies, the Brdička supporting electrolyte contained 1 mM Co(NH₃)₆Cl₃, 1 M NH₃(aq) and 1 M NH₄Cl, pH = 9.6; a surface-active agent was not added. The DPV Brdička reaction

parameters were as follows: an initial potential of -0.6 V, an end potential -1.9 V, a modulation time 0.057 s, an interval 0.2 s, a step potential of 1.05 mV/s, modulation amplitude of 250 mV, and accumulation time of 240 s.

Results and Discussion

The Brdička reaction has long been used for MT analyzes [3]. Urine samples after their thermal denaturation were electrochemically analyzed. The typical sample voltammograms are shown in Figure 1A. The area under the curve (AUC) was used to evaluate the obtained voltammetric curves. For the obtained voltammograms, we evaluated their AUC from -1.0 V to -1.6 V. RSDs of AUCs ranged from 20-40% ($n = 5$). We decided to apply the mathematical evaluation procedure to the electrochemical analysis of MT in a urine sample. The mean AUC of the PCa group ($n = 9$) was 151.7 ± 48.0 , RSD 53.7%. The difference between the control group and the PCa group was statistically significant ($P = 0.0099$). Signals in patients with prostatic hypertrophy did not show a statistically significant difference compared to the control group ($P = 0.7869$).

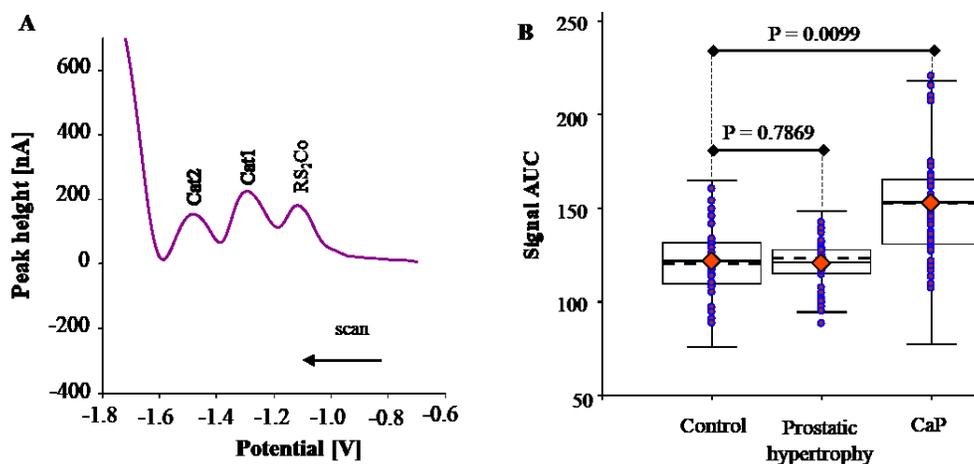


Figure 1. A) Typical average ($n = 5$) DP voltammogram in a urine sample with redox signal RS₂Co and catalytic signals Cat1, Cat2 and Cat3. 200 μ l of sample was dosed into 5 ml of basic electrolyte. B) Box plots of AUC signals. Comparison of the group of controls ($n = 13$), the group of patients with prostatic hypertrophy ($n = 9$) and the group of patients with PCa ($n = 14$).

Conclusion

Metallothioneins are determined in a number of different matrices, especially in organ samples. Recently, we have paid attention to the detection of MT in blood and serum. Another matrix in which MT can be analyzed is urine. A pilot study of electrochemical analysis of MT in urine was performed. We decided to mathematically evaluate the individual catalytic signals as AUC in four potential zones. We applied the mentioned methodological approaches to monitoring changes in

MT content in patients with PCa and prostatic hypertrophy. Differences were demonstrated between the tested groups, the values in patients with PCa were increased, but they must be studied in more detail

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Study of the Catalytic Effect of Metal Nanoparticles towards Insulin Oxidation

I. Šišoláková^{a*}, J. Shepa^a, F. Chovancová^a, R. Oriňaková^a

^a Department of Physical Chemistry. Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 040 01, Košice, Slovak Republic

*ivana.sisolakova@upjs.sk

Diabetes mellitus (DM) can be considered as one of the most serious worldwide disease. Enzymatic glucose sensors are currently commercially used to diagnose DM. Because blood insulin concentration is indirectly dependent on glucose concentration, the development of a non-enzymatic insulin sensor may be identified as a new approach in the diagnosis of DM [1-3]. Screen printed carbon electrode (SPCE) is used as the base material, mainly due to the low carbon price and the low amount of analysts required for the determination, which results from the small size of the used working electrode (only 4 mm in diameter). SPCEs were modified by the combination of multi walled carbon nanotubes (MWCNT) and chitosan, which were used to increase the active area of the electrode and eliminate Cl⁻ ions on the electrode surface [2]. Various types of metal nanoparticles (Cu, Co, Zn, and Ni) or metal oxide (NiO) nanoparticles were used for MWCNTs-chitosan/SPCE modification and their electrocatalytic activity towards insulin oxidation was studied. Based on our study and established analytical characteristics of prepared electrodes, we can achieve that NiONPs/chitosan-MWCNTs/SPCE is the most suitable for insulin determination. Mentioned SPCE displayed the lowest limit of detection (19.6 nM), the highest sensitivity (7.06 $\mu\text{A}/\mu\text{M}$) and widest linear range for insulin determination (600 nM to 10 μM). Influence of interferences on insulin determination on NiONPs/chitosan-MWCNTs/SPCE was also studied with no oxidation peak in the potential window related to insulin oxidation.

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Acknowledgements

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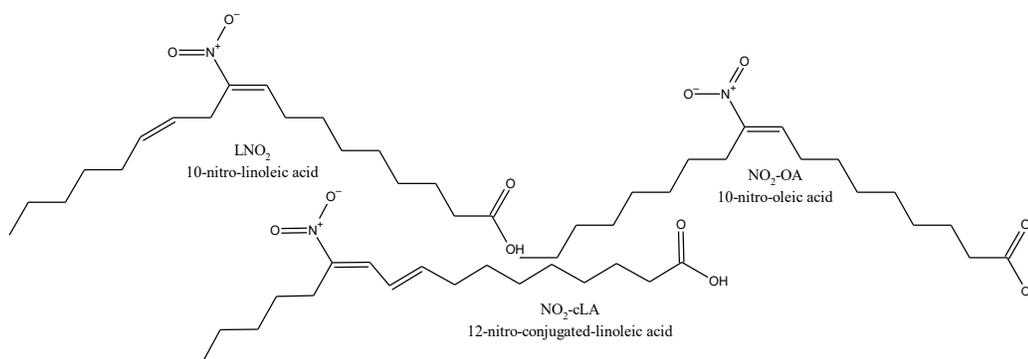
Electrochemical Characterization of Nitro-Fatty acids

M. Zatloukalova^{a*}, D. Novak^a, J. Vacek^a

^a Department of Medical Chemistry and Biochemistry,
Faculty of Medicine and Dentistry, Palacky University, Hnevotinska 3, Olomouc 775 15, Czech
Republic

*martina.zatloukalova@seznam.cz

Nitroalkene fatty acids (NO₂-FAs) are endogenous electrophiles produced *via* interaction of reactive nitrogen species (RNS) with unsaturated fatty acids. NO₂-FAs are usually investigated for being reactive lipidic species produced during inflammatory and metabolic reactions. NO₂-FAs act as pleiotropic mediators in signaling response of the cell and regulating redox homeostasis. Nitro-oleic acid (NO₂-OA) and conjugated nitro-linoleic acid (NO₂-cLA), have been demonstrated to have anti-inflammatory properties in a broad spectrum of pathologies. NO₂-FAs are powerful biological electrophiles which can react with biological nucleophiles [1]. In this study, we focused on the evaluation of the redox properties of NO₂-OA, NO₂-cLA and nitro-linoleic acid (LNO₂), Scheme 1.



Scheme 1 Structure of studied NO₂-FAs.

The nitro group of NO₂-FAs undergoes electrochemical reduction at a potential of around -0.8 V (vs. Ag/AgCl) at pH 7.4 in an aqueous milieu [2], Fig. 1. Based on this reduction signal, the reactivity and stability of NO₂-FAs can be monitored. EPR and fluorescence methods were used for the evaluation of NO· release. The stability of NO₂-FAs is derived from the environment where NO₂-FAs occur. Relatively rapid degradation occurs in aqueous media. NO₂-FAs are more stable in a non-polar environment such as adipose tissue or cell membranes [3].

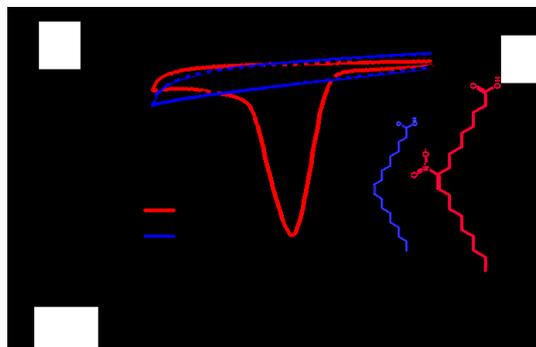
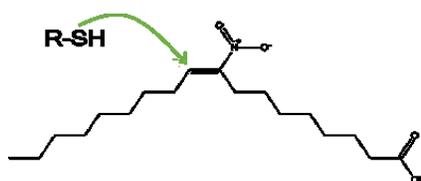


Figure 1 Cyclic voltammograms of 20 μM $\text{NO}_2\text{-OA}$ and OA measured on pyrolytic graphite electrode in 0.1 M phosphate buffer pH 7.4. CV conditions: start potential -0.25 V, vertex potential -1.25 V, step potential 5 mV, scan rate 1 V/s.

As was mentioned above, these electrophilic species react with a variety of biological nucleophiles such as Cys, His and Lys amino acid residues in proteins through Michael's addition (Scheme. 2).



Scheme 2 Scheme of interaction of 9- $\text{NO}_2\text{-OA}$ acid with $-\text{SH}$ group of proteins.

Constant-current chronopotentiometric stripping (CPS) analysis was utilized to evaluate the interaction of $\text{NO}_2\text{-FAs}$ with proteins. In a single CPS scan we can observe the reduction peak of $\text{NO}_2\text{-FAs}$ and also the peak H related to electrocatalytic process in which proton-donating amino acid residues of protein are involved. Interaction with proteins was monitored, based on the changes in the reduction peaks [2]. In addition to the electrochemical approach, mass spectrometry (peptide mapping) and spectrophotometric methods were applied to evaluate the formation of Michael's adducts.

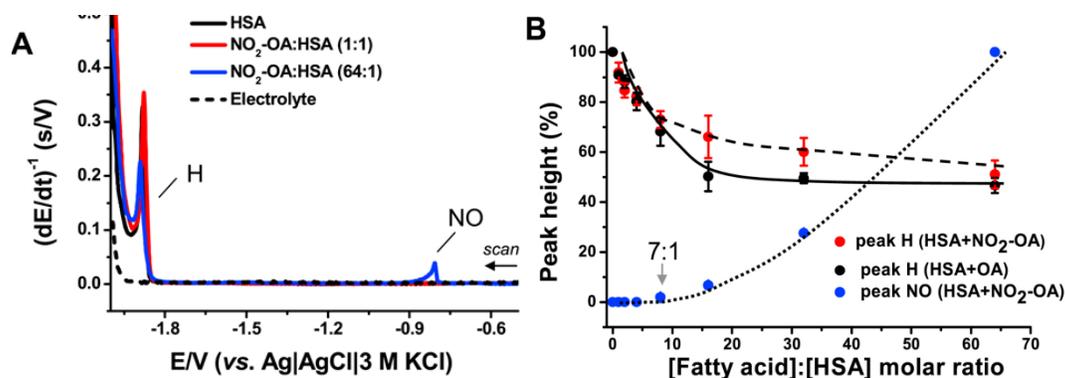


Figure 2 A) Constant-current chronopotentiometric stripping analysis of 0.5 μM HSA after incubation with increasing concentration of $\text{NO}_2\text{-OA}$. B) Dependence of peak H and NO heights on concentration of $\text{NO}_2\text{-OA}$ after their incubation with HSA.

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