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INVESTIGATION OF ANILINE ELECTROCHEMICAL POLYMERIZATION

ON DIFFERENT ELECTRODES

Summary of doctoral dissertation
Physical sciences, chemistry (03 P)

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VILNIAUS UNIVERSITETAS

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ANILINO ELEKTROCHEMINĖS POLIMERIZACIJOS TYRIMAS

ANT ĮVAIRIŲ ELEKTRODŲ

Daktaro disertacijos santrauka
Fiziniai mokslai, chemija (03 P)

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1. INTRODUCTION

Electrically conductive polymers (ECP) – are organic polymers, which are characterized by electrical, electronic, magnetic and optical properties of metals and maintain as a simple polymer mechanical properties. ECP in literature are described as synthetic metals or organic semiconductors. Conjugated polymers, which links of atoms are not fully, are mostly characterized by good electronic properties. These are artificially derived substances, which in certain conditions can be transformed from insulator to electrically conductive polymers. Both the structure and conductive properties of polymers are mutually different. Consequently, the electrical properties of these polymers can be used in many fields, such as electronics, catalysis, nanotechnology, optical technology, medicine, anti – corrosion coatings, catalysts, sensing[1,2,3,4,5] and others. Biological sensors are the one of electrically conductive polymers practical application examples.

Currently, well – researched are conjugated polymers: polyaniline (PANI), polypyrrole (PPy), polythiophene (PT) and polyparaphenylene (PPP). All these polymers in common can have positive and/or negative charge in an atom shall maintain a common chain π orbitals. However, the most studied and mostly wide – used is the PANI, due to the easy – going synthesis, high conductivity, chemical stability, low cost and the ability to create different redox forms[6,7].

Polyaniline compounds are of interest to a charge transfer mechanism of electrically conductive polymers and chemical and electrochemical sensor development. Conduction across and along the polymer chain depends on both degrees of oxidation and of protonation of the polymer, both on and off doping ion nature that cause the polymer structure. ECP surface and internal structure, that is to say structural defects in the chain length of crystallinity depends on the synthesis method doping anion, aniline concentration, and other, often more difficult to control elements such as electrode preparation or maintenance before the start of synthesis solution time.

Conductive polymer study is needed to find the link between the synthesis conditions and the resulting material properties. Despite the large number of scientific studies in the field of conductive polymers, synthesis conditions for selection to be controlled by the electrical properties and the structure is not resolved. Once Nano – sciences, found that the polymer structure is very important in applications. Process mechanism of polymerization, charge transfer phenomena in polymer and ion incorporation kinetics is not fully examined. Electrochemical polymerization of aniline is often arises in polymer degradation and by – products in the reaction problem.

The aim of the work is to determine the optimal conditions for polyaniline layer formation on the pencil graphite, titanium and electrochemically anodized

[1] Ziadan K. M., Saadonb W. T., Energy Procedia 2012 (19):71 – 79.
[2] Lua H., Zhou Y., Vongehra S., Hua K., Meng X., Synthetic Metals, 2011 (161):1368 – 1376.
[3] Kumar S.A., Meenakshi K.S., Sankaranarayanan T.S.N., Srikanth S., Progress in Organic Coatings, 2008 (62):285 – 292.
[4] Zhong L., Zhu H., Hu J., Xiao S., Gan F., Electrochimica Acta, 2006 (51):5494 – 5501.
[5] Cases F., Huerta F., Garces P., Morallon E., Vazquez J. L., Journal of Electroanalytical Chemistry 2001 (501):186 – 192.
[6] Albuquerque de J.E., Mattoso L.H.C., Faria R.M., Masters J.G., MacDiarmid A.G., Synthetic Metals 2004 (146):1 – 10.
[7] Shinde V. P., Patil P. P., Electrochemica Acta 2012 (78):483 – 494.

titanium electrodes using cyclic voltammetry method and investigate the electrochemically synthesized PANI coating properties. To investigate the $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ oxidation/reduction process on the Au electrode modified with PANI.

The main objectives of the work were as follows:

• To select the optimum conditions for the electrochemical polymerization of aniline on the pencil graphite electrode by cyclic voltammetry method. Characterize the obtained coatings.

• Investigate the availability of precipitated polyaniline acid after electrochemical modification of pencil graphite electrode.

• To select the optimum conditions for the electrochemical polymerization of aniline on titanium and electrochemically anodized titanium electrodes.

• To evaluate the gold surface of the filling polymer degree of active and coated polymer surface area measurements, depending on the amount of electrochemically synthesized polyaniline.

• To identify gold electrode double layer capacitance neutral solution dependence on the degree of surface coverage of polyaniline. To calculate the electrical double layer capacitance of polyaniline – coated Au electrode.

The novelty and significance of the work

This work was formed by electrically conductive polymer – polyaniline layer on the pencil graphite, titanium and titanium dioxide electrodes, as well as studies on the gold electrode, the solution changed from medium acid to neutral, where polyaniline becomes insulator. In addition to the electrochemical system introduced by $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ salts of oxidized and reduced only non – coated polymer metal surface. The experimental set of iron complexes in the oxidation/reduction of dependencies has been solved on the formed polyaniline layer structure. Similar research in general, the abundance of literature cannot be found.

All the mentioned problems, work to get the experimental results and their interpretation, particularly in the distribution of the polymer pencil graphite, Ti and TiO_2 electrode on the surface of the investigation and also PANI coating study in neutral solution using Au electrode – this is a doctoral dissertation novelty and originality.

The defense statements of the work

- The oxidized form of PANI – emeraldine obtained during electrochemical polymerization of aniline on the pencil graphite electrode.
- Polyaniline material as precipitate forms was precipitated in 2 M H_2SO_4 solution by cyclic voltammetry method on modified with PANI layer pencil graphite electrode.
- Aniline electrochemical polymerization on titanium and electrochemically anodized titanium electrodes undergoes in a complex way. The resulting surface is completely oxidized form of PANI – pernigraniline.

- Depending on aniline electropolymerization cycles (the synthesized polyaniline content) on the Au electrode, the surface coating of polymer grade increases from 11 to 96.7%. Average active (bare polymer) island radius varies from ~ 10 to ~ 100 nm, while the average distance between them of ~ 0.05 to 1.1 nm. Electric double layer capacity of the neutral medium decreases linearly from 65 (Θ = 0) to 10 (Θ = 1) $\mu F/cm^2$.
- The macrostructure of polyaniline films formed on gold surface is changing in neutral solutions when potential is cyclically changing. Adsorbed polymer levels remain constant. Upon termination of the scan, the initial structure of polyaniline is recovers.

Dissertation contents

The dissertation is written in Lithuanian and contains the following parts: Introduction, Literature review, Materials and Methods, Results and Discussion, Conclusions, List of References (109 positions), List of Publications (2), Tables (3) and Figures (60). Total 118 pages.

ABBREVIATIONS

AFM – atomic force microscopy; **ANI** – aniline; **BQ** – benzoquinone; **CPE** – constant phase element; **CV** – cyclic voltammetry; **E** – potential; **EIS** – electrochemical impedance spectroscopy; **ECP** – electrically conductive polymers; **EM** – emeraldine; **FTIR** – Fourier transformation InfraRed; **HQ** – hydroquinone; **H₂Q** – p-hydroquinone; **LEB** – leucoemaraldine; **RS** – Raman Spectroscopy; **SEM** – scanning electron microscopy; **PANI** – polyaniline; **PAP** – p-aminophenol; **PG** – pernigraniline; **QI** – benzoquinoneimine.

2. MATERIALS and METHODS

The materials, reagents, solvents and electrodes

Research solution was made from a "clean" and "pure for analysis" qualifying reagents. The solutions were made using $KHCO_3$, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ (Reachim, Russia) p. a.; $HClO_4$ (Fluka, Germany) purum p. a. 70%; H_2SO_4 (Penta, Czech Republic) purum p. a. 96%. Measurements were performed at room temperature (20 ± 2 °C).

Aniline experiment was distilled in two ways: 1) distilled in oil pump vacuum 60-65 °C; 2) distilled at 184-185 °C, in the order to remove impurities in solution. It was held at 4 °C in the dark glass container, because it splits the light. The reagent has been renewed every six months. Suitability for the task was assessed visually, distillation repeated emergence of yellowness.

Product of aniline solution by dissolving 0.5 M $HClO_4$ or 0.5 M H_2SO_4 acids required aniline milliliters (ζ = 1.04 g/ml) and diluting to the desired volume. The solution is used for a single measurement. If the series has been written for two days in a row, the same solution was used, stored at 4 °C.

All measurements, in except for titanium anodizing were carried out in a three – electrode system, which consists of working, auxiliary and comparative

electrodes. For different investigated systems were used several working electrodes: metallurgical Au (0.22 cm^2), pencil graphite (0.16 cm^2, Schneider, HB 0.5), titanium and electrochemically anodized titanium (2 cm^2). As an auxiliary electrode used a cylindrical – shaped platinum sheet electrode, reference electrode was used Ag/AgCl saturated KCl electrode EVL – 1M4 (Russia), the potential of the standard hydrogen electrode (according to the manufacturer's description) is ≈ 200 mV. Everywhere, unless otherwise indicated by the potential of this electrode.

Titanium anodizing was carried out in a two – electrode system with a total volume of 10 ml of electrolyte. Working electrode (anode) was used for 2 cm^2 titanium (99.9% purity) plate electrode and an auxiliary electrode (cathode) – the two plates of Cu (99.9% purity). This process has been used to carry power supply Б5 – 44 (USSR).

Electrode surface preparation

Electrode surfaces were cleaned mechanically or electrochemically, in dependence on the nature of the electrode.

Metallurgical Au in the first experiment was mechanically polished one with lime and washed with water. The lime particles were washed out from metal surface by potentially disposed hydrogen bubbles in amperostatic 5 mA electrolysis of the chosen acid solution for 5 minutes. Since hydrogen on Au, in the contrast to Pt does not oxidize spontaneously to H$^+$, to remove its final traces were held in 0.5 V potential for 2 min. In subsequent experiments abandoned the mechanical effect, since the initial ANI polymerization conditions are very sensitive to metal preparation, including roughness. Since mechanical polishing roughness failed to replicate the surface preparation was launched, the electrode immersed in dichromate (K$_2$Cr$_2$O$_7$ + conc. H$_2$SO$_4$ + distilled H$_2$O) solution overnight. Adsorbed chromium compounds on the surface were removed by holding it for 2 hours in water, which has been amended periodically. The surface was later carried out by electrolysis of cyclic acid (up to oxygen and hydrogen separation potential) until the selected voltamperogram coincided with the clean Au voltamperogram.

Ti electrode before anodizing and ANI layer formation was mechanically polished with diamond paste to obtain a smoother surface, and then in the ultrasonic bath rinsed with acetone and distilled water (after 360 s) to remove residues of diamond paste and distilled H$_2$O residues were dried drained with wipes.

Pencil graphite electrode for research was taken every time a new one. Additional surface preparation not needed.

Auxiliary electrodes used for Pt or Cu plates were polished before the experiment with Viennese lime and washed with water jet.

TiO$_2$ layer calculations

TiO$_2$ layer was formed electrochemically on titanium electrode in 0.5 M H$_2$SO$_4$ solution, while maintaining a certain period of time. Process time was calculated using the first and second laws of Faraday cumulative formula:

$$m = \frac{M \times I \times t}{n \times F} \qquad t = \frac{m \times n \times F}{M \times I}$$

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where *m* – mass of a compound released on the electrode (mass was calculated using the density (TiO_2), and volume (i. e., TiO_2 layer thickness); *M* – molar mass of the substance; *n* – the number of electrons involved in electrodynamics process; *F* – Faraday constant; *I* – current; *t* – electrolysis time.

Time of electrolysis was carried out in 18, 36, 180 and 360 s. Accordingly, 50, 100, 500 and 1000 nm thick layer of titanium dioxide resulted.

Experimental methods

Cyclic voltammetry (CV)

Current – voltage studies were carried out by µAUTOLAB (Type III) (EcoChem, Netherlands), multi – purpose device, enabling the use many of the electrochemical methods of investigation and to carry out of their data a mathematical – processing. Cyclic voltammetry curves were recorded using the appropriate potential range of experiments carried out (from - 0.2 to 2 V). Seeding rates were used: 20, 50, 70, 100, mV/s. The number of cycles depended on the electrochemical polymerization of ANI. Measurements were performed in a three electrode electrochemical cell. In all cases as the reference electrode was used Ag/AgCl electrode, as the auxiliary electrode – 32 cm² Pt cylinder. Working electrodes were used: Au – made from 0.5 mm wire gold infused into glass (0.22 cm²), Ti – plate electrode (2 cm²), pencil graphite electrode (0.16 cm²).

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy studies were carried out using µAUTOLAB (Type III) potenciostat. Electrochemical data analysis was carried out with "Zview" (Scribner Associates, JAV) program, the equivalent scheme for modeling the electrolyte resistance, a double electric layer and parallel to it on – screen, charge transfer resistance and diffusion impedance were used. EIS spectra were written in the frequency range from 0.1 to 12,000 Hz. Measurements were performed in a three electrode electrochemical cell. As the comparator Ag/AgCl electrode was used as the comparator and 32 cm² Pt cylinder as an auxiliary electrode. Working electrode was made of 0.5 mm wire gold infused into glass. The test electrode area is 0.22 cm². Electrochemical measurements were carried out at room temperature. A neutral $K_3[Fe(CN)_6]$ + $K_4[Fe(CN)_6]$ solution was used as the test of electrical properties.

Atomic Force Microscopy (AFM)

Titanium and electrochemically anodized TiO_2 electrode surface were analyzed with AFM system (Nanoscope III, USA). PANI synthesized material was used for visualization on atomic force microscopy system Dimension Icon (Bruker, USA). The surfaces were measured by contact and tapping mode, using the NP – S (k = 18 – 19 kHz) and FESP (k = 75 – 100 kHz) tips (Bruker, USA). Contact mode is when the tip contacts with the sample and the probe scans the surface of a lower magnification than 1 Å away, for this reason, there is a strong repulsive force, and also received the highest resolution compared to other AFM modes. PANI material dissolved in dist. H_2O was covered on atomically smooth V–4 quality mica (SPI

Supplies, USA) and incubated for 10 min at room temperature and then rinsed with water and dried in N_2 stream.

Fourier transformation InfraRed (FTIR)

FTIR measurements were performed on Perkin-Elmer spectrometer (Spectrum GX, USA). Spectrometer resolution is 4 cm^{-1}. In order to increase the signal/noise ratio was compounded 50 interferograms. Spectra were recorded using a compressed tablet. Recorded FTIR spectra of pure (without test substance) KBr tablets are concerned.

Preparation of tablets:

- ✓ It was taken about 1 mg of the test substance (PANI) and grind the spec. mill with 200 mg of KBr salt for about 30 seconds. To remove the larger crystals, and materials to mix together well.
- ✓ All placed in a clamp and extruded (10^5 N) for 10 – 15 min.

Raman Spectroscopy (RS)

Raman spectra were registered by LabRam HR800 spectrometer (Horiba Jobin Yvon, France), the placing of material (PANI) on the plate. Measurement conditions: excitation 633 nm wavelength laser, whose power at the sample was about 1 mW; cell – 600 lines/mm; lens is 10x; storage time – 400 s.

Scanning electron microscope (SEM)

Morphology study of pencil graphite, titanium and electrochemically anodized TiO_2 electrode surface were taken on Hitachi scanning electron microscope (TM – 3000).

3. RESULTS and DISCUSSION

Electrically conductive polymers and particularly their modified electrodes are one of the most exploratory fields of science around the world. In Vilnius University, Faculty of Chemistry, Physical Chemistry Department the first explorer of this area was prof. Gintaras Baltrūnas. The main aim of this work was to develop electrochemical PANI film on Au and Pt electrodes using cyclic voltammetry method and to examine the properties of the polymer by using electrochemical impedance method.

Because these metals are relatively expensive, so this work was an attempt to determine the optimal conditions for the formation of polyaniline layer on the titanium electrochemically anodized, titanium and pencil graphite electrodes. Also being studied $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ oxidation/reduction process on the Au electrode modified electrically conductive polymer – PANI.

3.1 Electrochemical formation of polyaniline on pencil graphite electrode

The electropolymerization of aniline on the pencil graphite electrode were recorded by cyclic voltammetry curves of 0.5 M H_2SO_4 and 0.5 M $HClO_4$ acids at a constant 50 mV/s the scan speed. The scan range was chosen -0.2 to 1.2 V range. As

can be seen from the results (Figure 1), sulfuric acid (curve 1) and perchloric acid (curve 2) plotted unobservable no voltammetry peak. This confirms that the cyclic time on the pencil graphite electrode does not undergo any oxidation/reduction processes.
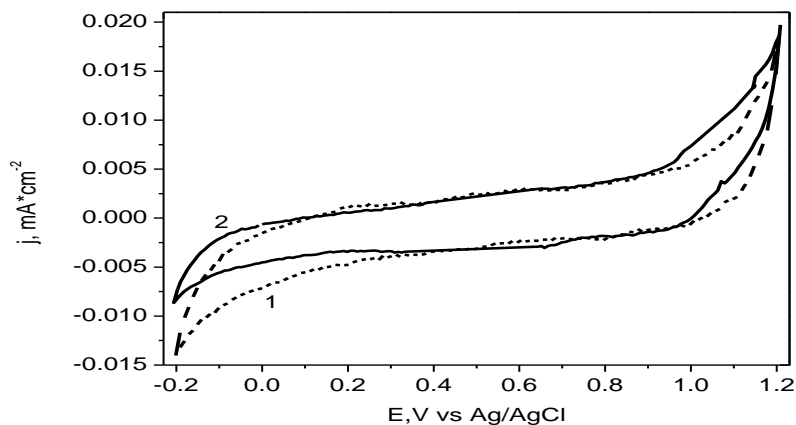

Figure 1. *Cyclic voltammograms recorded on pencil graphite electrodes in 0.5 M H_2SO_4 (curve 1) and 0.5 M $HClO_4$ (curve 2) without aniline at a scan rate of 50 mV/s.*

When appropriate potential limits were sedimented polymer coating of sulfuric and perchloric acid solutions containing 0.05 M aniline. Polymer formation was controlled by emerging anode and cathode current peaks. Visually noticeable thick enough layer of polyaniline in sulfuric acid formed after 7 – 10 cycles and perchloric acid after 15 – 20 cycles. Increasing the number of cycles observed in cyclic voltammetry current peak increases until the polymer formation and decay rates coincide. Figure 2 and 3 represent the cyclic voltammograms data of the aniline electropolymerization in time.
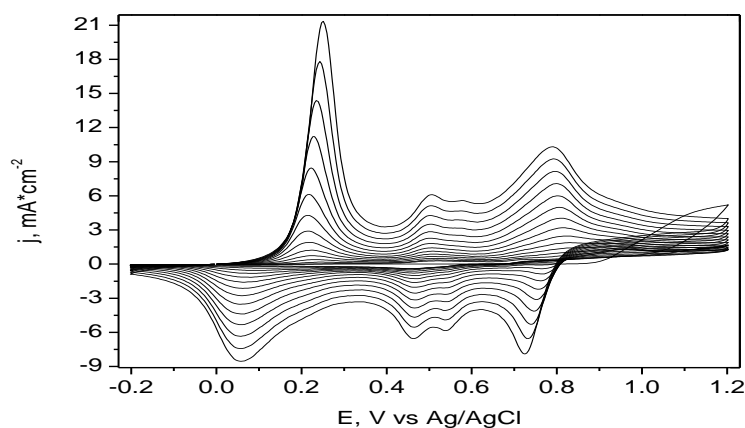
Figure 2. *Cyclic voltammograms recorded on pencil graphite electrode in a solution of 0.5 M H_2SO_4 and containing 0.05 M of aniline. The scan rate of 50 mV/s.*
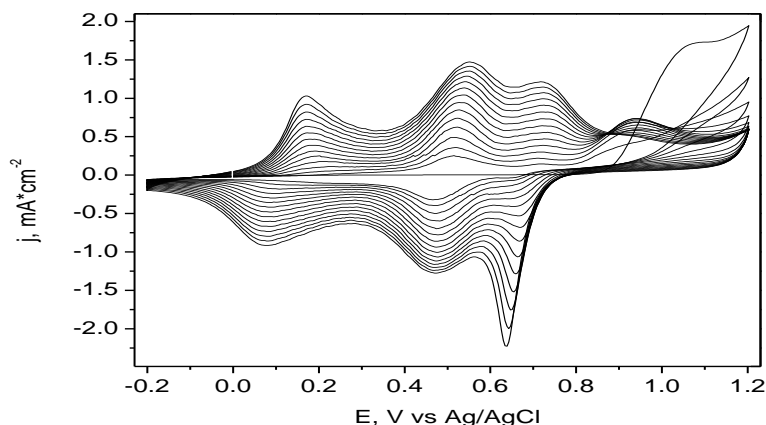
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Figure 3. *Cyclic voltammograms recorded on pencil graphite electrode in a solution of 0.5 M HClO$_4$ and containing 0.05 M of aniline. The scan rate of 50 mV/s.*

Cyclic voltammograms revealed a number of peaks that occur due to process complexity of the electrochemical oxidation of PANI. Peaks arising from anode side show that the polymer oxidation process takes place, and the cathode side of the reduction process is going on. With increasing number of cycles and current increases, as well as differences and polymerization curve shape, depending on the electrolyte used in the polymerization.

It is important to emphasize that different acids from the cyclic voltamperogram anodic current peaks are located differently, and their values, depend on the number of cycles. For sulfuric acid the highest observed peak in anode section is at 0.25 V with current density of 21 mA/cm^2. Meanwhile, observed maximum value of the current density for perchloric acid at the anode in 0.55 V is only 1.5 mA/cm^2.

Is well known that polymer oxidation is a complex process, in which not only the oxidation/reduction reactions are held together, but deprotonization reaction too, in which the proton is removed. The analysis of the results obtained on the pencil graphite electrode: the PANI layer, which is formed at the electrode potential less than 0.25 V is induced tight leucoemeraldine (LEB) form. When potential is sweeping from 0.25 to 0.75 V, the oxidation of PANI going to semi – conductive PANI oxidized forms – emeraldine (EM)[8]:
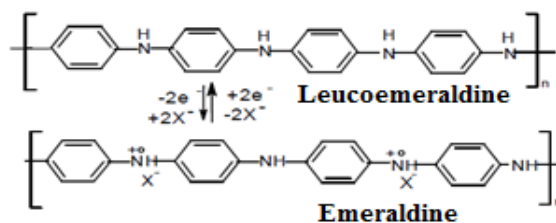

Emeraldine PANI structure is not a stable shape. After some adjustments to the chain it can exist as an emeraldine base or salt[8]:

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[8] Q. Qin, J. Tao, Y. Yang, Synthetic Metals 2010 (160):1167 – 1172

Emeraldine salt
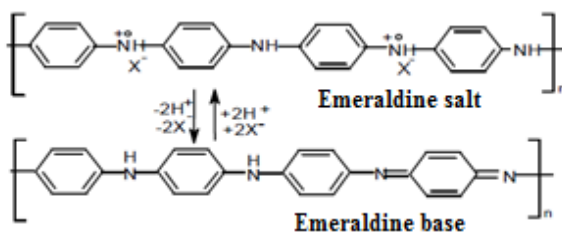
Emeraldine base

When potential values varies from 0.75 V to 1.2 V, emeraldine oxidized to form fully oxidized pernigraniline (PG) form, while at higher potential values chain cracking is performing[8]:

Emeraldine

Pernigraniline
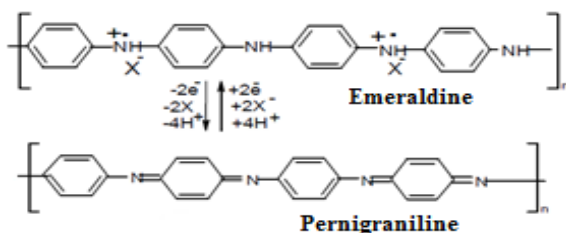
At 0.4 to 0.6 V potential the demanding polymerization of aniline takes place. The second oxidation peak of current is observed, which corresponds to the polymer degradation and by – products formation potential. These processes can be attributed to benzoquinone/hydroquinone (BQ/HQ) and p-aminophenol/benzoquinoneimine (PAP/QI) oxidation/reduction reactions. Electrochemical oxidation of aniline goes with H_2Q breakdown adsorption of the product (p-hydroquinone), which takes place in acidic solution. In general, the more developed is the surface, the more cationic salt is formed emeraldine EM^{+2} and easier adsorption of H_2Q. On the cover layer of PANI electrodes H_2Q oxidation reaction takes place in the same potential in the field, which produces a conductive emeraldine form, while undergoing this reaction[9].

$$H_2Q \leftrightarrow Q + 2H^+ + 2e^-$$

$$EM^{2+} + 2e^- \leftrightarrow LE$$

$$EM^{2+} + H_2Q \leftrightarrow LE + 2H^+ + Q$$
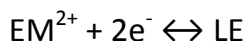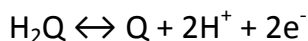
From the above equations it can be said that at one time are held not only emeraldine's shape transition to leucoemeraldine, but and other side reactions.

In order to verify the electrochemically formed PANI layer durability and adhesion to the electrode surface have been carried out experiments in 2 M H_2SO_4 solution. At the end, the electrode with molded PANI layer was transferred to a 2 M H_2SO_4 solution and cyclic voltammetry aid was recorded until the CV curve will coincide with the curve recorded on a graphite electrode in 0.5 M H_2SO_4 solution without aniline (Figure 1., Curve 1), until the polyaniline layer is washed away from the electrode surface and the solution will fall deposits form. The resulting PANI precipitate was filtered from the solution and analyzed by FT-IR (Figure 4) and Raman spectroscopy (Figure 5).

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[9] Duic Lj., Grigic S., *Electrochimica Acta* 2001 (46):2795 – 2803

The resulting PANI materials FT-IR spectra (Figure 4) were recorded using the core IR spectral range – from 2.5 to 25 μm (from 4000 to 400 cm^{-1}). In examined spectrum the peak at 3433 cm^{-1} was observed, which is evidence of the vibrations of the N–H group, which are asymmetric valence vibrations. The absorption bands at 2940 and 2868 cm^{-1} in the spectrum is characterized by asymmetric C–H vibrations. This band area is not very informative, because the most common material is used for various C–H vibrations. They have the ability to interact with each other and bands overlap in this area by making blurred peaks. Polymer absorption bands at 1610 – 1590, 1600 – 1580, 1510 – 1490 cm^{-1} are characteristic for aromatic rings, and 1670 – 670 cm^{-1} vibrations of C–H single bond. 2000 – 1560 cm^{-1} valence vibrations of C = N double bond.
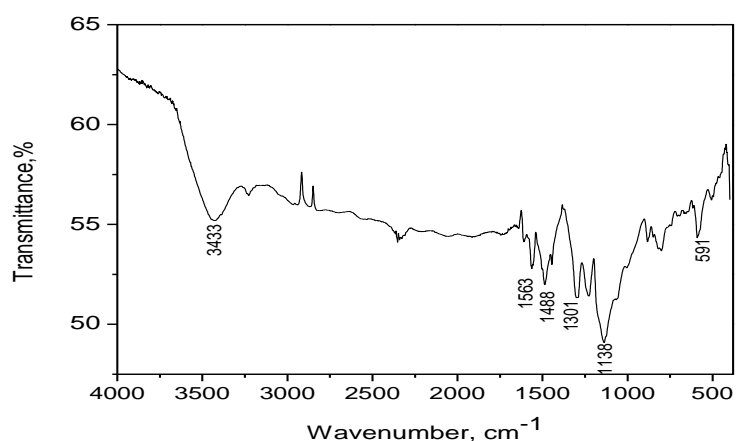

Figure 4. *FT – IR spectrum of synthesized polyaniline.*

The analysis of the resonance Raman spectra (Figure 5) shows that the intense band at 1162 cm^{-1} corresponds to planar deformation vibrations of the six – membered C-H communications ring. Six – membered ring stretching vibration appears at 1579 cm^{-1}, and a less pronounced band at 1617 cm^{-1} is related to the stretching vibration of the benzene ring. Vibrations at 1483 cm^{-1} attributed (C = N) vibration coupling quinone ring pair (according to Wilson aromatic ring systems). PANI vibrations in 1300 – 1400 cm^{-1} frequency range commonly associated with the C-N single and double bonds overlap. Both of these areas are at 1322 and 1374 cm^{-1} are clearly visible in Raman spectrum of PANI materials. According to the results, we can conclude that our material is synthesized PANI emeraldine shape.
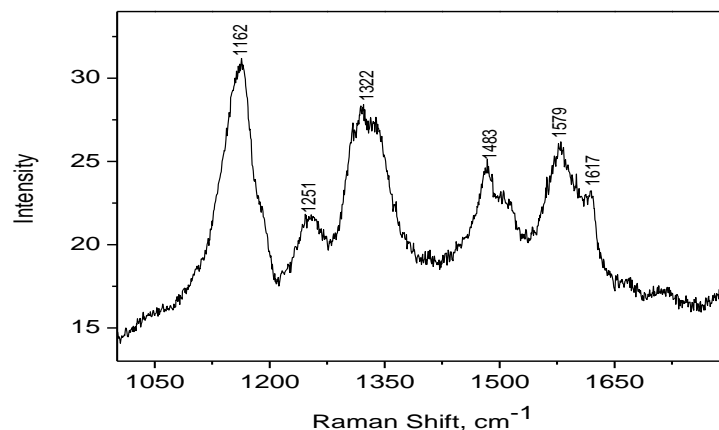
Figure 5. Raman spectrum of synthesized PANI in the 1000 – 1800 cm^{-1} frequency domain. Samples rekindle the 633 nm light. The pumping time is 400 s, and the power of 1 mW.

In order to ascertain whether the PANI layer is removed from the electrode surface was relatively SEM images obtained by scanning a clean pencil graphite electrode surface (Figure 6., a)) and the PANI layer coated pencil graphite electrode surfaces before and after cyclic 2 M H_2SO_4 solution (Figure 6, b) and c)). As we can see, the pencil graphite electrode surface is not smooth, but has a layered structure (Figure 6., a)). Electrochemically formed polyaniline layer is spread evenly across the electrode surface (Figure 6., b)). After 60 cycles, the scan of 2 M H_2SO_4 solution (Figure 6., c)) pencil graphite electrode surface becomes perfectly clean, but most of the PANI is removed from the electrode surface. Observed residue of the polymer film is possibly related to the electrode surface discontinuities that PANI adhesion of the electrode is enhanced.

a)   Non – coated PANI layer graphite electrode surface.
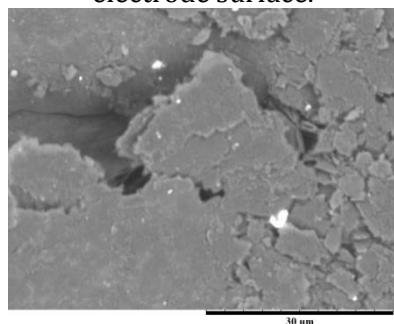
b)   Electrochemically coated with PANI coating graphite electrode surface.

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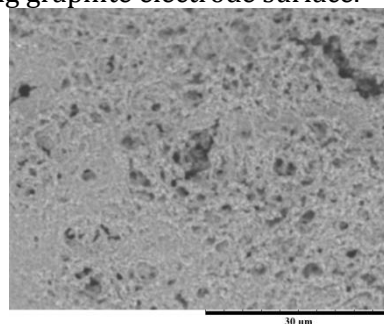
c) PANI – coated graphite electrode
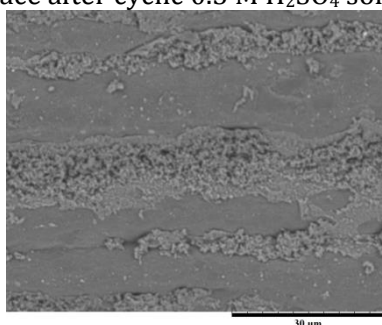surface after cyclic 0.5 M H$_2$SO$_4$ solution

Figure 6. *SEM images of pencil graphite electrodes.*

3.2 Electrochemical formation of polyaniline on Ti and electrochemically oxidized Ti electrodes

Two kinds of titanium electrodes have been used for electropolymerization of aniline. One of them relates to "naked" titanium. This kind was prepared by a simple polishing of electrode, without any subsequent electrochemical treatment. Because titanium metal shows a high chemical activity towards ambient oxygen and water, the "naked" electrode obviously contains a thin layer of titanium dioxide on its surface. However, this surface layer is rather of uncontrolled thickness. Therefore, a different kind of electrodes has been prepared by the controlled potentiostatic anodization of titanium in 0.5 M solution of sulfuric acid for definite time periods. Following this way, four different electrodes have been prepared, containing a surface-bound titanium dioxide layer with the thickness of 50, 100, 500, and 1000 nm, respectively. Figure 7 compares cyclic voltammograms for these four TiO$_2$ coated electrodes. No specific redox processes are observed within entire potential window used, ranging from −1.00 to 2.00 V, except for negligible increase of background current at anodic and cathodic ends of potential scan.
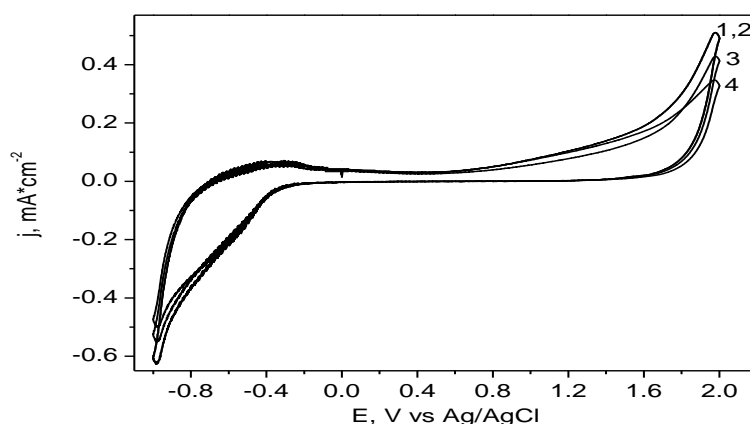

Figure 7. *Cyclic voltammograms recorded on electrochemicaly oxidized titanium electrodes in 0.5 M H2SO4 without aniline at a scan rate of 50 mV/s. Thickness of TiO2 layer (nm): 1, 2 – 50 and 100; 3 – 500; 4 – 1000.*

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The morphology of anodized titanium electrodes was characterized by atomic force microscopy. The images obtained (Figure 8) show no clear relationship between the thickness of TiO_2 layer and its roughness. In a common sense, the surface of anodized titanium becomes more homogeneous with increasing thickness of TiO_2 layer. By comparing the images of anodized and naked titanium surface, and taking into account the roughness parameters for naked titanium (R_{ms} = 4.1 nm) and anodized titanium (R_{ms} ranging from 1.7 to 3.9 nm), it could be concluded that the surface area diminishes to some extent upon anodization.
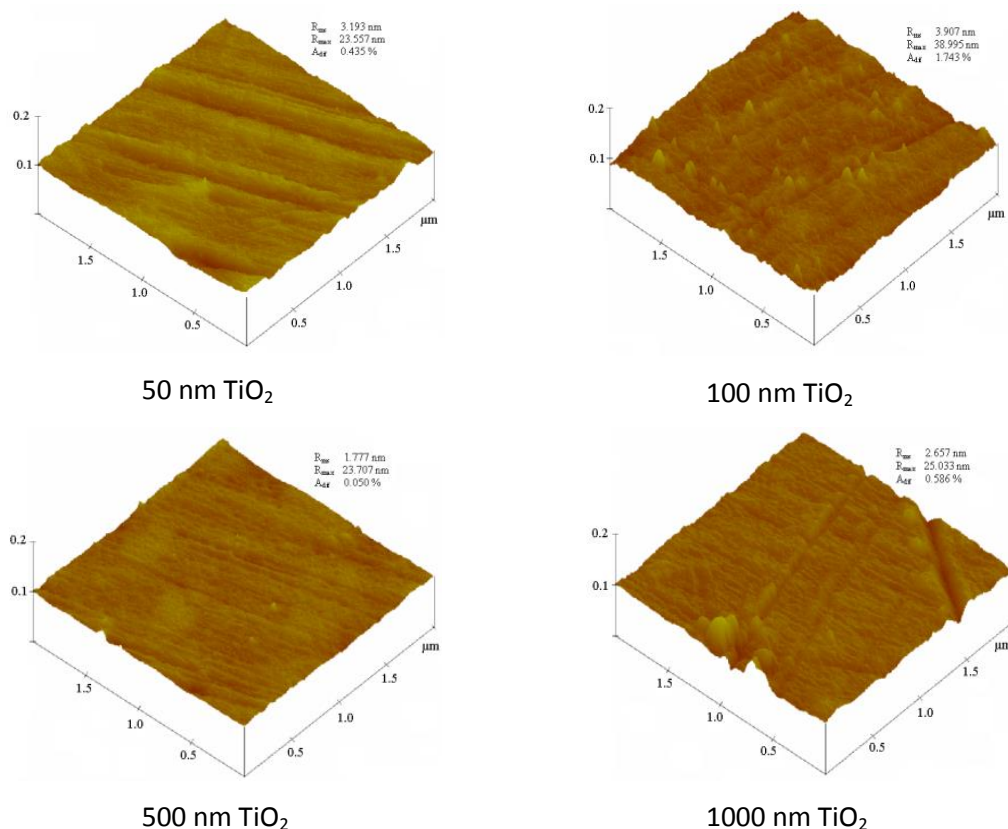

50 nm TiO_2 100 nm TiO_2

500 nm TiO_2 1000 nm TiO_2

Figure 8. *AFM images of anodized titanium surface containing TiO_2 layer of different thickness.*

An anodic potential scan, performed at a naked titanium electrode in an acidic solution containing aniline, as expected, results in a relatively high anodic current at electrode potentials exceeding 0.7 V, corresponding to electro oxidation of aniline. After a few repeating potential scans, cyclic voltammogram stabilizes in its shape. At the same time, the electrode surface appears to be covered with deeply blue layer of polyaniline at positive electrode potentials. Figure 9 shows stabilized cyclic voltaperograms for naked titanium electrode in a solution containing aniline, obtained after a few repeating potential scans at a scan rate of 50 mV/s. Well expressed anodic peak is seen located at 0.77 V, whereas no other anodic peaks are observed at lower potentials. As compared to the corresponding CVs, obtained at a platinum electrode, this peak appears to be shifted by ca. 0.4 V towards positive direction. Also, no second anodic peak around 0.8 V is observed, characteristic for polyaniline deposited at platinum or related inert electrodes. Noteworthy, the

anodic current does not drop to zero after passing this anodic peak, indicating electro oxidation to proceed even at higher potentials. In the back cathodic potential scan, two cathodic peaks are observed, located at 0.03 and -0.51 V (Figure 9). Again, as compared to platinum electrode (E_{pa} around 0.2 V), these peaks appear shifted to lower potentials. Surprisingly, the number and the position of these peaks depend on the potential scan rate applied. By decreasing the scan rate up to 20 mV/s, little changes are observed for anodic peak potential, however, the only cathodic peak (instead of two peaks) is observed around 0.55 V. Adversely, an increase of potential scan rate up to 100 mV/s results in a shift of anodic peak to lower potentials up to 0.50 V, whereas the two cathodic peaks appear at 0.19 and -0.26 V, viz. shifted to more positive potentials.
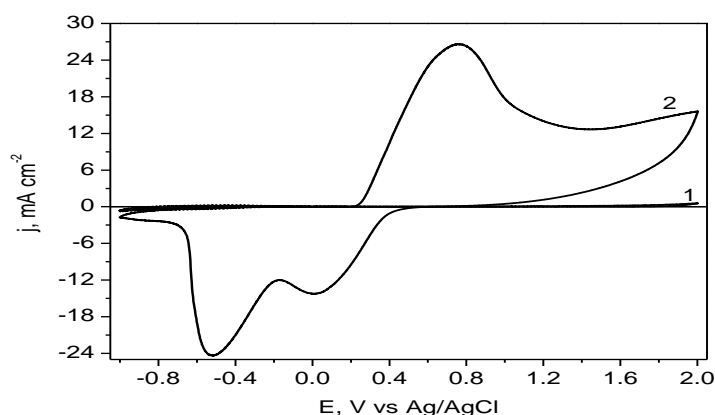

Figure 9. Multicycle voltammogram (as obtained in the 10th cyclic potential scan) of naked titanium electrode within potential scan limits of −1.00 to 2.00 V at a potential scan rate of 50 mV/s in a solution of 0.5 M of sulfuric acid (1), and in the same solution, containing additionally 0.05 M of aniline (2).

Related tendencies have been observed at anodized titanium electrodes. Figure 10 presents a set of CVs, obtained for anodized titanium electrodes, containing TiO_2 layer of different thickness. For the thinnest TiO_2 coating, an anodic peak at 0.68 V is observed for the lowest potential scan rate of 20 mV/s, followed by the second not well resolved anodic wave around 1.00 V. Thickening of TiO_2 layer results in development of two well separated anodic peaks at 0.54 and 0.90 V (for TiO_2 layer of maximum 1000 nm thickness). In a cathodic part of CVs, the only peak is observed, located around -0.48 V, and shifted to -0.33 V for the thickest TiO_2 coating (Figure 10). As for naked titanium electrode, an increase of potential scan rate results in a shift of anodic peak to lower potentials, and the development of two well separated cathodic peaks, subjected to variations in their position on the potential scale depending on the thickness of TiO_2 layer.

50 nm TiO$_2$

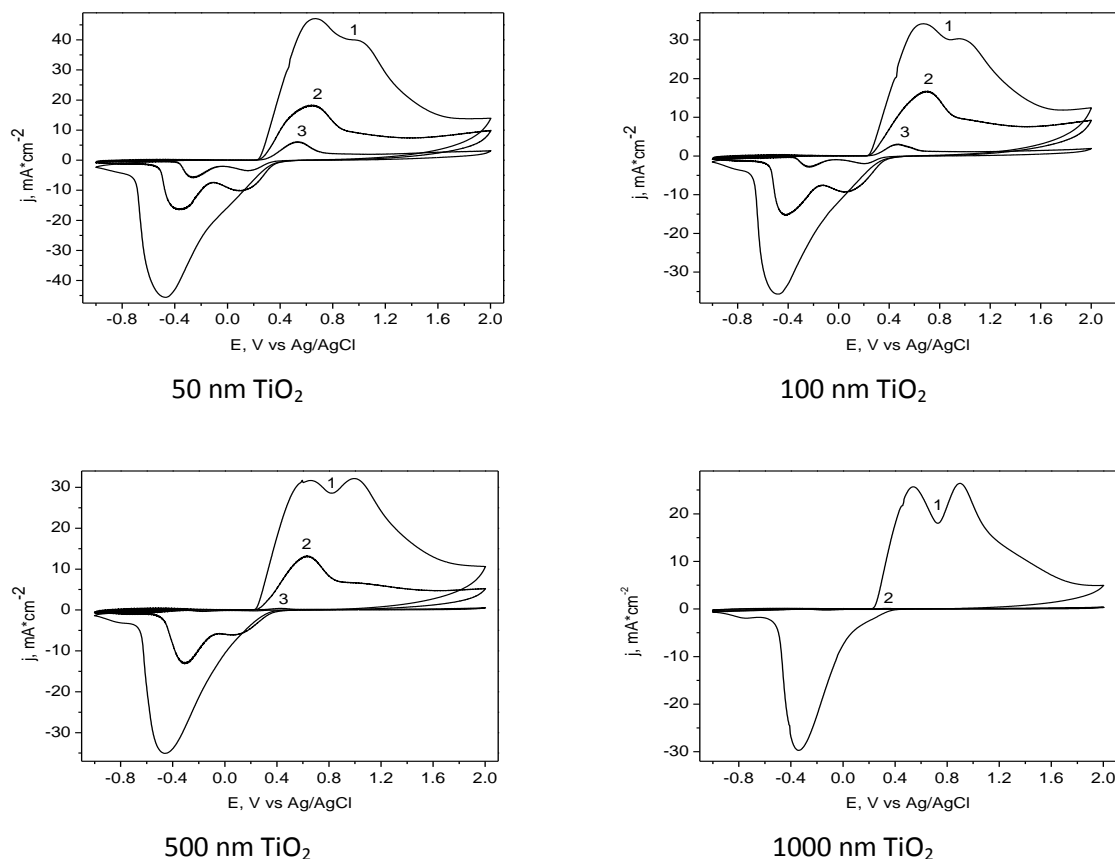100 nm TiO$_2$

500 nm TiO$_2$

1000 nm TiO$_2$

Figure 10. Multicycle voltammogram (as obtained in the 10th cyclic potential scan) of anodized titanium electrode, containing TiO$_2$ layer of different thickness ranging from 50 to 1000 nm (as indicated), obtained within potential scan limits of -1.00 to 2.00 V at a scan rate (mV/s): 1 – 20; 2 – 50; 3 – 100 in a solution of 0.5 M of sulfuric acid, containing 0.05 M of aniline.

The most striking observation, as it could be concluded from Figure 10, is the decrease of peak currents with increasing potential scan rate. This relates both to anodic and cathodic peaks (Figure 11). For thin layers of TiO$_2$ (50 or 100 nm), the peak current drops up to 10-15% of its initial value by changing the potential sweep rate from 20 to 100 mV/s, whereas for thick TiO$_2$ films (1000 nm) both peaks almost disappear by fastening of potential sweep from 20 to 50 or even more to 100 mV/s (Figure 11). The reasons for this unexpected effect remain unknown; however, it deserves a more detailed discussion.
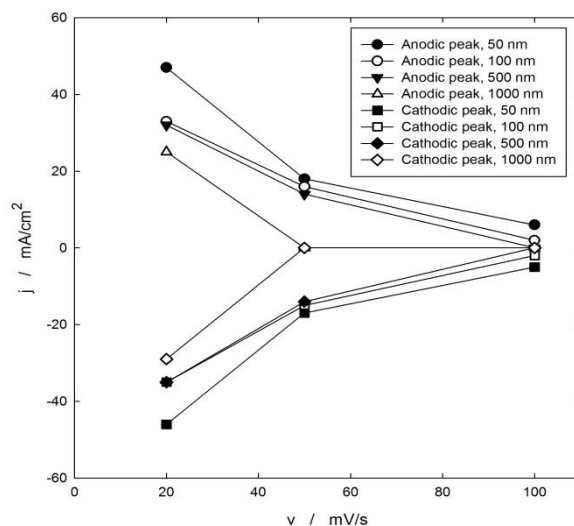
Figure 11. *Dependence of anodic and cathodic peak currents on the potential scan rate, as obtained for polyaniline-modified titanium electrodes containing TiO₂ layer of different thickness (as indicated).*

At least three reasons should be taken into account. First, somewhat related effect has been described earlier for polyaniline, electropolymerized at aluminum electrode[10]. Within a low range of potential sweep rate (*v*), not exceeding 50 mV/s a linear increase of anodic peak current with increasing *v* has been observed, as it could be expected for surface – bound redox couple, whereas a gradual decrease of peak current proceeded at *v* exceeding 50 mV/s. The authors attributed this behavior to the presence of passive (non – conducting) Al_2O_3 layer at aluminum surface that prevent fast electron transfer between the background electrode and polyaniline layer[10]. This reason seems to be very likely also for titanium electrode, covered with a semiconducting or insulating TiO_2 layer. However, following this model, it is difficult to understood, why the peak heights depend on the sweep rate, since the electric conductivity of a passive layer does not depend on it.

The second possible reason relates to possible electrocatalytic processes taking place at TiO_2 surface. The corresponding reaction scheme includes electrochemical oxidation of the reduced form of polyaniline, leucoemeraldine (LM) to its half-oxidized form emeraldine (EM):

LM + ne → EM,

and a catalytic regeneration of LM supported by the catalyst, e.g. by TiO_2 (Cat):

EM + Cat → LM.

Following this scheme, the ratio of catalytic to noncatalytic peak current is given by equation[11]:

$$\frac{i_{cat}}{i_p} = \frac{k^{1/2}[Cat]^{1/2}}{0.446a^{1/2}}$$

[10] Pournaghi – Azar M. H., B. Habibi, *Electrochimica Acta* 2007 (52):4222.
[11] Galus Z., Fundamentals of electrochemical analysis, Chapter 10, Halsted Press, 1976.

Where k denotes the rate constant for catalytic reaction, [Cat] – an initial concentration of catalyst, and a is a function of potential sweep rate (v):

$$a = \frac{nFv}{RT}$$

Although this approximation, derived for the case of a homogeneous catalytic reaction, cannot be directly applied for the system studied, it is seen that the ratio of catalytic to noncatalytic peak current, and thus the height of anodic peak should diminish with increasing v.

The third possible reason relates to specific nature of redox transformation of polyaniline. Electrooxidation of LM form of polyaniline in an acidic solution, as it is common accepted, involves the doping of polymer film by solution anions, most likely by sulfate anions. Because of a porous structure of TiO_2 layer, the diffusion of solution anions to polyaniline, contained within the pores, appears to be restricted. Therefore, the anions cannot penetrate into polyaniline film during a short time of anodic potential scan, performed at a high v. Adversely, slow potential scan facilitates anion transport, and higher peak currents are observed.

3.3 PANI layer on electrochemical system $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$

Polyaniline layer on the surface of the Au electrode was formed in 0.5 M $HClO_4$ acid and 0.05 M aniline solution by cyclic spreading electrode at the potential of 0.0 V to 1.05 V range, the scan speed of 50 mV/s. These parameters were selected according to G. Batrūnas and his group's carried out the experiments on the Au electrode surface[12]. Perchloric acid was chosen because the electrochemical polymerization of aniline in it produces a more compact and tight – fitting PANI film at the electrode surface and this is confirmed by the results obtained on the pencil graphite electrode.

Using cyclic voltammetry method was tested at least qualitatively explore the emerging influence of polyaniline film on electrochemical systems $[Fe(CN)_6]^{-3}/[Fe(CN)6]^{-4}$ oxidation/reduction rate, depending on the electrical double and assessing the stability of the resulting film. Mostly interesting were Au surfaces with different polyaniline layer thicknesses, so for research has been selected six different electropolymerization series: 1 – 2 cycles; 2 – 7 cycles, 3 – 17, 4 – 27, 5 – 37, 6 – 47 potential replacement cycles. Au electrode modified with PANI layer studies have been carried out ready for transfer to a neutral electrode $K_3[Fe(CN)_6]$ + $K_4[Fe(CN)_6]$ solution. As is known from the literature, a neutral medium of polyaniline becomes insulator, so the iron complexes in the oxidation/reduction of the polymer takes place only on non – coated gold surface. Cyclically changing the electrode potential, the current density on the polyaniline coated electrodes are smaller than in the clean Au electrode case. Such dependency example (6 series) made is represented in Figure 12.

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[12] Baltrūnas G., Valiūnienė A., Vienožinskis J., Gaidamauskas E., Jankauskas T., *Journal of Applied Electrochemistry* 2008 (38):1519 – 1526
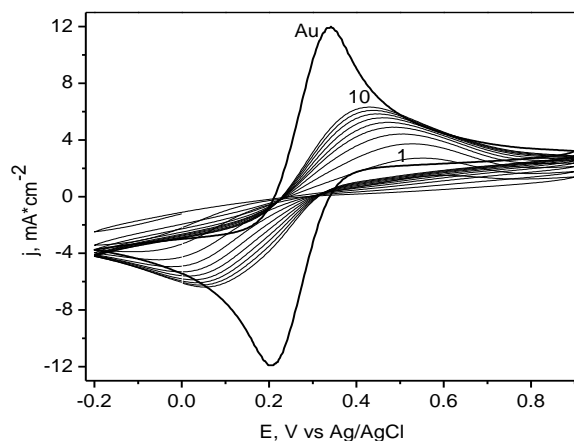
Figure 12. *Cyclic voltammograms dependence on the electrically impermeable coated with polyaniline (6 series) Au electrode. Solution composition: 0.04 M $K_3[Fe(CN)_6]$, 0.04 M $K_4[Fe(CN)_6]$, 0.5 M $KHCO_3$. Thickened line - polymer coated Au surfaces. CV presented in ascending order from 1 to 10. Potential scan rates of 0.1 V/s.*

As can be seen from the cyclic voltammetric dependences, the each subsequent cycle flows by increasing current. As the total amount of polyaniline electrode surface does not change, it means that the potential varies cyclically changing the structure of the film. Current growth in a declining degree of blocking the electrode surface, i.e. the start of a fairly densely adherent to the surface membrane (Figure 12, curve 1), then is roughened. In the case of polyaniline uncoated Au surface the current density is reached, because after 10 – 20 cycles of voltage – current dependence ceases to change. Upon termination of cyclic potential change within a few hours recovering the initial state of the surface – again, can replicate the first curve. This once again proves that the experiment polyaniline remained stable.

The current increase can occur when there is a solution of the polymer doping anions. This process occurs when the PANI oxidation due to the generation of positive ions to compensate the polymer chain from the solution into the polymer matrix, the negative ions are inserted.
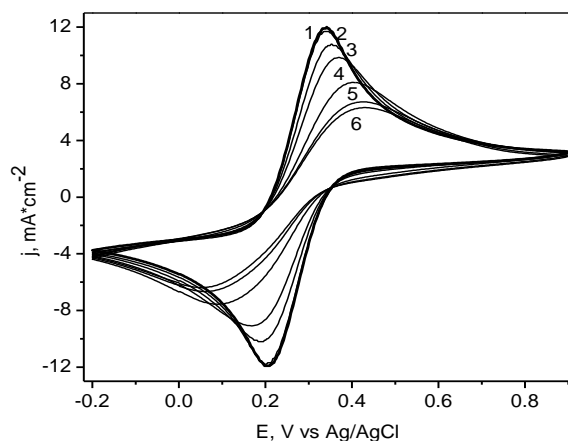

Figure 13. *Cyclic voltammograms dependence on the polyaniline – coated Au electrode. The digits to the curves indicate electropolymerization serial number.*

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Figure 13 provides details of all six series electropolymerization and polyaniline coated Au electrode voltage-current tenth cycle of addiction. The results show that the 1 – series electropolymerization curves coincide within the error range of the polyaniline coated on the Au electrode current – voltage dependence, and all other current densities consistently declining. This shows that increasing the amount of polymer on the surface of the electrode, the film is decreasing its defects (pores).

For quantification of polyaniline electrode surface blocking parameter (Θ and a) in the cyclic voltammetry method is not convenient, so for further investigation, we used the EIS method. After each in Figure 13 represented the cyclic voltage – current dependence detection, the electrode potential variation was stopped when E = 0.257 V $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ steady potential of our solution. After waiting for 30 seconds was measured impedance spectrum of 0.1 – 12,000 Hz field distribution of log 120 alternating current frequency values.
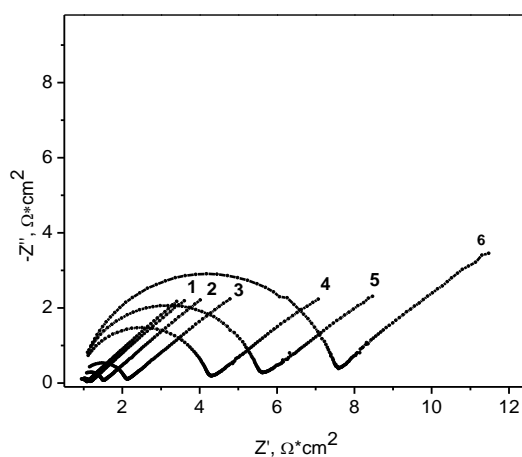

Figure 14. *Electrochemical impedance spectra to determine the polyaniline – coated Au electrode. The digits to the curves indicate Electropolymerization serial number. Solution composition: 0.04 M $K_3[Fe(CN)_6]$, 0.04 M $K_4[Fe(CN)_6]$, 0.5 M $KHCO_3$.*

Experimentally determine the electrochemical impedance spectra (Figure 14). Were analyzed using the model shown in equivalent diagram (Figure 15).
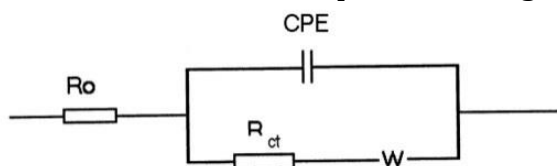

Figure 15. *R_0 – uncompensated solution resistance; CPE – constant phase element; R_{ct} – charge transfer resistance; W - Warburg (diffusion) impedance.*

The calculated electrochemical impedance Equivalent Circuit parameters shows that the surface of the inefficiency relatively little distortion of electric double layer capacitance physical meaning: in all cases, n> 0.9. The second mathematical impedance spectra processing stage was experimentally set Z 'and Z "frequency dependencies subtract R_0 and C_D (Table 1) contributions.

Table 1

	Au	1	2	3	4	5	6
R_0, Ω	0.85	0.90	0.90	0.92	0.88	0.87	0.90
C_D, µF/cm^2	65.3	55.6	32.9	22.3	14.8	13.4	10.5
n	1.0	1.0	1.0	0.97	0.95	0.94	0.92
R_{ct}, Ω cm^2	0.214	0.241	0.557	1.11	3.15	4.47	6.52
1-Θ	1.0	0.89	0.39	0.19	0.068	0.048	0.033

The calculated electrochemical impedance equivalent circuit parameters shows that the surface of the inefficiency relatively little distortion of electric double layer capacitance physical meaning: in all cases, n > 0.9. From the obtained data were calculated for the remaining parameters of polyaniline films: bare polymer film islets average radius (*a*) and the average distance between islands (*d*). Calculation results are presented in Table 2.

Table 2

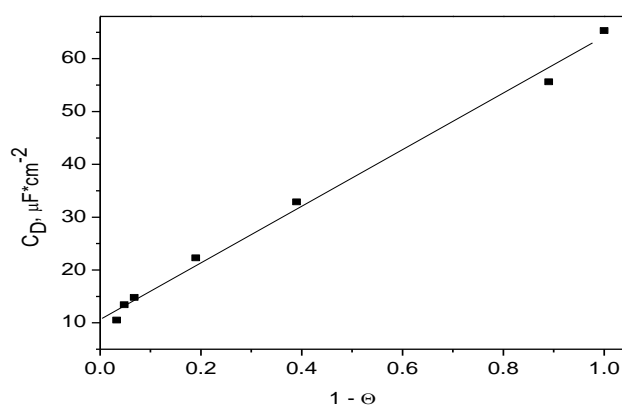|	Au	1	2	3	4	5	6
Θ	0	0.11	0.61	0.81	0.932	0.952	0.967
a, nm	-	-	14.7	25.3	85.5	100	105
d, nm	-	-	47.5	115	656	922	1160

Figure 16. *The test electrode electrical double layer capacitance on the Au surface coating polyaniline degree.*

Capacity varies linearly (Figure 16) of clean gold (C_D = 65 µF/cm^2) and entirely covered with polyaniline (C_D = 10 µF/cm^2) surface. A linear relationship

was found, confirm that the electrochemical impedance spectra analysis of the choice of the model (equivalent circuit), and the calculation of the parameters meets the requirements of reality.

CONCLUSIONS

- The electrochemical polymerization of aniline on pencil graphite electrode in sulfuric acid and perchloric acid, obtains coating is a semi oxidized form of PANI - emeraldine.
- Polyaniline material as precipitate forms was precipitated in 2 M H_2SO_4 solution by cyclic voltammetry method on modified with PANI layer pencil graphite electrode. AFM data showed that the PANI deposited material is rod – shaped, with a height ranging from 50 to 60 nm and lengths – from 30 to 100 nm.
- Electrochemical polymerization of aniline can be deposited on titanium and electrochemically anodized titanium electrodes surface, despite the fact that the scan interval is significantly higher, than of the pencil graphite or inert electrodes. It was able to get PANI coating by using H_2SO_4 solution.
- Electrochemically deposited PANI layer on the Ti and TiO_2 electrodes is blue in color which suggests the being of fully oxidized form of PANI – pernigraniline.
- The higher the TiO_2 layer thickness, the electrochemical polymerization of aniline is harder.
- Cyclically changing the electrode potential of changing the structure of the polymer film, this terminated the scan within a few hours of recovery.
- With the increasing amount of formed polyaniline on the gold surface from 0.056 to 0.46 $nmol/cm^2$, the degree of surface coverage by the polymer increases from 11 to 96.7%. Average active (bare polymer) islet radius varies from $\sim$ 10 to $\sim$ 100 nm, while the average distance between them, from $\sim$ 0.05 to 1.1 μm. Electric double layer capacity of the neutral medium decreases linearly from 65 (Θ = 0) to 10 (Θ = 1) $\mu F/cm^2$.

List of papers

1. **B. Rakovska**, A. Valiūnienė, A. Malinauskas, V. Kubilius, R. Valiūnas. Electrochemical formation of polyaniline on Ti and electrochemically oxidized Ti electrodes. Chemija. 2012:Vol.23:No.1:12-17

2. J. Vienožinskis, **B. Rakovska**, R. Unsys, G. Baltrūnas. Polianilino plėvelės struktūros kitimai aukso elektrodo paviršiuje. Cheminė Technologija. 2007: (3):26-30;

Conference materials/abstracts

1. **B. Rakovska**, A. Malinauskas, A. Valiūnienė, H. Cesiulis. Electrochemical formation of polyaniline on Ti and electrochemically oxidized Ti electrodes.220th ECS Meeting & Electrochemical Energy Summit in Boston, Massachusetts, USA, October 9-14 (2011).

2. **B. Rakovska**, A. Malinauskas, A. Valiūnienė. The electrochemical polymerization of aniline on titanium and titanium dioxide coatings. 10-oji Lietuvos Chemikų tarptautinė konferencija "Chemija 2011"; Vilnius, Lithuania, October 14-15 (2011)

3. **B. Rakovska**, G. Baltrūnas. Polianilino plėvelės stabilumo kitimai Au elektrodo paviršiuje. Conference "Chemistry and Technology of Inorganic Compounds". Kaunas, Lithuania, April 22, (2009) 55-56;

4. J. Vienožinskis, **B. Rakovska**, R. Unsys, G. Baltrūnas. *„Polianilino plėvelės struktūros kitimai aukso elektrodo paviršiuje".* Conference "Chemistry and Technology of Inorganic Compounds". Kaunas, Lithuania, April 21-22, (2007) 78–80;

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ANILINO ELEKTROCHEMINĖS POLIMERIZACIJOS TYRIMAS ANT ĮVAIRIŲ ELEKTRODŲ

REZIUMĖ

Darbo tikslas – parinkti optimalias sąlygas polianilino (PANI) sluoksnių formavimuisi ant pieštukinio grafito, titano ir elektrochemiškai anoduoto titano elektrodų, naudojant ciklinės voltamperometrijos metodą bei ištirti elektrochemiškai susintetintų PANI dangų savybes. Ištirti $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ oksidacijos/redukcijos procesą ant Au elektrodo, modifikuoto PANI.

Nustatyta, jog anilino elektrocheminė polimerizacija ant įvairių elektrodų vyksta skirtingai. Priklausomai nuo darbinio elektrodo prigimties, taip pat nuo monomero bei elektrolito koncentracijos, gaunamos dangos gali būti skirtingos struktūros ir pasižymėti skirtingomis savybėmis. Vykdant anilino elektropolimerizaciją ant pieštukinio grafito, gaunama danga yra pusiau oksiduota PANI forma, t.y. emeraldinas – laidi elektros srovei medžiaga. Tuo tarpu, naudojant Ti arba elektrochemiškai anoduotą titaną gaunama danga yra visiškai oksiduota PANI forma, t.y. pernigranilinas – elektros srovei nelaidi medžiaga. $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ redokso procesas ant Au elektrodo, modifikuoto PANI, buvo tirtas naudojant elektrocheminio impedanso spektroskopijos metodą.

Šie tyrimų rezultatai leis spręsti apie tolimesnį tirtų elektrodų panaudojimą elektrai laidžių polimerų sintezės srityje.

Darbo išvados:

1. Naudojant ciklines voltamperometrijos metodą, polianilino medžiaga buvo nusodinta 2 M H_2SO_4 tirpale nuosėdų pavidalų, prieš tai pieštukinio grafito elektrodą modifikavus PANI sluoksnių. AJM tyrimai parodė, kad nusodinta PANI medžiaga yra lazdelės formos, kurios aukštis svyruoja nuo 50 iki 60 nm, o ilgys – nuo 30 iki 100 nm.

2. Anilino elektrocheminė polimerizacija gali vykti ant titano ir elektrochemiškai anoduoto titano elektrodų paviršiaus, nežiūrint į tai, kad potencialo skleidimo intervalas yra žymiai didesnis, negu ant pieštukinio grafito arba inertinių elektrodų. PANI dangą pavyko gauti naudojant H2SO4 tirpalą.

3. Kuo didesnis TiO_2 sluoksnio storis, tuo anilino elektrocheminė polimerizacija vyksta sunkiau.

4. Cikliškai keičiant elektrodo potencialą keičiasi polimero plėvelės struktūra, kuri nutraukus potencialo skleidimą per kelias valandas atsistato.

5. Didėjant susidariusio polianilino kiekiui aukso paviršiuje nuo 0,056 iki 0,46 $nmol/cm^2$, paviršiaus padengimo polimeru laipsnis didėja nuo 11 iki 96,7 %. Vidutinis aktyvių (nepadengtų polimeru) salelių spindulys kinta nuo $\sim$10 nm iki $\sim$100 nm, o vidutinis atstumas tarp jų: nuo $\sim$0,05 iki 1,1 µm. Dvigubojo elektros sluoksnio talpa neutralioje terpėje tiesiškai mažėja nuo 65 ($\Theta = 0$) iki 10 ($\Theta = 1$) $\mu F/cm^2$.