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CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY  
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**STUDIES OF CONDUCTING POLYMER- MODIFIED ELECTRODES AND  
THEIR APPLICATION FOR ELECTROANALYSIS**

Summary of Doctoral dissertation  
Physical Sciences, Chemistry (03 P)

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VILNIAUS UNIVERSITETAS  
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO  
CHEMIJOS INSTITUTAS

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**ELEKTRODŲ, MODIFIKUOTŲ LAIDŽIAIS POLIMERAIS, TYRIMAS  
IR TAIKYMAS ELEKTROANALIZĖS TIKSLAMS**

Daktaro disertacijos santrauka  
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## INTRODUCTION

Polyaniline-modified electrodes are known to catalyze electrochemical redox processes of selected inorganic and organic species [1]. The lowering of an anodic oxidation potential for some species due to electrocatalytic action of polyaniline enables one to use modified electrodes for amperometric detection of these species.

One of the important analytes that can be electrocatalytically oxidized at polyaniline electrodes is ascorbic acid (vitamin C). Electrocatalytic oxidation of ascorbic acid at polyaniline-modified electrodes has been studied with the use of many electrochemical techniques. A significant problem arises concerning the use of polyaniline-modified electrodes for electroanalytical purposes, particularly for ascorbate assay. Most analyses of biologically related species must be provided in nearly neutral solutions. At pH value exceeding 4.0, polyaniline presents in its non-conducting form, and no electrocatalytic processes could be expected to take place at electrodes, covered with this insulating form of polyaniline, especially in nearly pH-neutral solutions, where most of assays for ascorbate are provided. Despite of this assumption, many papers published during the last decade demonstrate the possibility for the successful application of polyaniline modified electrodes for amperometric assay of ascorbic acid, even in nearly pH-neutral buffered solutions. The present study, however, addresses the problem of deeper understanding for the function of polyaniline as an electrocatalyst for ascorbate oxidation in pH-neutral solutions.

We used electrode modified with a structural analogue of polyaniline poly(*N*-methylaniline). Despite of closely related structures of both polymers, poly(*N*-methylaniline) differs in that it shows good electrochemical activity even in pH-neutral and slightly alkaline media [2]. Thus, ‘normal-shaped’ current transients could be expected for electrodes, modified with this conducting polymer, in contrast to sigmoid transient, characteristic for polyaniline coated electrode, confirming the autocatalytic mechanism proposed for polyaniline-based sensors.

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1. A. Malinauskas, Electrocatalysis at conducting polymers, *Synth. Met.* 107 (1999) 75–83.  
2. R. Sivakumar, R. Saraswathi, *Synth. Met.* 138 (2003) 381.

### **The goal of the work:**

The aim of this work - to investigate patterns of electrochemical oxidation of ascorbic acid on the polyaniline and poly(N-methylaniline) modified electrodes, in order to develop sensitive sensors for ascorbate.

### **The tasks of the work:**

1. To modify Pt electrodes layers of PANI and PNMA, using a variety of electrochemical coating techniques and conditions, and monomer concentrations.
2. To characterize obtained polymer coatings (electrochemical activity and electrochemical behavior in sulfuric acid and buffer solutions).
3. To use modified electrodes for oxidation of ascorbic acid in buffer solutions.
4. To investigate the possibility of using PANI and PNMA modified electrodes as amperometric ascorbate sensors.

### **Scientific novelty and practical value of the work.**

Scientific novelty: a detailed study of various factors affecting aniline and N-methylaniline electrochemical polymerization and the resulting properties of PANI and PNMA layers was carried out for this purpose. Comparative study of modified electrodes in solutions of different acidity was performed and it was shown that PNMA had a better redox activity in slightly acidic and neutral solutions compared to polyaniline. The nature of amperometric response of modified electrodes to ascorbate was investigated and autocatalytic mechanism of ascorbate electrooxidation on PANI modified electrode was suggested. Using PANI and PNMA modified electrodes, prototypes of amperometric ascorbate sensors have been developed and their comparative studies were carried out.

**Approbation of the dissertation.** Three publications have been published in the international scientific journals on the theme of dissertation. The research results have been presented at 2 Lithuanian national and 6 international scientific conferences.

# 1. EXPERIMENTAL

## 1.1. Reagents

Aniline and *N*-methylaniline were obtained from *Aldrich* and have been distilled prior to use. All other chemicals were of analytical or reagent grade, and were used as received.

## 1.2. Methods

### 1.2.1. Electrochemical study on Pt electrode

PI-50-1 model potentiostat, arranged with PR-8 model programmer and a custom built A/D converter with appropriate software for data acquisition has been used throughout the work. The experiments have been done at ambient temperature in a one-compartment electrochemical cell. Platinum wire electrode, 0.5 mm diameter and 5 mm length, and platinum foil electrode, 1.5 cm<sup>2</sup> in area, were used as a working and auxiliary electrodes, respectively. A saturated Ag/AgCl reference electrode has been used as a reference electrode. All potential values reported refer to this reference electrode. Electropolymerization of *N*-methylaniline has been performed in a solution of 0.5 M of sulfuric acid containing 0.1 M of *N*-methylaniline by applying a controlled potential of 0.8 V for definite time periods ranging from 30 to 300 s. After that, the modified electrode has been rinsed with water. By studying the electrode response to ascorbate, the electrolyte has been continuously stirred with magnetic stirrer, and aliquots of ascorbate solution have been added. 0.01 M phosphate buffer solutions with pH ranging from 5.5 to 7.2, containing 0.1 M of potassium chloride, have been used in these experiments. For comparison, polyaniline modified electrode has been prepared in a similar way using aniline instead of *N*-methylaniline as a monomer present in electropolymerization solution.

### 1.2.2. Morphology of PANI and PNMA

The morphology of PANI was characterized by scanning electron microscopy (SEM, JEOL JSM-6700 F). The electrochemical performance of PANI/Pt and PNMA/Pt was characterized by 1.2.1 section. The electrolytes used in the characterization of PANI/Pt were degassed with purified nitrogen gas at least 20 min before use.

### 1.2.3 Hydrodynamic voltammetric analysis on carbon electrode

A BASi-Epsilon potentiostat and BASi RDE-2 rotating disk electrode (both of Bioanalytical Systems Inc., West Lafayette, IN, USA) have been used in experiments. Electrochemical experiments were performed in a single-compartment 20 ml in volume three-electrode glass cell, containing glassy carbon rotating disk working electrode, 3 mm in diameter, press-fitted into a Teflon holder, a custom-built glassy carbon rod (Sigradur K, HTW, Germany) counter electrode, 3 mm in diameter and 10 mm in length, and RE-5B (Bioanalytical Systems Inc.) Ag/AgCl reference electrode, filled with 3 M NaCl solution. All potentials are quoted versus this reference electrode. The potential of glassy carbon electrode (GCE) RDE ( $E$ ) was scanned slowly ( $0.005 \text{ V s}^{-1}$ ) during rotation.

## 2. RESULTS AND DISCUSSION

### 2. 1. Receipt of polymer layers

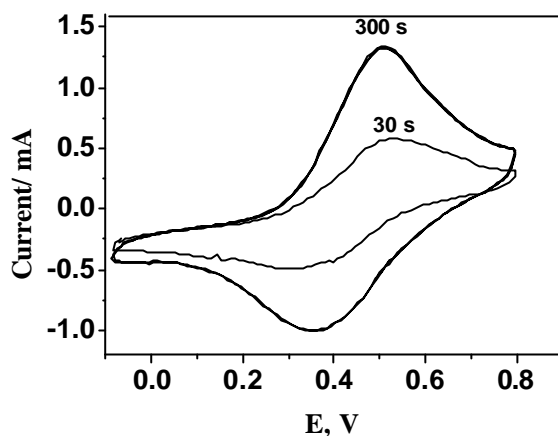
In the present work, we used electrolysis at a controlled potential, provided in an acidic solution containing *N*-methylaniline and aniline. In order to reduce the degradation processes [3] which occur simultaneously with electropolymerization [4], The polymerization for PNMA has been done at a relatively low potential of 0.8 V. Fig. 1 shows typical cyclic voltammograms for PNMA and PANI modified electrodes. The CVs obtained show clear anodic and cathodic peaks, whose shape and position on the potential scale vary to a little extent with varying the duration of electropolymerization. For PNMA films obtained by electropolymerization for 300 s, anodic and cathodic peaks with the midpoint potential  $E_m$  of 0.43 V and peak separation  $\Delta E_p$  of 0.16 V are observed (Fig. 1). The values obtained are close related to those, reported elsewhere [3]. The amount of PNMA deposited onto electrode depends on the duration of electropolymerization. It could be calculated from the data presented in Fig. 1, that PNMA films with the redox capacity of 6.6 and 44  $\text{mC cm}^{-2}$  are obtained by providing the electropolymerization for 30 and 300 s, respectively.

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3. R. Mažeikienė, G. Niaura, A. Malinauskas, J. Solid State Electrochem. 11(2007) 923.

4. R. Mažeikienė, A. Malinauskas, Synth. Met. 123 (2001) 349.



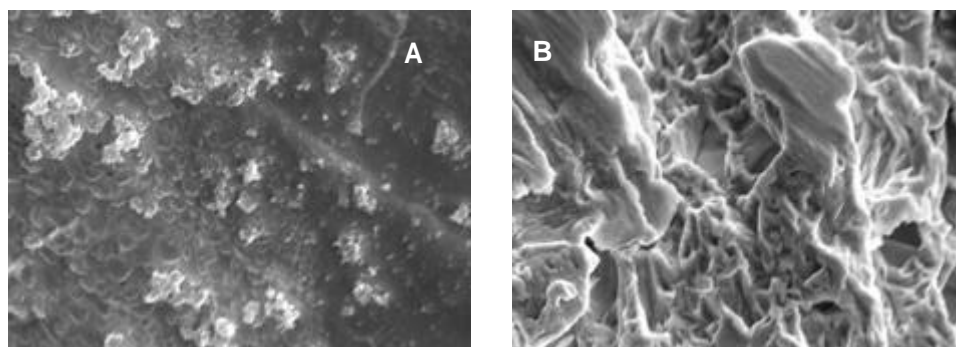


**Fig. 1.** Multicycle voltammograms, obtained in a solution of 0.5 M sulfuric acid at potential scan rate of  $0.1 \text{ V s}^{-1}$  for electrode, modified in a solution containing 0.5 M of sulfuric acid and 0.1 M of N-methylaniline by applying controlled potential of 0.8 V for 30 or 300 s (as indicated).

By varying the polymerization time within these limits, intermediate redox capacity of resulting PNMA films is obtained, varying between the given limits, although no linear dependence of redox capacity on electropolymerization time has been observed. It is an open question whether an entire surface of electrode appears to be uniformly covered by the polymer film under the conditions used. For the thinnest films with the lowest redox capacity it is very probable that the polymer builds separate islands, whereas thick films with a high redox capacity present most probably a uniform coating of the electrode surface.

### 2. 1. 2. Morphology of PANI and PNMA

The morphology of PANI and PNMA deposited on Pt substrate was characterized by SEM. The results of the research are presented here (Fig. 2).



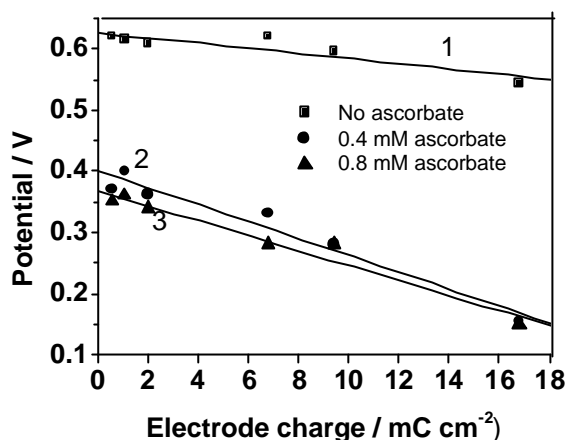
**Fig. 2.** Polymer films obtained at Pt electrodes in 0.1 M monomer (A- ANI, B-NMA) and 0.5 M sulphuric acid solutions.

Polymer morphology studies have shown, that under the potentiodynamic conditions complete coverage of the surface is obtained and the structure is influenced by  $E_{lim}$ . The structure of PANI is papillae like, consisting of small globules, while the morphology of PNMA is a sponge-like, and even though the thickness of PNMA under the same covering conditions is thinner than that of PANI, the coating looks more fluffy, due to the by-products inclusion into the bulk of polymer.

### **2.1.3. Open circuit potential of PANI-modified electrode**

For the preparation of polyaniline-modified electrodes we used two traditional electropolymerization procedures - potential cycling with extending the upper scan limit to high anodic potentials, where the formation of aniline cation radicals proceed, and, as an alternative, electropolymerization at a controlled anodic potential. Both techniques used gave close similar results, thus, electropolymerization at a controlled potential has been chosen as a main procedure. It is well known that the structure and morphology of polyaniline film depends greatly on many polymerization variables. Polyaniline coatings obtained by electropolymerization procedure, present usually porous films consisting of spheres, fibrils, or other related structures, and contain a large void volume filled with a supporting solution. Therefore, the thickness of polyaniline films obtained has been characterized by an anodic (i.e. oxidation) electric charge (relative to electrode area), obtained by potential cycling of the modified electrode within definite potential limits in a supporting electrolyte not containing aniline monomer. The thickness of a polyaniline coating (electrode charge) thus expressed shows a specific amount of electrochemically active polyaniline, deposited at the electrode. The thickness of polyaniline coating deposited grows with an increase of both electropolymerization potential and the process duration. Within the reasonable limits of polymerization duration, ranging from 45 s to 300 s, a linear dependence of a specific electrode charge on electropolymerization time has been obtained with a slope of  $6.12 \times 10^{-2} \text{ mC cm}^{-2} \text{ s}^{-1}$  ( $r = 0.997$  for  $n = 5$ ) for electropolymerization potential of 1.0 V. The modified electrodes, prepared under these conditions, had well mechanically stable polyaniline coatings with specific electrode charges ranging from 1.04 to 16.8  $\text{mC cm}^{-2}$ . In a solution of sulfuric acid, the open-circuit potential (OCP) of polyaniline-modified electrode ranges between 0.62 and 0.54

V, and tends to decrease with increasing electrode charge, i.e. with an increasing amount of polyaniline deposited (Fig. 3).



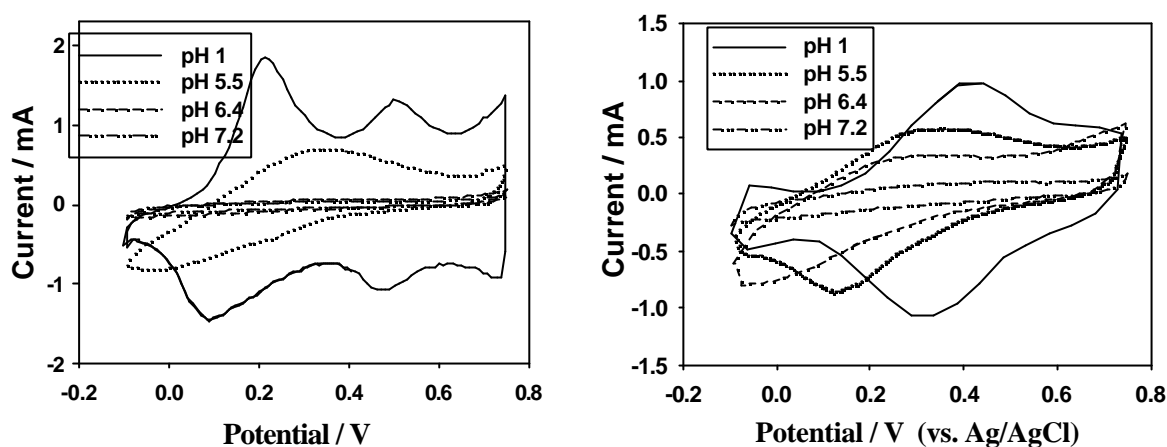
**Fig. 3.** Dependence of open circuit potential of polyaniline-modified electrode in 0.5 M sulfuric acid solution of on electrode charge (active polyaniline content) in absence or presence of ascorbate (as indicated).

By adding ascorbic acid to the background solution, OCP drops by ca. 0.20–0.25 V, and, again, tends to decrease with increasing electrode charge, and with an increase of ascorbate concentration as well (Fig. 3). The OCP of polyaniline-modified electrode shows a negligible or almost no dependence on the electropolymerization potential applied in the electrode preparation step. Since, in a solution of sulfuric acid, polyaniline presents in its conducting, doped, and electrochemically active form, it could be concluded from the dependencies obtained that a redox interaction of ascorbate with polyaniline proceeds, resulting in a shift of OCP towards lower values, indicating a partial reduction of a polyaniline film. A higher potential drop, obtained at a higher ascorbate concentration, supports this assumption.

## 2.2. Investigation of coating polymer in solutions of different pH

The acidity of electrolyte exhibits a crucial effect to the redox properties of PNMA and other polymers of polyaniline family. Fig. 4 compares CVs for polyaniline (PANI) and PNMA modified electrodes in solutions of different pH. As for PANI, well-expressed pair of anodic and cathodic peaks, characterized by  $E_m$  of 0.15 V and  $\Delta E_p$  of 0.12 V, is observed in pH 1.0 solution (Fig. 4, left). This pair of peaks corresponds to well-known quasi-reversible redox transition between the leucoemeraldine (reduced),

and emeraldine (half-oxidized) forms of this polymer. The second well-expressed pair of peaks with  $E_m$  of 0.49 V and  $\Delta E_p$  of 0.04 V corresponds obviously to some destruction



**Fig. 4.** Representative cyclic voltammograms for polyaniline (as on the left) and poly(*N*-methylaniline) (as on the right) modified electrodes, as obtained at a potential scan rate of  $0.1 \text{ V s}^{-1}$  in solutions of different pH (as indicated). The electrodes have been prepared by applying of a controlled potential of 0.8 V for 180 s in a solution containing 0.5 M of sulfuric acid and 0.1 M of either aniline or *N*-methylaniline, respectively.

products, usually present in as-prepared PANI film. Both the shape of CVs and the redox capacity of PANI film drastically change by increasing the solution pH. A nearly total loss of redox activity and thus of a redox capacity is observed in pH 6.4 and 7.2 solutions, whereas an intermediate shape of CV has been observed in pH 5.5 electrolyte (Fig. 4, left). For PNMA films, however, the corresponding changes in redox properties occur less drastic. In pH 1.0 solution, PNMA shows under the conditions used a pair of anodic and cathodic peaks with  $E_m$  of 0.36 V and  $\Delta E_p$  of 0.12 V, whereas turning to pH 5.5 solutions causes a shift of  $E_m$  to 0.23 V and an increase of  $\Delta E_p$  up to 0.20 V (Fig. 4, right). Also, the redox capacity of PNMA film diminishes by approximately 1/3 by turning from pH 1.0 to 5.5 electrolytes. Further increase of pH causes a decrease of redox capacity, however, PNMA film still shows significant redox capacity even in pH 6.4 and 7.2 solutions (Fig. 4, right).

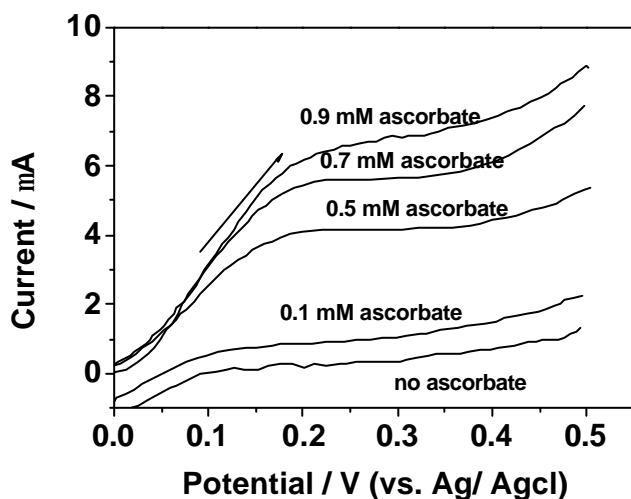
The difference in pH-dependencies of electrochemical behaviour and redox capacity for both conducting polymers, PANI and PNMA, appears to be of crucial importance due to potential use of these polymers as electroactive materials for electrocatalysis and thus for amperometric sensor applications. Since most of biology- and medicine-related sensors operate in nearly pH-neutral solutions, the use of PANI as

electrode material appears to be doubtful because of absence of electrochemical activity related to electrocatalytic properties of this electrode modifier. Also, it is well known that PANI loses its electric conductivity along with the loss of redox capacity in pH-neutral solutions. By contrast, PNMA exhibits significant electrochemical activity and redox capacity even in pH-neutral or slightly acidic media, thus, its electrocatalytic properties towards some substances of analytical importance could be expected, making this polymer potentially suitable for sensor applications.

## 2.3. Electrocatalytic oxidation of ascorbate (vitamin c) at modified electrodes

### 2.3.1. Electrocatalytic oxidation of ascorbate at polyaniline modified electrode

In a pH-neutral phosphate buffer solution, polyaniline modified electrode shows well defined anodic current waves, related to ascorbate oxidation. The half-wave potential of these waves is located at 0.10–0.12 V, and a plateau current is observed within a potential window of 0.20–0.35 V. The height of these anodic waves grows up with an increasing concentration of ascorbate. In nearly pH-neutral solutions, the slope of these dependencies drastically depends on the pH value of the solution used.

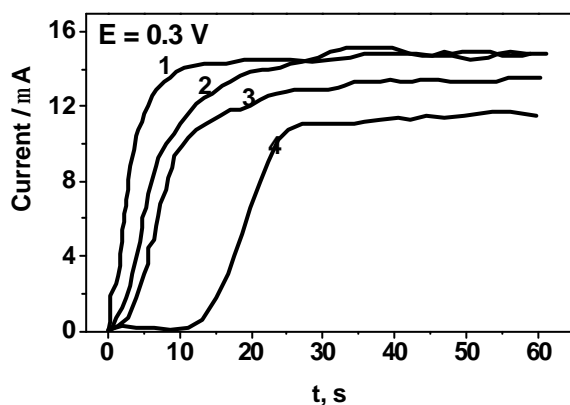


**Fig. 5.** Voltammograms of polyaniline-modified electrode (electrode charge  $1.89 \text{ mC cm}^{-2}$ ), obtained in pH 6.95 solution containing different concentrations of ascorbate (as indicated) at potential sweep rate of  $10 \text{ mV s}^{-1}$ .

containing polyaniline coating of  $1.89 \text{ mC cm}^{-2}$  (as in Fig. 5), the slope drops ca. two-fold, from  $10.1$  to  $4.99 \text{ } \mu\text{A mM}^{-1}$  with an increase of solution pH from 6.95 to 7.2.

### 2.3.1.1. Autocatalytic electrooxidation mechanism of ascorbate on the PANI modified electrode

In a pH-neutral solution, polyaniline presents in its insulating and electrochemically inactive form. Therefore, it seems surprising that the anodic oxidation of ascorbate proceeds at polyaniline-modified electrode even at neutral pH values, as depicted in Fig. 5. To clear the possible reasons for this, in a further set of experiments the modified electrode has been operated at a constant potential, that corresponds to ascorbate oxidation, and aliquots of ascorbate solution have been injected into a stirred solution. Fig. 6 shows the time resolved dependencies thus obtained. It is well seen that, in pH 7.2 solution, a delay in anodic current evolution is observed upon the addition of the first aliquot of ascorbate. The delay time depends both on solution pH and ascorbate concentration added. For pH 7.2 solutions, a delay of ca. 10–14 s is observed for 0.1 mM of ascorbate added. The delay time decreases at higher ascorbate concentrations injected, e.g., it decreases up to 2–4 s for 1.0 mM of ascorbate added. Otherwise, a nearly 1.5-fold increase of the delay time has been observed by injecting 0.04 mM of ascorbate. Noteworthy, almost no delay is observed by adding the second and next following aliquots of ascorbate. The decrease of solution pH results in a gradual decrease of delay time, whereas almost no delay is observed at solution pH of 5.5 or lowers (Fig. 6).



**Fig. 6.** Response of polyaniline-modified electrode (electrode charge  $6.6 \text{ mC cm}^{-2}$ ) on ascorbate added (0.1 mM), obtained at different pH values 1-5,5; 2-6,4, 3-6,95, 4-7,2. Electrode operated at 0.2 V.

The most prominent changes in delay time occur at pH around 7. All these peculiarities have been observed within an entire operating potential window studied, i.e. 0.1–0.3 V.

The dependencies observed can be understood taking into account that the oxidation of ascorbic acid is accompanied by the proton liberation. In an aqueous solution, ascorbic acid shows two steps of ionization with  $pK_a$  values of 4.17 and 11.57 [5]. Therefore, a mono-deprotonated anionic form of ascorbic acid (ascorbate) should be predominant in nearly neutral buffered solutions used in the present work. Thus, a two-electron electro-oxidation of ascorbate mono-anion should be accompanied by the liberation of one proton. Then, since electro-oxidation of ascorbate proceeds in a thin porous layer of polyaniline, a local acidifying of this layer should proceed. Obviously, a local decrease of pH within this layer leads to proton doping of polyaniline. As a result, polyaniline turns into its protonated, and thus electrically conductive and electrochemically active form, which enables an efficient electro-oxidation of ascorbate to proceed. Therefore, autoaccelerating oxidation of ascorbate is observed in pH 7.2 solution, manifesting in a sigmoid-like current transition, typical for autocatalytic processes (Fig. 6). Assuming an autocatalytic mechanism for anodic oxidation of ascorbate at polyaniline-modified electrode, all experimental features observed can be well understood. The observed lengthening or shortening of a delay time by adding of a lower or higher concentration of ascorbate, respectively, relates obviously to slower or faster initial increase of a local proton concentration, accordingly. The increase of an initial ascorbate concentration added leads to a faster acidifying of electrode layer, faster protonation of polyaniline and its conversion into an active conducting form. Thus, more efficient autocatalytic oxidation proceeds. Moreover, once the process of ascorbate oxidation reaches its steady state, i.e., a steady diffusion-controlled anodic current, polyaniline turns into its active conducting form, and no delay is thus observed by adding of the next aliquot of ascorbate. Also, lowering of solution pH favours the protonation of polyaniline at an initial step of autocatalytic process, thus, consequent shortening of delay time is observed by lowering of pH for buffer solutions used. Under the conditions used, a steady current response to each addition is reached within 5–15 s, depending on solution pH and other experimental variables. The dependence of anodic

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5. J.A. Dean (Ed.), Lange's Handbook of Chemistry, 15th ed., McGraw-Hill, New York, 1999.

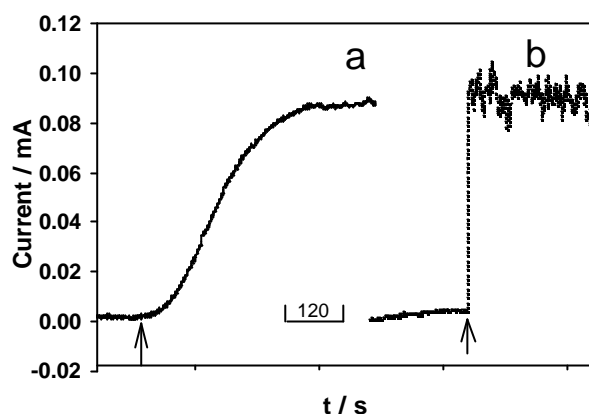
response on ascorbate concentration shows a nearly linear part, suitable for analytical applications, up to ascorbate concentrations not exceeding 1 mM. The slope of this linear part, i.e. the sensitivity of the sensor, depends on solution pH, the thickness of polyaniline coating, and operating potential used. The sensitivity grows up with an increase of sensor operating potential within the limits of 0.1–0.3 V studied. Good correlations could be obtained from these dependencies, e.g., the sensitivity of 124 and 185  $\mu\text{A mM}^{-1}$  for operating potential of 0.1 and 0.2 V, respectively, were obtained up to the concentration of 0.6 mM with  $r = 0.999$  (for  $n = 6$ ). The sensitivity depends to some extent on the polyaniline content at electrode. A relative steep increase of sensitivity has been obtained by increasing the electrode charge up to ca. 2  $\text{mC cm}^{-2}$ , whereas slow increase is noted with the further thickening of polyaniline layer up to 16  $\text{mC cm}^{-2}$ . Independent of the electrode charge, the sensitivity appears some higher for more acidic solutions, however, this difference diminishes with increasing thickness of polyaniline layer.

Again, this difference could be well understood taking into account an autoacceleration mechanism proposed. Obviously, protons liberated during ascorbate electro-oxidation either participate in the doping of polyaniline, or diffuse out of a polyaniline layer. For a thin layer, the diffusion of protons into a surrounding solution prevails over their binding to polyaniline. Adversely, the diffusion of protons into solution appears probably retarded within a thick layer of polyaniline, thus, the protonation of polyaniline prevails over proton leach. Therefore, a local acidifying of a reaction layer appears to be more efficient for thicker polyaniline coatings. Thus, a weaker dependence of electrode sensitivity on solution pH is observed for thicker polyaniline coatings.

### **2. 3.2. Amperometric ascorbate sensor based on conducting polymer: Poly(N-methylaniline) versus polyaniline**

Fig. 7 displays anodic current responses to ascorbate added for PANI and PNMA modified electrodes operated in a batch mode at a controlled potential. For PANI electrode, an autoaccelerating character of current response is well observed. After





**Fig. 7** Representative anodic current responses on ascorbate additions (added at aliquots of 1.0 mM at the moments indicated by the vertical arrows), as obtained in pH 7.2 buffer solution at operating potential of 0.2 V for polyaniline (a) and poly(*N*-methylaniline) (b) modified electrodes. The electrode has been modified by applying of a controlled potential of 0.8 V for 180 s in a solution of 0.5 M of sulfuric acid containing 0.1 M of either aniline or *N*-methylaniline.

adding of ascorbate, almost no current is observed at an initial time period of a few seconds. Somewhat later, the current grows in an accelerating manner reaching a steady state value. Earlier we discussed this specific sigmoid response of PANI modified electrode to ascorbate in terms of autoacceleration. Since PANI layer possesses no electric conductivity at solution pH around 7, the process of anodic oxidation of ascorbate starts obviously at electrode surface not covered with a polymer layer. The protons expelled during ascorbate oxidation lower the local pH near or within the polymer film, and, as a result, PANI turns to its protonated, i.e. conducting form, causing an acceleration. As distinct from PANI, PNMA possesses a better redox activity and conductivity in pH-neutral solution, as it follows from CVs obtained in nearly neutral solutions (Fig. 4). Therefore, the anodic current response starts immediately after adding ascorbate, and no acceleration effect is observed (Fig. 7) (note, that in order to get kinetic characteristics, the kinetic curves like those in Fig. 7 have not been smoothed, resulting in a relatively high noise). The difference in current transients for PANI and PNMA modified electrodes presented in Fig. 7 supports our autoacceleration mechanism proposed. As a result of different redox behavior of the two conducting polymers studied in pH-neutral solution, the net kinetics of current response to ascorbate appears to be quite different. It is seen from Fig. 7 that it takes about 1 min to reach the steady state for

ascorbate oxidation at PANI modified electrode, whereas the response for PNMA electrode is reached in a few seconds. Since this net kinetics is of a great importance for sensor applications, it should be analyzed in more details. A characteristic sigmoid dependence as presented in Fig. 7 can be treated according to a three-parameter sigmoid equation as follows:

$$I = \frac{I_{\max}}{1 + \exp(-(t - t_0)/b))} \quad 2.3.2.1$$

where  $I$  represents an anodic current,  $I_{\max}$  its maximum value, attained at a sufficient long time period,  $t$  and  $t_0$  the time and its value at  $I = I_{\max}/2$ , respectively, and  $b$  is an empirical coefficient which characterizes the steepness of the  $I, t$  transient, i.e. the net kinetics of the current response.

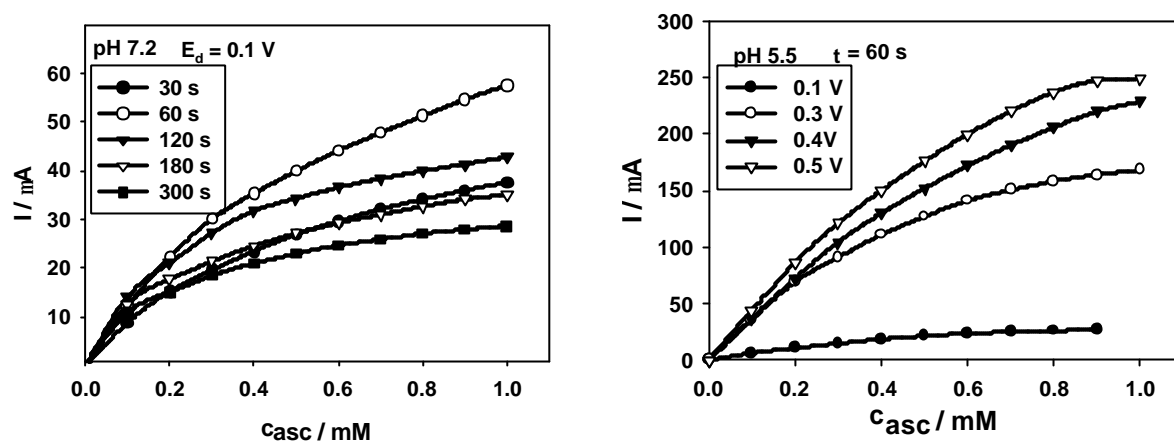
Treating the data for PANI modified electrode in accordance with this equation yields  $I_{\max} = 87.4\mu\text{A}$ , and  $b = 9.26 \pm 0.04$  s with correlation coefficient  $r = 0.998$ . For PNMA modified electrode the corresponding treatment yields  $I_{\max} = 88.5\mu\text{A}$ , and  $b = 0.029 \pm 0.007$  s with  $r = 0.993$ . Close related values of  $I_{\max}$  obtained show very probably that, once a steady state is reached, ascorbate oxidation appears to be a diffusion-controlled process for both modified electrodes. The main difference between the two electrodes relates to the coefficient  $b$ , which is approximately 320 times higher for PANI modified electrode than for PNMA one. This means that the response of PNMA electrode for ascorbate is more than 300 times faster than for PANI based sensor. It follows that PNMA modified electrode is much more suited to electroanalytical use as an amperometric ascorbate sensor, compared to PANI based electrode because of a faster response related to a better redox performance in pH-neutral solutions.

### **2.3.3. Electrocatalytic oxidation of ascorbate (vitamin C) on the PNMA modified electrodes**

When plotted as a function of ascorbate concentration, calibration graphs can be obtained (

Fig. 8). From these, the dependence of current response and of electrode sensitivity on various parameters could be obtained and analyzed. Particularly, the

dependence of sensitivity on electrode preparation conditions, solution pH, and operating



**Fig. 8** *On the left:* Dependence of anodic current response on ascorbate concentration as obtained in pH 7.2 buffer solution operating potential of 0.1 V for electrode, modified in a solution of 0.5 M of sulfuric acid containing 0.1M of N-methylaniline by applying of a controlled electropolymerization potential of 0.8 V for different time periods (as indicated).

*On the right:* Dependence of anodic current response on ascorbate concentration as obtained in pH 5.5 buffer solution at operating potential ranging from -0.1 to 0.5 V (as indicated) for electrode, modified in a solution of 0.5M of sulfuric acid containing 0.1 M of N-methylaniline by applying of a controlled electropolymerization potential of 0.8 V for 60 s.

potential are of great importance. For pH 7.2 solutions, the sensitivity increases with extending the electropolymerization time spent during electrode preparation procedure up to a definite limit, i.e. with increasing redox capacity and thus a thickness of a polymer layer for the prepared electrode. At a polymerization time of 60 s, the sensitivity reaches its maximum, and then decreases with extending of electropolymerization time up to 300 s (

Fig. 8 left). Same tendencies are observed for different electrode operation potentials. This dependence shows that an optimum net thickness of a polymer layer exists. At a low electrode coverage by the polymer (i.e., at a short electropolymerization time), an increase of polymerization time results obviously in an increase of electrode coverage, causing more efficient electrocatalysis of the resulting modified electrode. By increasing the polymerization time over an optimum limit, however, polymer destruction processes could proceed to a considerable extent [3], leading to increasing content of inactive material that diminishes the efficiency of electrocatalytic oxidation of ascorbate.

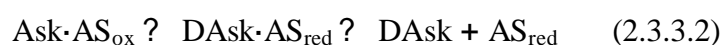
In a pH 5.5 solution, the electrode responses to ascorbate appear to be some higher (by the factor of 1.5–2) as compared to pH 7.2 solution (Fig. 8 right). This is in accordance with a better redox performance of PNMA modified electrode in slightly

acidic solutions compared to neutral ones. Also, it is seen from Fig. 7 on the right that an optimum time of electropolymerization exists regarding the response of electrode prepared. The response of PNMA electrode depends also on the operating potential applied. Increase occurs by shifting  $E_{op}$  from 0.1 to 0.3 V can be well understood taking into account that the relative content of an oxidized form of PNMA within the film increases by shifting the electrode potential from 0.1 to 0.3 V. In a pH 5.5 solution, the midpoint potential for PNMA film of 0.23 V has been estimated based on CVs (Fig. 4). This means that at  $E_{op}$  around 0.2 V, roughly a half of PNMA within the film presents in its oxidized state. Assuming a one-electron redox process for PNMA to proceed (relating to one elementary unit of this polymer), it could be concluded that only 1 % of PNMA presents in its oxidized state at  $E_{op}$  around 0.1V, and, adversely, that the polymer appears almost completely oxidized at  $E_{op}$  around or over 0.3 V. Since the efficiency of redox interaction of ascorbate with PNMA should be proportional to the relative content of the oxidized form of polymer, more efficient electrocatalysis should proceed at a higher  $E_{op}$ . Therefore, a higher response of the electrode to ascorbate is observed at higher operating potentials. Over the limits of 0.3 V, a further increase of electrode response is observed, however, high  $E_{op}$  values present little or no practical interest because other substances usually present in a real analyte solution could discharge at a high electrode potentials, yielding substantial bias in ascorbate assay.

Some lower curvature of current–concentration profiles is observed for lower ascorbate concentrations; however, even in this case the dependence appears to be non-linear. There are at least two possible reasons for the deviations from linearity. One of them relates to a possible two-step mechanism of ascorbate electrooxidation. In accordance with this scheme, the formation of a complex of ascorbate (Asc) with the oxidized active site of PNMA ( $AS_{ox}$ ) is expected:



followed by spontaneous fast electron transfer from  $A_{sc}$  to  $AS_{ox}$  and dissociation of the resulting complex:



where  $DAsc$  and  $AS_{red}$  represent dehydroascorbate and a reduced form of PNMA active site, respectively.

Assuming the intrinsic electron transfer within the complex to proceed very fast, the reaction scheme could be treated in analogy to chemical reactions which proceed via the transient complex (e.g., to enzyme-catalyzed reactions [6]). Then, the following kinetic equation could be derived:

$$v = \frac{k_2 [AS_{ox}] [Asc]}{(k_{-1} + k_2)/k_1 + [Asc]} ; \quad (2.3.3.3)$$

where  $v$  represents the reaction rate,  $k_1$  and  $k_{-1}$  the rate constants for the forward and backward reactions (1), respectively,  $k_2$  the rate constant for reaction (2.3.3.2), and  $[Asc]$  and  $[AS_{ox}]$  are concentrations of ascorbate and active sites of a polymer, respectively.

Turning now to electric current units and simplifying Eq. (2.3.3.3) following the known transformation, one can obtain:

$$I = \frac{I_{max} [Asc]}{[Asc]_{1/2} + [Asc]} ; \quad (2.3.3.4)$$

where  $I$  is a relative electric current,  $I_{max}$  its maximum value, attained at an indefinitely high  $[Asc]$ , and  $[Asc]_{1/2}$  is the ascorbate concentration that corresponds to the half of a maximum current.

Treatment of the results obtained according to (2.3.3.4) yields the values of  $I_{max}$  and  $[Asc]_{1/2}$ , which are collected in Table 1.

It is seen that the maximum current values depend on all variables studied—electrode preparation conditions, solution pH and operating potential. An increase of operating potential within the limits of 0.1–0.4 V causes a drastic increase of  $I_{max}$ . Also, higher  $I_{max}$  are obtained in more acidic buffer solutions.

In pH 7.2 buffer solutions, the highest value of  $I_{max}$  has been obtained for  $t = 60$  s, whereas some higher  $t$  of ca. 120 s is required for pH 5.5 buffer solutions. This means probably that there is a definite optimum thickness of PNMA layer which ensures the highest rate of electrocatalytic reaction, resulting in the highest electrode output. For thicker polymer films, however, the charge carrier transport within this film could become rate limiting, resulting in lower  $I_{max}$  values. This could be partially supported by comparing the data obtained in pH 7.2 and 5.5 solutions.

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6. D.L. Nelson, M.M. Cox, Lehninger Principles of Biochemistry, fourth ed., W.H. Freeman & Co., New York, 2004

In the latter case, the highest  $I_{\max}$  values have been obtained for longer electropolymerization (for  $t$  about 120 s or more), i.e. for thicker polymer films, since the electric conductivity of PNMA appears to be higher in more acidic solution.

**Table 1.** The values for maximum current ( $I_{\max}$ ) and concentration at a half of maximum current ( $c_{1/2}$ ), as obtained by treating the data according to Eq. (2.3.3.4) for PNMA modified electrodes operated in pH 7.2 and 5.5 buffer solutions at different operating potentials ( $E_{op}$ )

t / s	pH 7.2 $E_{op}=0.1V$		pH 7.2 $E_{op}=0.2V$		pH 7.2 $E_{op}=0.3V$		pH 5.5 $E_{op}=0.2V$	
	$I_{\max}/$ mA	$c_{1/2}/$ mM	$I_{\max}/$ mA	$c_{1/2}/$ mM	$I_{\max}/$ mA	$c_{1/2}/$ mM	$I_{\max}/$ mA	$c_{1/2}/$ mM
30	60	0.60			120	0.59	350	0.84
60	95	0.66	230	0.63	250	0.64	490	1.12
120	57	0.37					580	1.16
180	46	0.31	140	0.49			540	1.15
300	36	0.27	120	0.39	200	0.53	230	0.53

The values of ascorbate concentration at a half of maximum current ( $c_{1/2}$ ) are also important characteristics for the possible use of electrodes prepared as sensors for ascorbate assay. It follows from (2.3.3.4) that a linear dependence of electrode output on analyte concentration could be obtained only for low concentrations, not exceeding  $c_{1/2}$ . Surprisingly, the values of  $c_{1/2}$  obtained do not differ drastically for electrodes, prepared at different conditions. Also, these values do not depend essentially on the operating potential used. In general, the values of  $c_{1/2}$  vary within the limits of ca. 0.3–0.7 mM for pH 7.2 solution, whereas some higher values have been obtained for pH 5.5 solution (Table 1).

An alternative reason for the non-linear dependence of electrode current on ascorbate concentration could be derived taken into account a limited rate of charge carrier transport within PNMA film. Recently, mathematical modeling of electrocatalytic processes taking place at conducting polymer modified electrodes has been provided [7]. Taking into consideration the most important parameters for electrocatalytic process, viz. the thickness of a conducting polymer layer, the rate of redox reaction of analyte with

active sites within the polymer layer, and the rate of charge carrier diffusion within the polymer film, the possibility for the deviation from linearity has been shown for the cases with relatively low charge carrier mobility within the film, and higher reactant concentration. The third possible reason for non-linearity could be the electrochemical (anodic) degradation of PNMA film during its prolonged polarization. Based on our kinetic studies on electrochemical degradation of PNMA [3] and PANI [8], however, this reason could be excluded from consideration, since at a relatively low electrode potential, and relatively high solution pH used in the present study, the degradation proceeds at a low rate, which do not impact the results significantly.

#### 2.4. Electrocatalytic oxidation of ascorbate at pnma modified rotating disk electrode

In accordance with Levich equation, a linear dependence of limiting current for ascorbate electrooxidation on the square root of rotation velocity should be observed [9]:

$$i = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}c \quad (2.4.1)$$

where  $i$  is the mass transfer limited anodic current density,  $n$  – the number of transferred electrons,  $F$  – Faraday constant,  $A$  – rotating disk electrode surface area,  $D$  – diffusion coefficient for ascorbate,  $\omega$  – rotation angular velocity,  $\nu$  – kinematic viscosity of solution, and  $c$  – ascorbate concentration.

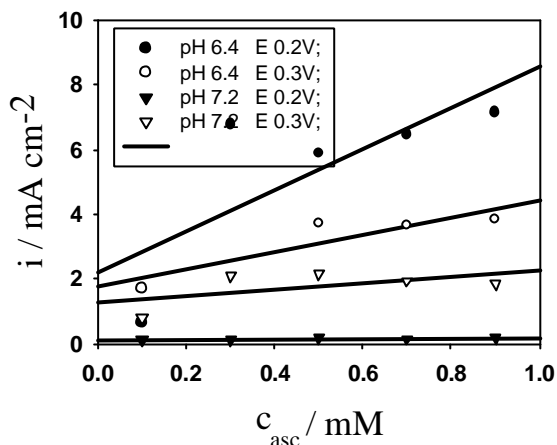
In a pH 7.2 solution, a linear dependence according to Levich equation is retained within a narrow range of relatively low rotation velocity. Obviously, the deviation from linearity at higher rotation velocities is determined by limited rate of electron transfer reaction. In any case, all factors mentioned above are included into kinetic current density that can be attained at an indefinite high rotation velocity.

In accordance with Koutecky-Levich equation, a net current can be divided into two components – mass transfer limited, and kinetic (or reaction limited) current. Dependencies of kinetic current density on ascorbate concentration for both solutions has been studied and analysed for a selected electrode potential of 0.2 and 0.3 V (*Fig.*).

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8. R. Mažeikienė, A. Malinauskas, Synth. Met. 123 (2001) 349.

9. A. J. Bard, and L. R. Faulkner, Electrochemical Methods. John Wiley & Sons, New York. 1980, p. 230–231.



**Fig.9.** Treatment of the data obtained at PNMA modified electrode in pH 6.4 and 7.2 solutions for different ascorbate concentrations and different electrode potentials (as indicated) in Koutecky-Levich coordinates.

The results obtained show an efficient electrocatalytic oxidation of ascorbate at the PNMA modified electrode to proceed in solutions with a pH 6.4 and 7.2. Within the electrode potential window of 0.2 to 0.3 V and electrode rotation velocity of 100-4000 rpm, catalytic current obeys Koutecky-Levich equation at a millimolar ascorbate concentration.



### 3. CONCLUSIONS

1. Polymer morphology studies have shown, that under the potentiodynamic conditions complete coverage of the surface is obtained and the structure is influenced by  $E_{lim}$ . The structure of PANI is papillae like, consisting of small globules, while the morphology of PNMA is a sponge-like, and even though the thickness of PNMA under the same covering conditions is thinner than that of PANI, the coating looks more fluffy, due to the by-products inclusion into the bulk of polymer.

2. It has been ascertained that poly(*N*-methylaniline) shows better redox properties in slightly acidic or neutral solutions compared to those of PANI, due to slow oxidation of aniline in an alkaline media.

3. The autocatalytic reaction mechanism has been proposed for anodic oxidation of ascorbate in nearly pH-neutral buffered solutions: protons liberated during ascorbate oxidation cause a local pH drop within a thin polyaniline layer, turning it into a proton-doped conducting form which shows electrocatalytic activity towards oxidation of ascorbate. The proposed mechanism explains the ability of polyaniline to electrocatalyze the anodic oxidation of ascorbate even in pH-neutral solutions, where polyaniline is present in its undoped and non-conducting form.

4. Poly(*N*-methylaniline) modified electrodes can be used for ascorbate (vitamin C) assay in pH-neutral solutions. The response of PNMA electrode for ascorbate is more than 320 times faster than for PANI based sensor. It has been shown that the fast response is due to a better redox activity of poly(*N*-methylaniline) in slightly acidic or neutral solutions compared to polyaniline.

5. It is shown that at optimal operating conditions modified PNMA and PANI electrodes can be used for ascorbate (vitamin C) testing in the pH- neutral solutions. It has been shown that polyaniline-modified electrodes can be used for ascorbate assay within a pH range of 5.5–7.2, operating potential window of 0.1–0.3 V versus Ag/AgCl, showing a linear range of response up to 0.6 mM, and a lower detection limit of 0.05 mM.

6. Oxidation of ascorbate using a PNMA modified glassy carbon rotating electrode occurred at more negative potentials than on unmodified electrode. Using the electrode potential from 0.2 to 0.3 V and the electrode rotation speed from 100 to 4000

rpm the catalytic current satisfies Koutecky-Levich equation conditions at a millimolar ascorbate concentration.

7. It has been shown that pt and glassy carbon electrodes modified by PNMA and PANI can be used for the determination of ascorbate concentration in juice.

## LIST OF PUBLICATIONS

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1. K. Brazdžiuvienė, I. Jureviciute, A. Malinauskas. Amperometric ascorbate sensor based on conducting polymer: Poly(*N*-methylaniline) versus polyaniline. *Electrochimica Acta*, 2007, vol. 53, p. 785-791.
2. I. Jureviciute, K. Brazdžiuvienė, L. Bernotaite, B. Šalkus, A. Malinauskas. Polyaniline-modified electrode as an amperometric ascorbate sensor. *Sensors and Actuators B*, 2005, vol.107, p. 716-721.

### ISI Proceedings

1. I. Jureviciute, L. Baršyte, K. Brazdžiuvienė, A. Malinauskas. The electrochemical formation of PANI and PNMEA films at steel electrodes in oxalic acid solutions. *Proceedings of Baltic Polymer Symposium 2007*. Druskininkai, Lithuania, p. 30-34.

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1. I. Jureviciute, K. Brazdžiuvienė, L. Bernotaite, B. Šalkus, A. Malinauskas, S. Bruckenstein. The Investigation of the Electrochemical oxidation of Ascorbic Acid on Polyaniline modified Pt electrodes. *IV Baltic Electrochemistry Conference Greifswald*, Germany, 2005.
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# ELEKTRODU, MODIFIKUOTU LAIDŽIAIS POLIMERAIS, TYRIMAS IR TAIKYMAS ELEKTROANALIZES TIKSLAMS

## REZIUME

Elektrochemiškai modifikuoti elektrodai padidina reakcijos greiti, jautruma ir selektyvuma, tuo tarpu kai biologiškai aktyvios medžiagos oksidacijos-redukcijos reakcija ant nemodifikuotu elektrodu dažnai vyksta labai greitai, jautri pašaliniais poveikiams, ir prasciau atsikartoja. Elektrodai, modifikuoti polianilinu (PANI), poli(N-metilanilinu) (PNMA) gali buti panaudoti askorbo rūgšties tyrimams dėl to, kad polimeras mažina jos oksidacijos potenciala. Ji dalyvauja ivairiuose organizmo fiziologiniuose procesuose. Tokio jutiklio, kuris galetu nustatyti askorbo rūgštį ne tik silpnai rūgščiuose bet ir neutraliuose tirpaluose, bei neskaidriose biologinese sistemose, kurimas išlieka labai svarbus. Todėl, pagrindinis šio darbo tikslas - ištirti askorbo rūgšties elektrochemines oksidacijos ant elektrodu, modifikuotu polianilinu ir poli(N-metilanilinu), desningumus, siekiant sukurti jautrius askorbatui jutiklius.

Ištirta ivairiu faktoriu itaka anilino ir N-metilanilino elektrocheminei polimerizacijai bei gautu PANI ir PNMA sluoksniu savybems. Atlikti palyginamieji PANI ir PNMA modifikuotu elektrodu tyrimai skirtingo rūgštingumo tirpaluose ir parodyta, kad PNMA pasižymi geresniu aktyvumu silpnai rūgščiuose ir neutraliuose tirpaluose, nes šarmineje terpeje anilino oksidacija vyksta labai greitai.

Ištirtas abiejų tipu modifikuotu elektrodu amperometrinio atsako į askorbatą pobudis, ir pasiulytas autokatalizinis askorbato elektrooksidacijos ant modifikuotu elektrodu mechanizmas. Vykstant askorbo rūgšties oksidacijai dėl atskylancio protono vyksta galimi PANI struktūros pakitimai ir polianilinas protonizuojasi igydamas elektrochemiškai aktyvia emeraldino druskos struktura, kuri leidžia pratesti askorbo rūgšties oksidacija. Poli(N-metilanilinu) modifikuotas elektrodas rodo 320 kartų greitesnį askorbato atsaką, lyginant su polianilinu modifikuotu elektrodu.

Ištirta askorbato oksidacija ant sukamojo stiklo anglies elektrodo. Esant elektrodo potencialui nuo 0,2 iki 0,3 V, elektrodo sukimosi greičiui nuo 100 iki 2000 aps./min ir milimoliarinei askorbato koncentracijai, katalizine srove atitinka Koutecky-Levich lygties sąlygas.

Panaudojus PANI ir PNMA modifikuotus elektrodus, sukurti amperometriniai askorbato jutiklio prototipai ir atlikti jų palyginamieji tyrimai.

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