

Electrochemical Template-Free Synthesis of Nanofibrous Polyaniline Modified Electrode for Ascorbic Acid Determination

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Electrochemical formation of polyaniline (PANI) modified electrode was performed galvanostatically from aqueous solution of 1.0 mol dm^{-3} HCl containing 0.2 mol dm^{-3} aniline at current densities ranging from $0.5\text{-}3.0 \text{ mA cm}^{-2}$. The morphology of PANI electrode consisted of highly developed nanofibrous network with electrocatalytic features towards oxidation of ascorbic acid, reflected in increase of the peak current ~ 2.5 times and shift of the oxidation potential by 0.32 V to less positive values. Response of PANI modified electrode was obtained from anodic LSV curves. Current peak potentials decreased with increase of pH with slope of $\sim 32 \text{ mV pH}^{-1}$, indicating two electron charge transfer process with liberation of one proton characteristic of an electrochemical reaction followed by a chemical step.

Keywords: electrochemical polymerization, polyaniline, nanofibres, ascorbic acid, electrocatalysis

1. INTRODUCTION

Electrochemical techniques are widely used in many fields of analytics, including quality control in pharmaceuticals and food industry, environmental monitoring, chemical and biochemical analysis. Electrochemical techniques offer simple, fast and low-cost way for sensing of numerous important electroactive compounds, such as hormones, medications, antioxidants, etc. [1-4]. The principle of electroanalytical determination is based on a charge transfer process at the

electrode/electrolyte interface, which is measured, depending on the selected technique, as electrical quantity (current, potential or charge), [5].

Beside the fact that ascorbic acid is an electroactive compound that may be oxidized at anode, its electrochemical determination at unmodified common electrodes such as Pt or glassy carbon is faced by high anodic overpotentials, leading to electrode fouling and poor reproducibility. Another significant problem is low selectivity, since some other compounds can be also oxidized at similar potentials, causing overlapping of the signals [6-10]. Having in mind the wide-spread importance of ascorbic acid, efforts have been made in formulation of modified electrodes which would enable reliable, reproducible and sensitive sensing of ascorbic acid in various samples [11-25]. Determination of ascorbic acid on, either chemically or electrochemically, modified electrodes is based on electrocatalytic process. An electrocatalytic process enables selective determination at lower anodic potential (lower over-potential) and higher peak current or higher current depending on whether voltammetry or amperometry is used [6].

Various, modified electrodes, mostly based on carbon materials, have been considered. Zhang and Lin [7] have used covalently grafted aspartic acid modified glassy carbon electrode for determination of dopamine and ascorbic acid by differential pulse voltammetry. Paulikante et al. have investigated both chemically and electrochemically deposited copper hexacyanoferrate onto carbon film electrode for amperometric sensing of ascorbic acid, chemically deposited films were shown to be more efficient for long term and stable determination in wines and juice [12]. Teixeira et al. have proposed a carbon paste electrode modified with copper phosphate immobilized in polyester resin for cyclic voltammetric determination of ascorbic acid in pharmaceuticals, they have also shown that the proposed electrode was suitable for amperometric measurements [15]. Recently, He et al. have shown that zeolite functionalized with copper nanoparticles and graphene oxide modification of glassy carbon electrode might be successfully used for simultaneous determination of dopamine and ascorbic acid [8]. Wu et al. have also used glassy carbon modified with palladium nanoparticles supported on graphene oxide for studies of electrocatalytic oxidation of ascorbic acid [9]. A lot of attention has also been paid to application of electroconducting polymers in electrocatalytic determination of ascorbic acid. Among numerous electroconducting polymers, polyaniline based electrodes are probably the most studied, due to high conductivity, redox activity, stability and low cost monomer. Polyaniline can be easily synthesized by either chemical or electrochemical oxidative polymerization. Electrochemical polymerization is of great practical importance particularly when polymer modified electrode is needed, since the polymer is directly deposited onto electrode enabling further analysis. Among electrochemical techniques used to deposit polyaniline onto electrodes, galvanostatic technique provides constant rate of the polymerization process and possibility of control and estimation of the polymer thickness. It is well known that polyaniline can exist, depending on its oxidation and protonation level, in different forms of which emeraldine salt is the only conductive one [26,27]. The existence of emeraldine salt at pH lower than 4, restricted practical application of polyaniline in biological system operating at nearly neutral pH. This problem might be overcome by application of so called self doped polyanilines or copolymers of aniline and its derivatives, whose conductivities are lower than those of the parent polymer [27]. However, O'Connell et al. have shown, that it was possible to obtain selective and reliable response of ascorbic acid at polyaniline modified carbon

electrode [16]. Jurevičiūtė et al. have successfully used polyaniline modified electrode for amperometric determination of ascorbic acid in neutral pH [20]. Bartlett and Wallace have investigated and proposed a mechanism of electrocatalytic oxidation of ascorbic acid at polyaniline-polyvinyl sulfonate composite electrode; the proposed mechanism involved two electron and one proton charge transfer [6]. Kilmartin et al. have also examined electrocatalytic oxidation of ascorbic acid at Pt microelectrode modified with polyaniline doped by polyvinyl sulfonate and polystyrene sulfonate, this electrode has given practically no interference during amperometric experiments in neutral buffered beverages [19]. Ambrosi et al. have used polyaniline nanoparticle drop-coated onto screen printed carbon-paste electrode for oxidation of ascorbic acid. Zhang et al. have investigated polyaniline nano-networks on *p*-aminobenzenesulfonic acid functionalized glassy carbon electrode for selective and simultaneous sensing of ascorbic and uric acid [17]. Milakin et al. proposed polyaniline based material obtained by chemical oxidative polymerization on screen printed electrode [25]. They have pointed out the influence of the synthesis conditions on the potentiometric sensor response. Having in mind that nanostructuring of materials improves most of its physical and chemical properties compared to those of the bulk materials; the aim of this work is to establish conditions for simple templateless electrochemical synthesis of nanostructured polyaniline to be considered as an electrode for electrochemical determination of catalytically oxidized ascorbic acid.

2. EXPERIMENTAL

2.1. Electrochemical polymerization of aniline

Electrochemical oxidative polymerization of aniline at graphite electrode was carried out galvanostatically, from acidic aqueous solution of 1.0 mol dm^{-3} HCl (p.a. Merck) containing 0.20 mol dm^{-3} aniline (p.a. Fluka). In order to estimate the optimal conditions for electrochemical formation of polyaniline (PANI) modified graphite electrode, both cathodic and anodic chronopotentiometric curves, obtained at different current densities were recorded.

Prior to polymerization aniline was distilled in Ar atmosphere, while cylindrical graphite electrode, inserted into Teflon holder, was mechanically polished by fine emery papers (2/0, 3/0 and 4/0, respectively) and polishing alumina ($1 \mu\text{m}$, Banner Scientific Ltd.) on polishing cloths (Buhler Ltd.), the traces of the alumina were removed ultrasonically during 5 min.

Scanning electron microscopy (SEM) micrograph of nanofibrous PANI electrode surface was taken by field emission SEM, MIRA3 TESCAN at 10 kV.

2.2. Electrochemical characterization of ascorbic acid oxidation on PANI electrode

Electrochemical characterization of PANI modified graphite electrode was performed by cyclic voltammetry (CV) in the potential range of -0.3 to 1.0 V (SCE) with different scan rates in buffered solution containing $10.0 \cdot 10^{-3} \text{ mol dm}^{-3}$ L-ascorbic acid. Stock solution of L-ascorbic acid, (p.a. Merk) was prepared in phosphate buffer solution (PBS), 0.1 M at pH 6.8.

The dependence of the current signal on ascorbic acid concentration was evolved from linear scanning voltammetry (LSV) results, recorded at scan rate of 20 mV s^{-1} . The solutions with different concentration of ascorbic acid were obtained by diluting of the stock solution with PBS. LSV was also used to determine the influence of pH on the electrocatalytic process of ascorbic acid oxidation at different pH (PSB).

2.3. Electrochemical cell and instrumentation

All experiments were carried out at ambient temperature ($23 \pm 1 \text{ }^\circ\text{C}$) in three compartment electrochemical cell. Saturated calomel electrode (SCE) served as reference electrode (all potentials in the text were referred to SCE), while Pt wire was used as counter electrode. The experiments were performed using SP-300 BioLogic Science Instruments, potentiostat/galvanostat connected to PC.

3. RESULTS AND DISCUSSION

3.1. Electrochemical formation of PANI modified electrode

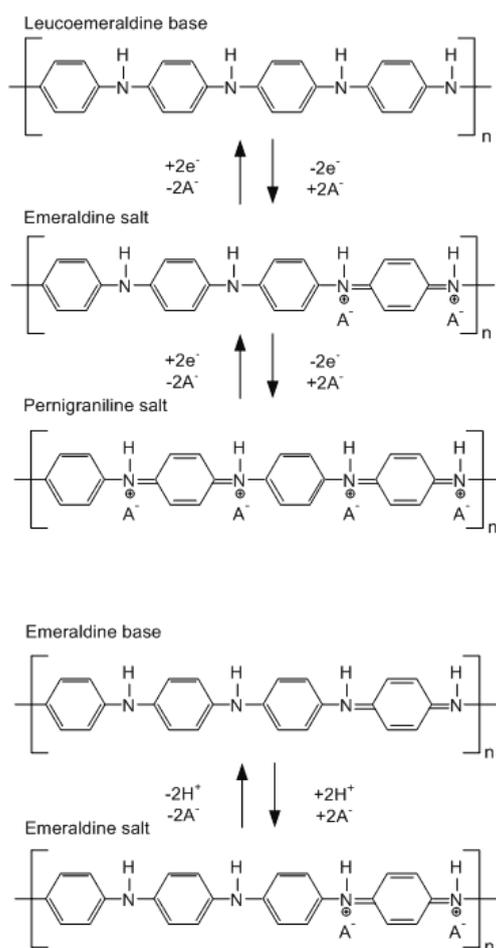


Figure 1. Schematic presentation of mutual conversion between different polyaniline forms.

It is well known that PANI can exist in different oxidation forms of which only emeraldine salt is conductive. Emeraldine salt can be obtained either by doping or by protonation of half-oxidized form of polyaniline known as emeraldine base [26, 27], these forms can be easily converted by both chemical and electrochemical reactions, displayed schematically in Fig.1.

3.1.1. Electrochemical synthesis of PANI

Electrochemical synthesis of polyaniline was performed galvanostatically with current densities ranging from 0.5 to 3.0 mA cm⁻², during 600s. In order to estimate the amount of emeraldine salt, which is capable for charge exchange, all electrodes were discharged with the same current density of 1.0 mA cm⁻² (dedoped) in the same solution, and results are given in Fig.2.

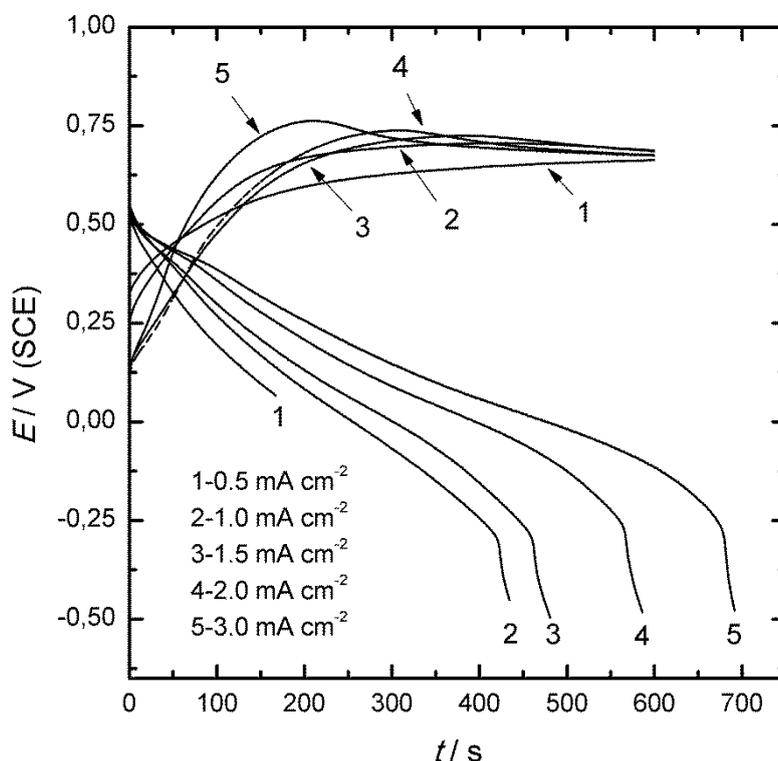


Figure 2. Chronopotentiometric curves of electrochemical synthesis of polyaniline with current densities ranging from 0.5 -3.0 mA cm⁻² and potentiometric discharge (dedoping) curves ($j = 1.0 \text{ mA cm}^{-2}$) of graphite electrode from aqueous solution of 1.0 mol dm⁻³ HCl and 0.15 mol dm⁻³ aniline.

All chronopotentiometric curves, except those obtained by current density of 0.5 Acm⁻², of electrochemical polymerization of aniline are characterized by increase of the potential, often referred as induction period, followed by potential plateau. Increase of the potential up to 0.7 V is required for formation of dimmers, after the polyaniline layer was formed, polymerization proceeded at nearly

constant potential characterized by the potential plateau. The potential increased faster for higher current density, while for current density of 0.5 A cm^{-2} potential plateau occurred at lower potential. As it can be seen from discharge curves at Fig.2, current density of 0.5 A cm^{-2} was not sufficient for growth of adherent polyaniline film on electrode since practically no charge was obtained in the discharge process, as a result of a weak adhesion of the obtained PANI film. Other current densities all resulted in more or less uniformly deposited PANI films. The dependence of discharge and polymerization capacities ratio (which corresponds to amount of conductive form PANI, i.e. emeraldine salt) on polymerization current density is given in Fig. 3. As seen, this ratio decreases with increase of the polymerization current density, probably as a result of increase of the amount of formed nonconductive pernigraniline and degradation products due to higher potentials. Since the best results were obtained when polymerization was performed with 1.0 mA cm^{-2} , this current density was used in further experiments.

In order to estimate the optimal time of polymerization, electrochemical polymerization of aniline was performed at current density of 1.0 mA cm^{-2} during 300, 600, 900, 1200 and 1500 s. After polymerization, the electrodes were discharged with the same current density and ratio of discharge and polymerization charge was evaluated and presented in Insert of Fig 3.

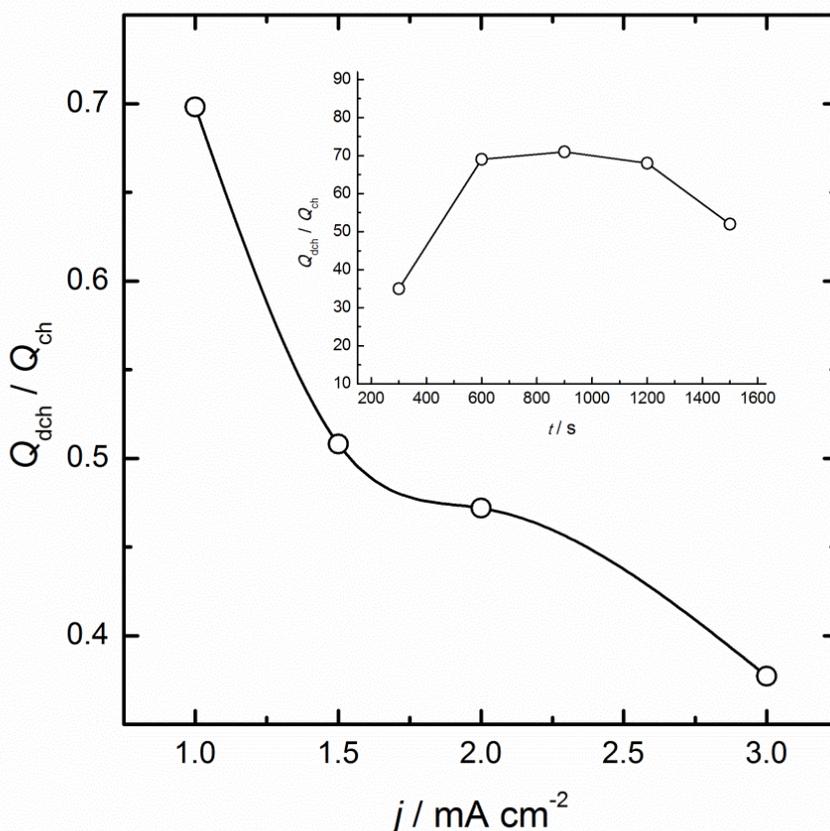


Figure 3. Dependence of discharge and polymerization capacities ratio on polymerization current density. Insert: Dependence of discharge and polymerization capacities ratio on polymerization time.

As it can be seen the discharge and polymerization capacity ratios are nearly the same for polymerization time of between 600 and 1200 s, meaning that charge can be exchanged through the whole deposited film, while for higher polymerization time, decrease of this ratio is due to loss of the polymer film from electrode. Shorter polymerization time, on the other hand, led to nonuniformly deposited film, which was visually confirmed. In order to achieve greater available charge, PANI modified graphite electrode was deposited with current density of 1.0 mA cm⁻² during 1200 s and used in further investigations.

Since, electrochemical oxidative polymerization of aniline proceeds at anode together with insertion (doping) by chloride ions fulfilling the request of electro neutrality according to:



where y refers to degree of doping, defined as the number of charges in the polymer and number of monomer units, the amount of both deposited and active mass of polyaniline can be estimated using [30]:

$$m = \frac{j t (M_m + y M_a)}{(2 + y) F} \quad (2)$$

where m , g, is the mass of deposited polyaniline, j , A cm⁻², polymerization or discharge current density, t , s, polymerization or discharge time, M_m and M_a are molar mass of aniline monomer (93 g mol⁻¹) and chloride anion (35.5 g mol⁻¹) respectively, $F = 96500$ A s mol⁻¹ is Faraday constant and y is degree of doping.

Assuming that current efficiency of the polymerization process was 100 % and taking for polymerization current density 1 mA cm⁻², polymerization time of 1200 and doping degree of $y = 1.0$ which corresponds to fully oxidized form of pernigraniline salt, due to high potentials of polymerization, it could be calculated that the overall deposited mass of polyaniline on graphite electrode was about 0.46 mg cm⁻². On the other hand, taking into account discharge time of 560 s and discharge current density of 1 mA cm⁻² and $y = 0.5$ for emeraldine salt, active conductive mass of polyaniline can be estimated to 0.24 mg cm⁻², meaning that 52 % of overall deposited mass of polyaniline was active.

3.1.2. Morphology of PANI modified electrode

SEM micrographs of electrochemically synthesized polyaniline are presented in Fig 4.

Electrochemically synthesized polyaniline is uniformly deposited on graphite electrode. The morphology refers to highly developed surface area of nanofibrous network with average diameter of 120 nm. The obtained structure would facilitate heterogeneous electron transfer and enhance catalytic reaction of electroactive compound.

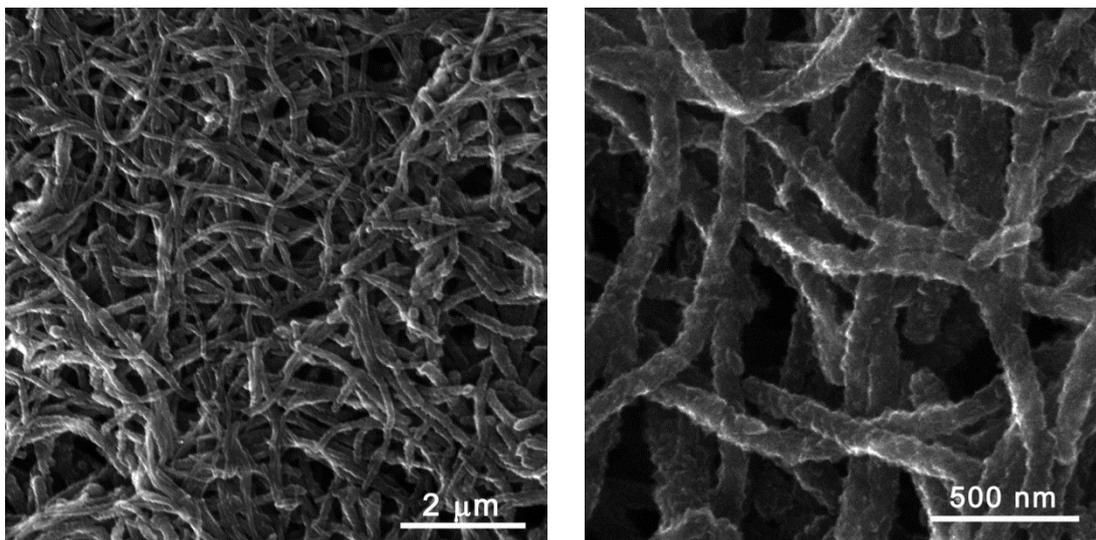


Figure 4. SEM micrographs of electrochemically synthesized nanofibrous PANI on graphite electrode from aqueous solution of 1.0 mol dm^{-3} HCl and 0.15 mol dm^{-3} aniline, at different magnifications.

3.2. Electrocatalytic oxidation of ascorbic acid on PANI modified electrode

CVs of electrochemical oxidation of ascorbic acid on both graphite and PANI modified electrode is given in Fig. 5.

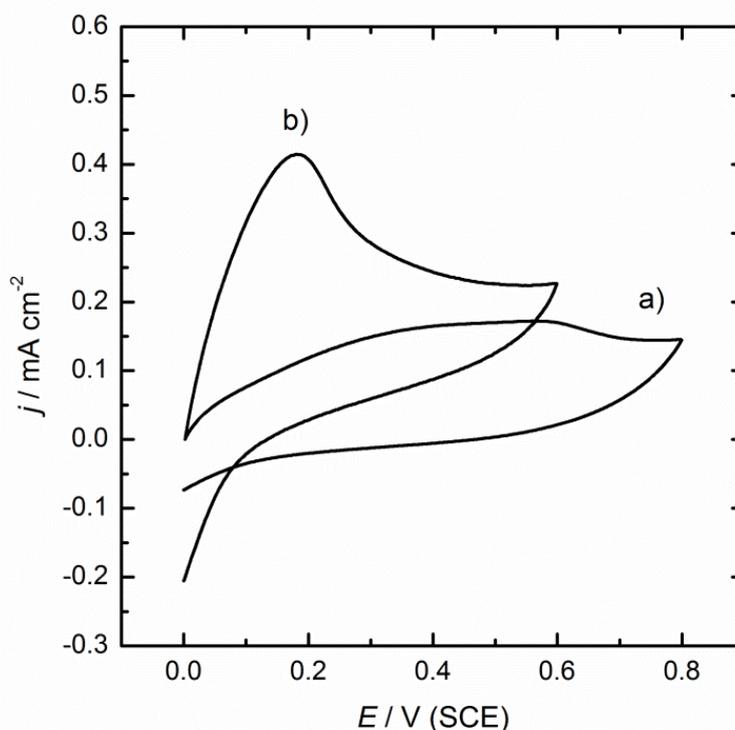


Figure 5. Cyclic voltammograms ($\nu = 20 \text{ mV s}^{-1}$) in PBS (pH = 6.8) containing $10.0 \cdot 10^{-3} \text{ mol dm}^{-3}$ ascorbic acid on a) graphite and b) PANI modified graphite electrode.

As can be seen from Fig. 5., electrochemical oxidation on graphite electrode is characterized by very broad response with poorly defined current peak positioned at 0.5 V (SCE). On the other hand, electrochemical oxidation of ascorbic acid on PANI modified electrode proceeded with well defined anodic peak at potential of 0.18 V (SCE). Electron transfer kinetics of ascorbic acid oxidation is highly depends on surface properties of the electrode [6,9] therefore, both the increase of the peak current for ~ 2.5 times and shift of the oxidation potential for 0.32 V to less positive values, clearly indicates electrocatalytic oxidation of ascorbic acid on PANI modified electrode [14].

CVs of PANI modified electrode in PBS solution containing ascorbic acid, recorded with different scan rates are given in Fig. 6., while Insert of Fig.6. refers to dependence of the peak current density on square root of the scan rate.

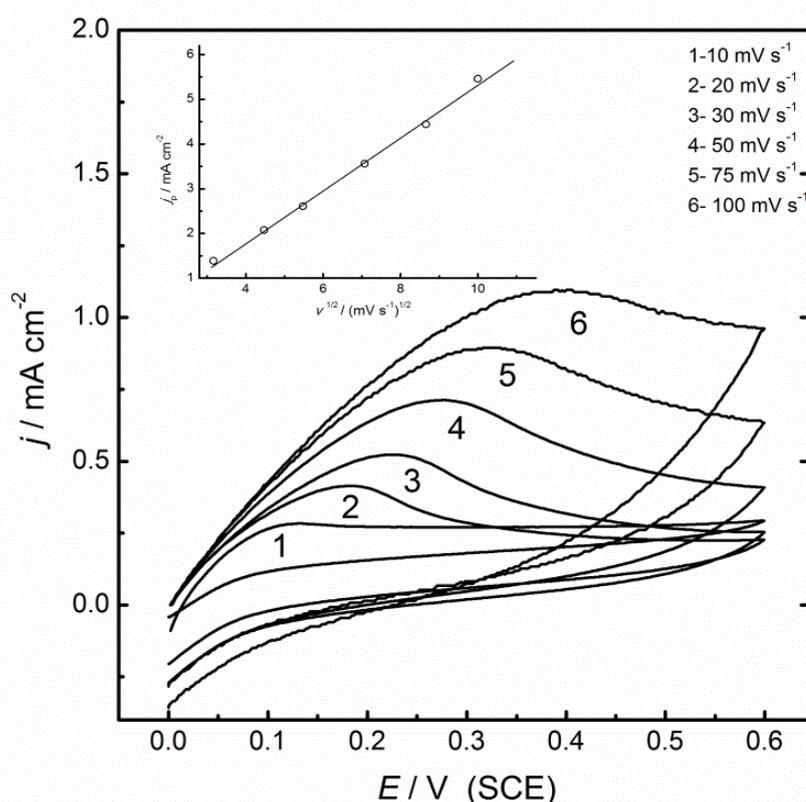


Figure 6. Cyclic voltammograms of PANI modified electrode in PBS (pH = 6.8) containing $10,0 \cdot 10^{-3}$ mol dm⁻³ ascorbic acid obtained by different scan rates. Insert: Dependence of current peak density on square root of scan rate.

The shape of CVs refers to defined anodic wave associated with electrochemical oxidation of ascorbic acid, followed by a fast chemical reaction associated to absence of reverse peak in cathodic part of CV [5]. Position of the catalytic peak potentials shifts to more positive values for higher scan rates, while the values of the peak currents increase. Dependences of the peak current density on square root of the scan rate is linear indicating diffusion control of electrochemical oxidation of ascorbic acid on PANI modified electrode [14].

3.3. Electrochemical determination of ascorbic acid on PANI modified electrode

Response of PANI modified electrode in terms of current peak intensity on ascorbic acid concentration was obtained from anodic LSV curves and given in Fig.7. LSV curves were (Insert of Fig.7.) recorded in different concentration of ascorbic acid in PBS in the range of 0.5 – 50.0 at scan rate of 20 mV s^{-2} (for simplicity only several curves are given obtained at concentrations marked on Fig.7)

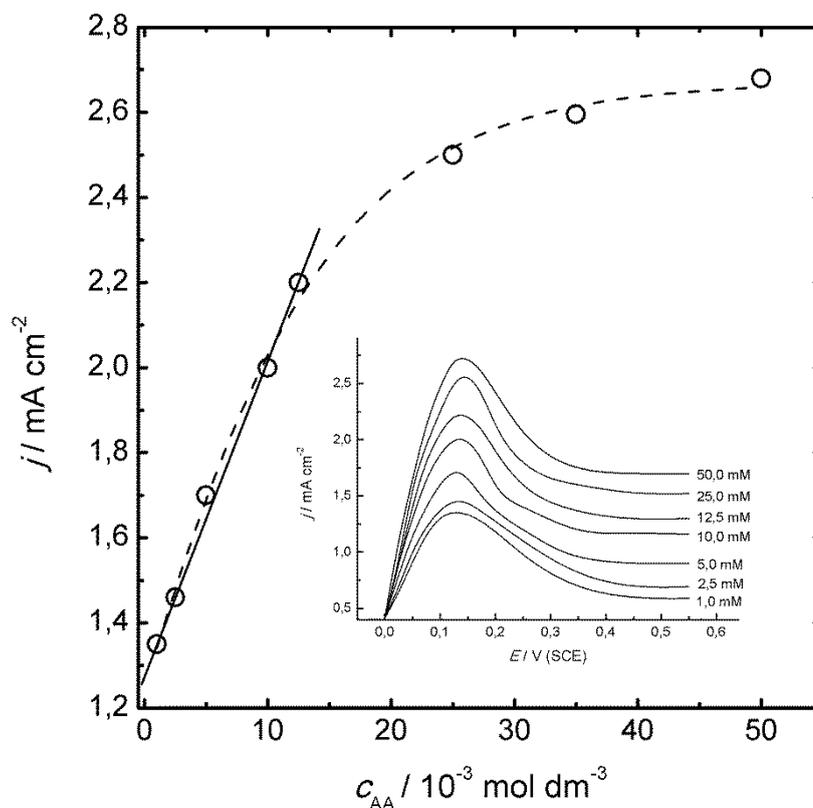


Figure 7. Dependence of the current density peak on ascorbic acid concentration. Insert: LSV curves ($v = 20 \text{ mV s}^{-1}$) for electrochemical oxidation of ascorbic acid in PBS (pH = 6.8) on PANI modified electrode obtained in different concentration of ascorbic acid in the range of $0.5 - 50.0 \cdot 10^{-3} \text{ mol dm}^{-3}$

As it can be seen, the intensity of the oxidation peak current increased by increasing ascorbic acid concentration ranging from 0.5 to $50.0 \cdot 10^{-3} \text{ mol dm}^{-3}$, with linearity in the range between 0.5 and 18.0 mol dm^{-3} . The linearity region, at lower ascorbic acid concentrations, corresponds to reaction occurring at the polymer surface, whilst the diffusion limitation resulted in deviation from linearity, finally reaching the steady state. The dependence of current (i.e. rate of the electrochemical reaction) on ascorbic acid concentration has a shape of rectangular hyperbola typical for chemical reactions proceeding via reactive complex, which might refer to formation of reactive polyaniline–ascorbic acid complex, as proposed by Brazdživuviene et al. [21].

The influence of pH on the position of the current peak potentials was investigated using LSV in buffered solutions containing $10,0 \cdot 10^{-3} \text{ mol dm}^{-3}$ ascorbic acid and the results are given in Fig. 8.

In the pH range between 5.6 and 8.1, current peak potentials decreased with increase of pH with slope of $\sim 32 \text{ mV pH}^{-1}$, indicating two electron charge transfer process with liberation of one proton characteristic to an electrochemical reaction followed by a chemical step [6,14,20].

The protons liberated during electrochemical oxidation of ascorbic acid locally decrease pH and since the polyaniline layer has accessible developed surface, protonation is likely to occur leading to existence of PANI in its conductive and electrochemically active form needed for electrochemical oxidation [20].

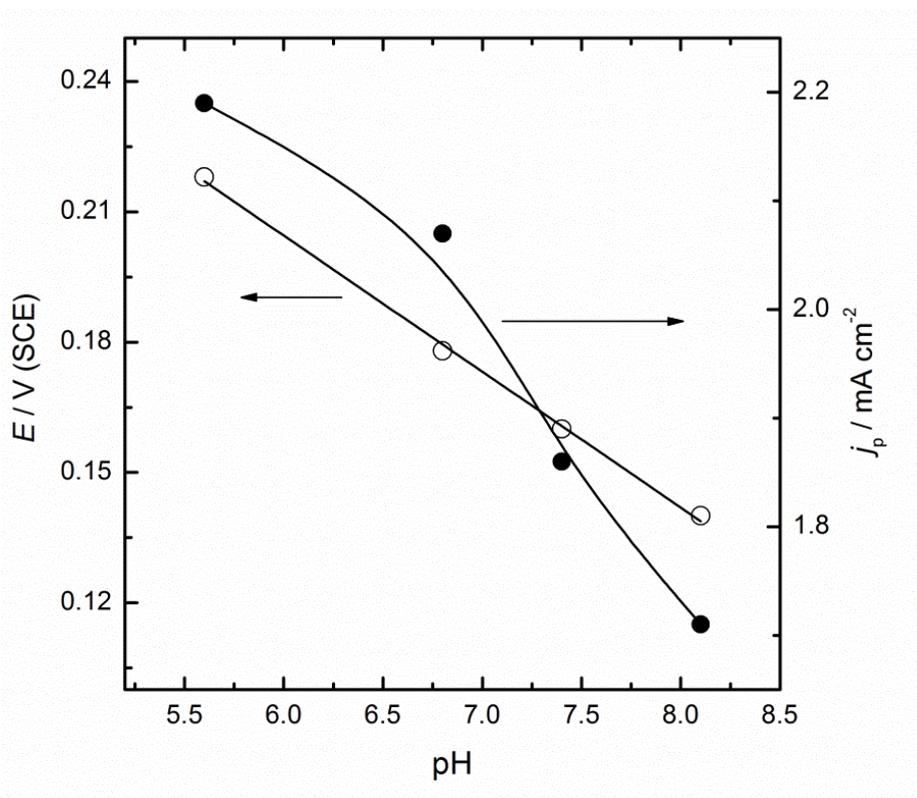


Figure 8. The dependence of: a) current peak potential and b) current density on pH

The peak current density decreased with increasing of pH, which is consistent with data from the literature [14,19]

3.3.1. Stability and real sample analysis

For estimation of the storage stability of PANI modified electrode, the electrode was refrigerated at 8°C in PBS at pH 6.8, and LSV curves for ascorbic acid concentration of $10.0 \cdot 10^{-3} \text{ mol dm}^{-3}$ were recorded after 10, 15, 20 and 30 days and results, in terms of relative signal intensity, are given in Fig 9.

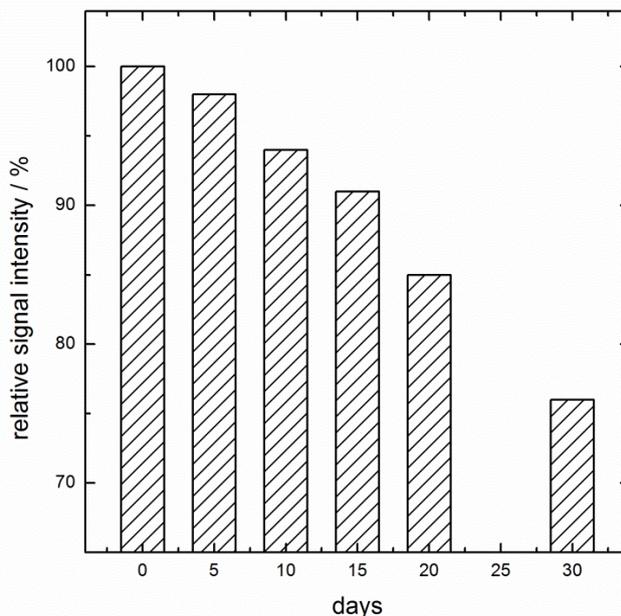


Figure 9. Storage stability of PANI modified electrode.

As it can be seen from Fig.9., during first 5 days of storage PANI modified electrode lost about 2 % of the initial signal intensity, while after a month of storage electrode kept 75 % of signal. The decrease of the signal intensity during long term storage might be a consequence of the lost of PANI film conductivity and degradation at pH 6.8.

PANI modified electrode was also tested in C vitamin for kids (Ivančić i sinovi). Concentrations evaluated from the calibration plot had showed mean values around 98% of those quoted by the manufacturer.

4. CONCLUSION

Nanostructured polyaniline modified electrode was successfully formed in templateless electrochemical synthesis onto graphite electrode. Morphology of the formed polyaniline consisted of highly developed surface suitable for heterogeneous electron transfer. Electrochemical catalytic oxidation of ascorbic acid on polyaniline modified electrode occurred under diffusion control. The pH dependence of the signal indicated two electron process with liberation of proton maintaining conductivity of the polyaniline layer. The storage stability of polyaniline modified electrode slightly increased, while long term lost of the signal indicated lost of the polyaniline conductivity. Polyaniline modified electrode was suitable for real sample analysis.

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