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## Electrochemical determination of ascorbic acid using electrochemically deposited polyaniline

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### Introduction

Electroconducting polymers are promising materials to be used in various fields including: batteries, capacitors, electronic devices, corrosion, biosensors and sensors [1,6]. Polyaniline is probably the most investigated electroconducting polymer, due to low cost monomer, conductivity, environmental stability. Polyaniline can be obtained by chemical or electrochemical oxidative polymerization of aniline. Electrochemical synthesis is performed in anodic process directly from acidic aqueous electrolyte containing aniline. Polyaniline can be used as electrode material for electrochemical determination of ascorbic acid based on electrocatalytic oxidation of ascorbic acid.

### Experimental

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

Prior to polymerization aniline was distilled in argon 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 μm, Banner Scientific Ltd.) on polishing cloths (Buhler Ltd.), the traces of the alumina were removed ultrasonically during 5 min.

Electrochemical characterization of PANI modified graphite electrode was performed by cyclic voltammetry (CV) in the potential range of -0.3 1.0 V (SCE) with different scan rates in buffered solution containing 10.0·10<sup>-3</sup> mol dm<sup>-3</sup> L-ascorbic acid. Stock solution of L-ascorbic acid, (p.a. Merck) was prepared in phosphate buffer solution (PBS), 0.1M 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<sup>-1</sup>. The solutions with different concentration of ascorbic acid were obtained by diluting of the stock solution with PBS

All experiments were carried out at ambient temperature (23±1 °C) in three compartment electrochemical cell. Standard 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 synthesis of PANI on graphite electrode

Electrochemical synthesis of polyaniline was performed galvanostatically with different current densities between 0.5 to 3.0 mA cm<sup>-2</sup>, during 600s. In order to estimate the amount of conductive form of polyaniline i.e. emeraldine salt, all electrodes were discharged with the same current density of 1.0 mA cm<sup>-2</sup> (dedoped) in the same solution. 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. 1. The ratio decrease 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<sup>-2</sup>, 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  $1.0 \text{ mA cm}^{-2}$  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 1.

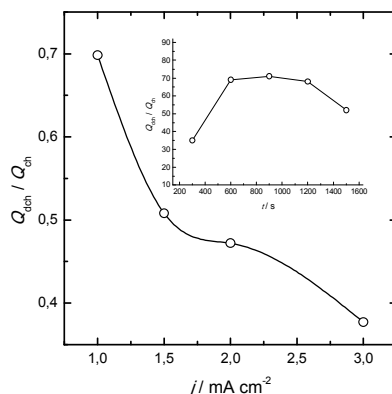


Fig.1. Dependence of discharge and polymerization capacities ratio on polymerization current density. Insert: Dependence of discharge and polymerization capacities ratio on polymerization time.

As it can be seen the discharge and polymerization capacities ratio are nearly the same for polymerization time of between 600 and 1200 s, while for higher polymerization time, decrease of this ratio is due to lost of the polymer film from electrode. Lower polymerization time, on the other hand, led to nonuniformly deposited film. In order to achieve greater available charge, PANI modified graphite electrode was deposited with current density of  $1.0 \text{ mA cm}^{-2}$  during 1200 s and used in further investigations.

### 3.2. Electrocatalytic oxidation of ascorbic acid on polyaniline electrode

CVs of electrochemical oxidation of ascorbic acid on both graphite and PANI modified electrode is given in Fig. 2.

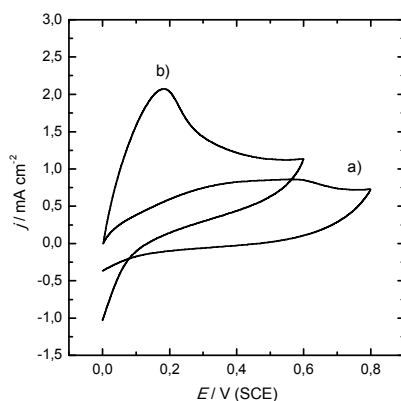


Fig. 2. Cyclic voltammograms ( $\nu = 20 \text{ mV s}^{-1}$ ) in PBS (pH = 6.8) containing  $10,0 \cdot 10^{-3} \text{ mol dm}^{-3}$  ascorbic acid on a) graphite and b) PANI modified graphite electrode

Electrochemical oxidation on graphite electrode is characterized by very broad response with not well 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 dependent on surface properties of the electrode [6,9] therefore, both the increase of the peak current for  $\sim 2.5$  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. 2., while Insert of Fig.2. refers to dependence of the peak current density on square root of the scan rate.

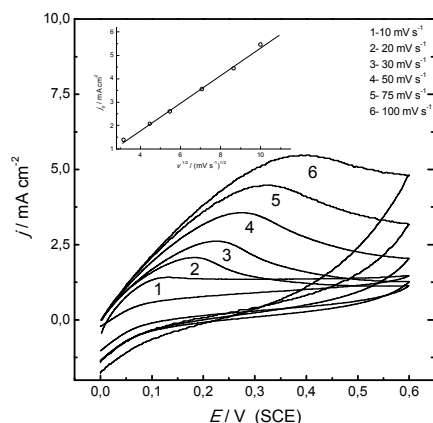


Fig.2. Cyclic voltammograms of PANI modified electrode in PBS (pH = 6.8) containing  $10,0 \cdot 10^{-3} \text{ mol dm}^{-3}$  ascorbic acid obtained by different scan rates. Insert: Dependence of current peak density on square root of scan rate.

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.

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.3. LSV curves were (Insert of Fig.3.) recorded in different concentration of ascorbic acid in PBS in the range of 0.5 – 50.0 at scan rate of  $20 \text{ mV s}^{-2}$  (for simplicity only several curves are given obtained at concentrations marked on Fig.3)

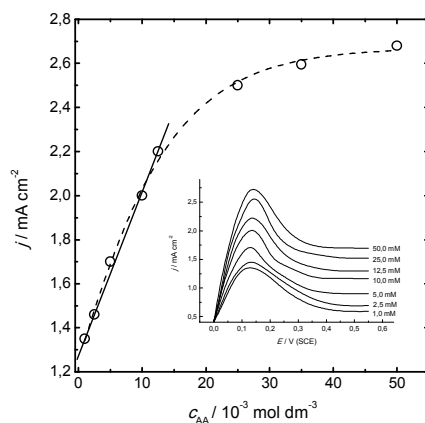


Fig. 3. Dependence of the current density peak on ascorbic acid concentration. Insert: LSV curves ( $v = 20 \text{ mV s}^{-1}$ ) for electrochemical oxidation of ascorbic acid in PBS (pH = 6.8) on PANI modified electrode obtained in different concentration of ascorbic acid in the range of  $0.5 - 50.0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

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  $18.0 \text{ mol dm}^{-3}$ .

### 3.3.1. Stability and real simple analysis

For estimation of the storage stability of PANI modified electrode, the electrode was refrigerated at  $8^{\circ}\text{C}$  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 4.

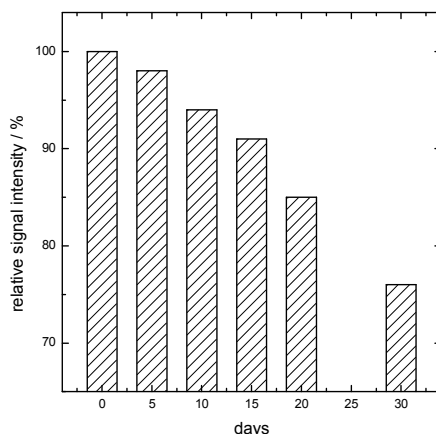


Fig. 4. Storage stability of PANI modified electrode.

As it can be seen, 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.

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