ELECTROCHEMISTRY AND ELECTROCHROMISM OF POLYANILINE AND CO-POLYMER OF ANILINE AND ANTRANILIC ACID LAYERS

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Introduction

The aim of this communication is to describe electrochemical and electrochromic properties of polyaniline and its co-polymer with anthranilic acid.

Polyaniline is one of the most common conductive polymers. It is also a popular electrochromic material. It is stable in aqueous solutions and it is oxygen resistant. The potential application of polyaniline is very wide e.g. it can be used in batteries [1, 2], in electronics [3, 4], in electrochromic display [5,6], in light-emitting devices [7], as corrosion inhibitors [8-11] etc. Through the modification of the polymer structure it is possible to change its properties, such as electrochromism, conductivity, stability. The structure of polyaniline can be modified by different methods. Firstly, its structure can be modified by means of a chemical reaction method, the second method is polymerisation of aniline derivatives, the third is copolymerisations of two different derivatives of aniline. In the group of these compounds it is possible to obtain copolymers of substituted and unsubstituted aniline by means of electrochemical methods.

Aniline and its derivative or, two different aniline derivatives can be used as monomers. The layers are prepared by electrochemical methods. Some of aniline derivatives, such as e.g. sulfonated anilines or carboxylic acids of aniline, are also very interesting for electrochemistry but, in contrast with aniline, many of them cannot form an adherent film, and so the oxidation products diffuse away from the electrode surface to the solution.

Experimental

Aniline was redistilled over zinc and stored in the dark under argon. Anthranilic acid (ortho-aminobenzoic acid (Aldrich) was used without purification. The solutions were prepared in Mili-Q grade water. The voltammetric measurements were carried out in a three-electrode cell. A Pt (99.99%) wire of geometric area $A=0.96 \pm 0.02$ cm^2 was used as a working electrode. A Pt mesh was a counter electrode and SCE (saturated NaCl) in a separated cell was used as a reference electrode. The measurements of voltammetry and EIS (Electrochemical Impedance Spectroscopy) were performed using the potentiostat PAR 273A and the analyser of frequency Solartron 1255. The measurement system was controlled by the microcomputer with CorrWare and ZPolt software v.2.7 by SAI (Scribner Associates Inc.). All the electrochemical measurements were carried out in the solutions containing 1 mol/dm^3 $HClO_4$ used as supporting electrolyte. Polyaniline and co-polymer of aniline with anthranilic acid were synthesised by means of cyclic voltammetry. The

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potential range equalled from 0 to 0.8V and the sweep potential rate was 200 mV/s. The layers were synthesised during 700 voltammetric cycles. Such conditions of polymerisation should enable the formation of polymers with the highest participation of linear structure (emeraldine), which guarantees high stability and resistance to degradation of the obtained layers.

In the measurements conducted by means of UV-vis spectroscopy, a special electrochemical cell was used in which working and counter electrodes were ITO plates. The examined polyaniline layers and co-polymer of aniline with anthranilic acid were synthesised on ITO base. UV-vis spectra were done *in situ* in the electrochemical cell, which was also the absorption cell of the spectrophotometer Specord M42 (Carl Ceiss Jena, Germany).

Results and Discussion

The electropolymerisation processes proceeding in aqueous aniline solutions and antranilic acid were examined by means of cyclic voltammetry.

Figure 1 presents the voltammetric curves obtained for polyaniline (A) and co-polymer of aniline and anthranilic acid (B) in 1 M $HClO_4$.

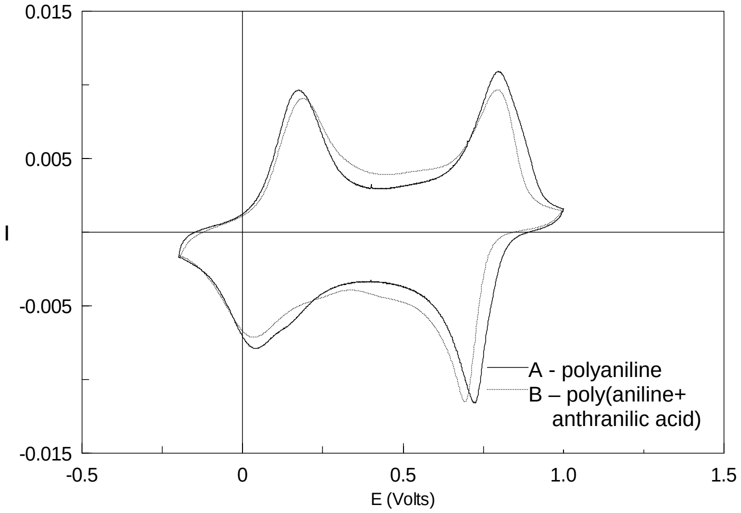

Fig. 1 *Voltammetric curves for polyaniline (A) and co-polymer of aniline with anthranilic acid (B) in 1M $HClO_4$, v=200mV/s.*

The obtained curves are in accordance with literature data [12-21]. Here we can observe the peaks connected with the first stage of polyaniline oxidation (I) of about 0.2 V and with the second stage of polyaniline oxidation (II) of about 0.7 V.

At such a narrow range of polarisation potentials (0 to 0.8V) the peaks connected with the formation of phenazine links and the processes of degradation in polymer structure are not visible. These processes usually reveal peaks at potentials about 0.5V. On this basis it can be stated out that the obtained layers are little cross-linked and their main components are linear structures (emeraldine).

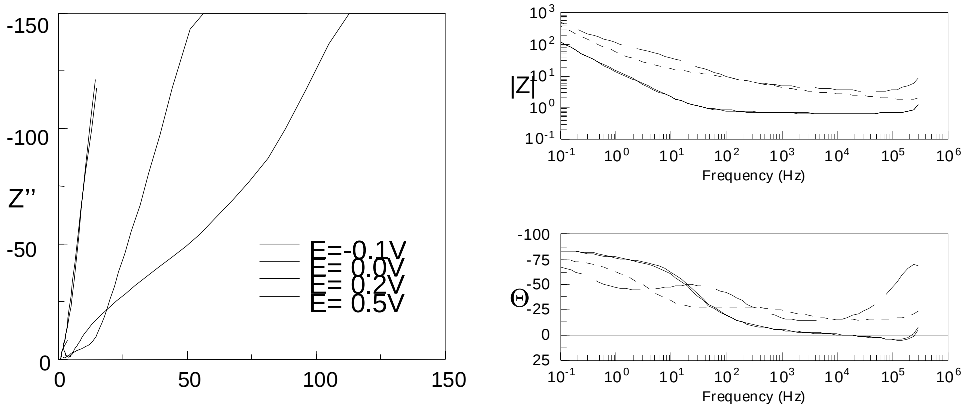

***Fig. 2** Nyquist's and Bode's diagrams for polyaniline layer in 1M $HClO_4$ at different polarization potentials.*

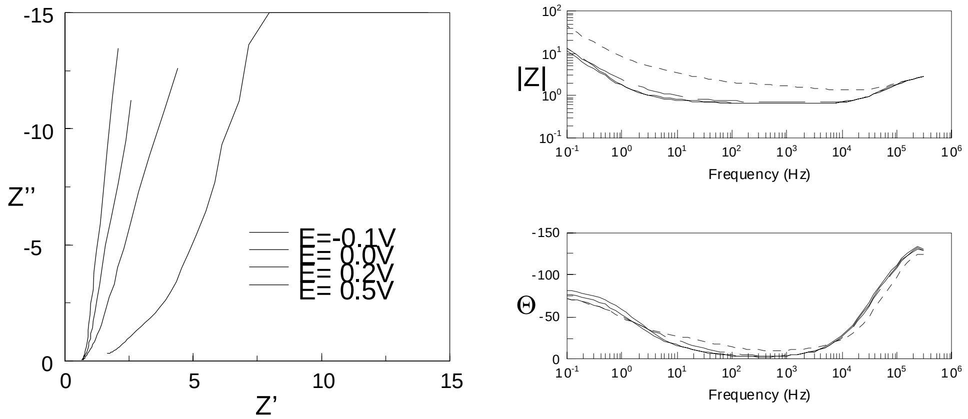

***Fig. 3** Nyquist's and Bode's diagrams for co-polymer of aniline with anthranilic acid layer in 1M $HClO_4$ at different polarization potentials.*

Figures 2 and 3 present Nyquist's and Bode's diagrams for the examined layers. The measurements were done for the potentials corresponding with the reduced layers (E=-0.1V), the areas of the first oxidation peak (E=0.2V) and the oxidation layers (E=0.5V). As it is seen in the presented diagrams, after oxidation polyaniline layers show the evidence of high conductivity and, as it results from Nyquist's diagrams, there are no kinetic limitations connected with charge transfer.

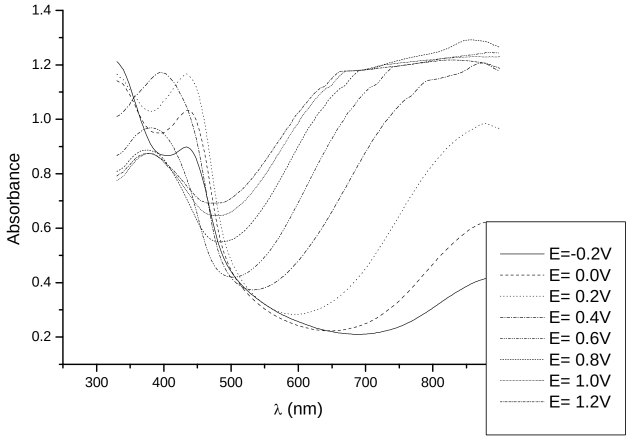

***Fig. 4** UV-vis spectra for polyaniline layer in 1M $HClO_4$ at different polarization potentials.*

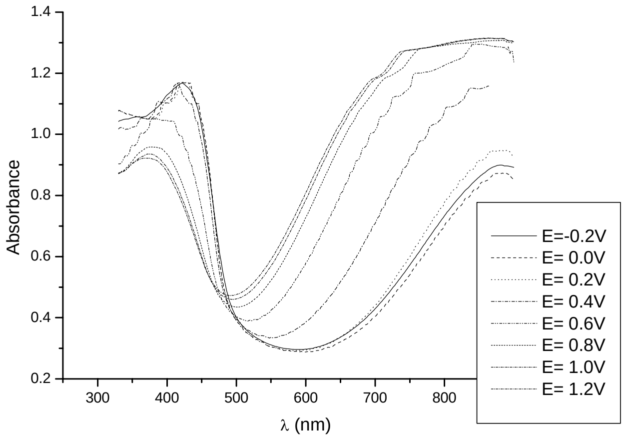

***Fig. 5** UV-vis spectra for co-polymer of aniline with anthranilic acid layer in 1M $HClO_4$ at different polarization potentials.*

Figures 4 and 5 present UV-vis spectra done for both examined layers at different polarisation potentials (E=-0.2, 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2V). The changes in the length of wave of adsorbed light caused by the degree of polymer oxidation are clearly seen. The changes are in accordance with literature data [22]. The reduced form (leukoemeraldine) is yellow or yellow-green, the oxidated form (emeraldine) is dark green, while completely oxidated form (pernigraniline) is dark blue.

However, there are some differences between the layers of polyaniline and co-polymer of aniline with anthranilic acid. Co-polymer layers in reduced form absorb light from the range about 700nm in greater extent than polynaline layers, for which the absorbance in this range equals about 0.2. While in the oxidated form (more than 0.8V pernigraniline) polyaniline layers absorb light from the higher range of the wave length and in greater extent than co-polymer.

Conclusions

The obtained polymer layers demonstrated very good structure. They were very little cross-linked. Both polymers underwent oxidation very quickly and at potentials 0.2V and higher did not reveal any kinetic limitations in electric conductivity. Polyaniline layers showed higher absorption of light in the oxidated form and lower in the reduced form in comparison with co-polymer. Both polymers presented not only high stability, but the repeatability of the results at subsequent polarisation cycles all well.

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