ELECTROCHEMICAL CHARACTERIZATION OF HYBRID MATERIALS OF PRUSSIAN BLUE-POLYANILINE OR CO-POLYMERS OF ANILINE AND ANTRANILIC AND METHANILIC ACID

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Introduction

For many years there has been considerable interest in the research connected with modified electrodes. The experiments are based on the application of layers having redox properties (e.g. Nafion®, polyvinylopyridine) or layers with electronic conducting (e.g. polypyrrole, polyaniline). The layers are usually organic substances, but inorganic substances also present similar properties. The example can be metal hexacyanoferrates, which contain in their structure redox centres of changeable stages of oxidation, while polyoxometalates and heteropolyanions layers demonstrate ion-electron conductivity. One of the new approaches in modified electrodes experiments are hybrid materials. These are conductive layers built of organic and inorganic materials interchangeably. Depending on the composition, they can be divided into organic-inorganic materials (OI) in which in their organic matrix inorganic particles are immobilized and inorganic-organic materials (IO) in which the inorganic matrix contains the addition of organic polymers. Between these two groups there are materials in which the fractions of organic and inorganic compounds are comparable. These materials are called nanocomposites. Contemporary electrochemistry enables to design the systems on the nanoparticles level. One of the widely used techniques to obtain ultra-thin layers of hybrid materials is the method of self-assembly [1]. Hybrid materials have a lot of applications, among others, in the construction of batteries [2-4] and electrochemical capacitors [5-8]and as electrochromic materials. The experiments presented in this communication deal with hybride materials based on the organic matrix built of polyaniline (Pani) or co-polymers of aniline with anthranilic acid (AA) or aniline with metanilic acid (MA). The inorganic component is Prussian blue (PB). In this material the following redox processes are possible:

for the polymer matrix:

$$\mathrm{Pani} \rightleftharpoons \mathrm{Pani}^{+2n} + 2ne + 2nH^+ \qquad (1)$$

$$\mathrm{Pani}^{+2n} \rightleftharpoons \mathrm{Pani}^{+4n} + 2ne + 2nH^+ \qquad (2)$$

for the Prussian blue:

$$K_4Fe^{II}_4[Fe^{II}(CN)_6]_3 \; - \; 4e \; - \; 4K^+ \rightleftharpoons Fe^{III}_4[Fe^{II}(CN)_6]_3 \qquad (3)$$

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 \; - \; 3e \; + \; 3A^- \rightleftharpoons Fe^{III}_4[Fe^{III}(CN)_6A^-]_3 \qquad (4)$$

Experimental

Aniline was redistilled over zinc and stored in the dark under argon. Anthranilic acid (ortho-aminobenzoic acid (Aldrich)) and metanilic acid (meta-aminobenzosulfonic acid (Aldrich)) were 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 electrodes. 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 were performed using the potentiostat PAR 273A. The measurement system was controlled by the microcomputer with CorrWare software v.2.8 by SAI (Scribner Associates Inc.).

The layers of hybrid materials were obtained by means of a single-stage electrochemical synthesis. The layers based on polianiline (Pani-BP) were synthesised from the solutions containing aniline (c=0.1M), $K_3Fe(CN)_6$ (c=0.001M), $Fe_2(SO_4)_3$ (c=0.001M), H_2SO_4 (c=0.5M), $KHSO_4$ (c=0.5M).

The layers based on co-polymers aniline with anthranilic acid (Poly(An-AA)-BP) were synthesised from the solutions containing aniline (c=0.05M), anthranilic acid (c=0.05M), $K_3Fe(CN)_6$ (c=0.001M), $Fe_2(SO_4)_3$ (c=0.001M), H_2SO_4 (c=0.5M), $KHSO_4$ (c=0.5M).

The layers based on co-polymers aniline with metanilic acid (Poly(An-MA)-BP) were synthesised from the solutions containing aniline (c=0.05M), metanilic acid (c=0.05M), $K_3Fe(CN)_6$ (c=0.001M), $Fe_2(SO_4)_3$ (c=0.001M), H_2SO_4 (c=0.5M), $KHSO_4$ (c=0.5M).

The synthesis was carried out using cyclic voltammetry, polarising the electrode within the range from -0.1V to 0.8V with sweep potential rate 50 mV/s. The thickness of the obtained layers depended on the concentrations of aniline and on the number of voltammertic cycles of the synthesis. The voltammetric measurements of the obtained modified electrodes were conducted in the solution of the supporting electrolyte (H_2SO_4 (c=0.5M), $KHSO_4$ (c=0.5M)).

Results and discussion

Figures 1-3 present voltammetric curves for the layers of Pani-Bp, Poly(An-AA)-BP and Poly(An-MA)-BP. The measurements were conducted for the sweep potential rate from20 mV/s to 300mV/s. The figures 1-3 also demonstrate the dependences of peak currents – anodic (E=0.22V) and cathodic (E=0.17V) in the function of square root of sweep potential rate. The results of the measurements for the layers built on the basis of polyaniline are in accordance with the results described in literature [9,10] – the number of peaks, their position and shape. It concerns mainly the characteristic peaks at potentials E=0.22V and E=0.17V, which correspond with the redox process (1) and (3).

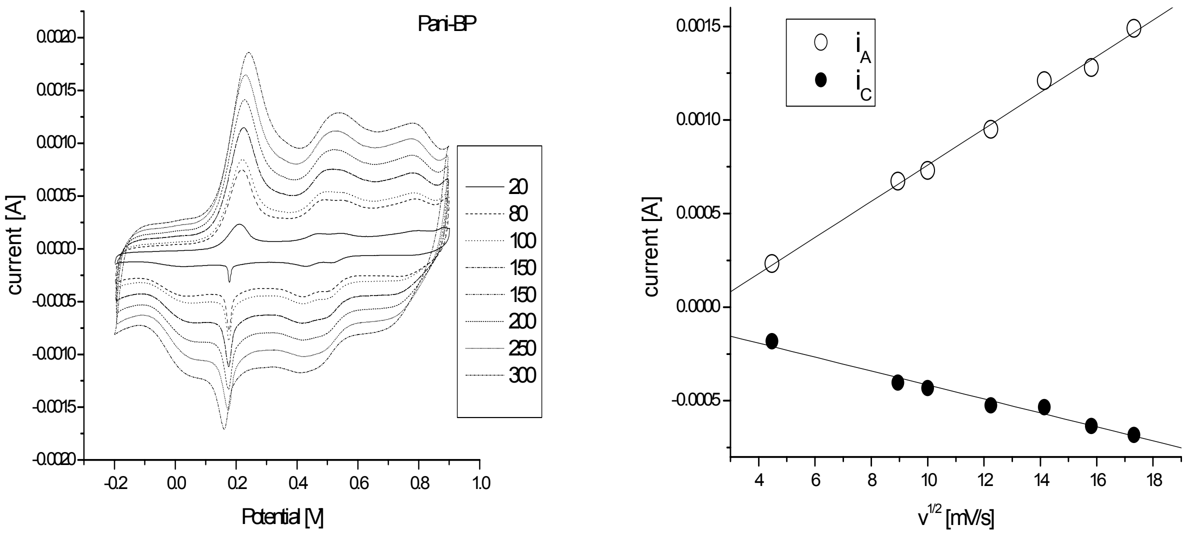

Fig.1 *Voltammetric curves of layer of Pani-PB and dependence of i_a and i_c on $v^{1/2}$*

The layer containing co-polymers demonstrate a lower degree of reversibility of electrode processes connected with peaks E=0.22V and E=0.17V.

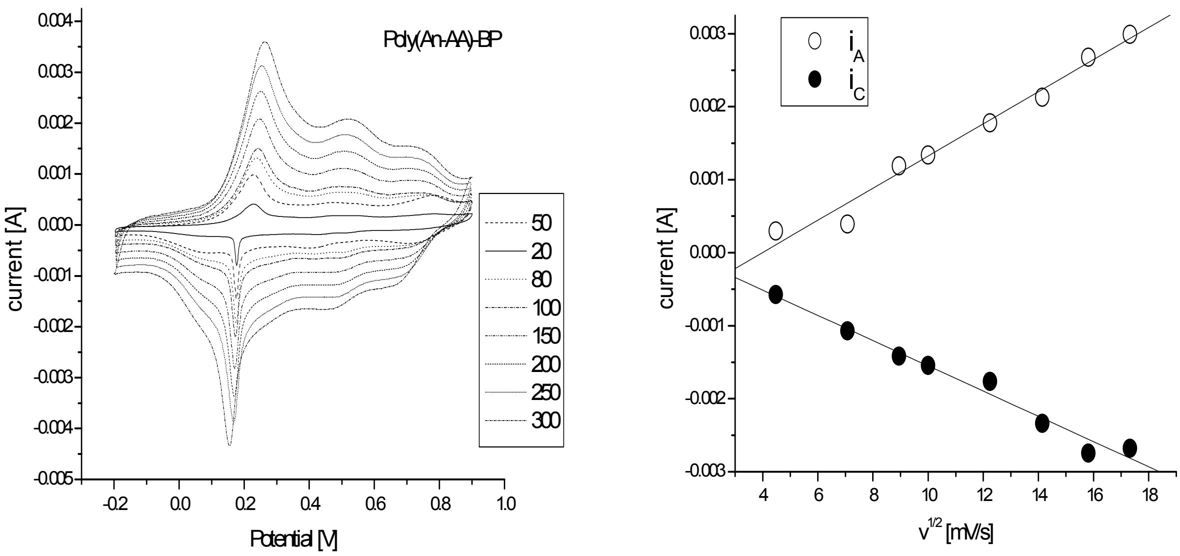

Fig. 2 *Voltammetric curves of layer of Poly(An-AA)-PB and dependence of i_a and i_c on $v^{1/2}$*

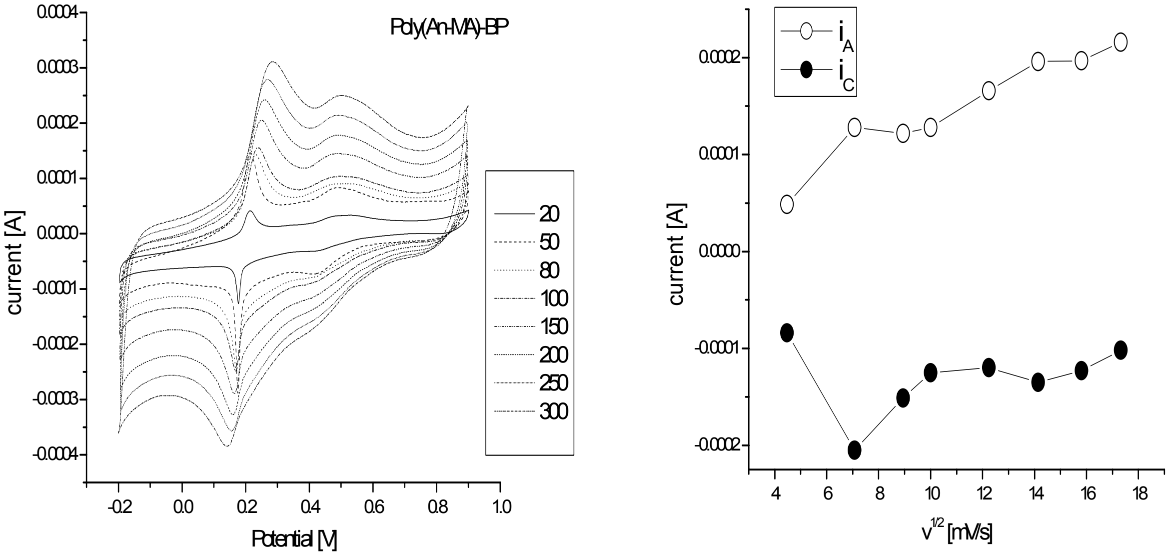

Fig. 3 *Voltammetric curves of layer of Poly(An-MA)-PB and dependence of i_a and i_c on $v^{1/2}$*

In case of co-polymers with metanillic acid the degree of irreversibility is the highest and the dependence of cathodic peak current on $v^{1/2}$ is irregular. For these layers, at rate over 100mV/s, the cathodic peak loses its characteristic shape. It might be supposed that the presence of sulphone groups causes the partial solution of organic layer, so it is unable to immobilise the particles of Prussian blue. The layers are unstable and they cannot be applied further. The results obtained for the layers with co-polymer of anthranilic acid indicate that they have similar properties as the layer with polyaniline only. Co-polymer of aniline and anthranilinc acid can be used as organic matrix to produce hybrid materials.

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