ELECTROCHEMICAL IMPEDANCE MEASUREMENTS ON PRUSSIAN BLUE FILMS DEPOSITED ON PLATINUM ELECTRODES

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În această lucrare sunt prezentate comportarea electrochimică şi spectrele de impedanţă electrochimică ale filmelor de Albastru de Prusia (PB) depuse pe electrozi de platină. BP a fost depus cu ajutorul metodei potenţiostatice la o valoare de potenţial de cca. +0.40 V vs. ECS. Spectrele de impedanţă electrochimică au fost înregistrate la diferite valori ale potenţialului de electrod. Au fost determinate rezistenţa filmului de BP şi rezistenţa la transferul de sarcină din spectrele de imedanţă electrochimică.

In this work, the electrochemical behaviour and the electrochemical impedance spectra of Prussian Blue (PB) films deposited on platinum electrodes are reported. PB was deposited by potentiostatic method at a potential value of +0.40 V vs. SCE. The impedance spectra of PB films have been recorded at different electrode potential values. The resistance of the PB film and the charge transfer resistance have been determined from electrochemical impedance spectra.

Keywords: modified electrode, Prussian blue, electrochemical impedance spectroscopy

1. Introduction

Iron(III) hexacyanoferrate(II), Prussian Blue (PB) is a mixed-valence compound that can be deposited onto the electrode surface as an electroactive film. There are two forms of PB that have been called "water insoluble PB", $Fe_4^{III}[Fe^{II}(CN)_6]_3$, and "water soluble PB", $KFe^{III}[Fe^{II}(CN)_6]$, respectively [1]. The soluble form of PB was supposed to be formed in the presence of an excess of potassium ions. A colourless compound called Everitt's Salt (ES) is obtained by reduction of PB, while oxidation of PB gives Berlin Green (BG).

Itaya and co-workers reported an electrochemical method of preparation of PB films, which is based on the electrochemical reduction of a solution of ferric-ferricyanide under galvanostatic conditions on platinum, glassy carbon and SnO_2 electrodes [1, 2]. It has been shown that the electrochemical behaviour of those galvanostatically deposited films is strongly dependent on the current density applied during the deposition reaction. PB films are deposited also by

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potentiodynamic and potentiostatic methods [3-6]. Initially, the PB film is obtained as insoluble form, but the film is converted into the soluble form by cycling the electrode potential repeatedly around the potential of PB/ES system in a KCl solution. The PB deposit presents a zeolite structure, which allows the motion of different counterions, such as K^+, NH_4^+, Rb^+ and Cs^+, throughout the electroactive film. Recently, several studies regarding the charge transport, deposition efficiency, and redox behaviour of PB films using cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM) methods have been performed [7-9]. On the other hand, electrochemical impedance spectroscopy (EIS) has been successfully used for investigating the charge transport within electroactive films [10]. Impedance spectra of PB films deposited on indium-thin oxide (ITO) electrodes in KCl [11-15] and NH_4Cl, CsCl [16] solutions have been reported. Recently, the combination of EQCM and EIS methods in the study of the PB reduction has been reported [17, 18]. However, there is no consensus on the best method to obtain high quality PB films. Due to the different properties of these films, the deposition technique of choice depends on the final application. Furthermore, the deposition of PB films can be made by selecting the convenient method out from the general methods usually applied for the preparation of chemically modified electrodes. In the case of PB films deposited on ITO electrodes, the impedance spectra and also the cyclic voltammograms are affected by the uncompensated resistance of the ITO electrodes.

In this paper, the electrochemical impedance spectra of PB films deposited on Pt electrodes in KCl solutions are presented. The impedance spectra of PB films were recorded at different potential values ranging from 0.00 V to +1.00 V *vs.* SCE. A good stability of the modifying layer was observed by using cyclic voltammetry after each electrochemical impedance measurement. The use of Pt electrode as substrate for the PB deposition resulted in smaller value of the uncompensated resistance in comparison with indium-tin oxide electrodes.

2. Experimental

2. 1. Chemicals

All chemicals: $FeCl_3$ (97%, Merck), $K_3[Fe(CN)_6]$ (p.a., Feinbiochemica), HCl (p.a., Aristar), and KCl (p.a., Carlo Erba, RPE) were used as received. Double distilled water was always used to prepare aqueous solutions for electrochemical use. In order to de-aerate the solutions for electrochemical tests, argon was bubbled through, for 20 min before the experiments. The argon flow was maintained continuously over the sample solution during the electrochemical measurements.

2. 2. Electrodes and Instrumentation

The electrochemical experiments were carried out with a PC-controlled Autolab PGSTAT 20 potentiostat/galvanostat (Ecochemie, Utrecht, The Netherlands). The electrochemical measurements have been carried out in a single-compartment cell (Metrohm), with a three-electrode configuration comprising a 3 mm diameter Pt disk electrode (Metrohm, Switzerland) as the working electrode, a saturated calomel electrode (SCE, Amel) as the reference electrode, and a Pt wire as the auxiliary electrode. Prior the modification, the working electrode was subsequently polished with 1, 0.3 and 0.05 μm alumina powder to a mirror finish, dipped into an ultrasonic bath for 5 min, and then rinsed with double distilled water.

Impedance measurements were carried out in the frequencies range between 0.01 and 10^5 Hz and 0.01 V of signal amplitude.

2. 3. Procedures for the preparation of modified electrode

Prussian blue was deposited onto Pt electrode using potentiostatic method from a solution containing 0.002 M $FeCl_3$, 0.002 M $K_3[Fe(CN)_6]$, 0.01 M HCl, and 0.1 M KCl. The potential of the working electrode was maintained at +0.40 V for 60 s. After the deposition of PB, the modified electrode was rinsed with double distilled water and dipped into the transfer solution containing 0.1 M KCl, and 0.01 M HCl, where the PB films were activated by cycling the potential between -0.10 and +1.00 V at a potential scan rate of 0.05 V s^{-1} until a stable cyclic voltammogram was obtained.

3. Results and Discussion

3. 1. Electrochemical behaviour of Pt/PB modified electrode in aqueous medium

A typical cyclic voltammogram recorded on a Pt/PB modified electrode, obtained as described in the Experimental section, is shown in Figure 1. A colourless compound called Everitt's Salt (ES) is obtained by reduction of PB, while by PB oxidation is formed Berlin Green (BG) [1, 2]. The signals in Figure 1 should be hence ascribed to the following processes, considering both the soluble and insoluble forms of PB:

- peak system at *ca.* +0.2 V:

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e^- + 4K^+ \Leftrightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 \qquad (1a)$$

PB 'insoluble form' ES

$$KFe^{III}[Fe^{II}(CN)]+e^{-}+K^{+} \Leftrightarrow K_2Fe^{II}[Fe^{II}(CN)_6] \quad (1b)$$

PB 'soluble form' ES

- peak system at *ca.* +0.9 V:

$$Fe_4^{III}[Fe^{II}(CN)_6]_3-3e^{-}+3A^{-} \Leftrightarrow Fe_4^{III}[Fe^{III}(CN)_6A]_3 \quad (2a)$$

PB 'insoluble form' BG

$$KFe^{III}[Fe^{II}(CN)]-e^{-}-K^{+} \Leftrightarrow Fe^{III}[Fe^{III}(CN)_6] \quad (2b)$$

PB 'soluble form' BG

The dependence of the anodic and cathodic peak current intensities on the potential scan rate is linear up to 0.10 V s^{-1} for the peak system at *ca*. +0.20 V. The cathodic peak current is larger than the backward associated anodic one. In what concerns the peaks recorded at *ca*. +0.90 V, the cathodic peak current increases very slowly with increasing scan rate, while the anodic peak current increases more rapidly with the scan rate.

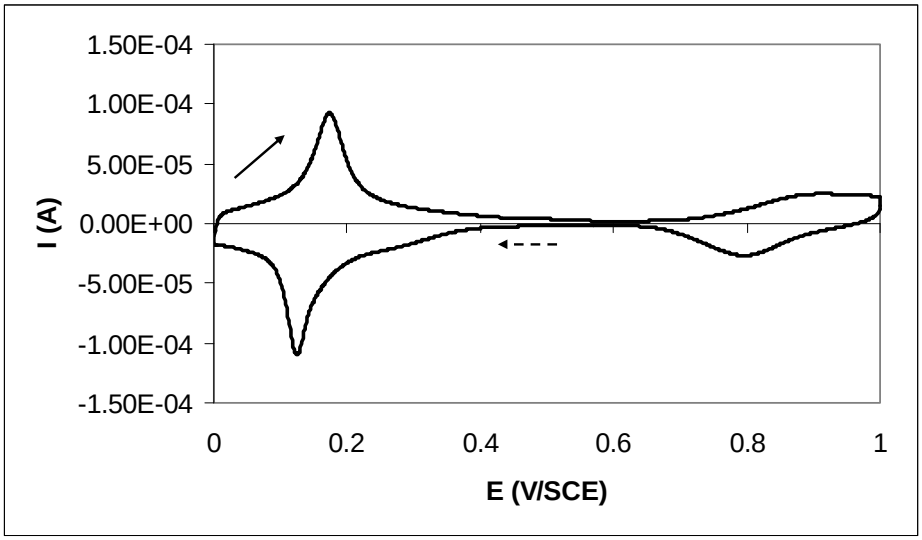


Fig. 1. Cyclic voltammogram (0.05 V s^{-1}) recorded at Pt/PB modified electrode in aqueous solution containing 0.1 M KCl, 0.01 M HCl

The peak potential separation for the system at *ca*. +0.20 V is equal to 0.048 V at the scan rate of 0.05 V s^{-1}, and grows with increasing the scan rate, no ohmic drop compensation being applied. The value of the peak potential separation indicates that PB is confined to the electrode surface and that the PB layer is thin enough – less than 50 nm, according to previously reported values for the PB film thicknesses [11, 19]. However, the peak potential separation is higher than that predicted by theory for surface confined redox species, i.e. 0 V, and this difference may imply some limitations in the redox reactions of PB/ES redox system due to the transport of counterions in and out of the PB layer. Concerning the peak system recorded at *ca*. +0.90 V, the peak potential separation is of 0.084 V at a scan rate of 0.05 V s^{-1} and slowly grows only with increasing the scan rate.

The excellent stability of the modified electrode over 100 repetitive scans between 0.00 and +1.00 V in 0.1 M KCl and 0.01 M HCl solution should be emphasized. Only a slight decrease of *ca.* 5% of both anodic and cathodic peak currents of the system at 0.2 V is observed. The stability of the peak system at 0.9 V is even higher, and only a decrease of the peak currents of 2% is correspondingly observed.

3.2. Electrochemical impedance spectroscopy of Pt/PB modified electrode

The impedance spectra were recorded at different potential values in the range between 0.00 V and +1.00 V. Before the EIS experiments, the PB films were cycled for 10 times around the PB/ES redox system until a stable voltammogram was obtained. Cyclic voltammograms were recorded before and after each impedance measurement in order to check the stability of the PB film. Figure 2 shows the electrochemical impedance spectrum of the Pt/PB modified electrode in the transfer solution (0.1 M KCl and 0.01 M HCl), recorded at a potential value of about +0.20 V.

Three distinct regions could be distinguished: i) a semicircle is observed at high frequencies, attesting the charge transfer at the electrode / solution interface; ii) a transition zone at intermediary frequencies; iii)a Warburg line at low frequencies characteristic for diffusion process. The first region is situated at high frequencies where a semicircle may be observed showing charge transfer behaviour. From the top of this semicircle, a corresponding value of the frequency, denoted as ω_{max}, can be determined. The charge transfer resistance, R_{ct}, and double layer capacitance, C_{dl}, could be determined by using the equation [20]:

$$\varpi_{\max} = \frac{1}{R_{ct}\, C_{dl}} \tag{3}$$

The exchange current density can be calculated using the equation [20]:

$$j_0 = \frac{RT}{nFAR_{ct}} \tag{4}$$

where A is the geometric surface area of the electrode, n the number of transferred electrons (n = 1), and the other symbols have the usual significance.

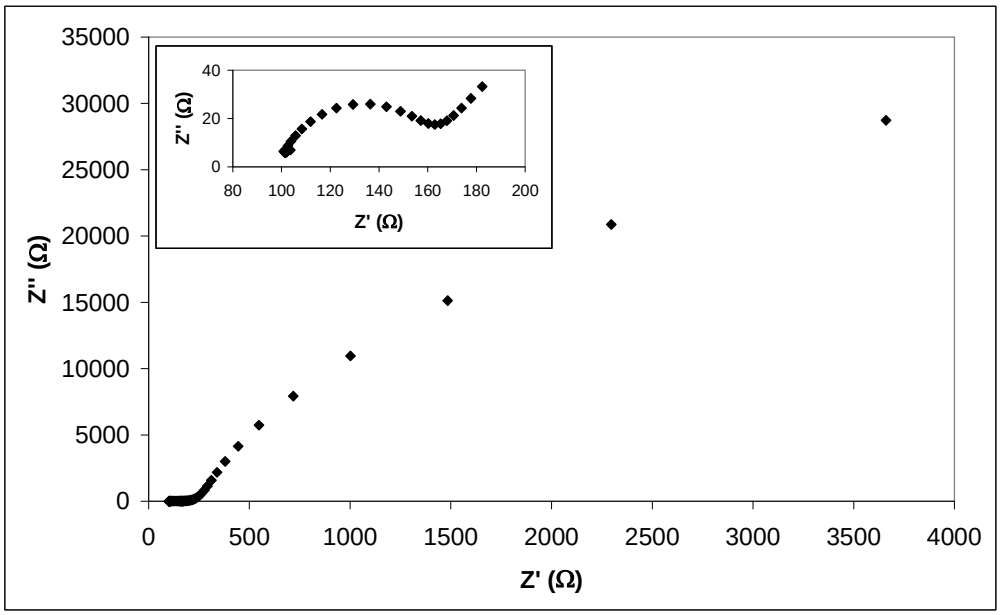


Fig. 2. Electrochemical impedance spectrum of Pt/PB modified electrode recorded in aqueous solution containing 0.1 M KCl, and 0.01 M HCl at a fixed potential value of 0.20 V; the inset shows the impedance spectra at high frequencies

The impedance measurements were performed at a fixed potential value of 0.2 V, which is close to the formal potential of the redox couple ES/PB where the electrode reaction (1) occurs. The left intercept of the semicircle with the Z' axis gives the sum between the solution and film resistances, which is the total ohmic drop, and the right intercept gives the sum of this total ohmic drop and the charge transfer resistance. Values of about 98.1 Ohms and 72.4 Ohms were obtained for the solution and film resistance, and the charge transfer resistance, respectively. A value of 5.02 mA cm^{-2} for the exchange current density and a value of 1.20 mF cm^{-2} for the double layer capacitance were also obtained.

After the EIS measurements, the PB modified electrode was investigated in the transfer solution by cyclic voltammetry. Figure 3 reports the cyclic voltammograms recorded before and after the EIS measurements at 0.2 V. It can be observed that both the anodic and cathodic peak currents corresponding to the ES/PB redox system increased after EIS measurement. However, a better criterion

is the charge of the corresponding peaks. The following values of 1.62 10^{-4} C and 1.91 10^{-4} C were obtained for the cathodic charges before and after EIS measurement, respectively. An increase of ca. 18% in the cathodic charge after EIS measurement is observed. These values are in agreement with the expected behaviour, i.e. the incorporation of potassium ions takes place during the reduction of PB. The anodic charge decreased from 2.39 10^{-4} C before EIS measurement to 2.21 10^{-4} C after EIS measurement, that is a decrease in the anodic charge of ca. 8%. This suggests that the incorporation of potassium ions is faster than its release. Therefore, this behaviour can be due to the incorporation/release of potassium ions during the EIS measurement performed at 0.2 V, which is a potential value that differs by 0.05 V to that of the formal potential of the ES/PB redox wave ($E_{1/2}$ = 0.15 V). The EIS measurement takes place during a period of time large enough. Therefore, the transport of potassium ions into and out of the film is necessary in order to maintain the electroneutrality (see equation (1)). The redox wave located at ca. 0.9 V is not affected by the EIS measurement. This behaviour is expected taking into consideration that the electrode was polarized at 0.2 V.

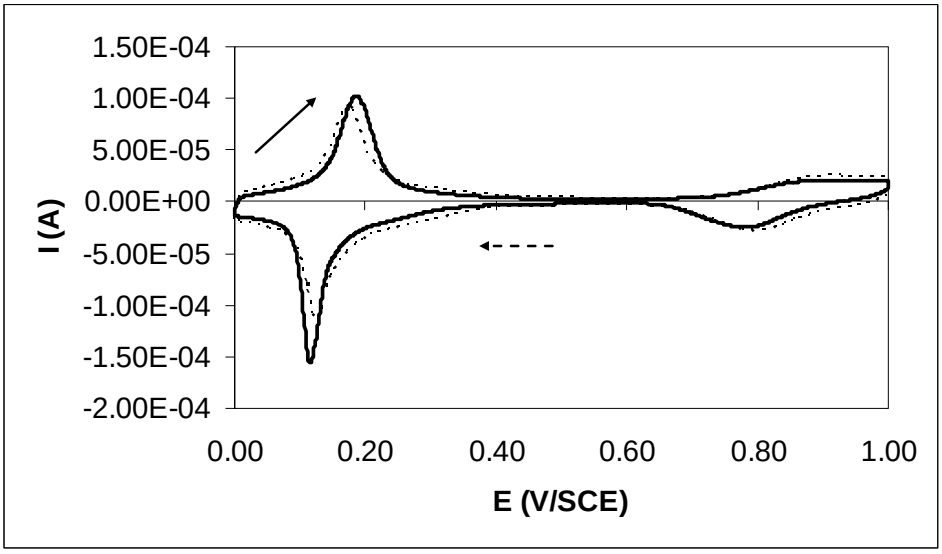


Fig. 3. Cyclic voltammograms of Pt/PB modified electrode recorded in aqueous solution containing 0.1M KCl, 0.01M HCl before (dotted line) and after (solid line) impedance measurement at 0.2V. Potential scan rate: 0.05V s^{-1}

The EIS spectrum was also recorded at 0.8 V potential value, which is near the second redox wave BG/PB. This spectrum is represented in Figure 4. The shape of the spectrum is quite different than that recorded at 0.2 V. In this case,

there is no semicircle at high frequencies. Furthermore, a capacitive loop is observed for high frequencies region, followed by the Warburg line at low frequencies. The appearance of the capacitive loop at high frequencies can be a result of an artefact due to the reference electrode. The shape of the spectrum attests a capacitive behaviour of the PB film under these experimental conditions. Taking into account the dependence of the cathodic peak current of the BG/PB redox wave on the potential scan rate, such behaviour could be expected.

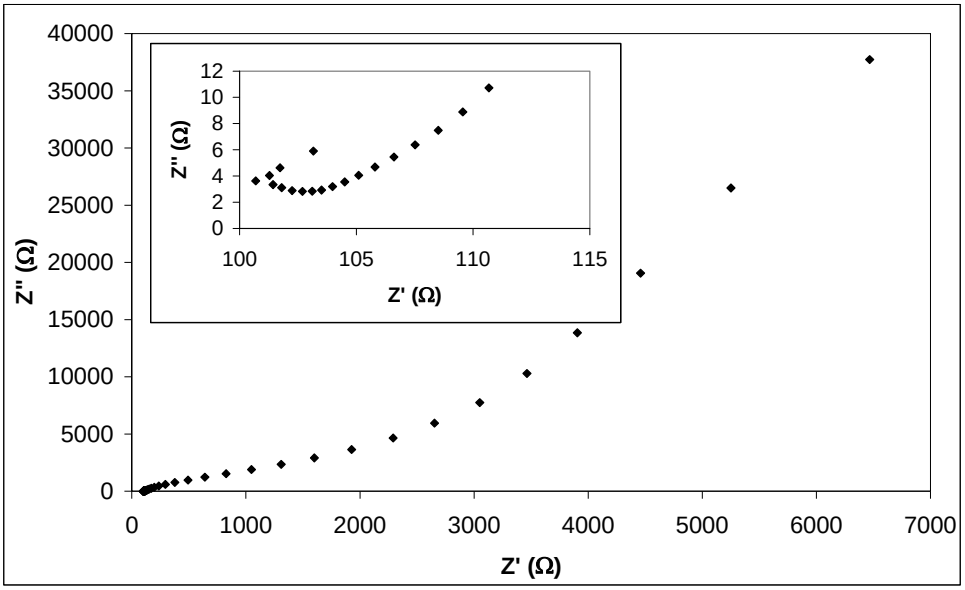


Fig. 4. Electrochemical impedance spectrum of Pt/PB modified electrode recorded in aqueous solution containing 0.1M KCl, 0.01M HCl at a fixed potential value of 0.80V;the inset shows the impedance spectra at high frequencies

The stability of PB film was further checked after the impedance measurement by using CV. The corresponding cyclic voltammograms recorded in the transfer solution before and after the impedance measurement are depicted in figure 5. A small decrease of the anodic and cathodic peak currents corresponding to the PB/ES redox wave and a stable BG/PB redox wave can be observed.

The EIS spectra were also recorded at various potential values from 0.0 to 1.0 V (see figure 6). The impedance spectrum recorded at 0.0 V has a shape similar to that recorded at 0.2 V (see figure 6B). Therefore, in the high frequencies domain a semicircle can be observed which is due to the charge transfer at the electrode / solution interface according to equation (1). At potential values comprised between the two redox waves a capacitive behaviour is observed, as expected because in this potential range PB is not electroactive. This result is in

agreement with the cyclic voltammogram experiments, which show a very small current in this potential range. The impedance spectrum recorded at 1.0 V is similar to that recorded at 0.8 V, and the shape of this spectrum is dominated by the second redox wave BG/PB (see figure 6). The most important result is the behaviour of PB film in the potential range from 0.0 to 0.2 V where the charge transfer at the electrode / solution takes place according to equation (1), and this behaviour could be exploited in the construction of electrochemical sensors based on inorganic redox mediators modified electrodes. Furthermore, the use of Pt electrode substrate for the deposition of PB films resulted in a reduced value of the uncompensated resistance by comparison with that of the indium-tin oxide electrode reported in the literature [11-16].

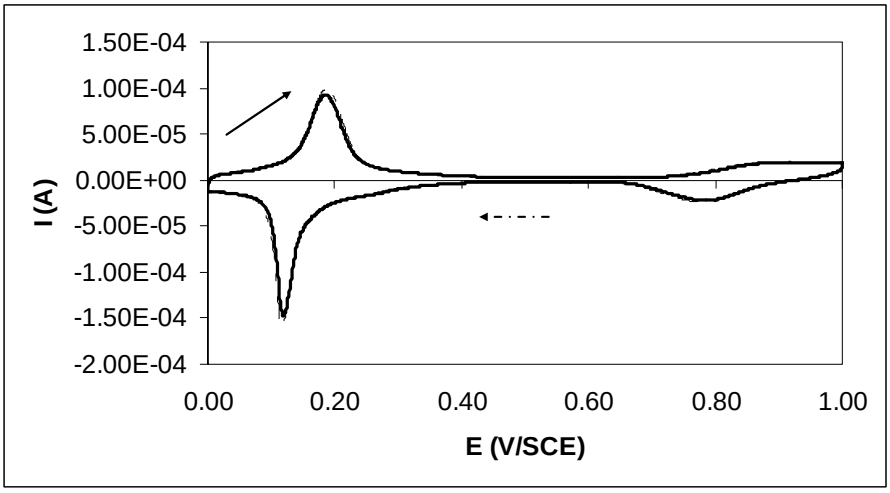
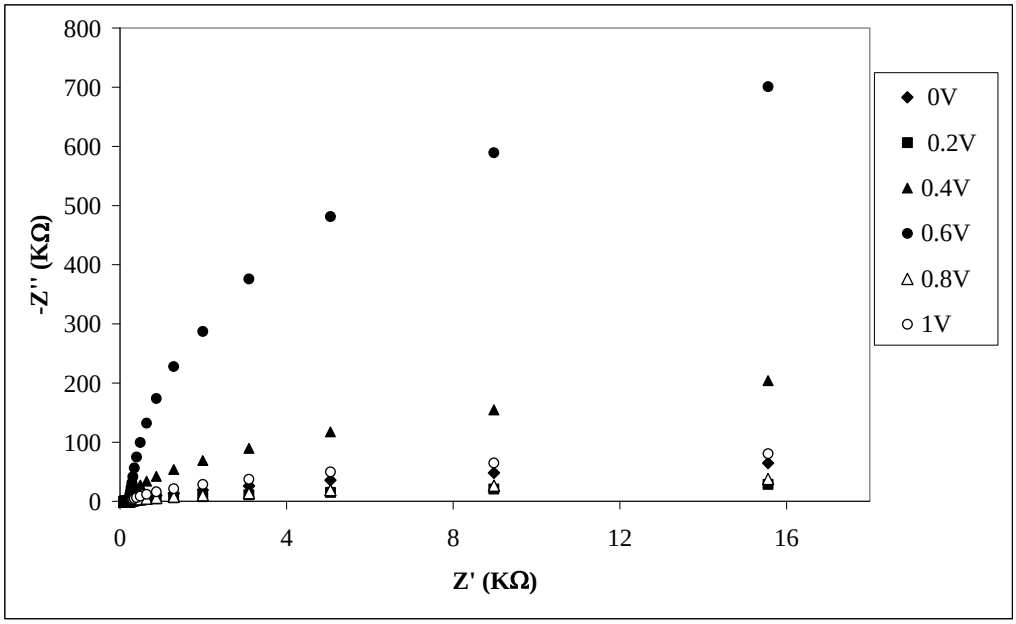
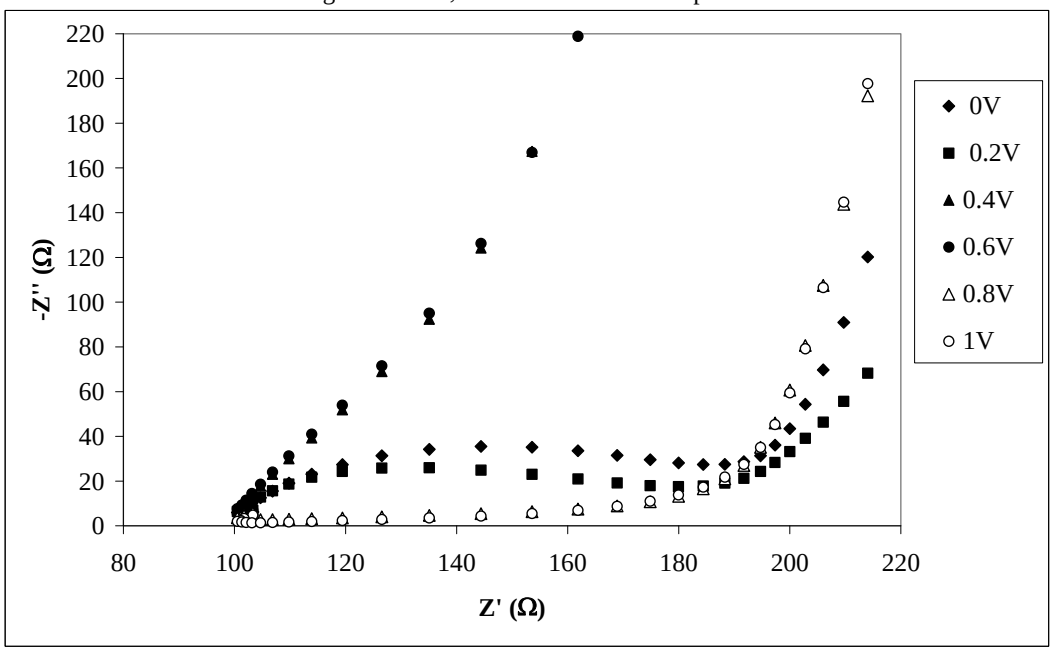


Fig. 5. Cyclic voltammograms of Pt/PB modified electrode in aqueous solution containing 0.1M KCl, 0.01M HCl before (dotted line) and after (solid line) impedance measurements at 0.8V; potential scan rate: 0.05V s^{-1}



(A)

Fig. 6. (A) Electrochemical impedance spectra of Pt/PB modified electrode recorded in aqueous solution containing 0.1 M KCl, 0.01 M HCl at various potential values



(B)

Fig. 6. (B) Their impedance spectra at high frequencies

4. Conclusions

PB films were deposited onto Pt electrodes and investigated by using cyclic voltammetry and electrochemical impedance spectroscopy. The film resistance and charge transfer resistance were determined from impedance spectra recorded at different fixed potential values. The electroactivity of PB films was higher at a fixed potential value of 0.2 V, which differs by 0.05 V with respect to the formal potential of the ES/PB redox wave. The results obtained by using EIS confirmed the potential range where the charge transfer takes place, i.e. from 0.0 to 0.2 V. In the potential range from 0.2 to 0.8 V no faradaic reaction takes place and a capacitive behaviour is observed.

The use of Pt electrode as substrate resulted in a smaller value of the uncompensated resistance in comparison with indium-tin oxide electrodes. EIS connection with CV measurements allow to establish the excellent stability of the PB films which is a key parameter for the design of new electrochemical sensors based on modified electrodes.

R E F E R E N C E S

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