Polish J. Chem., **78**, 1423–1429 (2004)

Impact of an Electrolyte Used for Electrodeposition of Polypyrrole on Ion Transfer and Bulk Resistances of the Polymer Electrode[*]

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(Received February 27th, 2004; revised manuscript April 19th, 2004)

Different electropolymerization counterions induce differences in the performance characteristics of the polypyrrole electrode. The primary counterion polypyrrole electrode, prepared in aqueous solution of sodium hexafluoroaluminate, was compared to the secondary counterion polypyrrole electrode, prepared in a presence of the sodium chloride solution. In general, the EIS and CV characteristics of the two system are similar due to the most marked contribution of the electrolyte to the electrical characteristics of the polymer electrode through ion transfer and ion transport resistances. The impact of electropolymerization counterion on the interfacial resistance was found to be more significant than on the bulk resistance. The effective polymer charge transport diffusion coefficients were found in the range of 10^{-7}–10^{-9} cm^2s^{-1} and the polymer redox capacitances were found in the range 50–100 Fcm^{-3}.

Key words: polypyrrole, thin film electrode, ion transfer resistance, EIS, CV

Due to broad time scale measurements, electrochemical impedance spectroscopy (EIS) is a powerful tool for a quantitative evaluation of numerous parameters characterizing complex electrode processes. This technique is used very often to characterize electrodes modified with a layer of the conducting polymer, *i.e.* polymer electrodes. For a purpose of the analysis, two types of polypyrrole electrodes can be considered: the primary counterion electrode, when the electrolyte anion used in electrodeposition of the polymer is identical with the electrolyte anion during its redox performance, and the secondary counterion electrode, when the two anions in question are different.

Our earlier EIS results on the polypyrrole electrodes with secondary hexafluoroaluminate counterions indicated a decrease in the ion transport diffusion coefficients and an increase in the ion transfer resistances at the polymer/electrolyte interface as compared to the primary chloride – polypyrrole system [1]. The hexafluoroaluminate – polypyrrole system was characterized by higher values of the effective diffusion coefficients for the reductive direction of the redox/conductivity state change than for the oxidative one. The charge transfer resistance of that system was higher than for the other systems studied.

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[*] Dedicated to Prof. Z. Galus on the occasion of his 70th birthday.

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The ac response of the polypyrrole electrodes was first investigated by Bull *et al.* [2]. They found that the polymer layer behaves like a porous metal. Later on, in series of papers, Ren and Pickup analyzed impedance of polypyrrole electrodes [3–5]. A relationship between transport of anions and/or cations and film structure was indicated. They concluded that electrochemically deposited films of polypyrrole consist of permselective polymer aggregates which enclose pores containing an electrolyte solution. Such films appear to work as permselective membranes because of the poor interconnectivity between pores [3].

A purpose of this study was to compare some impedance parameters, namely values of the model resistances, evaluated for primary and secondary polypyrrole – aqueous sodium hexafluoroaluminate systems [6].

EXPERIMENTAL

Preparation of polypyrrole electrodes. The primary counterion electrode was prepared by the potentiostatic electrodeposition of polypyrrole on gold (geometric area = 0.07 cm^2) at +0.800 V *vs*. SSCE using aqueous solutions being 0.6M in pyrrole and 0.04M in sodium hexafluoroaluminate. The film thickness was estimated from the polymerization charge assuming that 240 mC/cm^2 corresponds to a 1 μm polypyrrole film [7]. The secondary counterion electrode was prepared using the aqueous solution of pyrrole and sodium chloride as described in [1]. After the formation the electrodes were washed in water and subsequently in the supporting electrolyte.

Measurements of the electrode performance. It was done at 25°C in a thermostated conventional three electrode cell with a platinum gauze as a counter electrode and SSCE as a reference electrode. The polypyrrole electrodes were working in 0.04M (or 0.05M) Na_3AlF_6 aqueous solution which was purged with nitrogen before measurements. EIS were carried using FRA instrumentation (Autolab Electrochemical Instruments, Ecochemie). The dc potential of measurements ranged from +0.4 V to –0.7 V. Thus, the overoxidation of the polymer is assumed to be avoided [8]. The dc potential steps of 0.05 V or 0.10 V were used in the EIS measurements. The electrode was equilibrated for 10 minutes at each dc potential. Ac signals were 0.010 V in amplitude and (50 kHz – 0.1 Hz) in frequency; the 100 frequency points impedance/admittance spectra were recorded. The EQUIVCRT.PAS program was used to fit experimental impedance data to the circuit models [9].

Chemicals. Pyrrole (p.a. Merck) was distilled under a reduced pressure. Sodium hexafluoroaluminate (p.a. Aldrich) was used as received. All solutions were prepared with doubly distilled water.

RESULTS AND DISCUSSION

The small amplitude sinusoidal perturbation is superimposed on several dc potentials, corresponding to various redox states of the polymer, during the routine EIS measurements. The obtained impedance spectra of the thin film polymer electrodes can be used to separate characteristics of the bulk and interfacial phenomena of a polymer phase. Representative complex plane impedance data recorded for two hexafluoroaluminate-polypyrrole systems at the same dc potential/redox state are shown in Figure 1.

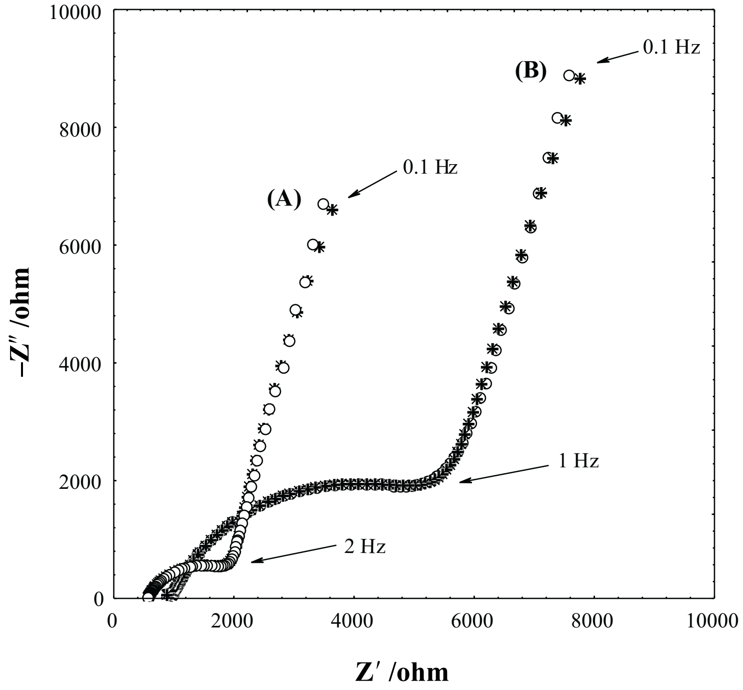

Figure 1. The complex plane impedance plot of the polypyrrole – aqueous sodium hexafluoroaluminate electrodes at +0.100 V, the oxidation path, frequency range (0.1 Hz, 50 kHz), temperature = +25°C: (A) the secondary counterion system, solution concentration = 0.05 M, polymer thickness = 0.29 μm; (B) the primary counterion system, solution concentration = 0.04 M, polymer thickness = 0.21 μm. Symbols: o – experimental data, $*$ – fit to equ. (5).

There, the primary **(B)** counterion system has been compared with the secondary **(A)** counterion system. At a given dc potential, the impedance of the former system is higher than the later system. The data for the another primary hexafluoroaluminate counterion electrode of thickness 0.29 μm corroborate this finding. A main contribution to the increased impedance comes from the higher charge transfer resistance for the ions at the polymer/electrolyte interface (a diameter of the depressed semicircle in the complex plane impedance plot is determined mainly by a value of the ion transfer resistance at the polymer/electrolyte solution interface [1]). No ideal capacitive characteristics are observed at the low frequencies. An origin of the behavior can be sought in a detailed analysis of the charge transport in the polymer layer. Two contributions to the transport impedance were assumed in the earlier analysis of the polymer film electrodes, both of a diffusional character but differing in the characteristic time parameter and a nature of the electrical connection to the bulk electrolyte phase [1,10]. The spectra shown in Figure 1 were fitted to the impedance – frequency function of the following general formula [1]:

$$Z(j\omega) = \mathrm{R}_{\mathrm{sol}} + \frac{\mathrm{R}_{\mathrm{x}}}{1 + j\cdot\omega\cdot\mathrm{R}_{\mathrm{x}}\cdot\mathrm{C}_{\mathrm{x}}} + \frac{1}{\mathrm{Y}_{0,\mathrm{dl}}\cdot[j\omega]^{\mathrm{n}} + [\mathrm{R}_{\mathrm{ct}} + \mathrm{Z}_{\mathrm{tr}}(j\omega)]^{-1}} \qquad (1)$$

where:

$$\mathrm{Z}_{\mathrm{tr}}(j\omega) = \mathrm{Y}_{0,\mathrm{tr}}^{-1}\cdot[j\cdot\omega]^{-1/2}\cdot\coth[j\cdot\omega\cdot\tau]^{1/2} \qquad (2)$$

with [1,11]:

$$\mathrm{Y}_{0,\mathrm{tr}} = \frac{\tau^{1/2}}{\mathrm{C}_0} = \frac{\left[\frac{\mathrm{R}_0}{3}\cdot\mathrm{C}_0\right]^{1/2}}{\mathrm{C}_0} = \left[\frac{\mathrm{R}_0}{3\cdot\mathrm{C}_0}\right]^{1/2} \qquad (3)$$

$\mathrm{Z}_{\mathrm{tr}}(j\omega)$ is the transport impedance of the polymer characterized by two frequency independent parameters: $\mathrm{Y}_{0,\mathrm{tr}}$ and τ, or alternatively C_0 and τ, or alternatively C_0 and R_0. Parameters C_0 and R_0 correspond to the limiting low frequency capacitance and resistance, respectively, that describe ionic transport in the polymer. C_0 is known as the redox pseudocapacitance [12]. The characteristic time constant τ can be related to the effective diffusion coefficient of counterions [1]. $\mathrm{Y}_{0,\mathrm{dl}}$ and n are the frequency independent parameters of the double layer admittance of the polymer/electrolyte interface. R_{ct} is the ion transfer resistance at the polymer/electrolyte solution interface, $\mathrm{R}_{\mathrm{sol}}$ is the electrolyte solution resistance, ω is the angular frequency, $\mathrm{j} = (-1)^{0.5}$. The C_{x} and R_{x} symbols indicate capacitance and resistance, respectively, that give minor contributions to the electrode impedance. Their physical meanings as the geometric capacitance and the bulk resistance of the polymer layer, respectively, were considered previously [1]. However, they can represent electrical properties of the metal/polymer interface, namely its double layer capacitance and electron transfer resistance, respectively (the C_{x}-values found for our polypyrrole electrodes are mostly in the range of 10^{-1} μF/cm^2).

Here, a detailed analysis of the transport impedance will be omitted as it requires a critical approach to the impedance transport function used in the previous study. Nevertheless, the best fit to the experimental data for the hexafluoroaluminate – polypyrrole systems is observed when the two contributions to the transport impedance, described in [1], are linked in parallel, not in series. The former was used in the fits of Figure 1. Although determined without the high accuracy, values of the effective charge transport diffusion coefficients and the redox capacitances for the primary hexafluoroaluminate – polypyrrole systems, appeared similar to those for the secondary one [1]. The values obtained for the primary system fall in the range of $(2\cdot10^{-9}\text{–}5\cdot10^{-7})$ cm^{2}s^{-1} and (50–100) Fcm^{-3}, respectively. The polymer/electrolyte ion transfer resistance was found a much higher in values for the primary hexafluoroaluminate counterion electrodes than for the secondary ones. An increase in the R_{x}-values of the primary systems over the secondary system is much smaller.

It indicates that the different electropolymerization counterions induce differences in the performance characteristics of the polypyrrole electrode.

The ion-sieving was found earlier by Shirakawa and coworkers for the polypyrrole – monovalent counterion systems [13]. Our present results indicate that mostly the properties of the outer interface of the polypyrrole electrode are affected by the counterions used in the electrode preparation and performance. The relevant resistive components of the cell impedance are shown in Table 1.

Table 1. The solution, bulk polymer, and charge transfer resistances of polypyrrole – sodium hexafluoroaluminate systems.The oxidation path. Temperature 25°C.

E_{dc} /V	System	R_{sol} /kΩ	R_x /kΩ	R_{ct} /kΩ
+0.300	primary[a)] secondary[b)]	0.87 0.58	0.16 0.06	5.42 1.40
	ratio	**1.5**	**2.6**	**3.9**
–0.300	primary[a)] secondary[b)]	0.98 0.75	1.02 0.55	24.03 4.56
	ratio	**1.3**	**1.8**	**5.3**

[a)] layer thickness = 0.21 μm (based on the electropolymerization charge);
[b)] layer thickness = 0.29 μm (based on the electropolymerization charge).

An increase in the resistances of the electrode is observed when the polypyrrole is reduced. However, the magnitude and rate of this change is low. The resistances are a much more complicated function of dc potential than for the polyaniline electrode case [14,15]. The change in the solution resistance accompanying the redox process is insignificant as compared to the changes in R_x and R_{ct}, which is the common feature for the thin film conducting polymer electrodes. The R_{sol}-values can be related to the active area or roughness of the polymer electrode.

A strong influence of the resistance of the polymer electrode on its dc faradaic currents is illustrated in Figure 2 where dc cyclic voltammograms of three polypyrrole electrodes are compared. There primary and secondary hexafluoroaluminate systems are characterized by much lower currents and more pronounced anodic – cathodic peak potential differences of cyclic voltammogram than the primary chloride system. It is in accord with a much lower bulk and interfacial resistances of the primary chloride electrode [1].

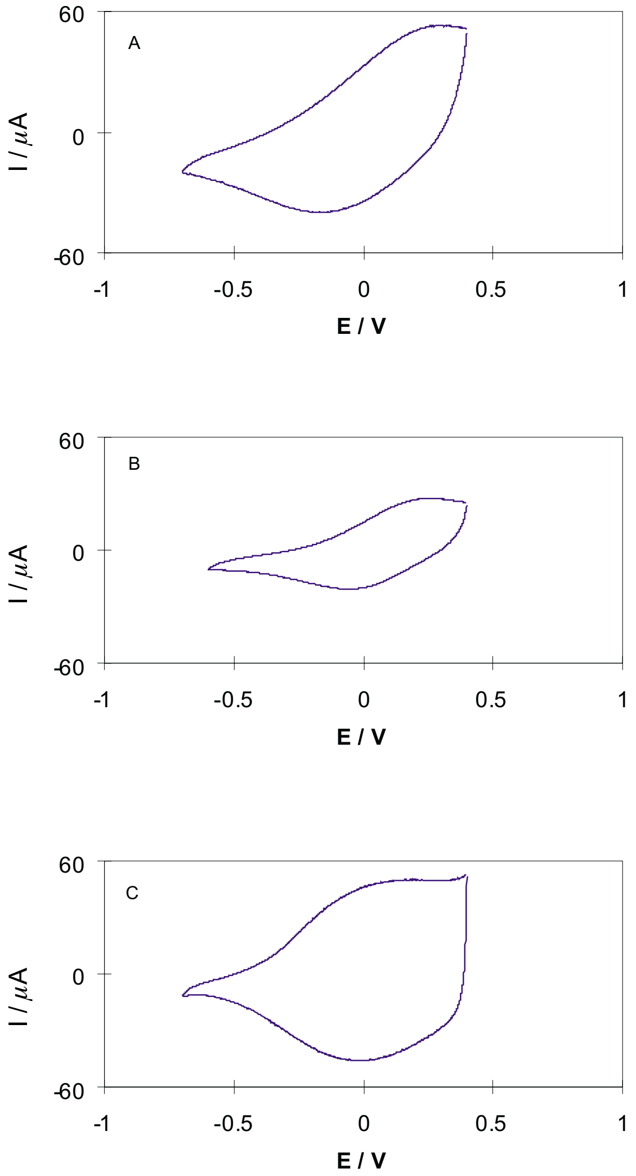

Figure 2. Cyclic voltammograms of the primary and secondary polypyrrole electrodes recorded at 100 mV/s and temperature +25°C: (A) – the primary counterion system, bathing solution = aqueous 0.05 M Na_3AlF_6, polymer layer thickness = 0.45 μm; (B) – the secondary counterion system, bathing solution = aqueous 0.04 M Na_3AlF_6, polymer layer thickness = 0.31 μm: (C) – the primary counterion system, bathing solution = aqueous 0.1 M NaCl, polymer layer thickness = 0.31 μm.

CONCLUSIONS

The involvement of hexafluoroaluminate anionic species in the charge transport was evidenced by EQCM results [6]. The EIS characteristics of the primary and secondary polypyrrole – sodium hexafluoroaluminate – water systems are determined predominantly by the nature of the bathing electrolyte. The quantitative EIS analysis has confirmed that the ion transfer at the polymer/solution interface prevails in determining the dc current response of the polypyrrole – aqueous sodium hexafluoroaluminate electrodes. This parameter appeared to be more sensitive to the type of the system (primary, secondary) than others, namely the bulk polymer resistance or the metal/polymer electron transfer resistance. The impact of the hexafluoroaluminate electrolyte used in the electrodeposition of the thin polymer film for a hindrance of ion transfer at the polypyrrole/solution interface is pronounced. Thus, one can expect similar effects in a performance of the charge trapping devices based on bilayers of polypyrrole [16].

Earlier, a competition between ion transfer and electron transfer at the other conducting polymer-electrolyte interface was shown based on EIS results [17]. A further study focused on the kinetics of the interfacial charge transfer at the polymer electrodes certainly would help to model the complex behavior of the conducting polymer electrodes [18,19]. Our studies were intended to differentiate between counterion effects in the preparation and performance of the polypyrrole electrode.

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