Effect of the Bathing Electrolyte on the Charge-Transport Process at Poly(o-aminophenol)-Modified Electrodes. An ac Impedance Study in Sulfate and Benzenesulfonate Solutions

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Abstract: The aim of this work was to study how charge-transport and charge-transfer processes at poly(o-aminophenol) film electrodes depend on the type and concentration of the external electrolyte solution in contact with the polymer film. To this end ac impedance measurements on poly(o-aminophenol) films contacting solutions of different anions such as sulfate and benzenesulfonate were carried out. These two different anions were chosen due to their differences in size and adsorbability. Impedance data were interpreted on the basis of a modified electron-hopping model, where the electron-transport rate within the polymer phase and the electron-transfer rate across the metal-polymer interface are represented by an effective diffusion coefficient \( D \) and a standard electrochemical rate constant \( k_{\text{rate}} \), respectively. It was found that both parameters are independent of the type and concentration of the electrolyte solution within the thickness range from 10 nm to 35 nm. However, these transport parameters depend strongly on both external variables within the thickness range from 38 nm to 70 nm. In this regard, the rate of charge conduction through thick poly(o-aminophenol) increases with the increase of the concentration of the electrolyte solution. The increase of poly(o-aminophenol) conductivity with the increase of film thickness was attributed to changes in the polymer morphology. It was assumed that the electrolyte incorporated into the open structure of a thick film reduces repulsive interactions between redox sites yielding a more compact distribution of redox centers as compared with that present in a thin film that does not incorporate the electrolyte. Lower distances between adjacent redox sites in a thick film facilitate the electron-hopping process, which in turn leads to a higher conductivity as compared with that of a thin film.

Keywords: Poly(o-aminophenol) Films, Sulfate, Benzenesulfonate, conductivity, morphology.

1. INTRODUCTION

It is well-known that without redox species in solution ("background electrolyte") the charge-transport process of an electrode modified by an electroactive polymer film is affected by ionic transfer at the polymer-electrolyte interface, ionic and electronic charge carrier transport inside the polymer and an electronic transfer at the metal-polymer interface [1]. In this connection, counterrions are able to cross the polymer film-solution interface to retain the bulk film electroneutrality. This process would only be dependent on the degree of oxidation of the polymer. However, it has also been suggested that the external supporting electrolyte contacting the polymer film could be incorporated into the polymer phase [2]. This internal electrolyte phase can play an important role in the charge-transport and charge-transfer processes of the polymeric material.

Poly(o-aminophenol) (POAP) is a typical electroactive polymer that has been employed as resistive and permselective material to build biosensors [3]. In this application, the resistive behavior of POAP films was only associated with the entrapment of nonconductive species into the polymer matrix [4], disregarding the effect of the external electrolyte solution on the conductivity of the polymer. In the present work, ac impedance measurements on POAP film electrodes in contact with solutions containing different anions such as sulfate and benzenesulfonate (BS) anions were performed in order to detect changes in the polymer conductivity due to the different electrolyte composition. The experimental results were quantitatively interpreted on the basis of a modified electron-hopping model [5], which allowed bulk and interfacial transport parameter values obtaining. The aim of this work was twofold: firstly to demonstrate the crucial effect of the electrolyte composition on the charge-conduction process of the polymer and secondly, to compare conductivity values of POAP in these two electrolytes. To the best of my knowledge, no work employing ac impedance measurements on POAP films contacting these two electrolytes has been reported in the literature so far. This work could help those engaged in the development of sensors based on POAP because its operating characteristics can be favorably modified by selecting a suitable electrolyte.

2. EXPERIMENTAL

2.1. The Gold Film Electrodes

In order to obtain a specular surface to deposit POAP films, gold thin-film electrodes of constant thickness \( \phi_m \sim 30 \) nm were prepared by vacuum evaporation as was previously described [6]. The samples were inserted into an electrochemical cell similar to that shown in a previous paper [7].

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and employed as working electrodes. An electrode area of 0.56 cm² was exposed to the solution. A gold grid of large area was used as counterelectrode. All the potentials reported in this work are referred to the SCE.

2.2. The POAP-Coated Gold Film Electrodes

POAP-coated gold film electrodes were obtained by immersing the gold films described in the previous section in a 10⁻³ M ortho-aminophenol + 0.4 M NaClO₄ + 0.1 M HClO₄ solution and cycling the potential between -0.25 V and 0.8 V at a scan rate ν = 0.05 V s⁻¹. The POAP thickness was increased by increasing the number of potential cycles in the solution containing the monomer. In order to measure the polymer thickness, these POAP-coated gold film electrodes were then rinsed and transferred to the supporting electrolyte solution (0.4 M NaClO₄ + 0.1 M HClO₄). Then, the voltammetric reduction charge, \( Q_{\text{Red}} \), in this solution was determined by integrating the cathodic current of the voltammetric response between -0.25 V and 0.5 V (\( ν = 0.05 \) V s⁻¹) [8]. Thus, \( Q_{\text{Red}} \) was considered as representative of the polymer thickness. Two POAP film thicknesses with \( Q_{\text{Red}} \) values of 0.42 nC cm⁻² and 1.5 mC cm⁻² were employed in this work. For this type of polymer, many researchers have correlated the charge obtained from the integration of the voltammetric response at -0.25 V to 0.5 V (\( ν = 0.05 \) V s⁻¹) [8]. The \( Q_{\text{Red}} \) values indicated above would correspond to polymeric thicknesses (\( \phi_p \)) of 19 nm and 70 nm, respectively. With these POAP-coated gold film electrodes, voltammetric responses (\( j-E \)) were recorded separately for each \( \phi_p \) value, within the potential range from -0.2 V to 0.5 V at a scan rate \( ν = 0.01 \) V s⁻¹ in solutions containing \( SO_4^{2-} \) and benzenesulfonate (C₆H₅SO₃⁻ = BS) anions, respectively. In CV measurements a PAR Model 173 potentiostat and a PAR Model 175 function generator were used. An X1-X2-Y Hewlett-Packard Model 7046 B Plotter was used to record the \( j-E \) responses.

Impedance spectra of the POAP-coated gold film electrodes in contact with solutions containing \( SO_4^{2-} \) and benzenesulfonate ions were also recorded. Impedance spectra were measured following a 30-min application of the steady-state potential ranging from -0.2 V to 0.2 V. Impedance measurements in the frequency range from 0.01 Hz to 10 kHz were performed with a PAR 309 System. Impedance values were determined at seven discrete frequencies per decade with a signal amplitude of 5 mV. The validation of the impedance spectra was done by using Kramers-Kronig transformations.

AR grade chemicals were used throughout. O-aminophenol (Fluka) was purified as described elsewhere [13]. The solutions were prepared with water purified using a Millipore Milli-Q system. NaClO₄, HClO₄, H₂SO₄, Na₂SO₄, benzenesulfonic acid and sodium benzenesulfonate were employed to prepare the corresponding solutions.

3. RESULTS AND DISCUSSION

\( j-E \) responses for the 30 nm thick gold film coated with POAP films of different thicknesses \( \phi_p (= 19 \) nm and 70 nm, respectively) were recorded in solutions containing \( SO_4^{2-} \) and BS anions. \( j-E \) responses at a given scan rate (\( ν \)) and POAP thickness in the presence of the different anions do not show big differences. This is shown in Fig. (1) for the 70 nm thick POAP film. In the inset of Fig. (1), the corresponding response for the thinner POAP film (\( \phi_p = 19 \) nm) is shown.

![Image](openphysicalchemistryjournal.com)
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(Fig. 4). Besides, spectra only consist of a high-frequency semicircle. This same impedance response shown in Fig. (4) was observed within the thickness range from 10 nm to 35 nm.

Fig. (2). Ac impedance diagram in the Nyquist coordinates (-Z' vs. Z) obtained at E = 0.1 V for a 70 nm thick POAP film in contact with a 0.4 M Na₂SO₄ + 0.1 M H₂SO₄ solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

Fig. (3). Ac impedance diagram in the Nyquist coordinates (-Z' vs. Z) obtained at E = 0.1 V for a 70 nm thick POAP film in contact with a 0.4 M C₆H₅SO₃ Na + 0.1 M C₆H₅SO₃H solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5]. The inset is a magnification of the high-frequency region.

Fig. (4). Ac impedance diagrams in the Nyquist coordinates (-Z' vs. Z) obtained at E = 0.1 V for a 19 nm thick POAP film in contact with: (Δ) a 0.4 M C₆H₅SO₃ Na + 0.1 M C₆H₅SO₃H solution and (●) a 0.4 M Na₂SO₄ + 0.1 M H₂SO₄ solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].

It is well-known that some impedance models consider a porous electrode with two superimposed phases where one (the polymer) transports electrons and the other (the electrolyte) transports ions [1]. In other models [14] the polymer is considered as a single homogeneous phase where the transport of both carriers occurs by diffusion-migration in a single phase. The problem arises because the different models can fit the same experimental results and the parameters obtained by impedance analysis are susceptible to different interpretations depending on the applied model. In this regard, the treatment of the impedance data is often complicated by accompanying not only experimental but also theoretical difficulties. With regard to experimental conditions, by employing a gold film as base electrode as is described in the experimental section, it is expected to reduce surface defects of the base electrode on an atomic scale, in such a way that the polymer film is deposited on a smooth enough surface. Gold films deposited under high vacuum conditions (~10⁻⁷ Torr), as in the present work, result polycrystalline with crystallite sizes between 0.01 and 0.1 μm [6, 7]. Studying the “Size effects” [6] on these gold films, a value of the specularity parameter, p = 0.91, was estimated. Parameter p correlates with the roughness of the surface topography and the presence of surface defects. More precisely, this parameter represents the probability of an electron being reflected specularly or diffusely (due to the presence of defects) at the film surface. The p value ranges from 0 for complete diffuse scattering to 1 for complete specular scattering. Thus, imperfections should lead to experimental p values much lower than 1. In this connection p values of our gold films, are high enough (p > 0.91) to assume a low amount of surface defects on an atomic scale, as compared with the surface of a bulk electrode mechanically polished to deposit a polymer film. Concerning the POAP layer deposited on the metal electrode, it has been demonstrated that when a POAP film that is thick enough [15] covers a gold film, the internal structure of the polymer layer contacting the metal surface is highly compact. Then, the experimental arrangement used in this work, that is, a gold base electrode of low surface roughness
coated with a thick POAP film ($\phi_h > 10$ nm), could be a good approximation to the existence of a homogeneous (uniform) polymer layer on an electrode surface to apply a homogeneous electrochemical model in its study. Then, impedance spectra recorded in the work were analyzed by using the following impedance expression:

$$Z(\omega) = R_{QX} + (R T n F^2 A c) \left[ k_f + k_b (K+1)/K \right] A(\omega)$$  \hspace{1cm} (1)

Eq. (1) was derived from a physical model previously reported by Rodríguez Nieto and Tuccerti [5], which considers effects of the degree of protonation of the polymer on the dynamics of the charge-transport process by electron hopping between redox sites. This model describes the charge-transport process within the polymer film by means of an effective diffusion coefficient, $D$, contained in $A(\omega)$ (see Eq. (1)), whose expression is

$$A(\omega) = \frac{\coth(\phi_D/j_0 D)}{(k_f/j_0 D)^{1/2}} + \frac{\coth(\phi_D/j_0 D)}{k_b^{-1}} \left[ j_0 + \frac{k}{1+K} \left[ 1 - \frac{1}{1+1/K} \right] \right]^{1/2} \left[ j_0 + \frac{k}{1+K} \right]^{1/2}$$  \hspace{1cm} (2)

Parameters $k_f$ and $k_b$ in Eqs. (1) and (2) are the forward and the backward electrochemical rate constants corresponding to the charge-transfer process, defined as

$$k_f = k_{sh} \exp[ b_f (E-E^o)]$$  \hspace{1cm} (3)

$$k_b = k_{sh} \exp[ b_b (E-E^o)]$$  \hspace{1cm} (4)

where $E^o$ is the standard potential of the redox couple, $b_f$ and $b_b$ are the Tafel coefficients ($b_f = anF/RT$ and $b_b = (1-a) nF/RT$) and $k_{sh}$ is the standard electrochemical rate constant for the interfacial charge-transfer process. $K$ is an equilibrium constant depending on the external proton concentration through $K = K'_{\text{pKa}} 10^{\text{pH}}$. $K'$ is related to the $pK_a$ of the polymer redox species. The parameter $k = (k_f + k_b)$ in Eq. (2) is related to the forward ($k_f$) and the backward ($k_b$) electrochemical rate constants corresponding to a protonation chemical step coupled to the charge-transfer step, as proposed in [5]. Besides, Eq. (2) contains the angular frequency of the perturbation, $\omega$, and the complex unit, $j$. $R_{QX}$ in Eq. (1) is a charge-transfer resistance related to the high-frequency semicircle in the impedance diagrams, whose expression is

$$R_{QX} = (R T n F^2 A c) \left[ (k_f + k_b) \left( k_f k_b \right)^{-1} + (k_f K)^{-1} \right]$$  \hspace{1cm} (5)

In both Eq. (1) and Eq. (5), $A$ is the electrode area, $c$ is the total redox site concentration and $n$ is the number of transferred electrons of the redox process of POAP.

The fitting of impedance diagrams was made by using the aforementioned expression (1), provided that $K$, $D$ and $k_{sh}$ are adjustable parameters of the model. Figs. from (2 to 4) show the fittings (solid lines) of experimental Nyquist diagrams (discrete points) by means of the expression given by Eq. (1). Also, the corresponding Bode diagrams were fitted by means of Eq. (1) (Fig. 5). In the simulations a value of $n = 0.44$ for the number of transferred electrons of the redox system of POAP [14] and a total concentration of redox sites in the polymer $c = 4.5$ M [13] were used. An electrode area of $A = 0.56 \text{ cm}^2$ was used. A $K'$ value around $8.5 \times 10^{-6} \text{ cm}^2 \text{ mol}^{-1}$ was adequate to obtain the best fits. The last value leads to $pK_a = 2.93$. This value is of the order of that expected for the deprotonation reaction of the aroylamine group of polyaniline [5]. With the $K'$ value, and the $pH$ of the solutions measured $\text{in situ}$, the $K$ value for each solution was calculated. To fit experimental impedance diagrams a double-layer capacitance $C_{\text{diff}} = 30 \times 10^{-6} \text{ F cm}^{-2}$, in parallel with the charge-transfer resistance at high frequency, was also considered. At fixed polymer thickness and solution $pH$, $D$ and $k_{sh}$ were considered dependent on the type of anion contained in the supporting electrolyte. Table 1 shows that for the thicker POAP film ($\phi_h = 70$ nm) both parameters $k_{sh}$ and $D$ decrease following the sequence $\text{SO}_4^2^- > \text{C}_6\text{H}_5\text{SO}_3^-$. While the diffusion coefficient value for BS anions is nearly two orders of magnitude lower than that for sulfate anions, the standard electrochemical rate constant for BS is almost 4 orders of magnitude lower than that for sulfate. However, Table 2 shows that for the thinner POAP film ($\phi_h = 19$ nm) both parameters remain nearly constant with the change of the electrolyte composition. Also, $D$ and $k_{sh}$ values for the thinner POAP film are several orders of magnitude lower than those corresponding to the thick one.

![Fig. (5). Ac impedance diagrams in Bode coordinates (Phase and Quadrature vs. Logarithm of the frequency) obtained at $E = 0.1 \text{ V}$ for a 70 nm thick POAP film in contact with a 0.4 M $\text{C}_6\text{H}_5\text{SO}_3\text{Na} + 0.1 \text{ M C}_6\text{H}_5\text{SO}_3$ solution. Discrete points are experimental data, and the continuous line represents the fitting by using Eq. (1) [5].](image-url)
for the thinner POAP film, the effect of the electrolyte solution on the charge-transport process seems to be negligible. As it has been indicated that electron hopping controls the charge-transport process at POAP [5, 14], the interpretation of electrolyte effects on the charge conduction can be made on the basis of the electron-hopping model [14]. In the limit of a large excess of supporting electrolyte in the film and noninteracting sites, \( D \) has been expressed in terms of the mean distance between adjacent redox sites, according to \( D = (a^2k_o) \). Parameter \( k_o \) is the intermolecular electron-transfer rate constant and \( a \) is the mean distance between two adjacent redox sites. The hopping rate \( k_h \) exhibits an exponential dependence on \( a \), through the energy - \( U(x+a) \) of a state with an electron in the position \( x \) along the current direction (see Eq. (23) in Ref. [16]). That is, the principal effect of the hopping distance \( a \) on \( D \) proceeds from the exchange rate. In this sense, the effect of increasing the mutual separation \( a \) between adjacent redox centers is to decrease the exchange rate \( k_o \), which in turn should lead to a \( D \) decrease. Then, it could be suggested that at low POAP thickness the intrinsic electron hopping controls the rate of the charge-transport process because the low quantity of electrolyte contained in the polymer matrix is unable to reduce the electrostatic repulsion between charged redox sites [17]. Then, the redox sites adopt an extended configuration with a large \( a \) value (low \( D \) value) so as to minimize the coulombic repulsion. In this connection, in previous work [15] it was demonstrated that within the thickness range from 0.4 mC cm\(^{-2}\) to 0.82 mC cm\(^{-2}\) (10 nm - 35 nm), POAP exhibits a rather continuous and compact structure. Thus, it is possible that only very low amounts of electrolyte can be incorporated into the compact structure exhibited by a thin POAP film (\( \phi = 19 \text{ nm} \)), and then transport parameters of POAP become independent of the external electrolyte composition. However, for large POAP thicknesses it is possible that considerable amounts of electrolyte can be incorporated into the polymer matrix. The electrolyte solution incorporated into the polymer can shield the redox centers from interaction between them and so the existence of a more compact distribution of these centers, as compared with that present in thin films, would reduce the \( a \) value, thereby increasing the rate of the charge-transport process by intrinsic electron hopping. Besides, it is possible that BS anions were more effective than sulfate anions to shield the redox centers from interaction between them; however, its larger size as compared with sulfate, should lead to a higher \( a \) value, and then to a lower \( D \) value as experimentally observed (Table 1).

The higher ability of the BS anion to shield redox centers, as compared with that of the sulfate anion, could be due to both its larger size (area of the BS anion between 0.44 and 0.54 ± 0.03 nm\(^2\)), and that of sulfate 0.18 nm\(^2\) [18] and a stronger interaction (anion with charged and noncharged parts) with the redox site. In this regard, SEM images of a thick POAP film (0.82 mC cm\(^{-2}\) - 1.5 mC cm\(^{-2}\)) show an external structure that is able to incorporate electrolyte solution [15].

With regard to the standard electrochemical rate constant, \( k_{\text{sh}} \), the electron injection at the metal|polymer interface must be accompanied by ion injection at the polymer|solution interface to maintain charge neutrality within the polymer phase. The ion motion across the film is not expected to affect the overall charge-transfer reaction. However, for thin PAOP films (see Table 2) the resistance to counterion motion through the polymer phase (low content of electrolyte) seems to reduce the apparent rate of charge injection (large high-frequency semicircle) as compared with values for thick films (Table 1) where higher amounts of electrolyte could be incorporated. On the assumption that the external electrolyte can be incorporated into open structures of a thick POAP film, the lower rate of charge injection (\( k_{\text{sh}} \)) at the gold|POAP interface in the presence of BS anions as compared with sulfate anions could be due to a more pronounced blocking effect of BS anions towards the electron exchange between redox sites and the gold surface [15]. However, at present we have no clear explanation about the dependence of this interfacial charge-transfer parameter on the content of electrolyte in a POAP film.

As was above-indicated, impedance diagrams were recorded at various potentials. Both parameters obtained from the model (\( D \) and \( k_{\text{sh}} \)) are independent of the net oxidation state of the polymer within a large potential range. However, they decreased slightly at low degrees of oxidation.

### Table 1. Comparison of the Standard Electrochemical Rate Constant (\( k_{\text{sh}} \)) and Diffusion Coefficient (\( D \)) Values for a Thick POAP Film in the Presence of Sulfate and BS Anions. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

<table>
<thead>
<tr>
<th>Anion</th>
<th>( 10^4 k_{\text{sh}} \text{ cm s}^{-1} )</th>
<th>( 10^{10} D \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( \phi \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{\circ} \text{SO}_4^{2-} )</td>
<td>1.04</td>
<td>3.72</td>
<td>70</td>
</tr>
<tr>
<td>( ^{\circ} \text{C}_6\text{H}_5\text{SO}_3^{-} )</td>
<td>2.25</td>
<td>5.32</td>
<td>70</td>
</tr>
</tbody>
</table>

\( e = 4.7 \text{ M, } K = 8.5 \times 10^{-2} \text{ cm mol}^{-1}, C_{\text{in}} = 30 \times 10^{-3} \text{ F cm}^{-2}. \)

Electrode potential: \( E = 0.1 \text{ V. Electrolytes: } 0.1 \text{ M SO}_4\text{H}_2 + 0.4 \text{ M Na}_2\text{SO}_4, 0.1 \text{ M C}_6\text{H}_5\text{SO}_3\text{H} + 0.4 \text{ M C}_6\text{H}_5\text{SO}_3\text{Na.} \)

### Table 2. Comparison of the Standard Electrochemical Rate Constant (\( k_{\text{sh}} \)) and Diffusion Coefficient (\( D \)) Values for a thin POAP Film in Contact with Sulfate and BS Solutions. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

<table>
<thead>
<tr>
<th>Anion</th>
<th>( 10^4 k_{\text{sh}} \text{ cm s}^{-1} )</th>
<th>( 10^{10} D \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( \phi \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{\circ} \text{SO}_4^{2-} )</td>
<td>1.04</td>
<td>1.72</td>
<td>19</td>
</tr>
<tr>
<td>( ^{\circ} \text{C}_6\text{H}_5\text{SO}_3^{-} )</td>
<td>1.22</td>
<td>1.83</td>
<td>19</td>
</tr>
</tbody>
</table>

\( e = 4.7 \text{ M, } K = 8.5 \times 10^{-2} \text{ cm mol}^{-1}, C_{\text{in}} = 30 \times 10^{-3} \text{ F cm}^{-2}. \)

Electrode potential: \( E = 0.1 \text{ V. Electrolytes: } 0.1 \text{ M SO}_4\text{H}_2 + 0.4 \text{ M Na}_2\text{SO}_4, 0.1 \text{ M C}_6\text{H}_5\text{SO}_3\text{H} + 0.4 \text{ M C}_6\text{H}_5\text{SO}_3\text{Na.} \)
In order to analyze in more detail the effects of electrolyte incorporation on the charge-conduction process of POAP, the ionic strength of the electrolyte solution was varied while the proton concentration remained constant. Impedance diagrams for the 70 nm thick POAP film in contact with solutions of different concentration of sulfate and benzenesulfonate anions are shown in Fig. (6) and Fig. (7), respectively. As can be seen, impedance plots depend on the electrolyte concentration. However, for the 19 nm thick POAP film impedance spectra do not depend on the electrolyte concentration (not shown).

The fitting of these impedance diagrams (also the corresponding Bode plots) gives the parameter values collected in Tables 3 and 4, respectively. As can be seen, both parameters \( (D \text{ and } k_{sh}) \) increase with the increase of the anion concentration. On the assumption that the external electrolyte was incorporated into the polymer phase, it would be expected that an increase in the ion concentration in the solution would cause an increase in the ion concentration within the film. If these ions (sulfate and benzenesulfonate) reduce the repulsive interaction between redox sites, an increase in their concentration within the film would cause a decrease in the resistance to the charge conduction by electron hopping through it. That is, an increase in the electrolyte concentration should cause an increase of the diffusion coefficient. Again, by comparing the adsorption capability of both anions (BS > sulfate) lower \( k_{sh} \) values are observed in the presence of benzenesulfonate anions as compared with sulfate ones. However, \( k_{sh} \) values in the presence of both anions increase with the increase of the ionic strength of the solution.

4. CONCLUSIONS

Charge-transport and charge-transfer parameters of poly(o-aminophenol) films were obtained by impedance measurements in solutions containing sulfate and benzenesulfonate anions, respectively. Experimental impedance spectra were interpreted on the basis of a modified electron-hopping model. The model gives an effective diffusion coefficient whose value represents the electron-transport rate within the polymer phase. Also, a standard electrochemical rate constant is obtained from the model, which describes the electron-transfer rate across the metal-polymer interface. While for film thicknesses within the range from 10 nm to 35 nm both transport parameters are independent of the type and concentration of the anion present in the external solution, in the thickness range from 38 nm to 70 nm, the parameter values increase with the increase of the electrolyte concentration. Besides, within the former thickness range, parameter values are nearly two orders of magnitude lower than within the latter thickness range. This indicates a resistive behavior of thin poly(o-aminophenol) films. However, at constant film thickness and electrolyte concentration, in the thickness range from 38 nm to 70 nm, parameter values are higher in the presence of sulfate ions than in the presence of benzenesulfonate ones. The influence of the type and concentration of the electrolyte on the charge-transport and charge-transfer rates at thick poly(o-aminophenol) films was explained in terms of the incorporation of the electrolyte into their open structures, which facilitates the electron-hopping process by reducing the repulsive interactions between redox sites. Strong repulsive interactions between redox centers should operate in thin poly(o-aminophenol) films whose compact structures hinder the incorporation of the electrolyte. These considerations on the basis of different structures of thin and thick films, respectively, are confirmed by SEM images. Although the simple impedance model employed in this work gives satisfactory results, more work is in progress to obtain a more complete series of charge-transport parameters, electron and ion diffusion coefficients, interfacial resistances and capacitances as a function of the type and concentration of ions present in the electrolyte solution in contact with poly(o-aminophenol) films. To this end the theory of
Table 3. Comparison of the Standard Electrochemical Rate Constant ($k_{oa}$) and Diffusion Coefficient ($D$) Values for a 70 nm thick POAP Film in Contact with Sulfate Solutions of Different Concentration. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

<table>
<thead>
<tr>
<th>Anion</th>
<th>$10^2 k_{oa}$/cm$^2$ s$^{-1}$</th>
<th>$10^6 D$/cm$^2$ s$^{-1}$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>1.04</td>
<td>3.72</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>3.02</td>
<td>6.27</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>5.22</td>
<td>9.83</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$c = 4.7 \text{ M, } K' = 8.5 \times 10^2 \text{ cm}^3 \text{ mol}^{-1}, C_{\text{H}} = 30 \times 10^4 \text{ F cm}^{-2}$. Electrode potential: $E = 0.1 \text{ V}$. Electrolytes: $0.1 \text{ M SO}_4\text{H}_2 + x \text{ M Na}_2\text{SO}_4$.

Table 4. Comparison of the Standard Electrochemical Rate Constant ($k_{oa}$) and Diffusion Coefficient ($D$) Values for a 70 nm Thick POAP Film in Contact with Benzenesulfonate Solutions of Different Concentration. Values Extracted from the Fitting of Experimental Data by Using Eq. (1)

<table>
<thead>
<tr>
<th>Anion</th>
<th>$10^2 k_{oa}$/cm$^2$ s$^{-1}$</th>
<th>$10^6 D$/cm$^2$ s$^{-1}$</th>
<th>$X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_5\text{SO}_3\text{Na}$</td>
<td>2.25</td>
<td>5.32</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>3.17</td>
<td>6.93</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>7.22</td>
<td>9.91</td>
<td>1.5</td>
</tr>
</tbody>
</table>

$c = 4.7 \text{ M, } K' = 8.5 \times 10^2 \text{ cm}^3 \text{ mol}^{-1}, C_{\text{H}} = 30 \times 10^4 \text{ F cm}^{-2}$. Electrode potential: $E = 0.1 \text{ V}$. Electrolytes: $0.1 \text{ M C}_6\text{H}_5\text{SO}_3\text{H} + x \text{ M C}_6\text{H}_5\text{SO}_3\text{Na}$.

Vorotyntsev et al., reported in Ref. [19], will be applied to study this system in more detail.

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