

Analysis of ion diffusion and charging in electronically conducting polydicarbazole films by impedance methods

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Abstract

An electrochemical impedance analysis of the doping kinetics of polydicarbazole films is reported. Polymer films of varying thickness were analyzed using an impedance model that considers spatially-restricted diffusion of ionic species. The main bulk parameters for diffusion and charge accumulation during doping were determined from fits. These parameters resulted independent of film thickness after considering the experimental error. The equilibrium (bulk) capacitance C_0 varies in the range of 100–800 F cm⁻³. The chemical diffusion coefficient D varies within the range of 10⁻¹⁰ to 10⁻⁸ cm² s⁻¹ and increases as the steady-state potential reaches the oxidation peak potential.

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1. Introduction

The kinetics of conducting polymer doping using electrochemical methods is a central issue in the investigation and development of useful applications for such compounds. In practical terms, slow kinetics prevents the inclusion of the conducting polymer in technologies that require fast responses [1]. Assuming electroneutrality in equilibrium conditions (ionic doping balanced by electronic charge), the relationship between the concentration of electronic and ionic species with the steady-state potential defines the low-frequency capacitive behavior of the polymeric film (isotherm of doping) [2]. In contrast, the double-layer interfacial capacitance relates the inhomogeneous charge distribution at the interface to the electric field between these charges. Among several mechanisms determining the kinetics of doping (interfacial electronic and ionic charge transfer, double-layer capacitance, charging capacity, ionic

and electronic diffusion in the polymeric film, electrode morphology) [3,4], it is widely acknowledged that the rate controlling factor for low-frequency processes depends mainly on two parameters: the chemical diffusion coefficient D and the diffusion thickness L . In this sense, when doping kinetics is studied by time- or frequency-resolved techniques it is important to verify if the specific film parameters such as chemical diffusion coefficient and equilibrium capacitance correspond to real bulk properties, i.e. they result independent of thickness. This approach ensures that the measurement interpretation has physical relevance [5].

This paper is concerned with the doping kinetics of poly(2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester), a polydicarbazole based conducting polymer. Recently, the mechanism of the electrochemical polymerization of this polymer for biosensing applications was reported [6]. Here, the doping kinetics is studied by means of electrochemical impedance spectroscopy, measured at different steady-state potentials near the potential corresponding to the oxidation peak shown by cyclic voltammetry. The effect of the film thickness (in the 100–600 nm range) is investigated employing a spatially-restricted diffusion model to interpret the impedance spectra of polydicarbazole films. A good correlation is found between the experiment and

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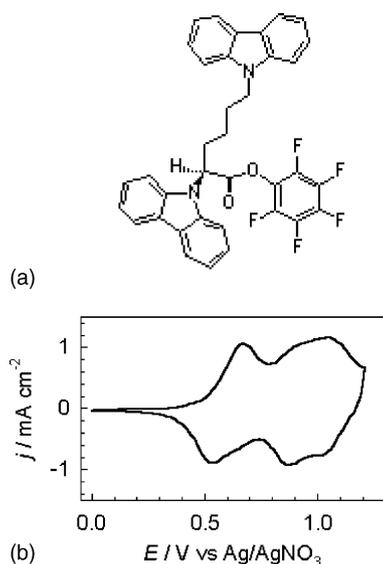


Fig. 1. (a) Chemical structure of the dicarbazole monomer used in this study. (b) Typical cyclic voltammogram of polydicarbazole films in a solution 0.2 M TBAClO₄ in dry acetonitrile. Scan rate was 100 mV s⁻¹.

the theoretical model. A reliable determination of kinetics and equilibrium parameters was thereby carried out.

2. Experimental

The synthesis of the monomer, 2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester (shown in Fig. 1a), was published elsewhere [6]. The electrochemical polymerization, characterization of the dicarbazole-monomer and the impedance measurements were done under a dry nitrogen atmosphere (<1 ppm H₂O and O₂), using an Eco Chemie Autolab 20 potentiostat. The experiments were carried out in a three-electrode cell using a Pt disk (∅ 1.0 mm) as working electrode, a Pt spring, surrounding the WE disk, as counter electrode and a Ag/AgNO₃/acetonitrile, reference electrode.

The background electrolyte consisted of 0.2 M battery grade TBAClO₄ (tetrabutylammonium perchlorate) in dry acetonitrile. For the polymerization process, 10 mM dicarbazole-monomer was added to the electrolyte. The fabrication and analysis of the polydicarbazole films were done in the following steps: First, electro-polymerization of the dicarbazole monomer by cyclic voltammetry varying between 0 and 1.2 V. Second, the typical electrochemical behavior of the polydicarbazole polymer was measured in the background electrolyte solution at the same voltage range. The cyclic voltammograms were done at a scan rate of 100 mV s⁻¹. Third, the film impedance was measured in the frequency range of 10 kHz to 0.1 Hz. The impedance spectra were measured following 30 min application of the steady-state potential ranging from 0.5 to 0.7 V versus Ag/AgNO₃.

Thickness measurements of the polymer films were performed using a Nanonics AFM scanner in a non-contact

mode. The polymer film was scratched to expose the substrate in several locations and the thickness reported was extracted from the step profile measured. The exposed substrate was relatively smooth and similar to that of the substrate before the polymerization process. Z-axis calibration was done before the thickness measurements using 3 different silicon gratings: 22, 97 and 485 nm. We note that the values calculated from the impedance spectra may vary in case of swelling changes the film thickness.

3. Results and discussion

A typical cyclic voltammogram of the polydicarbazole films in 0.2 M TBAClO₄/acetonitrile is presented in Fig. 1b. As explained in the previous publication [6], the peak corresponding to the polymer oxidation is situated between 0.4 and 0.7 V versus Ag/AgNO₃. The wide peak located between 0.7 and 1.1 V versus Ag/AgNO₃ results from oxidation of dangling carbazole units that did not cross-link with the polymer network. We restrict the impedance analysis within the potential range varying from the onset of the polymer oxidation up to the peak potential. Fig. 2 presents typical impedance response patterns of the polydicarbazole films at different steady-state potentials. Four different film thicknesses (from 100 up to 600 nm) were examined in this study. The spectra presented in Fig. 2 correspond to 400 nm thick films.

Electrochemical impedance response of electronically conducting polymers is known to be represented by a circuit model containing interfacial as well as diffusion elements in cases where the polymer films are regarded as homogenous [7]. In the simplest configuration the impedance model considers a single (ionic) charge carrier diffusing along such an active film. This model includes several circuit elements that are related to the different transport and capacitive mechanisms involved in the polymer oxidation (doping): a series resistance R_s , for the electrolyte and contacts contribution; a capacitance C_{dl} , for the double-layer at the electrolyte-polymer film interface; an ionic charge transfer resistance R_{ct} , and finally a diffusion element accounting for the ionic diffusion and charging of the film, Z_D . The spectra presented in Fig. 2 show some of the elements of the model. The high-frequency wing of such spectra (Fig. 2b) shows a small portion of an arc which corresponds to the parallel combination of C_{dl} and R_{ct} . At lower frequencies (<10³ Hz) the spectra are dominated by the spatially-restricted diffusion element Z_D [8,9]. The diffusion impedances undergo a change of pattern at a certain characteristic frequency, ω_d , at which a transition between a Warburg- and a capacitive-like behavior is observed. The frequency ω_d is located near the elbow of the impedance plot, as marked in Fig. 2c. Z_D exhibits in our case the so-called anomalous diffusion response [8,9].

As we are more concerned with the characterization of the ion diffusion process fits have been limited to the

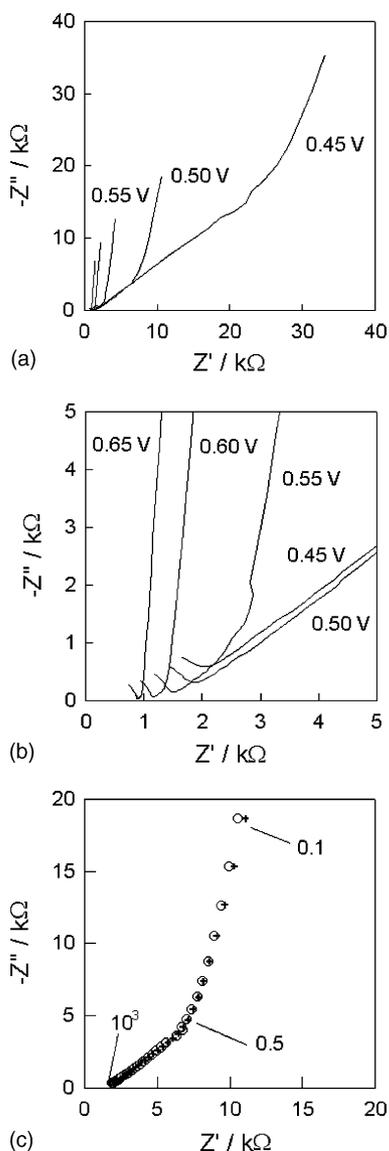


Fig. 2. Examples of electrochemical impedance measurements of polycarbazole films at different steady-state potentials (film thickness 400 nm). (a) General view showing the diffusion impedance, (b) high frequency detail showing the interfacial diffusion, and (c) comparison between experiment (○) and fit (+) for the spectra taken at 0.5 V vs. Ag/AgNO₃. Some frequencies are marked (in Hz). $\omega_d/2\pi \approx 0.5$ Hz.

low-frequency range ($<10^3$ Hz). The impedance spectra presented in Fig. 2 were fitted using the following diffusion element Z_D [9] in series with a resistance that summarizes the effect of R_s and R_{ct}

$$Z_D = R_d \left(\frac{i\omega}{\omega_d} \right)^{-\gamma/2} \left(\coth \left[\left(\frac{i\omega}{\omega_d} \right)^{\gamma/2} \right] \right) \quad (1)$$

where ω is the angular frequency, R_d the resistance associated with diffusion, and γ relates to the deviation from the ordinary spatially-restricted diffusion impedance ($\gamma = 1$). High fitting accuracy was reached as deduced from the values attained by the statistical confidence level ($>99\%$) and the regression coefficients $r^2 > 0.999$. At high frequencies,

$Z_D \propto (i\omega)^{-\gamma/2}$ gives a straight line inclined at less than 45° (the common response of ordinary diffusion), whilst at frequencies lower than ω_d the capacitive behavior due to the film charging is generalized by means of a constant phase element (CPE) $Z_D \propto (i\omega)^{-\gamma}$. Values for γ obtained from fits lie within the range of 0.90–0.95 indicating that the diffusion mechanism is slightly dispersive. As pointed out in ref. [9] the origin of the CPE behavior and the Warburg-like response ($\gamma < 1$) may be related to structural disorder effects which yield distributions of microscopic hopping rates for ion diffusion.

The characteristic diffusion frequency ω_d , obtained from fits enables determination of the chemical diffusion coefficient D as [9]

$$\omega_d = \frac{D}{L^2}. \quad (2)$$

As well known, D represents the effective chemical diffusion coefficient of both the counter anions D_i and the electronic species (polarons) D_e , as $D = D_e D_i / (D_e + D_i)$ (assuming electroneutrality in the film bulk). However, under usual experimental conditions, it seems that the slow carriers, i.e. ionic species, determine the actual value of D , because $D_e \gg D_i$ [1,10,11]. (In fact, an ionic diffusion model has been assumed from the beginning). Fig. 3a presents the dependence of the chemical diffusion coefficient with the steady-state potential for four different film thicknesses. D varies within the range of 10^{-8} to 10^{-10} cm² s⁻¹, showing similar values for the different thickness. In order to check the effect of irreversible changes in the polymer film resulting from the potential application (reproducibility and stability during the measuring time), a set of impedance measurements were performed at fixed potential for a duration similar to that elapsed during a potential scan experiment. This is shown in Fig. 3 by the bars that summarize the total parameter change associated with potential application only. The bars indicate that the effect of potential (at long time), both at 0.55 and 0.60 V versus Ag/AgNO₃ is negligible compared with the changes associated with the potential-induced polymer doping.

The increment of D observed might be related to structural, conformational changes undergone by the polymer film during the doping process. One should also regard the influence of the thermodynamic factor on the variation of D with the potential [12] or interaction effects between mobile species [13]. These values for D lie within the range encountered for other conducting polymers [14], although it has been recognized that the actual film morphology may be the most important determining aspect for ion diffusion. In this sense, several authors [1,5,14,15] have reported D values for polypyrrole films varying within the range of 10^{-12} to 10^{-8} cm² s⁻¹.

A useful estimation of the equilibrium bulk capacitance (per unit electrode volume) C_0 may be approximated from the low-frequency capacitive behavior C_{lf} [4] as $C_0 = C_{lf}/AL$ (A stands for the film active area). C_0 is related to

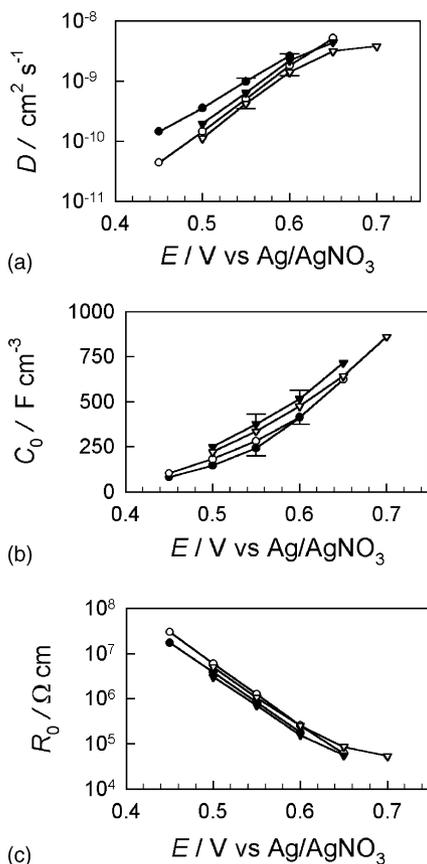


Fig. 3. (a) Chemical diffusion coefficient, (b) charging capacity and (c) diffusion resistance as a function of the applied potential (in V vs. Ag/AgNO₃) for four different film thickness: (●) 100 nm, (○) 300 nm, (▼) 400 nm, and (▽) 600 nm. Lines are marked for eye guiding only. Error bars denote parameter variation induced by the potential application during a time similar to that used to perform a potential scan impedance measurement.

the variation of the carrier concentration \bar{n} with the applied steady-state potential \bar{E} (bars denote equilibrium parameters and e corresponds to the positive elementary charge) in the following way [16]

$$C_0 = -e \frac{d\bar{n}}{d\bar{E}}, \quad (3)$$

and is shown in Fig. 3b. Here we present the correlation between C_0 and the steady-state potential for the different polymer film thickness (including long time variation at some potentials as explained previously). C_0 shows high values ranging from 100 to 800 F cm⁻³ and smooth variation with E . The averaged slope ~ 225 mV/decade implies that the charging process in these polydicarbazole films departs heavily from a Nernstian behavior (~ 60 mV/decade) [17]. A variety of mechanisms has been proposed to explain this behavior: sites with different redox potential [18], mobile species interaction effects [19], ion association [20] or gaussian distribution of electronic states [21].

The third diffusional parameter of interest corresponds to the diffusion specific resistance $R_0 = R_d A/L$. It relates to

the characteristic frequency as $\omega_d = 1/L^2 R_0 C_0$, which in terms of the diffusion coefficient is given by the following expression [22]

$$R_0 = \frac{1}{eD|d\bar{n}/d\bar{E}|}. \quad (4)$$

Therefore it is not an independent parameter and can be calculated from C_0 and D . However it is worth showing its variation with potential because R_0 represents the ionic resistivity of the film. The dependence of R_0 on the applied potential is presented in Fig. 3c (long time variations of the order of point size). R_0 decreases monotonically with the increase of the steady-state potential. Its values are also independent of the polymer layer thickness.

It is important to note that all three, non-independent parameters shown in Fig. 3, namely diffusion coefficient, charging capacity and diffusion resistance, summarize the thermodynamics and kinetics of the polymeric film charging. It is also worth mentioning that behaviors are rather similar regardless the film thickness after taking into account parameter variation during the measuring time.

4. Concluding remarks

We have analyzed the doping kinetics of polydicarbazole (2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester) films by impedance methods. The impedance response can be interpreted in terms of the spatially-restricted diffusion model. Precise parameters were derived from high accuracy fits showing that the charging mechanism is governed by the diffusion processes described by the model. In all cases the low frequency behavior is controlled by the relaxation of the equilibrium (low-frequency) capacitance. The analysis provides values for the bulk polymer parameters, namely chemical diffusion coefficient, equilibrium capacitance and diffusion resistance. As pointed out previously [5] the actual film morphology plays a central role in the kinetics of polymer charging. The fact that the obtained bulk parameters result independent of thickness (after considering parameter changes during the measuring time) enables us to consider the bulk of different films as structurally similar. Therefore our deposition procedure becomes reliable for the reproduction of morphology. Small variations of the dicarbazole monomer are currently being synthesized in order to examine both the model and the polymer. This work will be published when finalized.

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