

The Charge Transport Process at Polyorthoaminophenol Film Electrodes

Abstract

Poly(*o*-aminophenol) (POAP) films were deactivated and then reactivated, and dependences of the different charge-transport and charge-transfer parameters on the degree of deactivation (θ_c) were obtained by employing Electrochemical Impedance Spectroscopy. While some parameters, such as interfacial metal-film and film-solution resistances the high-frequency capacitance and the redox capacitance exhibit a continuous variation without hysteresis between deactivation and reactivation processes within the whole θ_c range, others, such as electron and ion diffusion coefficients show not only marked changes of slope from given θ_c values but also hysteresis between consecutive deactivation and reactivation processes.

Keywords: Poly(*o*-aminophenol); Deactivation; Reactivation; Charge-transport and charge-transfer parameters; Mediation reaction

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Introduction

Traditionally polymers were thought of as insulators and any electrical conduction in polymers was generally regarded as an undesirable phenomenon. The residual conductivity in common polymers can mostly be assigned to loosely bound protons. In the last decades an opposite trend has started inasmuch as investigations have been directed to the utilization of ionic conductivity of polymeric systems. The active research on thermodynamic and kinetic properties of ion-conducting polymers has led to the wide use of polymer electrolytes and polyelectrolytes in electrochemical systems, e.g. in power sources, sensors, and development of all-solid-state electrochemical devices [1-3]. Also in the 1970s somewhat surprisingly a new class of polymers possessing high electronic conductivity (electronically conducting polymers) in partially oxidized (or less frequently reduced) state was discovered. Electrochemistry has played a significant role in the preparation and characterization of these novel materials. Electrochemical techniques are especially suitable for controlled synthesis of these compounds and for tuning of a well-defined oxidation state. The preparation, characterization and applications of electrochemically active, electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry. There are at least two major reasons for this intense interest. First, the intellectual curiosity of scientists that focuses on understanding the behaviour of these systems, in particular on the mechanism of charge-transfer and charge-transport processes occurring in the course of redox reactions of conducting polymeric materials. Second, the wide range of promising applications in the field of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microwave screening and corrosion protection. Several excellent monographs have been published, e.g. [4-6] mostly reviewing the knowledge accumulated

regarding the development of polymer film electrodes and their applications.

Electroactive polymers contain electron donor and acceptor sites that usually consist of up to hundreds of molecular layers [7-9]. Oxidation and reduction of fixed sites introduce charged sites into the polymer, which, to achieve charge neutrality, require the ingress of counter-ions from the contacting electrolyte solution and, according to the Donnan relation, the egress of co-ions [10]. Electron hopping is believed to be the mechanism for electron transport, but it is also possible that ion motions may partially or totally control the rate of charge transport. Thus, the charge-transport rate in electroactive polymer films is quantitatively characterised by a heterogeneous constant of charge transfer and an effective (or apparent) diffusion coefficient for charge transport across the film [11,12]. The factors governing the magnitude of these parameters are not well understood. Furthermore, in general, these transport parameters depend on different variables such as degree of oxidation of the polymer, polymer film thickness, type of electrolyte, ionic strength and *pH* of the solution in contact with the polymer film. A combination of different electrochemical techniques was employed to determine the rates of the charge-transfer and charge-transport processes in electroactive polymers, such as Cyclic Voltammetry (CV), Rotating Disc Electrode Voltammetry (RDEV) and Electrochemical Impedance Spectroscopy (EIS) [12]. When redox species are present in the electrolyte solution, they can participate in an interfacial electron exchange with the polymer at the polymer|solution boundary [13-16]. In this regard, an electroactive polymer can act as a redox mediator. Redox mediators are substances containing redox centres that may be oxidized and reduced more or less reversibly. In general, redox mediation is a phenomenon by which a substance of low conductivity in contact with a metal, on one side, and in contact with a solution containing one or both components of a redox couple, on the other, is capable of mediating electron

transfer between the redox couple in solution and the metal. In the context of the RDEV and the EIS, the conduction properties of electroactive polymer films in the presence of redox species are often tested by analysing the electrochemical behaviour of the films as a function of the electrode rotation rate, polymer film thickness and redox couple concentration.

Poly-*o*-aminophenol (POAP) is an electroactive polymer, which has been characterized by using different electrochemical techniques [17]. Also, several practical applications of POAP in the field of biosensors [18] and electrocatalysis [19] have been reported in the recent literature. In practical uses of POAP, electrochemical conditions, such as applied potential, solution *pH* and thickness, must be taken into account, because they play a crucial role in the performance of the polymer. Besides the control of these critical variables, from the practical viewpoint it is also necessary that the conducting properties of POAP remain substantially unchanged, before and after the polymer has been used. In this regard, a study about deactivation of POAP films employing Rotating Disc Electrode Voltammetry (RDEV) was previously reported [20]. The aim of [20] was to deactivate POAP films, and then study how their permeation and charge-transport processes are modified by the degree of deactivation, especially in the interesting case where the polymer contacts an electroactive solution (hydroquinone/benzoquinone) and a mediation reaction occurs at the polymer|electrolyte interface. Deactivation of POAP films was carried out in [20] by soaking in a 50mM Fe₂(SO₄)₃ solution. This deactivation process was chosen in [20] because it was observed that the deactivated polymer film can be partially reactivated by treatment with a 0.1 M NH₄OH solution [21]. In the present work Electrochemical Impedance Spectroscopy (EIS) was applied to the same POAP/(hydroquinone-benzoquinone) system employed in [20], in order to extract a more complete series of transport parameters of deactivated POAP films than those obtained from RDEV, that is, electron and ion diffusion coefficients and interfacial resistances and capacitances. The present work can help gain further insights into the charge-propagation process at POAP, in such a way that the restrictive stability conditions of the polymer in its practical applications can be exploited more successfully. In this regard, this paper could be interesting not only to the colleagues who have worked for years in basic research related to the conducting properties of this polymer, but also to readers interested in biosensors based on POAP for clinical and industrial applications, where the polymer operates under limit conditions, which can affect its conductivity and then, reactivation of the polymer becomes necessary.

Experimental

POAP films were grown on the base electrodes following the procedure described in [17]. A series of 8 electrodes were prepared and each one of them was successively deactivated and then reactivated as described in [21]. RDEV experiments were performed with each one of the deactivated POAP films in the presence of a solution containing equimolar concentrations of *p*-benzoquinone (Q) and hydroquinone (HQ) species. Stationary current-potential curves (*I*-*E*) at different electrode rotation rates Ω were recorded for each one of the electrodes. Then, *ac* impedance diagrams were recorded at potential values $E < 0.0$ V.

Deactivated POAP films were reactivated by treatment with a 0.1M NH₄OH solution and then, RDEV and *ac* impedance measurements were carried out again in the presence and the absence of Q and HQ species.

Results and Discussion

The degree of deactivation

A degree of deactivation was defined as

$$\dot{\epsilon}_c = 1 - \left(Q_{\text{Red,c}} / Q_{\text{Red,T}} \right) \quad (1)$$

Where $Q_{\text{Red,c}}$ is the total reduction charge assessed by integration of the corresponding voltammetric response from $E = 0.5$ V towards the negative potential direction for a deactivated film, and $Q_{\text{Red,T}} = 2.8 \text{ mC cm}^{-2}$ is the total reduction charge for the nondeactivated film.

The impedance model

The general theory of *ac* impedance described by Vorotyntsev et al. [15] was employed to interpret experimental impedance data of this modified electrode system.

Dependences of the different charge-transport and charge-transfer parameters on the degree of deactivation

A reduction of the POAP electroactivity was observed after its interaction with ferric cations (Figure 1). The reduction of the POAP electroactivity was attributed to the interaction of iron ions with the redox sites of POAP, which impedes the protonation reaction of the polymer. Here, only some transport parameters vs. degree of deactivation dependences, will be shown. The metal-film resistance, $R_{\text{m|f}}$ exhibits an almost continuous increase from the beginning of the deactivation, that is, from $\theta_c = 0$ to $\theta_c = 0.6$ (Figure 2). This increase is consistent with an increasing number of inactive sites at the metal polymer interface, as the deactivation becomes more pronounced. The ion film-solution resistance, $R_{\text{i}^{\text{fs}}}$ as a function of θ_c (Figure 3) exhibits a different feature as compared with $R_{\text{m|f}}$. That is, while a strong $R_{\text{i}^{\text{fs}}}$ increase is observed within the range $0 < \theta_c < 0.35$, a less pronounced increase is obtained at values of $\theta_c > 0.4$. When deactivated POAP films are reactivated by alkaline treatment, all dependences (C_p , $R_{\text{m|f}}$, $R_{\text{e}^{\text{fs}}}$, $R_{\text{i}^{\text{fs}}}$ and C_H vs. θ_c) exhibit a univocal correspondence between deactivation and subsequent reactivation (Figure 2 & 3). However, this is not the case for the dependences that involve diffusion coefficients for electron (D_e) and ion (D_i) transport. These dependences are shown in Figure 4 & 5, respectively. Diffusion coefficients for electron and ion transport decrease as the degree of deactivation (θ_c) increases. Both dependences exhibit a univocal correspondence during deactivation and subsequent reactivation, for degrees of deactivation lower than 0.4. Slower electron transport with the increase of the degree of deactivation was attributed to the increase of the electron hopping distance caused by the presence of inactive sites in the redox site configuration of a deactivated film. Decrease of the ion diffusion coefficient with the increase of the degree of deactivation up to 0.4 was associated with the inhibition of nitrogen-containing groups that provide the binding of hydrogen ions that contribute to film conductivity. Both

dependences show a change of slope for degrees of deactivation higher than 0.5 together with the existence of hysteresis after reactivation. The less pronounced decrease of the electron diffusion coefficient with a higher degree of deactivation (θ_c) was attributed to a redistribution of the redox site configuration to maintain the electron hopping distance constant. In the case of the ion diffusion coefficient, the effect was attributed to inhibition

of nitrogen-containing groups that immobilize protons that do not participate in the diffusion process. These findings seem to indicate that electron and ion conduction of a deactivated poly(*o*-aminophenol) film can only be completely recovered by reactivation when its degree of deactivation is lower than 0.4. However, a permanent loss of conductivity is observed for degrees of deactivation higher than 0.5.

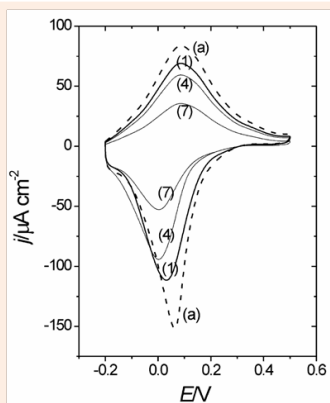


Figure 1: Voltammetric (j - E) responses for 2.8mC cm^{-2} thick POAP films: (a) (---) a freshly prepared POAP film. Numbers (1), (4) and (7) correspond to POAP films with different degrees of deactivation (θ_c): (1): $\theta_c = 0.13$; (4): $\theta_c = 0.44$; (7): $\theta_c = 0.60$. Electrolyte: $0.1\text{ M HClO}_4 + 0.4\text{M NaClO}_4$. Scan rate: $\nu = 0.01\text{ V s}^{-1}$.

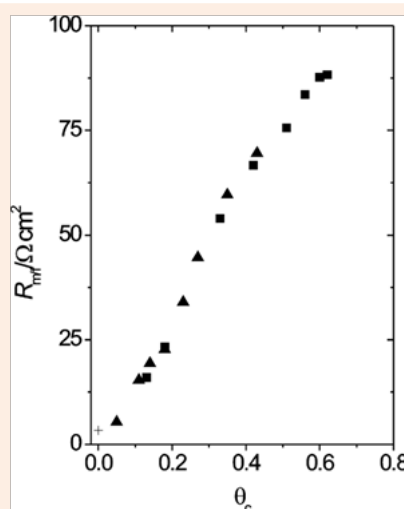


Figure 2: R_{mf} vs. θ_c .

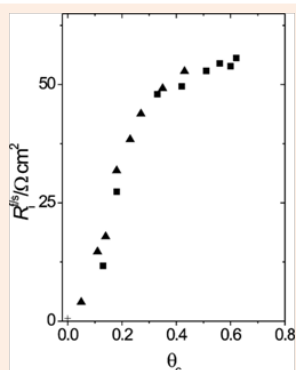


Figure 3: R_i^{ns} vs. θ_c .

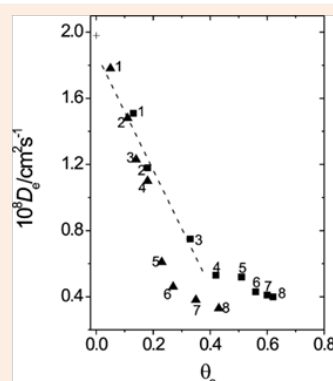


Figure 4: D_e vs. θ_c .

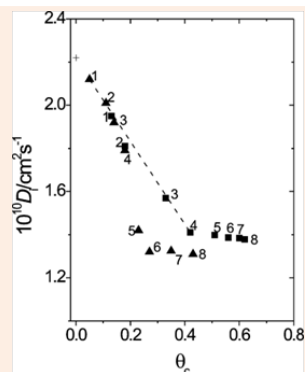


Figure 5: D_i vs. θ_c .

Conclusion

Electron and ion conduction of a deactivated poly(*o*-aminophenol) film can only be completely recovered by reactivation when its degree of deactivation is lower than 0.4. A permanent loss of conductivity occurs for degrees of deactivation higher than 0.5.

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Conflict of Interest

None.

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