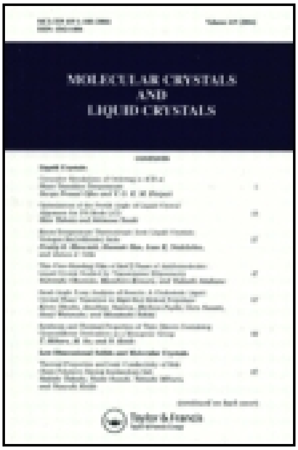

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Spectral and Impedance Study of the Charge Transport in Electrochromic Polymer Layers

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The optical transitions and charge transport in electrochromic polyaniline films have been studied by the impedance and spectroelectrochemical methods in aqueous and organic electrolytes containing proton acid. By means of impedance spectroscopy, the electron diffusion coefficients across the film for anode and cathode processes have been measured. It has been found that the higher rate of electron transport in the bleaching (cathode) process in comparison with the coloration (anode) process may be related to the conformation rebuilding of conducting polymer chains.

Keywords: diffusion coefficient; electrochromic film; impedance; polyaniline; spectroelectrochemistry

INTRODUCTION

A great interest in opto-electronic devices based on conducting polymers (polythiophenes, polyaniline, polyphenylenevinylene) such as "smart windows", optical memories, IR-switching, and electrochromic displays [1–8] has induced the study of the electrochromic materials in a wide spectral range – from near UV to visible and near IR-regions. Such devices are based on the electrochromic effect of changes in the optical spectrum (and color) in a polymer layer under an external electric field [9]. The outer form of this effect is similar to the observed one in liquid crystals [10], but the physical and chemical nature of such

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phenomena is different. The electrochromic effect is defined by the energy properties of molecules in the ground and excited states and by the transition from one state to another [9,10].

In the electrochromic devices, the existence of an electrolyte (liquid or solid) between the electroactive polymer layer and a transparent counter electrode is necessary [10]. Therefore, both the electronic and ionic charge transports in conducting polymer films play a great part. The oxidation (reduction) of a material is associated with the insertion of counter anions (cations) flowing from the electrolyte. They move to balance the electric charge ejected (injected) by the electroactive material which become an ion-doped anode (cathode). As a result, the electronic properties (e.g., the band gap) of the electrochromic material are varied [2]. This corresponds to the modified optical properties (e.g., absorption bands) and related color changes.

As the electrochromic transitions are caused by reduction-oxidation of a polymer with electron injection (ejection), their rate will be controlled by the rate of charge transport in the polymer layer immobilized on the electrode surface. Formally, this rate may be characterized by the heterogeneous constant of charge transport (k_s) or by the effective coefficient (D_{eff}) of diffusion through the film [8,11,12]. The study of the electrochemical behavior of polyaminoarene films in various electrolytes demonstrated that the charge transport across a film is limited by diffusion [6–8,12]. The effective diffusion coefficients (D_{eff}) calculated from the model of semi-infinite diffusion [11] with the use of voltammetry methods are very approximate [6,7,11] and give no possibility to estimate the electron transport rate separated from the ion transport.

Impedance spectroscopy is one of the best techniques for the determination of the electron diffusion coefficients (D_e) in electroactive polymer films [13]. This method was at first applied to a conducting polymer (polypyrrole) by Bard and his co-workers [14]. The comprehensive development of the theory applicable to conducting polymers is given by Albery and Mount [15,16].

In this article, the spectro-electrochemical behavior and the diffusion coefficients as the parameters of charge transport in electrochromic polyaminoarene films have been studied. As a model system, a thin polyaniline film on ITO electrodes has been considered.

EXPERIMENTAL

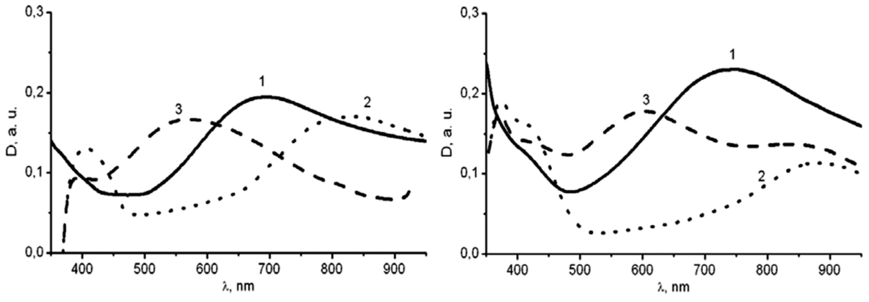
The polymer films on the ITO surface were obtained by means of the electrochemical polymerization of a 0.1 M aniline solution in 0.5 M sulfuric acid using the method of potential (E) cycling between 0 and 1.0 V at the sweep rate $\nu = 40\,\mathrm{mV/s}$ [8]. The sweep cycle number (N) regulated the film thickness which was also estimated with the help of a micro-interferometer MII-4. The glass plate (the area of $2.5\,\mathrm{cm}^2$) coated by indium-tin oxide was used as a working electrode. The counter electrode was a platinum wire, whereas Ag/AgCl in a saturated KCl solution was used as the reference electrode. The optical absorption spectra of PANI films were obtained on a spectrophotometer SP-46 in the spectral range 320...900 nm. To study the electrochromic properties of the films, a quartz cell disposed in the working camera of a spectrophotometer and connected by a three-electrode scheme with a potentiostat ΠI-50M has been used. As the reference electrode, $\mathrm{Pt/H_2}$ was employed [12]. The impedance experiments were carried out at the potential values corresponding to the electrooptical transitions in a polymer layer with the help of an AUTOLAB equipment over the frequency range from 0.01 Hz to 100 kHz, with an ac amplitude of 5 mV.

RESULTS AND DISCUSSION

The optical spectra of polyaminoarenes (polyaniline and its derivatives) are characterized by the existence of some absorption bands: at 380–450 nm related to the π–π^* transition in localized semiquinone cation-radicals (polarons) and at 750–780 nm caused by the polaron-bipolaron band absorption. The extension of this band to the nearest IR-region may be related to the free carrier's absorption [1,3]. The middle band at 650 nm corresponds to the n–π^* transition in the quinoid form of a polymer structure [17]. It is developed in the spectra of light doped polyaminoarenes and may be overlapped with the bipolaron band. The most remarkable changes at the applied potential are observed for the absorption band at 750–780 nm (Fig. 1a,b) corresponding to a transition in the polaron-bipolaron band [1,7].

Polyaniline, belonging to the family of multicolor electrochromic materials, exhibits the reversible electrochromic transitions (colorless-yellow-blue-green-violet) in the interval of potentials between $E = -0.2$ and $+1.0\,\mathrm{V}$ [1,6,7,12]. The color transitions in polyaminoarene films undergone the action of the applied potential (voltage) were observed both in the potentiodynamic mode (Fig. 2) and under the pulse voltage switching (Fig. 3). They respond to a displacement of the absorption bands (see Fig. 1) and to the changes in the polymer film's optical absorption (transmittance) at a fixed wavelength, as shown in Figures 2 and 3.

As for the characterization of the electrochromic properties of multicolor films, we propose to take the following parameters into account: a shift of the absorption peak under switching ($\Delta\lambda_{\max}$, nm); difference in optical absorption between the reduced or oxidized form of PANI at a



(a) (b)

FIGURE 1 Spectroelectrochemical response of a PANI film on the ITO electrode in 0.1 M $LiClO_4$ aqueous (a) and DMSO (b) solutions in the presence of 10^{-3} M $HClO_4$ (a,b) at potentials E, V (Pt/H_2): 0 (1); −0.2 (2); +0.2 (3). Film thickness is 360 ± 20 nm.

fixed wavelength (ΔA_{750}); and electrochromic contrast (CR_{750}) as the absorbance change (ΔA_{750}) per unit applied potential (ΔE, V) taking in account that $\Delta A = \lg CR$ [2]. An important characteristic of the electrochromic material is a degree of degradation of the optical absorption, defined in this work as a change in the film absorbance (A_{750}-A^{d}_{750}) after the 15-min polarization at the potential $E = 0.8$ V (Ag/AgCl).

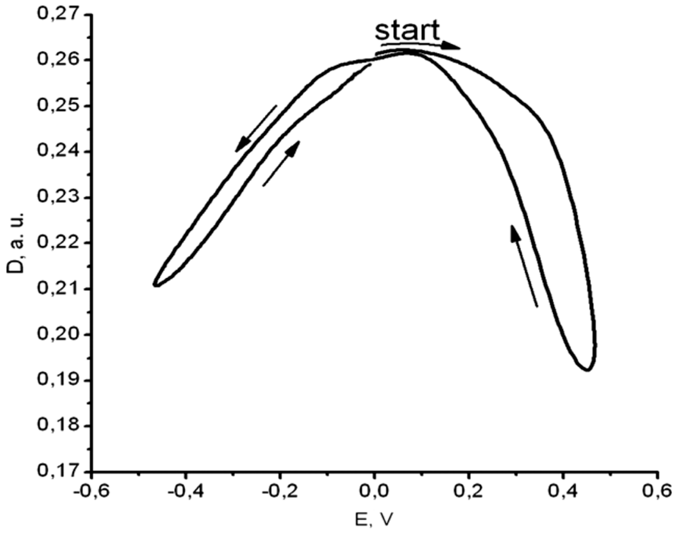


FIGURE 2 Dependence of the PANI film absorption at a wavelength of 750 nm under the potentiodynamic mode with a sweep rate of 10 mV/s.

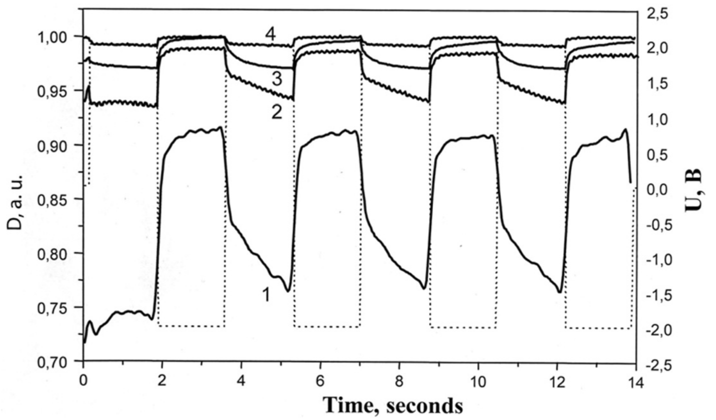


FIGURE 3 Change in the PANI film transmittance in the process of voltage imposition with an amplitude of ± 2V in the two-electrode control circuit. Wavelengths are 575 (1), 558 (2), 595 (3), and 610 nm (4). As an electrolyte, 0.5 M sulfuric acid was used.

In addition, a quick-acting parameter may be taking into consideration for completing the analysis of the electrochromic material. This parameter is related to the diffusion coefficient (D_e) concerning the charge transport across the film and should depend on the polymer structure, film thickness, and electrolyte type [6,10].

On the basis of spectroelectrochemical investigations (the typical spectra are shown in Fig. 1), the optimal concentration of proton acid and the type of a solvent providing the best electrochromic properties of PANI films have been defined (Table 1). As has been found, a higher electrochromic efficiency of the PANI films is observed in lithium perchlorate electrolytes at an acid concentration of $10^{-2} \ldots 10^{-3}$ M. The similar conditions were selected for studying the charge transport in polymer films by means of the impedance spectroscopy method.

The study of the impedance at potentials of the color transitions (yellow-green-blue) was performed at the polarization $\Delta E \pm 0.2\,\mathrm{V}$ versus the formal potential of the ITO-PANI electrode ($E_o = 0.54\,\mathrm{V}$, Ag/AgCl). The equivalent circuit of the electroactive film in an electrolyte solution is presented in Figure 4 (inset). The components of this hypothetical circuit correspond to real physical phenomena: the Faraday capacitance of the system (C_F), electronic resistance (R_e), ionic resistance (R_i) of the film, and solution resistance (R_s).

The obtained characteristic complex plane impedance plots (Nyquist diagrams) for the ideal case and for a response of the polyaniline film on the ITO surface are shown in Figure 4. In this plot, two distinct regions

TABLE 1 The Effect of Electrolytes on the Electrochromic Properties of a PANI Film on the ITO Electrode at Potentials ±0.2 V versus the Formal Potential of the ITO-PANI Electrode (0.54 V, Ag/AgCl). Film Thickness is 360 ± 20 nm

Solvent, electrolyte	Concentration of acid, M	Shift of the band, $\Delta\lambda_{max}$, nm	Absorbance difference at $\lambda = 750\,nm$, ΔA_{750}	Degree of degradation, $A_{750} - A^{d}_{750}$	Contrast, CR_{750}, $(\% \cdot V^{-1})$
Aqueous 0.1 M $LiClO_4$	10^{-1} $HClO_4$	150	0.112	0.06	32
80% Ethanol 0.1 M $LiClO_4$	10^{-1} $HClO_4$	106	0.125	0	33
Acetonitrile 0.1 M $LiClO_4$	10^{-2} $HClO_4$	84	0.110	0.006	32
Propylene-carbonate 0.1 M $LiClO_4$	10^{-2} $HClO_4$	99	0.160	0.01	36
DMSO 0.1 M $LiClO_4$	10^{-2} $HClO_4$	53	0.170	0.063	37
0.1 M $LiClO_4$, H_2O	$5 \cdot 10^{-3}$ H_2SO_4	177	0.050	0	27

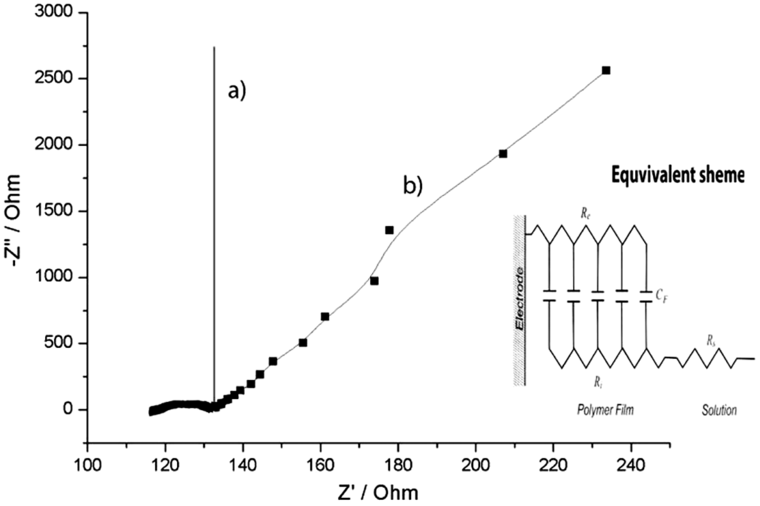


FIGURE 4 Complex plane impedance of the ITO electrode coated with a polyaniline film: (1) ideal, (2) experimental results. Inset: the equivalent circuit to model the electrochromic film in an electrolyte solution: R_e – electronic resistance, R_i – ionic resistance, C_F – Faraday capacitance, R_s – resistance of the electrolyte solution.

are distinguished: low-frequency and high frequency regions, whose origin stems from a diffusion process–electronic or ionic–within the film [15,16].

The effective coefficient diffusion of electrons (D_e) can be determined by the data on electrochemical impedance according to the relation [15]

$$D_e = \frac{d^2}{R_e C_{low}} \tag{1}$$

where d – film thickness; C_{low} – capacitance at low frequencies which may be obtained from the inverse slope of a plot of imaginary impedance Z'' versus reciprocal frequency $1/\omega$ (ω in $\mathrm{rad} \cdot \mathrm{s}^{-1}$) for the low-frequency data [15]; and R_e – electron resistance of the electrochromic film.

To define a value of R_e, the next considerations may be taken into account [15–18]. In the high-frequency limit, the impedance of the capacitance component C_F becomes negligible, and the transmission line behaves like two resistances in parallel:

$$\frac{1}{Z} = \frac{1}{R_e} + \frac{1}{R_i}. \tag{2}$$

The extrapolation of the 45°-region to the real axis in the Nyquist plot gives the intercept

$$R_{high} = R_s + \frac{1}{1/R_e + 1/R_i}, \tag{3}$$

where R_{high} – high-frequency resistance; R_{i} – ionic film resistance; and R_{s} – solution resistance.

The low-frequency response of the transmission line is described as

$$Z = \frac{R_\Sigma}{3} - \frac{i}{\omega C_F}, \tag{4}$$

where $R_\Sigma = R_e + R_i$.

The real impedance is theoretically constant at all frequencies, but this portion of the plot is not quite vertical in practice (see, for example, Fig. 4, curve 2). The real axis intercept of the low-frequency data gives cause for

$$R_{low} = R_s + \frac{R_\Sigma}{3}. \tag{5}$$

When $R_i << R_e$, the electronic resistance R_e is approximated by the difference between the real impedance intercepts of these two regions:

$$R_e = 3(R_{low} - R_{high}). \tag{6}$$

The transition line shape of the impedance demonstrates that at the external polarization equal to $\pm 0.2\,\mathrm{V}$, when the Faraday processes are insignificant, it turns out that the diagram with two linear sections is predominant. The complex resistance of the electrochromic film is modeled by the ohmic and capacity components. The measured values of these parameters and the diffusion coefficients calculated according to Eqs. (2–6) are presented in Table 2.

As follows from the obtained parameters of charge transport, the processes of coloration and bleaching (charge injection and charge extraction) in the polyaniline films are not symmetric phenomena. Probably, the coloration is controlled, in general, by properties of the polymer-injected electron contact interface, while the bleaching is determined by the proton transport in a polymer [10,12].

It has been recently shown that the rate of color switching is defined by both the polymer structure and electrolyte anion nature [6]. So the rate of writing-rewriting information in electrochromic memory devices [4] should depend significantly on the direction, interval, and rate of change in the electrode potential. As has been demonstrated in this work, the nature of a solvent considerably affects the

TABLE 2 Impedance of the Electrochromic Polyaniline Layer in Various Electrolytes. Film Thickness is 300 ± 20 nm

Electrolyte	Potential,V (Ag/AgCl)	R_e, Ω	C_{low}, mF	Diffusion coefficient, $D_e \times 10^9$, cm^2/s
Aqueous	0.74	129.3	10.9	0.64 ± 0.02
0.1 M $LiClO_4$	0.54	122.5	5.98	1.23 ± 0.02
10^{-3} M $HClO_4$	0.34	121.2	3.26	2.28 ± 0.04
80% Ethanol	0.34	164.6	9.18	0.60 ± 0.02
0.1 M $LiClO_4$	0.54	126.5	7.72	0.92 ± 0.02
10^{-3}M $HClO_4$	0.34	131.4	3.85	1.78 ± 0.03
Acetonitrile	0.74	256.6	6.20	0.56 ± 0.02
0.1 M $LiClO_4$	0.54	254.2	5.51	0.64 ± 0.02
10^{-3} M $HClO_4$	0.34	251.6	6.33	0.58 ± 0.02

electron diffusion coefficient (Table 2). A higher rate of electrochromic transition can be observed in aqueous and mixed electrolytes, but the best electrochemical stability is achieved in organic solvents with low donor number [18] such as acetonitrile (Table 1).

At the same time, the chromogenous processes in polymer layers are connected with the solvation of anions and their incorporation to the polymer backbone [12,18]. The oxidative process is accompanied by a reorganization of the polymer backbone structure. Conformation changes occurring in these processes take a certain time of relaxation. As a result, a hysteresis loop in the optical absorption of PANI is observed in the cyclic potentiodynamic mode (Fig. 2), as well as the asymmetry in the optical response of a PANI film under the voltage switching (Fig. 3). As was shown [6,12], the parameters of charge transport through the films correlate with the anion mobility, but we suggest that the most significant factor is the capability of a film to the quick and reversible relaxation.

CONCLUSION

By means of the spectral and impedance investigations of the polyaniline films on ITO electrodes in various electrolytes, the electrochromic properties and the parameters of charge transport (the electron diffusion coefficients) have been defined. It has been found that the nature of a solvent significantly influences the electron diffusion coefficient. A higher rate of electrochromic transition is observed in aqueous electrolytes, but the best electrochemical stability is achieved in organic solvents with low donor number. The experimental results obtained clearly confirm a difference in the parameters of charge transport in the case of the oxidation and reduction processes running in electrochromic polymer layers.

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