Charge Transport In Electrically Responsive Polymer Layers

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Abstract. The processes of charge transport in the conducting polymer electrochromic films have been studied by means of spectral-electrochemical method, impedance spectroscopy and cyclic voltametry measurements. It has been shown that charge transport during the coloration-bleaching processes is not symmetric phenomenon. By means of impedance spectroscopy the effective diffusion coefficients for anode and cathode charge transport have been measured. The higher rate of charge transport in the bleaching process as compared to coloration is considered in the frame of conformation rebuilding of conducting polymer chains.

1. Introduction
A great interest to nano-opto-electronic devices based on the conducting polymers (polythiophenes, polyaniline, polyphenylenevinylene) such as “smart windows”, optical memory devices, IR-switching, electrochromic displays and sensors caused a study of electrochromic materials in wide spectral range – from near UV to visible and near IR-region [1]. Such devices are based on electrochromic effect – changes in the optical spectra (and color) in organic polymer layer under external electric field. As a result of electrochemical doping-dedoping processes, the electronic properties (e.g. band gap) of the electrochromic material are remarkably varied [2]. This corresponds to modified optical properties (e.g. absorption bands) and related colour changes. The application of electrochromic organic films on the transparent electrodes also gives a possibility to create optoelectronic devices with long memory storage [3]. A number of constructions are proposed for electrochromic display based on WO³ layer with color change from white to blue following to applied potential [4] or hybrid nanostructured materials [5].

Recently, we offered novel electrooptical devices with conducting polymer layer on the transparent electrodes, which operate both on three- and two- electrode circuit basis, serving as a model of organic displays [6-8]. The application of the new principle of control as well as of new materials enables to provide a wide gamma of color transitions at the change of voltage within ±2V, stability of operation of the optical element during 1500-2000 cycles of switching as well as speed characteristics within the requirements for electrochromic displays [9]. In order to increase the colour contrast, quick-action and electrochemical stability of device a new electrochromic material based on nanostructured TiO² layer with immobilized conjugated polymers on the transparent tin oxide surface has been proposed.

In the electrochromic devices the presence of electrolyte (liquid or solid) between the electroactive polymer layer and transparent counter-electrode is necessary [9]. Therefore both
electronic and ionic charge transport in conducting polymer film plays a great role. The oxidation (reduction) of the material is associated with insertion of the counter anions (cations), flowing from the electrolyte. They move to balance the electric charge ejected (injected) by the electroactive material which become an anode (cathode) ion doped.

This paper presents the results of the study of electrochromic behavior and the charge transport parameters in the electrochromic polyaminoarene films on ITO electrodes.

2. Experimental
The polymer films on ITO surface were obtained by means of the electrochemical polymerization of the 0.1 M purified monomers (o-toluidine, o-methoxyaniline, aniline and o-aminophenol) in 0.5 M H\textsubscript{2}SO\textsubscript{4} using the method of potential (\(E\)) cycling between 0 and 1.0 V at the sweep rate \(\nu=40\) mV/s [6-8]. The sweep cycle number (\(N\)) regulated the film thickness, which was also estimated with the help of the micro-interferometer MII-4. The glass plate (area – 2.5 cm\textsuperscript{2}) coated by indium-tin oxide was used as a working electrode. The counter electrode was a platinum wire, whereas Ag/AgCl in saturated KCl solution and Pt/H\textsubscript{2} were used as a reference electrode. The optical absorption spectra of the films were collected using the spectrophotometer SP-46 in the spectral range of 350...1100 nm. To study the electrochromic properties of the films, the quartz cell, disposed in the work camera of the spectrophotometer and connected to the III-50M potentiostat by three-electrode scheme has been used. As a reference electrode Pt/H\textsubscript{2} was employed [10]. Impedance experiments were carried out at the potential values corresponding to the electrooptical transitions in the polymer layer with help of AUTOLAB equipment, over a frequency range from 0.01 Hz to 100 kHz, with AC amplitude of 5 mV.

3. Results and Discussion
Numerous investigations were carried out for electrochromic polyaniline films in organic and aqueous electrolytes [1-3], but complete polymeric electrochromic device, operating as display, screen or light filter is not yet realized. In the present report the electrochromic properties of polyaminoarenes with different nature of substitutes in benzene ring - poly-o-aminophenol (POAP), poly-o-toluidine (POTI), poly-o-methoxy-aniline (POMA) and polyaniline (PANI) have been studied as potential materials for using in three and two-electrode construction of electrochromic devices. Figure 1 presents the molecular structure of studied polyaminoarenes.

![Molecular structure of polyaminoarenes](image)

**Figure 1.** Molecular structure of polyaminoarenes: a – polyaniline; b – poly-o-aminophenol, c – poly-ortho-methoxyaniline, d – poly-ortho-toluidine.

Polyaminoarenes such as polyaniline and its derivatives, belonging to the family of multicolor electrochromic materials, exhibit, as shown in the Table 1, the reversible electrochromic transitions (colorless-yellow-blue-green-violet) in the interval of potentials between –0.2 and +1.0 V [6,7,10].
**Table 1.** The potentials of electrochromic color transitions in polyaminoarene films

| Conducting polymer layer on ITO | Electrode potential, V (Ag/AgCl) |
|----------------------------------|----------------------------------|
| Poly- o-aminophenol              | ![Poly- o-aminophenol](image1) |
| Poly- o-methoxyaniline           | ![Poly- o-methoxyaniline](image2) |
| Poly- o-toluidine                | ![Poly- o-toluidine](image3) |

The color transitions with potential (versus Pt/H₂) of the PANI films on the ITO electrode

At the potential range \( E > 0.6-0.8 \) V blue (PANI, POTI), violet (POMA) and brown (POAP) colors of the films are observed, which may be connected with appearance of over-oxidized permigraniline fragments in polyaminoarenes. At higher potential (\( E \geq 1.2 \) V) the color variations become irreversible; the loss of doping level and conductivity is observed. The optical spectra of polyaminoarenes (polyaniline and its derivatives) are characterized by the existence of some absorption bands: at 380-450 nm related to \( \pi-\pi^* \) transition in localized semiquinone cation-radicals (polarons); at 750-780 nm caused by polaron-bipolaron band absorption. Extention of this band to the nearest IR-region may be connected with the free carriers absorption [1,3]. The most remarkable changes at the applied potential are observed for the absorption band at 750-780 nm (Figures 2 and 3), corresponding to the transition in polaron-bipolaron band [1,7]. The color transitions in polyaminoarene films are responded to the displacement of the absorption bands as shown in Fig. 2, and asymmetry of the spectro-electrochemical response in the coloration-bleaching process (Fig. 3 and 4).

**Figure 2.** Spectroelectrochemical response of the PANI film on the ITO electrode in 0.1M LiClO₄ aqueous solution at the presence 10⁻³ M HClO₄ at potential V (Pt/H₂): 0 (1); -0.2 (2); +0.2 (3) V. Film thickness 360±20 nm.

**Figure 3.** The dependence of the PoTI film absorption at wavelength 750 nm under cyclic potentiodynamic mode with a sweep rate 5 mV/s.
According to cyclic voltametry (Figure 5) the electrochromic transitions in the polyaminoarenes are connected to electrochemical processes of the reducing - oxidation in polymer layers, which include an electron transport from electrode to polymer film. The study of polyaminoarene films electrochemical behavior in aqueous electrolytes (HCl, HClO₄, H₂SO₄, HNO₃, toluene sulfonic acid /TSA/) demonstrated that charge transport across the film is the diffusion limited and linear dependence of peak current from sweep rate iₓ = v₁/₂ is observed (Figure 6). Calculated by the model of semi-infinite diffusion [7,8,11] values of effective diffusion coefficients (Dₓ) and transition time of diffusion (τₓ = Tₓ/4Dₓ) are presented in Table 2. Obtained results allow one to suggest that the main factor determining the charge transport across the film is the molecular structure and segment mobility of polymer chains.

Table 2. Parameters of charge transport in polyaminoarene films in 0.5 M H₂SO₄.

| Conducting polymer layer | Film area, S, cm² | Film thickness, l 10⁻⁴ cm | Diffusion coefficient, Dₓ 10⁻⁷ cm²/s | Transition time, τₓ, s |
|--------------------------|-------------------|----------------------------|-------------------------------------|------------------------|
| POTI                     | 2.1               | 0.35                       | 2.62 ± 0.06                         | 0.5 ± 0.15             |
| PANI                     | 4.0               | 0.28                       | 9.02 ± 0.05                         | 0.02 ± 0.01            |
| POMA                     | 4.0               | 0.28                       | 3.56 ± 0.07                         | 0.8 ± 0.15             |
| POAP                     | 3.4               | 0.25                       | 0.23 ± 0.04                         | 6.4 ± 0.7              |
However, values of effective diffusion coefficients, calculated from the model of semi-infinite diffusion by means of voltammetry methods are much approximated [11] and do not give a possibility to estimate an electron transport rate separated from ion transport. Impedance spectroscopy is one of the best techniques for determination of different quantities in electrochromic films, particularly, it was applied to a conducting polymer (polypyrrole) by Bard and co-workers [12] in order to find the effective diffusion coefficients ($D_e$).

The study of impedance at potentials of the color transition (yellow-green-blue) was performed at polarization ±0.2 V versus a formal potential of ITO-PANI electrode ($E_f = 0.54$ V, Ag/AgCl). The obtained characteristic complex plane impedance plots (Nyquist diagrams), for ideal case and for the response of polyaniline film on the ITO surface are presented in the Figure 7. In this plot two distinct regions are distinguished: a low frequency region and high frequency region, whose origin stems from a diffusion process – electronic or ionic – within the film [13].

The effective diffusion coefficient of electron ($D_e$) may be determined from the electrochemical impedance data, according to the equation [13]:

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

where $d$ – film thickness; $C_{low}$ – capacitance at low frequency, which may be obtained from the inverse slope of a plot of imaginary impedance $Z'$ versus reciprocal frequency ($1/\omega$, $\omega$ in rad/s$^{-1}$) for the low frequency data [12]; $R_e$ – electron resistance of electrochromic film.

![Figure 7. The complex plane impedance of the ITO electrode coated with a polyaniline film: a)-ideal, b)-experimental results; inset: equivalent circuit of conducting polymer layer in electrolyte solution.](image)

| Electrolyte       | Potential, V (Ag/AgCl) | Electron Diffusion Coefficient, $D_e \times 10^9$, cm$^2$/s |
|-------------------|------------------------|---------------------------------------------------------------|
| Aqueous           | 0.74                   | 0.64 ± 0.02                                                   |
| 0.1M LiClO$_4$    | 0.54                   | 1.23 ± 0.02                                                   |
| 10$^{-3}$M HClO$_4$ | 0.34               | 2.28 ± 0.04                                                   |
| 80% Ethanol       | 0.34                   | 0.60 ± 0.02                                                   |
| 0.1M LiClO$_4$    | 0.54                   | 0.92 ± 0.02                                                   |
| 10$^{-3}$M HClO$_4$ | 0.34               | 1.78 ± 0.03                                                   |
| Acetonitrile      | 0.74                   | 0.56 ± 0.02                                                   |
| 0.1M LiClO$_4$    | 0.54                   | 0.64 ± 0.02                                                   |
| 10$^{-3}$M HClO$_4$ | 0.34               | 0.58 ± 0.02                                                   |
4. Conclusion

The obtained results show that the rate of color switching is defined by both the polymer structure (Table 2) and electrolyte nature. Thus, a rate of writing-rewriting of information in electrochromic memory devices should significantly depend on the direction, interval and rate of the changing of the electrode potential. As it has been demonstrated in this work, the nature of solvent plays an important role in the electron diffusion coefficient values. (Table 3). The higher rate of electrochromic transition may be observed in aqueous and mixed electrolytes, but the best electrochemical stability is achieved in organic solvent with a low donor number [14] such as acetonitrile. At the same time the chromogenius processes in polymer layer are connected with solvation of anions and their incorporation to the polymer backbone [10, 14]. The oxidative process is accompanied by reorganization of the polymer backbone structure. Conformation changes occurring in these processes, take certain time of relaxation. Consequently, the hysteresis loop in optical absorption of polyaminoarenes is observed in cyclic potentiodynamic mode (Figure 3) and also some asymmetry is noticeable in the optical response of PANI film at voltage switching (Figure 4).

It has been shown that charge transport during the coloration-bleaching processes is not symmetric phenomenon. By means of impedance spectroscopy the effective diffusion coefficients for anode and cathode charge transport have been measured. The higher rate of charge transport in the bleaching process in comparative to coloration is considered in the frame of conformation rebuilding of conducting polymer chains.

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