Charge transport in electrochromic films of poly-*ortho*-toluidine

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Optical and electrochemical properties of poly-*ortho*-toluidine films on SnO_2 electrodes have been studied in acid electrolytes. The electrochemical oxidation-reduction of films has been found to be accompanied by reversible electrochromic changes (colorless-yellow-blue-green-violet) in potential range of E from −0.3 to 1.2 V (Ag/AgCl). The effective diffusion coefficient D_{ef} for charge transfer across the film and transition time of diffusion τ_D have been calculated.

Изучены оптические и электрохимические свойства пленок поли-*орто*-толуидина на поверхности SnO_2 электродов в кислотных электролитах. Электрохимиче-ское окисление-восстановление пленкок сопровождается обратимыми изменениями цвета от полностью прозрачного до желтого, синего, зеленого и фиолетового в области потенциалов $E = -0,3...1,2$ В (Ag/AgCl). Рассчитаны значения эффективного коэффициента диффузии D_{ef} и характеристического времени τ_D для процесса переноса заряда через пленку.

Study of the charge transport processes in thin layers of organic semiconductor based on amino-containing polyarenes (poly-aniline and its derivatives) excites a great interest due to potential applications of these films as modified electrodes, sensors, non-emissive electrochromic displays, etc. [1−4]. Among the family of amino-containing polyarenes, an electrochromic polymer of good prospects is poly-*o*-toluidine (POTI), similar in molecular structure to polyaniline (PANI) and exhibiting electrophysical properties of interest due to the presence of electron-donor substitute (methyl group) in benzene ring [3, 4]. At the same time, the electrochemical properties of POTI defining the charge transport mechanism in functional devices, in particular, in electrochromic displays, in our opinion, are studied still insufficiently. Because the most of display materials operate mainly in proton media [5], in the present work, the electrochemical behavior of POTI films on transparent SnO_2 surface has been investigated in aqueous acid solutions as a model system for development of electrochromic devices.

The polymer films on SnO_2 surface were obtained by electrochemical polymerization of 0.1 M *o*-toluidine solution in 0.5 M sulfuric acid under cyclic potential sweeping between 0 and 1.0 V (Ag/AgCl) at the sweep rate $v = 40$ mV/s has been used. The sweep cycle number (N) and of anode and cathode current peak values in the cyclic volt-ampere curves were used to control the film thickness, which also was estimated using a MII-4 microinterferometer. The glass plate (2.5 cm^2 area) spin-coated with SnO_2, was used as the working electrode. Platinum wire was a counter electrode, Ag/AgCl in saturated KCl solution was used as the reference electrode. Electrochemical behavior of POTI on SnO_2 electrode was studied using cyclic voltammetry (CVA) in aqueous solutions of 0.5 M H_2SO_4, 1 M HCl, $HClO_4$, HNO_3, $CH_3C_6H_4SO_3$ at $T = 293$ К. Optical
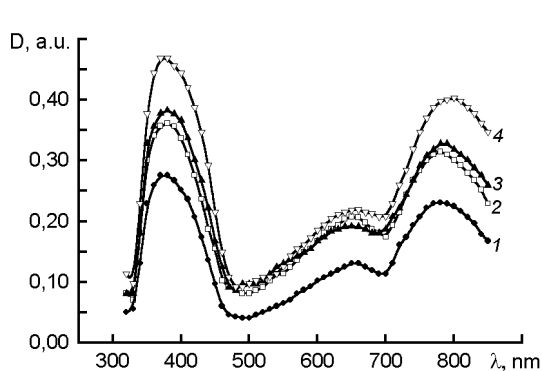
Fig. 1. Electronic spectra of poly-o-toluidine films on SnO_2 surface. Films obtained from 0.1 M o-toluidine solution in 0.5 M sulfuric acid during 15 (*1*), 20 (*2*), 22 (*3*), and 30 (*4*) cycles of potential sweep.
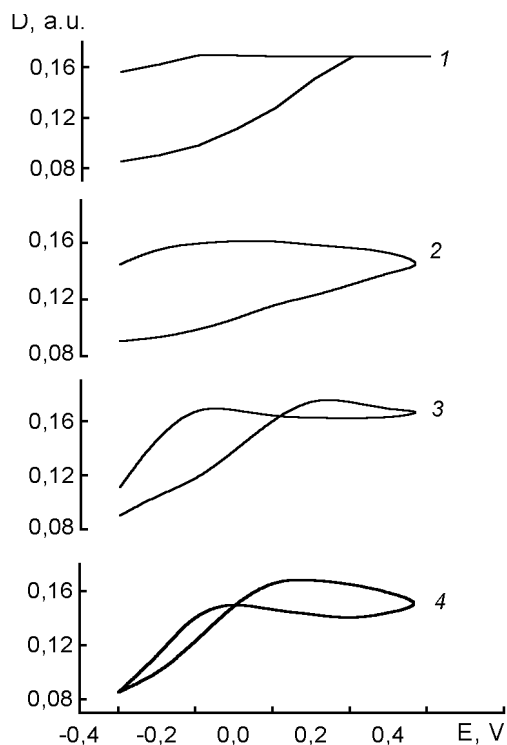

Fig. 2. Canges in optical density of POTI film at λ = 760 nm as a function of applied potential in 1 M toluene sulfonic acid solution at scan rate, v = 20 (*1*), 10 (*2*), 5 (*3*), 2 (*4*) mV/s.

absorption spectra of the POTI films were obtained on spectrophotometer SP-26 in spectral range of 320 to 900 nm. For testing of POTI electrochromic properties, a quartz cell placed in the spectrophotometer operating chamber and connected according to three-electrode scheme with potentiostat PI-50M has been used. The reference electrode was provided as a Pt wire in the same solution.

In the voltammetric study of the electrodeposition process, it has been found that the monomer (*o*-toluidine) oxidation on SnO_2 occurs after a potential E of 0.82 to 0.92 V is attained, while the polymerization process corresponds to a reversible redox maximum at potential values 0.55 to 0.57 V, that is, the primary formed layer acts as a catalyst of the process [6, 7]. The compact, uniform POTI films were deposited after 5 to 30 potential sweeps between E = 0 to 1.0 V. The molecular structure of the base POTI form obtained in these conditions, according to [3, 4], is similar to PANI with methyl substitute in *ortho*-position related to amino group of aniline link.

It follows from electron spectra that the increasing cycle number in the synthesis process results in increased optical density of the polymer film corresponding to its thickness (Fig. 1). The POTI films are characterized by two main absorption bands at 380 to 400 and 760 to 780 nm and a less intense intermediate band at 650 nm. These bands can be assigned to certain electron transitions by analogy with polyaniline and polymethoxyaniline [1, 2]. The absorption at 380 to 400 nm may be assigned to $\pi-\pi^*$ transition in localized semiquinone cation-

radicals (polarons), the 760 to 780 nm one is caused by delocalized states of free carries (bipolarons). The intermediate band at 650 nm corresponds to $n-\pi^*$ transition in quinoide form of POTI base structure.

Under applied potential the shape of electron spectra changes significantly. The POTI film, similar to polyaniline one [1], exhibits reversible electrochromic transitions (colorless-yellow-blue-green-violet) in the E interval between −0.3 and +1.2 V. In the electron spectra, the most remarkable changes are observed for absorption band at 760 to 780 nm, corresponding to transition from conducting to insulating form of POTI during potential sweeping. Depending on the potential sweep rate, the optical density changes in the band at 760 nm may exhibit the shape of loop, figure of eight, or ellipse (Fig. 2), agreeing well with results reported for poly-*o*-methoxyaniline [2, 8]). These transitions may be described analytically and consequently modeled, which is of importance for control of electrooptic devices [2]. At the same time, the optical response depends strongly on the potential variation rate, thus indicating the significant influence of charge transfer processes at the
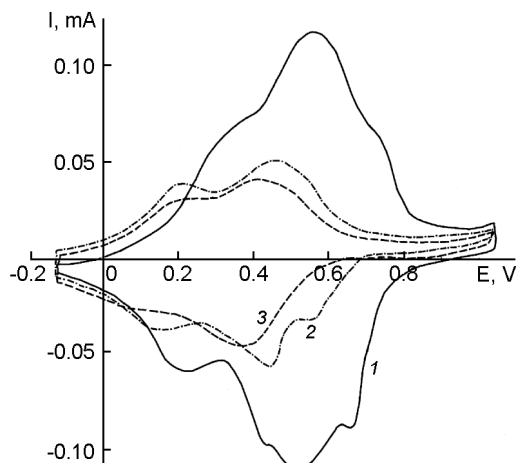
Fig. 3. CVA diagrams of POTI film in aqueous acid solutions: 0.5 M sulfuric (*1*), 1 M toluene sulfonic (*2*), 1 hydrochloric (*3*). Scan rate 40 mV/s. Film obtained at *N* = 15.

Fig. 4.(a) Dependence of peak current on potential sweep rate (*v*) for POTI film (*N* = 15) in 0.5 M H_2SO_4 (*1*), 1 M TSA (*2*), and 1 M HCl (*3*) and (b) for POTI film (*N* = 30) on *v* and $v^{1/2}$ in 0.5 M H_2SO_4. Solid line corresponds to anode peak, dotted one, to cathode peak.

polymer-electrolyte interface, complicated by relaxation processes in macromolecular structure of the polymer chain.

The electrochemical behavior of POTI films of different thickness was studied in solutions of protonic acids. The CVA curves of POTI are characterized by two reversible redox maximum (Fig. 3). The peak position and peak current depend on the kind of the background electrolyte anion. When toluene sulfonic acid (TSA) is used as electrolyte, the CVA curves contain two separated redox peaks, while in sulfuric and hydrochloric acids, broad overlapped maxims are observed. The first anode peak (*E* = 0.18 to 0.25 V) corresponds to oxidation of the completely reduced, insulating leuco-emeraldine form of poly-*o*-toluidine into conducting emeraldine (semi-quinone cation-radical) one. The second peak (*E* = 0.45 to 0.60 V) is caused by rapid oxidation of POTI ($\Delta E <$ 30 mV) into completely oxidized pernigraniline form [1]. The highest electrochemical activity of POTI films (estimated from peak current of CVA curves) is observed in sulfuric acid solutions. The different intensity of peak currents observed for the same films in different acid solutions also may be associated with diffusion phenomena at the polymer-electrolyte interface [6, 8, 9].

Because the electrochromic transitions are caused by reduction-oxidation of functional groups with electron transfer, their rate will be controlled by the rate of charge transfer in polymer layer immobilized on the electrode surface. Formally, this rate may be characterized by heterogeneous constant of ch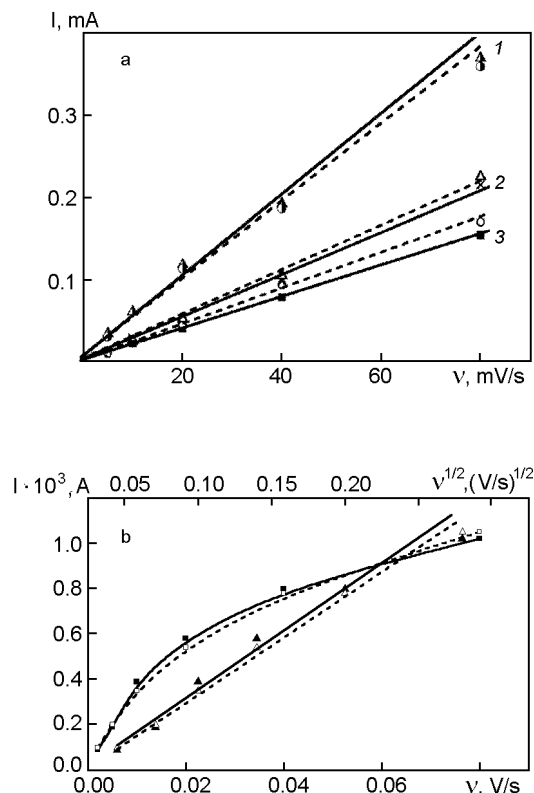arge transfer, k_s, or by effective diffusion coefficient, D_{ef}, for charge transfer across the film [10]. The existence of diffusion or kinetic control of the charge transfer process may be established by the study of CVA peak current dependence on potential sweep rate [11].

The electrochemical behavior study of POTI films in aqueous acidic electrolytes has shown that character of peak current dependence on the potential sweep rate is affected by thickness of polymer layer. The POTI films obtained on SnO_2 surface at sweep cycles number less than *N* = 20 exhibit the high reversibility of redox-processes. That is evidenced by the distribution potential $\Delta E = E_a - E_c$ in the range of 40 to 60 mV for the first redox maximum and 5 to 45 mV for the second one, and the ratio between currents of anode and cathode peak I_a/I_c near or equal to unity (Table 1). The peak current dependence on sweep rate is linear in all studied electrolytes (Fig. 4a).

Judging from CVA data, the first redox maximum at *E* = 0.18 to 0.25 V corre-

Table 1. Electrochemical parameters of CVA for POTI film ($N = 15$) in 1 M solution of TSA at $T = 293$ К

Scan rate, v, mV/s	First redox maximum			Second redox maximum		
	E_{rev}, V	ΔE, mV	I_a/I_c	E_{rev}, V	ΔE, mV	I_a/I_c
10	0.180	40	1.20	0.460	0.05	1.12
20	0.185	40	1.00	0.460	0.05	0.96
40	0.200	40	1.00	0.457	0.05	0.95
80	0.250	60	1.05	0.457	0.45	0.96

sponds to the more slow redox process in POTI films (transition of insulated form into conducting one and vice versa [1−4]) in comparison with next reversible redox maximum at $E = 0.4$ to 0.6 V. The value of reversible redox potential $E_{rev.} = (E_a + E_c)/2$ depends on the sweep rate (Table 1). This is typical of quasi-reversible electrochemical systems [11], which both kinetics and diffusion control is inherent to. The second redox maximum observed in CVA of thin POTI films exhibits the redox behavior, attributed to oxidation-reduction of redox particles strongly adsorbed or immobilized at the electrode surface [12]. It is known that linear dependence of anode and cathode peak currents on the sweep rate and small ΔE value is observed for thin layers of conjugated polymers, when the surface concentration of electroactive substance (Γ_i) does not exceed 10^{-8} mol/cm^2 [10]. As the film thickness increases, the symmetry of CVA is disturbed and diffusion limitation becomes more noticeable. This is expressed in deviation of the peak current dependence on sweep rate from linearity at increasing polymer layer thickness. In the case of studied POTI films, this deviation from linearity starts for polymer layer prepared at $N > 20$ at the sweep rate near to 50 mV/s.

In the case of relatively thick layers obtained during 30 and more sweeping cycles ($l = 0.3−0.5$ μm), the charge transfer is defined by diffusion, and linear dependence of peak current and square root of sweep rate, $i_p − v^{1/2}$, is observed (Fig. 4,b). This fact makes it possible to calculate the effective diffusion coefficient D_{ef} in films of poly-*o*-toluide using model of semi-infinite diffusion [10, 13] by means of equations (1) and (2):

$$i_p = 2.69 \cdot 10^5 n^{3/2} S D_{ef}^{1/2} v^{1/2} C^*, \qquad (1)$$

$$C^* = Q/nFSl, \qquad (2)$$

where n is a number of electrons involved in the redox process; S, the area of the film

(cm^2); C^*, concentration of active centers in the film (mol/cm^3); Q, total charge as calculated by integrating the anode or cathode cyclic voltammetric currents at slow sweep rate; d, the film thickness; F, Faraday constant.

By integration of CVA curve obtained at $v = 2$ mV/s (when all redox centers of the polymer layer have time to be oxidized or reduced), it is shown that in 0.5 M H$_2$SO$_4$ solution the charge quantities answering to anode and cathode process are almost equal to one another: $Q_a = 1.95 \cdot 10^{-4}$ C, $Q_c = 2.0 \cdot 10^{-4}$ C. The slope of lines obtained in $i_p − v^{1/2}$ coordinates (Fig. 4b) for anode and cathode peaks differ only slightly. This evidences a high reversibility of redox processes in POTI films and permits to suggest $D_a \approx D_c \approx D_{ef}$. The calculated charge transfer parameters in POTI film are presented in Table 2. Knowing D_{ef} and film thickness, the diffusion time (τ_D) which is the important characteristic of display materials [5] can be calculated according to equation (3).

$$\tau_D = l^2/4D_{ef}. \qquad (3)$$

The transition time, τ_D, values in POTI films are presented in the Table 2 in comparison with those obtained recently for polyaniline film [9].

The results obtained demonstrate that the presence of a donor substitute at the benzene ring of poly-*o*-toluidine causes a decreased electron transfer rate as compared to polyaniline, but to a lesser extent than for other polyaniline derivatives [1, 9]. In the case of POTI, this is reflected in somewhat lower values of effective diffusion coefficient (Table 2) as compared to unsubstituted polyaniline. The found τ_D values within the range 0.5−0.6 s in combination with a wide range of color transition and possibility of their control using low switching potentials permit to recommend this polymer to obtain electrochromic layers of satisfactory fast action in optical devices [5].

Table 2. Charge transfer parameters in polymer films in O.5 M sulfuric acid

Polymer films	Film area, S, cm^2	Film thickness, $l \cdot 10^4$, cm	Concentration of active centers $C^* \cdot 10^4$, mol/cm^3	Diffusion coefficient, $D_{ef} \cdot 10^9$, cm^2/s	Transition time, τ_D, s
Poly-*o*-toluidine	2.1	0.35	2.28±0.04	2.62±0.05	0.5−0.6
Polyaniline	4.0	0.28	7.34±0.03	9.02±0.05	0.02

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Транспорт заряду в електрохромних плівках полі-*орто*-толуїдину

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Вивчено оптичні та електрохімічні властивості плівок полі-*орто*-толуїдину на поверхні SnO$_2$ електродів у кислотних електролітах. Знайдено, що реакції окислення-відновлення у плівках супроводжуються оборотними змінами кольору від повністю прозорого до жовтого, синього, зеленого і фіолетового в області потенціалів $E = -0,3....1,2$ В (Ag/AgCl). Розраховано значення ефективного коефіцієнта дифузії D_{ef} та характеристичного часу τ_D для процесу переносу заряду через плівку.