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Spectroelectrochemical behaviour of poly (3-octylthiophene): application to electrochromic windows with polyaniline and iridium oxide

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The spectroelectrochemical behaviour of cast poly(3-octylthiophene) (POT) films (0.2 and 0.5 μm) on indium-tin-oxide (ITO) glass electrodes has been investigated in organic media. These thin films exhibit interesting electrochromic properties and their application in electrochromic devices has been examined in liquid ($CH_3CN + LiClO_4$ 0.3 M) and viscous electrolyte ($PEO + CH_3CH + LiClO_4$). Polyaniline (PANI) film appears to be a convenient complementary counter electrode since its transmission maximum corresponds to its oxidized state and that of POT film to its reduced state. Thin films of iridium oxide (IrO_2) are also possible counter electrodes, even in acetonitrile, the electrochemical behaviour being mostly capacitive with a low transmission change. However, the best contrast is obtained with the POT/PANI system.

1. Introduction

Conducting polymers, such as poly(3-alkylthiophenes), are promising industrial materials because of the recent progress in their processing [1]. Applications of poly(3-alkylthiophenes) are found in lithium secondary batteries [2] and especially in electrochromic cells [3–6]. It has been demonstrated for instance that poly(3-methylthiophene) has interesting electrochromic properties [5] with a response time of few milliseconds and a cyclability of more than 10^5 cycles. The aim of this paper is to report an investigation of the utilization of poly(3-octylthiophene) (noted POT) as an active electrochromic window. This polymer was chosen, since its solubility in organic solvents [7] allows the production of thin films on conductive electrodes by a chemical procedure. Moreover, it is known that increasing the length of the alkyl chain of 3-substituted thiophenes to 7–9 carbons produces an increase in the electrochemical reversibility of the undoped-doped process [8].

Though a polymer may display good electrochromic properties such as colour, response time and stability [3–6], it must be compatible with both electrolyte and counter electrode. The role of the counter electrode is to provide charge-balance during the electrochemical process. The question of the electrolyte choice is also important and, for a final product, solid electrolytes or at least gel electrolyte are required [9]. Since POT films give a dark-red colour in the reduced state and light-blue in the oxidized state, two types of counter electrode can be envisaged: (i) the material must be transparent and colourless in the reduced and oxidized state. The variations in the optical transmission must only be due to the electrochromic POT electrode; (ii) the material must participate in the electrochromic phenomena. The material must be almost colourless in the reduced state when the POT electrode is in the oxidized form and must be highly coloured in the oxidized state when the POT electrode is neutral (in reduced form). In such a case two electrodes can participate in the transmission variation in order to enhance the contrast.

From the organic polymers and inorganic metallic oxides which are compatible with POT we chose polyaniline (PANI) [10, 11] and iridium oxide (IrO_2) [9]. In aqueous medium the polyaniline is slightly yellow in the reduced state and turns into green or dark blue after oxidization. IrO_2 is almost transparent in the reduced state and blue in the oxidized state. These two compounds have been extensively studied in aqueous media [10, 11] and the electrochemical mechanism, which includes a proton insertion, is reversible. Since POT films are not stable enough in aqueous media, our electrochromic studies were carried out in organic medium: $CH_3CN + LiClO_4$ 0.3 M and polyethylene oxide (PEO) slightly swollen with acetonitrile.

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2. Experimental details

2.1. *Electrochemical and spectrochemical measurements*

Acetonitrile (BDH, HPL grade) and lithium perchlorate (Fluka) were used as received. The viscous electrolyte was prepared by dissolving 1 g of polyethylene oxide (PEO 20000) in 2 ml of CH_3CN containing $LiClO_4$ 0.3 M.

Spectroelectrochemical measurements were made in a conventional three electrode sandwich cell ($v = 1\,cm^3$) [12]. When studying the behaviour of electrochromic materials (POT, PANI and IrO_2), the working electrode was an ITO glass ($s = 1\,cm^2$) covered with the material under study. The counter electrode was a platinum wire.

The POT/PANI and POT/IrO_2 couples were studied in $CH_3CN + LiClO_4$ 0.3 M or in PEO + $CH_3CN + LiClO_4$ 0.3 M. In these electrochromic cells the distance between the two ITO-electrodes was respectively 0.9 and 0.2 cm.

The reference electrode against which all potentials in this paper are reported was an $Ag/10^{-2}\,M\,Ag^+$ in $CH_3CN + LiClO_4$ 0.3 M or PEO + CH_3CN + $LiClO_4$ 0.3 M.

Spectrophotometric measurements were made *in situ* during voltammetry and chronocoulometry experiments.

All electronic spectra were recorded with an OMA III spectrophotometer equipped with a 1421 detector and a 1463 controller (EGG Instruments). Results are presented in transmission mode, from 0 to 1 corresponding to 0 to 100%. Electrochemical experiments were carried out using a Princeton Applied Research Model 273 potentiostat-galvanostat equipped with a Schlumberger 8300 table recorder.

2.2. *Films*

Poly(3-octylthiophene) POT, was polymerized according to the method developed by Sugimito *et al.* [13]. The monomer was added to a slurry of $FeCl_3$ in chloroform under inert atmosphere. The reaction was left to run for 1–4 h after which the slurry was poured into boiling methanol, which does not dissolve the polymer. The precipitated polymer was then filtered and dissolved again in chloroform. This solution was washed with NH_3, HCl, MeOH and water repeatedly to reduce the residue of iron. The POT films were made by casting from chloroform solution on an optically transparent indium-tin-oxide (ITO) electrode. The resistivity of the ITO electrode was $30\,\Omega^{-1}\,cm^{-2}$. The thickness of the POT films was 0.5 or 0.2 μm and the electronic conductivity in the doped state was about $37\,\Omega^{-1}\,cm^{-2}$. This method led to reproductible films. The charge of doping calculated for ten samples by cycling films between −0.2 and 0.8 V in $CH_3CN + LiClO_4$ 0.3 M at a scan rate of $20\,mV\,s^{-1}$ was $5 \pm 0.5\,mC\,cm^{-2}$ or $1.5 \pm 0.2\,mC\,cm^{-2}$ for 0.5 and 0.2 μm films, respectively.

Polyaniline (PANI) films were synthesized on the ITO electrode in aqueous solution of 0.1 M aniline in 0.3 M perchloric acid by potential scanning between −0.5 and 0.5 V at a scan rate of $50\,mV\,s^{-1}$. 250 scans were needed to obtain a PANI film with a doping charge of approximately $5\,mC\,cm^{-2}$ for the first redox system. This charge was enough to compensate that of POT films (0.5 μm) in a complete electrochromic cell. Regular growth of an electroactive film of PANI was observed. The film adhered strongly to the ITO electrode surface. Polymerizations in perchloric acid solutions gave similar cyclic voltammograms to those obtained with platinum electrodes in NH_4F, 2.35 HF medium [10]. After the synthesis the PANI film was stepped to its oxidized state, washed with water, dried and transferred into $CH_3CN + LiClO_4$ 0.4 M.

IrO_2 films (0.4 μm) were deposited on SnO_2–In_2O_3 conductive glass (Saint-Gobain SA).

3. Results and discussion

3.1. *Electrochemical and spectroelectrochemical studies of POT films*

The cyclic voltammogram of a POT film (0.5 μm) in $CH_3CN + LiClO_4$ 0.3 M is shown in Fig. 1. This curve is similar to those reported for other poly(alkylthiophenes) [7] and displays the classical reversible system at $E = o.61$ V. It should be noted that the cathodic branch of the voltammogram, which involves the undoping process, is more complex than the anodic one and exhibits two successive steps corresponding to the doping–undoping process of the polymer [8]. Transmission spectra in the 410, 680 nm wavelength region as a function of the potential are shown in Fig. 2. As the potential was varied, the colour of the POT film reversibly changed from dark red in the reduced state to light blue in the oxidized state (0.8 V). The

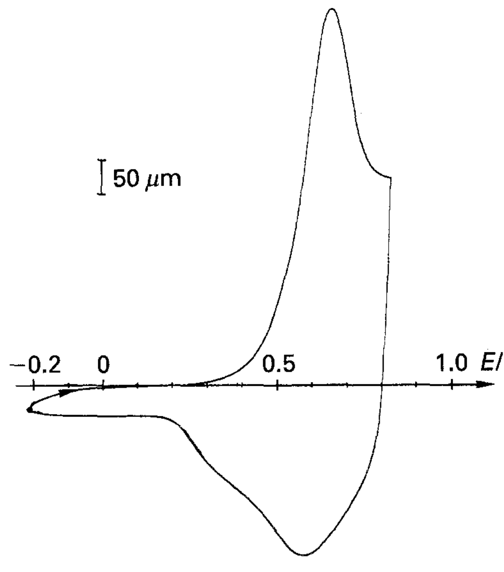

Fig. 1. Cyclic voltammogram of a POT film (0.5 μm) on an ITO electrode in $CH_3CN + LiClO_4$ 0.3 M; sweep rate $\nu = mV\,s^{-1}$.

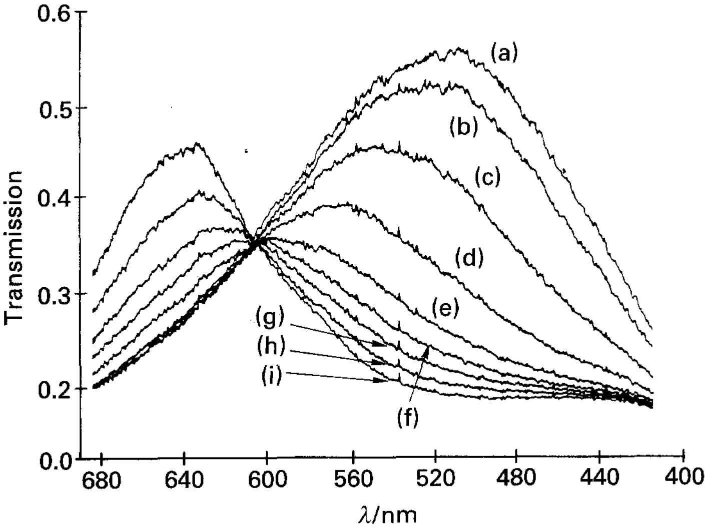

Fig. 2. Transmission spectra of a POT film (0.5 μm) in $CH_3CN + LiClO_4$ 0.3 M, during a potential scanning from 0.8 to −0.2 V: (a) 0.8, (b) 0.675, (c) 0.55, (d) 0.425, (e) 0.3, (f) 1.175, (g) 0.05, (h) −0.075 and (i) −0.2 V; sweep rate $\nu = 20\,mV\,s^{-1}$.

maximum change in transmission spectra is located at 510 nm. For a 0.5 μm film, transmission varies from 0.19 in the reduced state to 0.56 in the oxidized state when cycling between −0.2 and 0.8 V. (Transmission spectra were recorded in a few milliseconds during cycling without holding films at a constant potential.)

To evaluate the range of potential giving the best electrochromic response and film stability, POT electrodes were cycled at potential regions higher than 1 V and lower than −0.5 V. If the potential is cycled between −0.3 and 1.5 V, an irreversible peak appears at 1.2 V due to the overoxidation and degradation of the film and gradually the reversible system at 0.61 V becomes irreversible. After 8 successive cycles the redox charge of the film is reduced to one third of its initial value and the electrochromic response disappears, turning the film more transparent. The scanning at lower potentials, for example to −2 V, induces an anodic shift of the oxidation peak as well as a cathodic shift to the reduction peak. This phenomenon, previously observed with poly-(3-alkylthiophenes), is probably due to some irreversible reaction following the electron transfer during the n-doping of POT [14]. It appears that stable cycling of POT is possible only in the potential range of 0, 0.8 V.

POT films were also studied by continuous double potential step experiments which simulate the use of the electrochromic windows in applications and give access to the response time of films. Best results were obtained when films were cycled between 0 and 0.7 V. Figures 3 and 4 show the chronocoulometric curves and the corresponding transmission curves during a double potential step of 60 s for two POT films of different thickness (0.2 and 0.5 μm). After 1500 cycles the charge and transmission values had decreased by 25% compared to the initial values. However, it should be noted that the decrease in the charge between the cycles 1000 and 1500 is less significant than that between the first and 1000 cycle. This is probably due to the stabilization for the film after a few cycles. As a consequence good stability after 1500 cycles is expected. So, the response time of the film decreases as the thickness of the film decreases. For a 0.2 μm POT film, only 3 s are needed to reach the complete electrochromic response, while a time of 8 s is necessary for a film of 0.5 μm. After 1500 cycles the response time increases to 4 and 25 s for the films of 0.2 and 0.5 μm, respectively. It appears that the switching time of POT films is short enough for electrochromic window applications [9]. However, it should be noted that this material cannot be used in

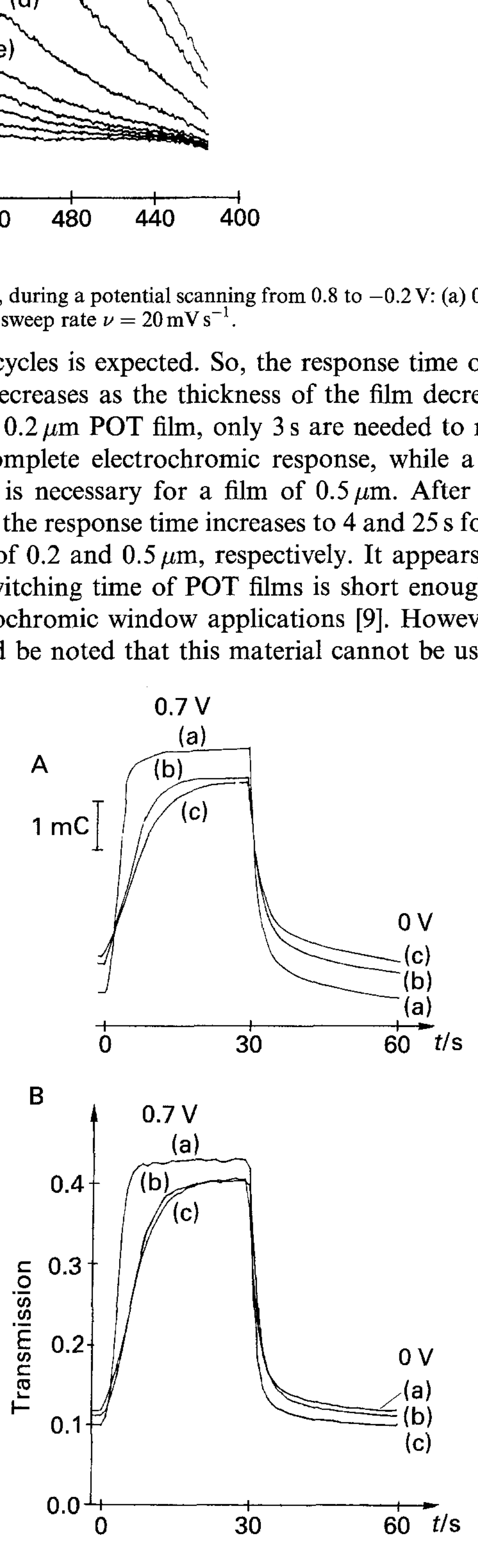

Fig. 3. Chronocoulometric (A) and corresponding transmission (B) curves at 510 nm of a POT film (0.5 μm) in $CH_3CN + LiClO_4$ 0.3 M, during continuous double potential step measurements between 0 and 0.7 V (step time 60 s): (a) 1st step measurement, (b) 1000th step and (c) 1500th step.

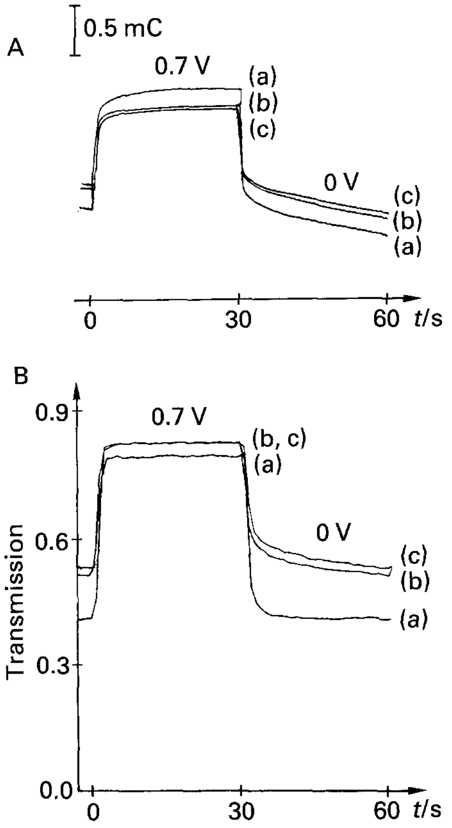

Fig. 4. Chronocoulometric (A) and corresponding transmission (B) curves at 510 nm of a POT film (0.2 μm) in CH_3CN + $LiClO_4$ 0.3 M, during continuous double potential step measurements between 0 and 0.7 V (step time 60 s): (a) 1st step, (b) 1000th step and (c) 1500th step.

displays in which very low response times (some milliseconds, e.g. electronic application [9]) are necessary.

For applications in a complete electrochromic cell device, we have also tested POT films of thickness of 1 μm. These films were too thick because the light beam of the spectrophotometer was completely extinguished. We assume that films of 0.5 μm are too thin. The ideal thickness of POT films for electrochromic windows is probably close to 0.75 μm.

3.2. *POT/CH_3CN + $LiClO_4$ 0.3 M/PANI cell*

Figure 5 shows the cyclic voltammogram of a PANI film in CH_3CN + $LiClO_4$ 0.3 M. To prevent the degradation of the film, the potential range was limited to −0.3, 0.5 V, corresponding to the first reversible redox couple of PANI [10]. It is well known that the degradation occurs after the second redox couple at potentials higher than 0.8 V [15]. When limiting the potential range to −0.3, 0.5 V, a stable behaviour after 800 cycles was noticed. It should be noted that the good reversibility of the first redox couple of the film is excellent since PANI was synthesized in acid solution. It has been shown that PANI retains its electroactive properties in unbuffered acetonitrile [10]. When PANI film was cycled in the potential range of its first redox couple, the colour of the film changed reversibly from pale transparent yellow (−0.3 V) to light green (0.5 V). The corresponding transmission variation at 510 nm was in the range 0.78 to 0.73, which is compatible with the large variation of transmission POT film at this wavelength.

To evaluate the performance of the electrochromic window, POT and PANI films were both placed in the same cell containing CH_3CN + $LiClO_4$ 0.3 M. One of the first examples of a complementary electrochromic system where both electrode materials are electrochromic polymers was recently given by Leventis *et al.* [16]. The present system was studied with continuous double potential steps between 0 and 0.7 V, the POT acting as the working electrode and PANI as the counter electrode (Fig. 6). Application of 0 V voltage means that PANI is oxidized while POT is reduced, which turns the window dark red. By cycling between 0 to 0.7 V the colour turns to light blue. The colour change almost corresponds to the colour change of the POT film alone since the PANI film exhibits only a slight absorption intensity, especially if the PANI film is cycled only in the potential region of its first redox system. Figure 6 shows the charge and transmission steps at 510 nm during change of the voltage from 0 to 0.7 V. A small increase of the contrast is observed for the combined cell ($\Delta T = 0.33$) compared with a cell containing only POT ($\Delta T = 0.32$). At 0 V, the light green colour of the oxidized form of PANI increases the red coloration of the POT and the quasi transparency of PANI in its reduced state does not influence the blue coloration of POT in its oxidized form. On the other hand, Fig. 6 shows that the response time of the combined cell is the same as that of the cell containing only POT.

3.3. *POT/POE + CH_3CN + $LiClO_4$ 0.3 M/PANI cell*

The two electrochromic electrodes were placed in a cell with a relative thin layer (0.2 cm) of a mixture of POE + CH_3CN + $LiClO_4$ 0.3 M. Evolution of the oxidation charge during a double potential step and corresponding transmission curves are shown in Fig.7. The use of a higher oxidation potential and a

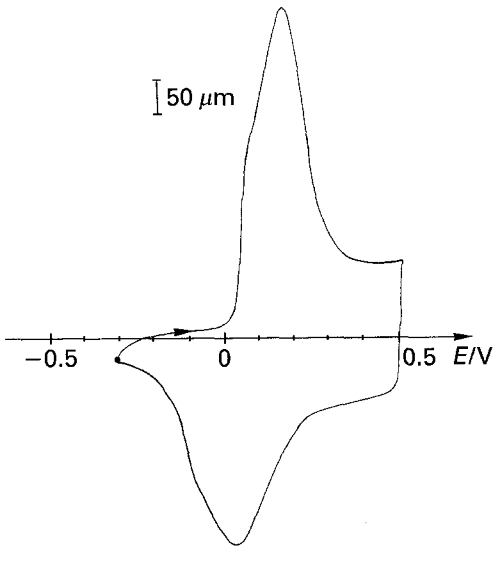

Fig. 5. Cyclic voltammogram of a PANI film (5 mC cm^{-2}) in CH_3CN + $LiClO_4$ 0.3 M; sweep rate $\nu = 20\,mV\,s^{-1}$.

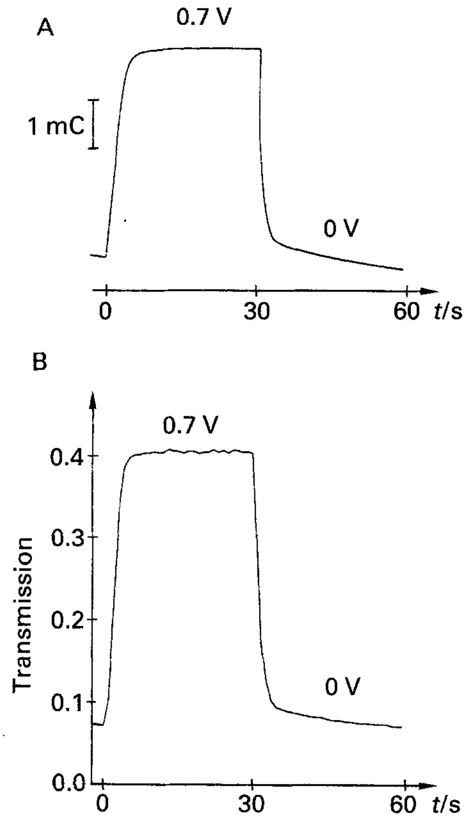

Fig. 6. Chronocoulometric (A) and corresponding transmission (B) curves at 510 nm of POT/CH_3CN + $LiClO_4$ 0.3 M/PANI cell during continuous double potential step measurements between 0 to 0.7 V (step time 60 s).

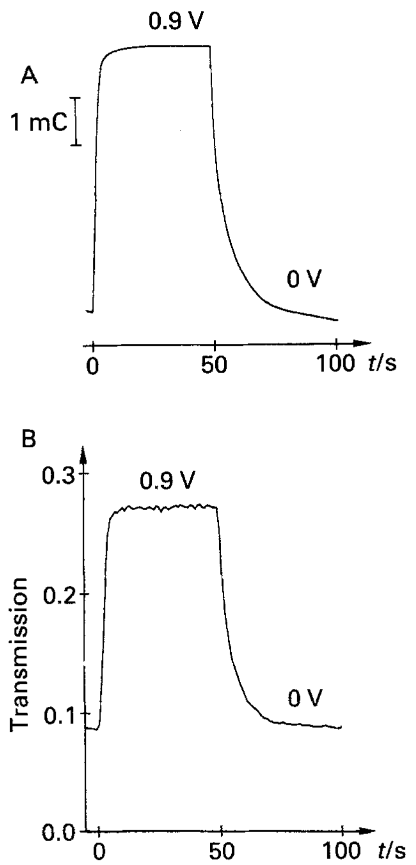

Fig. 7. Chronocoulometric (A) and corresponding transmission (B) curves at 510 nm of POT/POE + CH_3CN + $LiClO_4$ 0.3 M/PANI cell during continuous double potential step measurements between 0 to 0.9 V (step time 100 s).

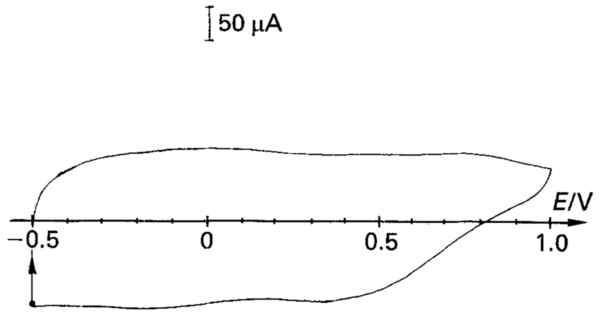

Fig. 8. Cyclic voltammogram of IrO_2 coating on ITO electrode in CH_3CN + $LiClO_4$ 0.3 M; sweep rate $\nu = 20\,mV\,s^{-1}$.

longer step time than in liquid electrolyte is due to the lower conductivity of the viscous electrolyte. A smaller transmission change at 510 nm was noticed compared to that obtained in liquid electrolyte, although the variation in the amount of charge is identical in both electrolytes. This is probably due to the fact that POE + CH_3CN + $LiClO_4$ 0.3 M electrolyte is not fully transparent at room temperature because it contains some crystallites [9].

3.4. *POT/CH_3CN + $LiClO_4$ 0.3 M/IrO_2 cell*

Figure 8 shows the cyclic voltammogram of an IrO_2 coating on ITO in CH_3CN + $LiClO_4$ 0.3 M. The shape of this voltammogram suggests a capacitive effect similar to that observed in other aprotic solvents [17]. The capacitive effect of IrO_2 coating in organic media

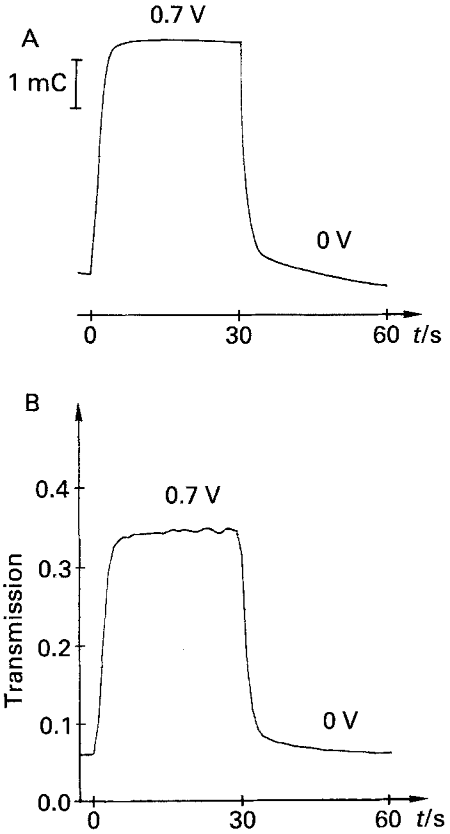

Fig. 9. Chronocoulometric (A) and corresponding transmission (B) curves at 510 nm of POT/CH_3CN + $LiClO_4$ 0.3 M/IrO_2 cell during continuous double potential step measurements with between 0 to 0.7 V (step time 60 s).

is probably due to the slow insertion and extraction of Li^+ ions [18]. When cycling between −0.5 and 1.1 V only a slight variation of transmission in the 410–680 nm wavelength region was observed: IrO_2 film changed from light blue (−0.5 V) to slightly more deep blue (1.1 V). The change in transmission at 510 nm in the range of (0.64, 0.54) indicates that the IrO_2 coating remains coloured in the reduced state. The stability of IrO_2 coating was evaluated by a double potential step from −0.6 to 1 V with a step time of 100 s. More than 800 steps were performed without any degradation of the coating. It should be noted that coloration and bleaching times (about 10 s) are close to these of POT films.

POT and IrO_2 covered ITO-electrodes were placed in a cell containing $CH_3CN + LiClO_4$ 0.3 M. New electrochromic devices based on the association of an organic polymer and an inorganic oxide, involve poly(N-benzylaniline) [19] or polyaniline as conductive polymer and WO_3 [20]. Figure 9 shows the evolution of the charge of the $POT/CH_3CN + LiClO_4$ 0.3 M/IrO_2 system during a double potential step between 0 and 0.7 V and the corresponding transmission curves at 510 nm. The injected charge passed through the electrodes was 4.9 mC cm^{-2} and the corresponding transmission variation was in the range 0.345 to 0.057. It appears that a lower contrast is obtained with the POT/IrO_2 couple compared to the POT/PANI couple, which is due to the remaining coloration of the IrO_2 window in its reduced state in organic solvents. However, the use of IrO_2 instead of PANI does not affect the response time of the electrochromic device. As previously pointed out for the POT/PANI cell, the use of a viscous organic electrolyte ($POE + CH_3CN + LiClO_4$ 0.3 M) decreases the contrast of the cell.

4. Conclusion

The study of two complementary electrochromic systems consisting of POT/PANI or POT/IrO_2 couples shows that a better contrast ($\Delta T = 0.33$) is obtained with the former couple. However, this contrast remains low because conducting polymers do not absorb stongly in their coloured states. An improvement of such devices may be obtained by incorporating other electrochromic material into the polymer films or by using functionalized polymers bearing chomohore groups.

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