SOLID STATE ELECTROCHROMIC DISPLAY BASED ON POLYMER ELECTRODE–POLYMER ELECTROLYTE INTERFACE

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Abstract—The electropolymerization of ortho-toluidine and ortho-anisidine gave uniform electroactive polymer films which were analysed by cyclic voltammetry, impedance and uv–vis absorption spectra. These films exhibit a reversible electrochemical response during cyclic voltammetry experiments in aqueous, non-aqueous and polymer electrolytes. Their electrochromic efficiency is high in aqueous and non-aqueous electrolytes but decreases in the polymer electrolyte. A solid state cell having the configuration ITO/TiO$_2$–CeO$_2$/LiN(SO$_2$CF$_3$)$_2$–PEO complex/polymer/ITO, has been assembled. The transmittance variation of this system between the oxidized and reduced state is about 20% at 632.8 nm.

Key words: electrochromism, polymer electrolyte, conducting polymer, electrochromic window.

INTRODUCTION

Electropolymerized polyaniline films have received considerable attention in the last few years due to their good electrical conductivity and wide application in interesting devices such as batteries, sensors and electrochromic devices[1–5]. The electrochemical synthesis of polyanisidine is described in the literature[6] and leads to a soluble conducting polymer. The electrochromic properties of poly(o-toluidine) have already been investigated in aqueous solution and during the polarization from −0.2 to 0.6 V vs. *sce* the colour of the film changed from yellow to violet[7].

This work reports on the electrochemical and electrochromic behaviour of polytoluidine and polyanisidine films in aqueous, non-aqueous and polymer electrolytes.

EXPERIMENTAL

All electrochemical measurements were performed using an EG & G Parc 273 potentiostat/galvanostat. Impedance were measured over a 100 kHz–0.01 Hz frequency range using a 5 mV *ac* excitation and a lock-in analyser EG & G model 5208 assisted by a computer. Electrochemical potentials in aqueous solutions were recorded vs. a hydrogen electrode in same solution (*hess*) and for non-aqueous solutions an Ag/20 mM AgClO$_4$/0.1 M LiClO$_4$ + acetonitrile was used as reference electrode.

Ortho-toluidine (2-methylaniline, Aldrich 99%) and ortho-anisidine (2-methoxyaniline, Aldrich 99%) were distilled under reduced pressure prior to use. All other chemicals were of analytical grade.

Poly(o-toluidine) and poly(o-anisidine) films were grown potentiodynamically on an indium–tin oxide (ITO) coated glass plate (Baltracon Z20, 200 Ω/□-Balzers) immersed in an aqueous solution containing 0.6 M H$_2$SO$_4$ and 0.1 M of monomer by cycling the potential between 0.0 and 1.0 V vs. *hess* at a sweep rate of 0.1 V s^{-1}. Poly(o-toluidine) and poly(o-anisidine) films were obtained after 23 and 15 cycles, respectively and the polymerization was stopped at 0.0 V. The total anodic charge for poly(o-toluidine) film was 60 mC cm^{-2} and their thickness, determined with a talystep (Rank Taylor–Robson Limited), was 1.3 μm. For poly(o-anisidine) film the total charge was 100 mC cm^{-2} and their thickness was 1.8 μm.

After formation, the polymeric films were washed with distilled water and placed in the monomer free solutions. The films were then cycled at least 20 times prior to experiments in order to establish equilibrium with the electrolyte.

The electrolyte was either a 0.1 M H$_2$SO$_4$ aqueous solution or a 0.1 M LiClO$_4$ non-aqueous acetonitrile (AN) solution or a PEO–LiN(SO$_2$CF$_3$)$_2$ complex with the ratio O/Li = 10. The preparation of this polymer electrolyte has been described in a previous paper[8]. The counter electrode used in the solid state cell was a transparent TiO$_2$–CeO$_2$ thin film (Ti/Ce = 1) deposited by the sol–gel dip-coating process[8] onto ITO coated glass.

The optical response of the solid state cell was measured by monitoring the transmission variation of a He–Ne laser light at $\lambda = 632.8$ nm.

RESULTS AND DISCUSSION

The potentiodynamic electropolymerization of o-toluidine gives uniform and insoluble films on ITO electrodes. Their cyclic voltammograms in aqueous

and non-aqueous solutions are shown in Fig. 1. In 0.1 M H_2SO_4, the polytoluidine film shows a cathodic peak at 0.55 V and an anodic peak near 0.75 V. In non-aqueous solutions, the polytoluidine film shows a cathodic peak at 0.58 V and a broad anodic wave, with a shoulder at about 0.69 V and a peak at 0.82 V. After the initial cycling the voltammograms for poly(o-toluidine) film in aqueous solutions exhibits only one redox process while in non-aqueous solution a broad peak is observed in the anodic region. This response indicates that this film degrades after repetitive cycling and a slight stability can be obtained cycling this film in non-aqueous media. Similar behaviour was reported for polyaniline films[9–11].

The blue polymerization product obtained from o-anisidine deposited on ITO electrode is easily solubilized and results in an uniform film. The electrochemical response of these films are shown in Figs 2 and 3. In 0.1 M H_2SO_4 (Fig. 2), two anodic peaks are observed at 0.50 V (I) and 0.68 V (II). The cathodic region of polyanisidine film shows a peak at 0.59 V (III) and a broad cathodic wave between 0.30 V and 0.37 V (IV).

In non-aqueous solvent (Fig. 3), the poly(o-anisidine) film shows an anodic peak at 0.34 V (I) and a large anodic wave between 0.40 V (II) and 0.55 V (III). In the cathodic region only two well-defined peaks are observed at 0.48 V (IV) and 0.30 V (V).

Poly(o-anisidine) film exhibit two well defined redox process either in aqueous or in non-aqueous solutions. The presence of the two redox process observed after several cycles is an indication of the stability of the polymeric film. The electrochemical response in acetonitrile indicates that the polymer is insoluble in this solution in either oxidation state. The first redox process was found independent of pH and according to the electrochemical reactions proposed for polyaniline[12, 13] this process might be related to oxidation of the amine nitrogen atoms to radical cations. The second redox process exhibits a dependence with pH as the peak potential shifts with increase of pH. From the mechanism reported for polyaniline, the oxidation of the radical cations to a
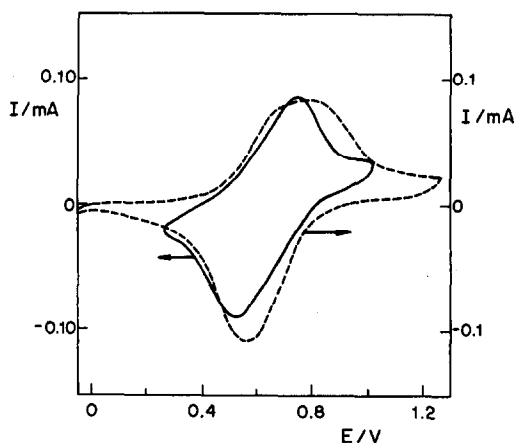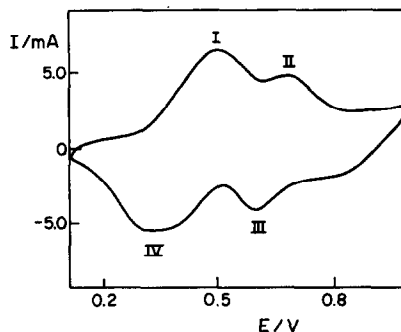

Fig. 2. Cyclic voltammetry of a glass/ITO/poly(o-anisidine) electrode in 0.1 M aqueous H_2SO_4; sweep rate 100 mV s^{-1}; electrode area = 5.6 cm^2.

fully oxidized polymeric form (pernigraniline) could involve the formation of an intermediate protonated form.

In correlation to the electrochemical processes shown in Figs 1–3, the poly(o-toluidine) and poly(o-anisidine) films exhibit multiple and reversible colour changes ranging from yellow to blue. The electronic adsorption spectra of both films are identical and are shown for poly(o-toluidine) in the reduced and oxidized states in Fig. 4. The maximum of adsorption near 560 nm that appears in the completely oxidized form (Fig. 4a) can be related to the formation of a complete quinoid form in this pH.

The conductivity of PEO-based polymer electrolyte complexed with LiN(SO$_2$CF$_3$)$_2$ is appreciable at room temperature[14] and, due to the elastomeric properties, a good electrolyte/electrode contact can be provided. The cyclic voltammogram shown in Fig. 5 was obtained by a sandwich composed of the following elements:

glass/ITO/polymer electrode/

PEO–LiN(SO$_2$CF$_3$)$_2$/TiO$_2$–CeO$_2$/ITO/glass.

Fig. 1. Cyclic voltammetry of a glass/ITO/poly(o-toluidine) electrode in (——) 0·1 M aqueous H_2SO_4; (– – –) 0.1 M LiClO$_4$ in AN; sweep rate 50 mV s^{-1}; electrode area = 3.2 cm^2.
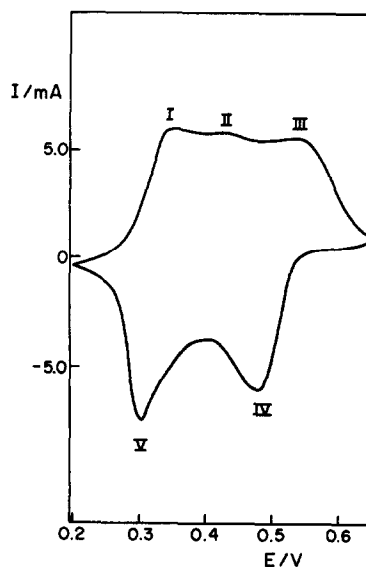

Fig. 3. Cyclic voltammetry of a glass/ITO/poly(o-anisidine) electrode in 0.1 M LiClO$_4$ in AN; sweep rate 50 mV s^{-1}; electrode area = 5.6 cm^2.
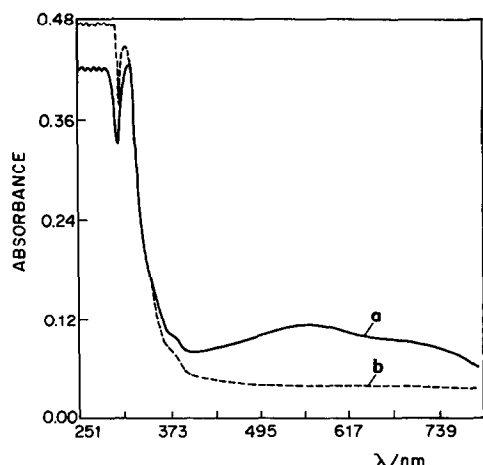
Fig. 4. Absorption spectra of poly(o-toluidine) (a) at 1.0 V; (b) at 0.27 V in 0.1 M aqueous H_2SO_4.

For a poly(o-anisidine) electrode the charge passed during the anodic cycle is similar to that released during the following cathodic cycle; this indicates that the process has a faradaic efficiency $\theta = Q_c/Q_a$ which approaches 100%. The cyclic voltammogram of poly(o-toluidine) film also indicates a faradaic efficiency of about 100%.

Impedance data for the solid state cell are shown in Fig. 6. The intercept of the linear portion with the real axis obtained at the equilibrium potential of the reduced film may be associated with the charge
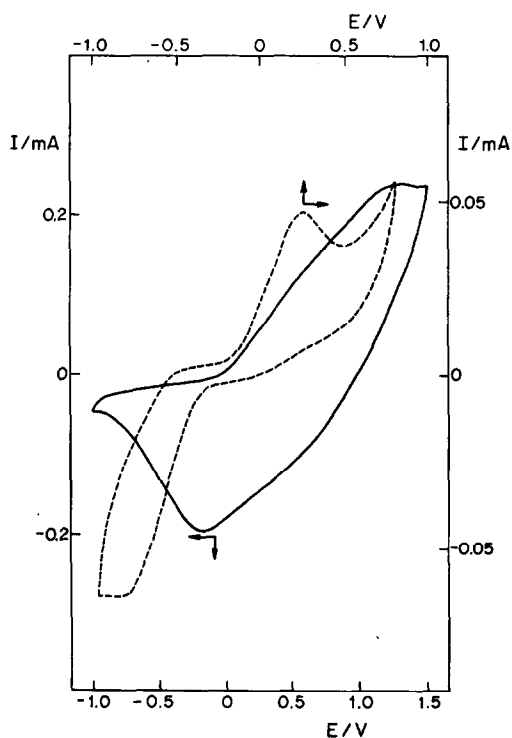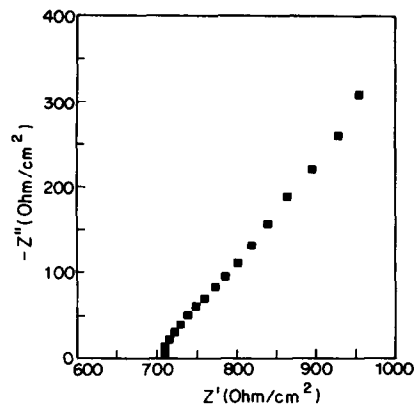

Fig. 6. Impedance plot of the poly(o-anisidine)/PEO–LiN $(SO_2CF_3)_2$ interface; frequencies from 100 kHz to 0.01 Hz.

transfer resistance and the low value of this resistance confirms the fast kinetics of the electrochemical process. The straight line observed at lower frequencies suggests that the rate of lithium injection is diffusion-controlled. The impedance at high frequency is associated with the resistance of the interface film/electrolyte and for the polymer electrolyte, in particular, this value is about 10 times higher than those obtained for the aqueous and non-aqueous solution.

Figure 7 shows the electrical and the optical transmission responses of a poly(o-anisidine) film during the application of a double potential step. The transmittance variation of ca 20% observed during the oxidation–reduction cycle indicates that the interaction between the poly(o-anisidine) and the polymer electrolyte changes the optical properties of the polymeric film. The loss in charge from the 25th cycle to the 2500th is smaller than 5%, demonstrating a good reversibility of the electrochemical reaction. Similar behaviour has been observed with the poly(o-toluidine) film.
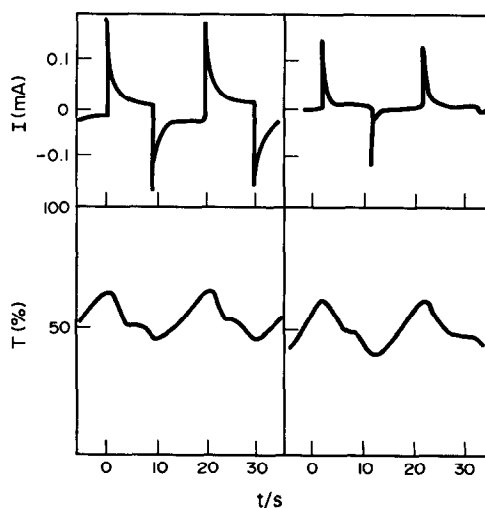

Fig. 5. Cyclic voltammetry of a cell composed of glass/ITO/ polymeric electrode/polymer electrolyte/CeO_2–TiO_2 electrode/ITO/glass; sweep rate 50 mV s^{-1}; (-----) poly(o-anisidine) with electrode area = 3 cm^2; (——) poly(o-toluidine) with electrode area = 4.6 cm^2.

Fig. 7. Electrical and optical transmission (at 632.8 nm) response vs. time of a glass/ITO/poly(o-anisidine)/polymer electrolyte/CeO_2–TiO_2 electrode/ITO/glass, submitted to a potential step from −0.8 to 1.5 V (vs. CeO_2–TiO_2); (a) 1st cycle; (b) 2500th cycle.

The optical response of the solid state cell shows a 20% change in transmittance at 632.8 nm. This response reveals a certain difference between the kinetics of the bleaching and colouring process, as well as a switching efficiency lower than 100%. This effect can be related to the contact between the electrode and electrolyte as can be inferred from analysis of the impedance data. Further studies are necessary to improve the contact between the polymeric electrode and polymer electrolyte.

The results reported in this work shows that the oxidation–reduction process that occurs in poly(*o*-toluidine) and poly(*o*-anisidine) films is reversible in the studied electrolytes and the poly(*o*-anisidine) film can be considered as a promising electrode for electrochromic devices.

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