Journal of Applied Electrochemistry **29**: 753–757, 1999.

A solid-state electrochromic device based on complementary polypyrrole/polythiophene derivatives and an elastomeric electrolyte

W.A. GAZOTTI, Jr[1], M.-A. DE PAOLI[1]*, G. CASALBORE-MICELI[2], A. GERI[2] and G. ZOTTI[3]
[1]*Instituto de Química, Universidade Estadual de Campinas, C.Postal 6154, 13083-970, Campinas/SP, Brazil;*
[2]*Istituto di Fotochimica e Radiazioni d'Alta Energia, Consiglio Nazionale delle Ricerche, Bologna, Italy;*
[3]*Istitituto di Polarografia e Elettrochimica Preparativa, Consiglio Nazionale delle Ricerche, Padova, Italy*
*(*author for correspondence, e-mail: mdepaoli@iqm.unicamp.br)*

Received 10 October 1998; accepted in revised form 11 November 1998

Key words: elastomeric electrolyte, electrochromic device, polypyrrole, polythiophene

Abstract

A device was assembled using optically transparent glass electrodes and combining two complementary electrochromic polymeric materials, poly(4,4′-dipentoxy-2,2′-bithiophene) and poly(N,N'-dimethyl-2,2′-bipyrrole). As electrolyte we used an ionically conductive polymer; poly(epichlorohydrin-*co*-ethylene oxide) containing a lithium salt. The optical contrast in the visible/near infrared region, stability to repeated redox cycles and electrochromic efficiency are reported and discussed.

1. Introduction

Electrochromism can be defined as a persistent but reversible optical change induced by electrochemical processes [1]. Materials that present this property are suitable for use in several technological applications, such as electrochromic devices, information displays and smart windows [1, 2]. The electrochromic properties of organic conducting polymers have been extensively studied in recent years [3, 4], and several devices based on these materials have been assembled [5–7]. Generally, the electrochromic process depends on the charge consumed in redox reactions (doping–undoping for conducting polymers) [8, 9].

An electrochromic device is an electrochemical cell in which one or both electrodes are coated with an electrochromic film [10]. Today, much research is directed to assembling all solid-state devices using solid electrolytes, involving not only electrochromics, but also batteries and photocells, minimizing solvent evaporation, avoiding leakage problems and increasing the possibility of technological applications. Solid-state electrochromic devices have been described in the literature [11–15]. The polymer which is most commonly used as solid electrolyte in combination with lithium salts is poly(ethylene oxide). However, its high crystallinity associated with the high T_m (70 °C) precludes its use at room temperature [13] . An amorphous material which presents high ionic conductivity at room temperature when mixed with $LiClO_4$ (10^{-5} S cm^{-1} in the absence of humidity: $H_2O < 1$ ppm), is poly(epichlorohydrin-*co*-ethylene oxide) [16], an elastomer produced under the trade name Hydrin-C®. The ionic conductivity of this polymeric electrolyte can be improved in humidity conditions. Recently, we were able to obtain an all solid-state electrochromic device assembled in air, by using Hydrin-C® + $LiClO_4$ as solid electrolyte and two *p*-doped conducting polymers: poly(*o*-methoxyaniline) doped with *p*-toluene-sulfonic acid and poly(4,4′-dipentoxy-2,2′-bithiophene), poly-(ET2) [17]. This device presented a good optical contrast in both the visible and NIR spectral regions, an optical response time lower than 1 s and high environmental and electrochemical stability was obtained. (Its optical characteristics remained unchanged after 3000 consecutive double potential steps.)

Poly(N,N'-dimethyl-2,2′-bipyrrole), poly(NNDMBP), is a polypyrrole derivative which can be obtained from N,N'dimethyl-2,2′-bipyrrole and has some important advantages with respect to the polymer produced from N-methylpyrrole. First, a blue-shifted onset of the absorbance spectrum of the neutral state permits a more transparent bleached form of the device to be obtained in the visible region. Moreover, the polymer produced from N,N'-dimethyl-2,2′-bipyrrole is oxidized at less positive potentials, presents more defined redox peaks and its in situ conductivity is 30 times higher than that of the polymer obtained from N-methylpyrrole, indicating that it has a more regular structure [18].

The synthesis of new conjugated polymers with low band gap has attracted great attention, owing to the possibility of obtaining new materials with uncommon electrochromic and electrochemical properties [19]. Electrochromic devices based on polythiophenes often show a high optical contrast and a good stability to electrochromic cycles [20]. Thiophene polymers with low energy gap can be obtained from substituted thiophenes by increasing the quinonic character of the π-electron conjugated systems [21]. These new materials, owing to the transparency in the oxidized state, open new perspectives in the field of electrochromic devices. Poly(ET2) is an example of these thiophene polymers with a high electrochemical stability; due to the electron-releasing property of the alkoxy group [22], it can be easily doped and, consequently, is very stable in the conducting state. It shows an optical spectrum complementary with respect to that of Poly(NNDMBP); it is transparent when fully oxidized and dark blue in the neutral form.

In this work, we describe a device assembled with two electrochromic electrodes obtained by coating ITO glasses with poly(NNDMBP) and poly(ET2), respectively, and using Hydrin-C® + $LiClO_4$ as solid electrolyte. Poly(NNDMBP) and poly(ET2) show complementary optical spectra and the device assembled with these materials works in the entire visible spectral range.

2. Experimental details

The monomers, 4,4′-dipentoxy-2,2′-bithiophene and N,N'-dimethyl-2,2′-bipyrrole, were obtained according to the methods of Gallazzi [22] and Sannicolò [18], respectively. Poly(NNDMBP) was synthesized by cyclic voltammetry (20 mV s^{-1}, from 0 to 0.8 V vs Ag|AgCl) on ITO electrodes (Balzer Baltracon, sheet resistance: $20\Omega\square^{-1}$), in a conventional three-electrodes cell, using platinum as auxiliary electrode and a 5×10^{-3} mol L^{-1} NNDMBP + 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ acetonitrile solution. Poly(ET2) was prepared in the same way, but using a 5×10^{-3} mol L^{-1} ET2 + 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$ acetonitrile solution and scanning the potential of the electrochemical cell from −0.2 to 1.1 V. The thickness of the films were controlled by the number of voltammetric cycles. Polymer films were deposited on 2.5 cm^2 ITO electrodes. The synthesis were performed using an AMEL 552 potentiostat interfaced to an AMEL 566 function generator and an AMEL 731 integrator. Cyclic voltammetry and chronoamperometry experiments were done using a platinum wire as auxiliary electrode and a 0.1 mol $L^{-1}(C_4H_9)_4NClO_4$ acetonitrile solution as electrolyte. All potentials are referred to the Ag | AgCl electrode.

The electrochromic device was prepared in the following way. The ITO | Poly(NNDMBP) and ITO | Poly(ET2) electrodes were separately polarized at 0.9 and 0 V, respectively, in the same liquid electrolyte used for the electrochemical experiments and, subsequently washed with acetonitrile and dried.

The solid electrolyte was prepared by dissolving 0.30 g of Hydrin-C® (Zeon Chemicals) and 0.035 g of $LiClO_4$ in 10 mL of tetrahydrofurane. Drops of this solution were distributed on the polymer surface of the ITO | Poly(ET2) electrode and the solvent was slowly evaporated (to retard THF evaporation, the electrode was covered with a Petri dish) until a plastic consistency of the electrolyte was achieved. Finally, the ITO | Poly(ET2) electrode recovered with Hydrin-C® + $LiClO_4$ was adhered by pressure to the ITO | Poly(NNDMBP) electrode. The device was maintained under dynamic vacuum for 15 min to assure complete solvent evaporation. The thickness of the solid electrolyte was controlled with an adhesive tape, 65 μm thick. Electrical characteristics of the device were studied by spectrochronoamperometry at several potential differences ($1.5 \rightarrow -1.5$ V, $0.8 \rightarrow -0.8$ V, $0.55 \rightarrow -0.55$ V: Poly(NNDMBP) electrode vs Poly(ET2) electrode). All spectrophotometric measurements were recorded with a Perkin Elmer λ9 spectrophotometer.

3. Results and discussion

The complementary electrochromic characteristics of poly(ET2) and poly(NNDMBP) films on ITO electrodes, having approximately the same charge capacity (6 mC cm^{-2}) and thickness (ca. 0.2–0.3 μm), are shown in Figure 1. The neutral form of poly(ET2) absorbs at 500–700 nm and the oxidized form of poly(NNDMBP) at $\lambda > 650$ nm. This indicates that an electrochromic device assembled with these two polymers would present a colored form absorbing over the entire visible region.

The cyclic voltammetries of the above films are shown in Figure 2(a) where it can be seen that they present a high capacitive current at positive potentials. The redox peaks of poly(NNDMBP), at 0.4 and 0.6 V, are more defined than those of Poly(ET2), occurring at 0.20 and

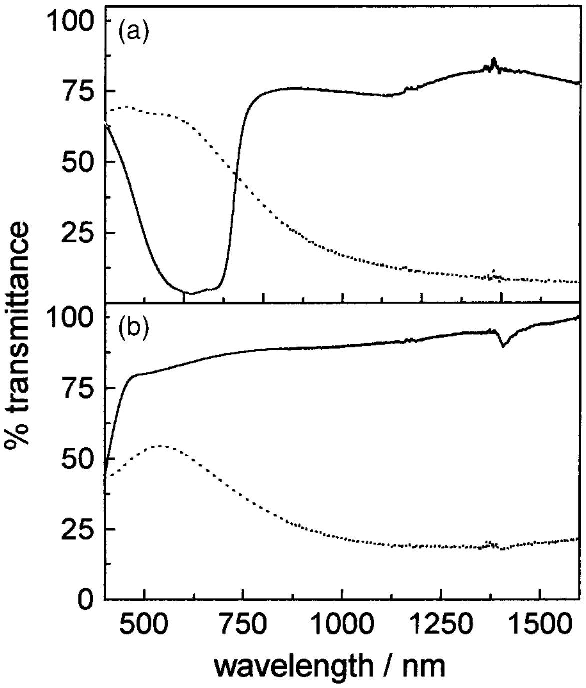

Fig. 1. Visible/NIR spectra for (a) poly(ET2) and (b) poly(NNDMBP). Full lines correspond to the reduced polymers and dotted lines to the oxidized polymers.

0.35 V. Moreover, both films present a coulombic efficiency close to 100%, which is an indication of high electrochemical reversibility.

The electrochromic kinetics between 0 and 0.9 V of single poly(ET2) and poly(NNDMBP) films deposited on ITO, Figure 2(b), show a chromatic variation of 57% (at 620 nm) and 35% (at 750 nm), respectively. Poly(ET2) undergoes a colour change from dark blue (reduced form) to pale grey (fully oxidized form) and poly(NNDMBP) from pale yellow (reduced form) to grey (fully oxidized form). Both polymers have faster electrochromic kinetics in the bleaching process; the optical response times are 1.5 s (bleaching) and 3.0 s (colouring) for poly(ET2), 1.5 s (bleaching) and 6.0 s (colouring) for poly(NNDMBP).

To be used in the construction of electrochromic devices, a material should present a large transmittance variation when cycled between its colored and bleached forms with a minimal consumption of energy. The parameter used to evaluate these characteristics is the electrochromic efficiency (η_λ), which is the ratio between the optical contrast at a given wavelength (λ) and the charge density used in the process. The values obtained for poly(ET2) ($\eta_{620} = 85\,\mathrm{C^{-1}\,cm^2}$) and for poly(NNDMBP) ($\eta_{750} = 79\,\mathrm{C^{-1}\,cm^2}$) indicate that they are suitable for utilization in electrochromic devices. These values are comparable to those found in the literature for other materials used for the same purpose [4, 5].

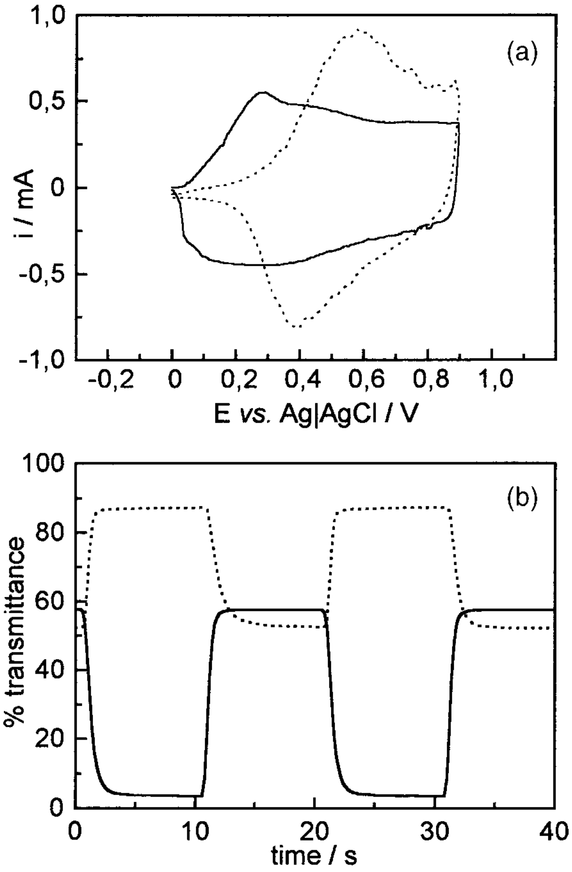

Fig. 2. Cyclic voltammetry at 20 mV s^{-1} for (——) Poly(ET2) and (- - -) Poly(NNDMBP) films, b) optical responses for the (——) poly(ET2) films at 620 nm and for the (- - -) poly(NNDMBP) films at 750 nm, when submitted to double potential steps between 0 and 0.9 V.

Taking advantage of these favourable properties, an electrochromic device was assembled. To improve further the properties of this device, we used a dry solid-state polymeric electrolyte. The device was assembled with the configuration: ITO|Poly(NNDMBP) ||Hydrin-C + LiClO$_4$|| Poly(ET2)|ITO. By changing the potential applied between the ITO electrodes from −1.5 to 1.5 V, the colour of the device varies from transparent pale gray to dark gray, due to the following electrochemical process:

$$\underset{\text{dark gray}}{-(\mathrm{ET2})_n- + -[(\mathrm{NNDMBP})^{+y}(\mathrm{ClO_4})_y]-}$$
$$\leftrightarrow \underset{\text{transparent pale gray}}{-[(\mathrm{ET2})^{+y}(\mathrm{ClO_4})_y] + -(\mathrm{NNDMBP})_n-}$$

Figure 3 reports the spectra of the dark and the bleached forms of the complete device. The spectra

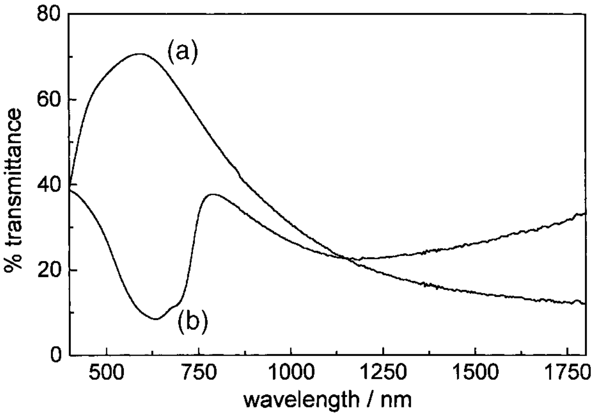

Fig. 3. Visible/NIR spectra for the device in its (a) bleached and (b) coloured forms.

were measured using an ITO/glass as background. When cycled between -1.5 V and $+1.5$ V, the device presents $\Delta\%T = 61.3\%$ at 620 nm. By considering the charge consumed in the electrochromic process, we calculated $\eta_{620} = 120\,\mathrm{C}^{-1}\,\mathrm{cm}^2$. This value is approximately the sum of η values for the single electrodes at this wavelength: $\eta = 85\,\mathrm{C}^{-1}\,\mathrm{cm}^2$ for Poly(ET2) and $\eta = 45\,\mathrm{C}^{-1}\,\mathrm{cm}^2$ for Poly(NNDMBP).

The stability to successive redox cycles for an electrochromic device based on p-doped conducting polymers mainly depends on the stability of the polymers at positive potentials. Figure 4(a) reports subsequent electrochromic cycles (%T at 620 nm) for the device at different potential switches. It can be observed that, by decreasing the potential difference from 3.0 (1.5 to -1.5 V) to 1.1 V (0.55 to -0.55 V), the transmittance variation remains acceptable, while the durability of the device considerably increases. Figure 4(b) shows that the device presents 50% of the initial transmittance variation at 620 nm after switching the potential 1200 times between 0.55 and -0.55 V. This result indicates that this system is very stable when compared to similar electrochromic devices [12, 13].

Deactivation of the device may be the result of crosslinking or overoxidation processes occurring in one or both polymeric materials. It is therefore reasonable that the deactivation is higher by cycling the device with a higher potential difference. Results presented in Figure 5 suggest that this is correct. Figure 5(a) shows the 1st and the 800th electrochromic cycle of the device switched between 1.5 and -1.5 V. In this Figure it is evident that the transmittance variation after 800 cycles is lower than in the first cycle. However, by increasing the switching time (dotted line), the transmittance change tends to reach the value attained in the first cycles (Figure 5(a), I). Therefore, by increasing the

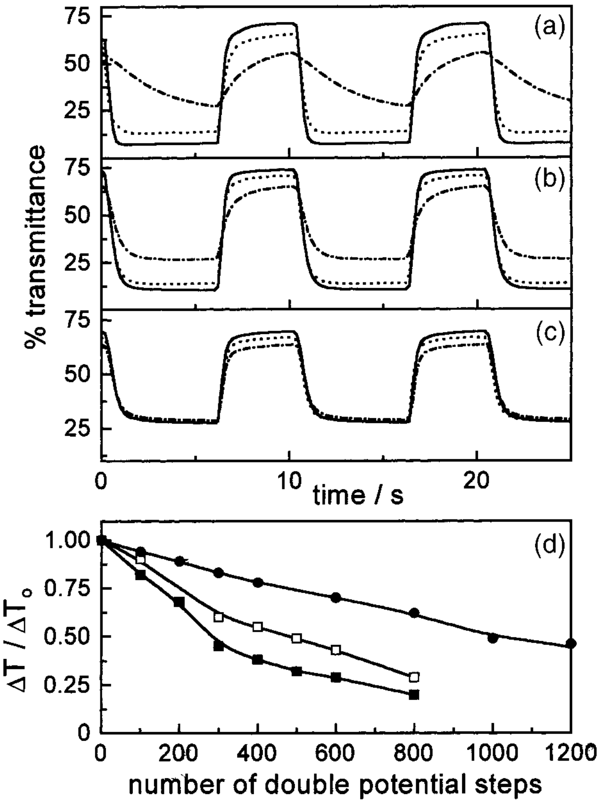

Fig. 4. Optical responses for the device (—— 1st cycle, ···· 100th cycle, – · – · – 300th cycle) by applying different potential switches: (a) 1.5 and –1.5 V, (b) 0.8 and –0.8 V, (c) 0.55 and –0.55 V. (d) Relative colour change (620 nm) of the device as a function of the electrochromic cycles, by applying different potential switches: (■) 1.5 and −1.5 V, (□) 0.8 and –0.8 V, (●) 0.55 and –0.55 V.

number of electrochromic cycles, the rate of ion diffusion decreases due to crosslinking or over-oxidation processes between the polymer chains. Figure 5(b) shows the spectrum of the dark form of the device at the beginning of the experiment (full line) and after 600 electrochromic cycles (dotted line). These spectra show that the absorption related to the π–π^* transition of poly(ET2) at about 600 nm is shifted to higher energies after the electrochromic cycles. This may be a result of shortening of the π-electron conjugation due to crosslinking reactions or scissions in the backbone. As the neutral form of poly(ET2) shows the strongest absorption in this region, it is reasonable to assume that these degradation processes occur mainly in this material.

4. Conclusions

In summary, the electrochromic device assembled and tested under atmospheric conditions showed promising

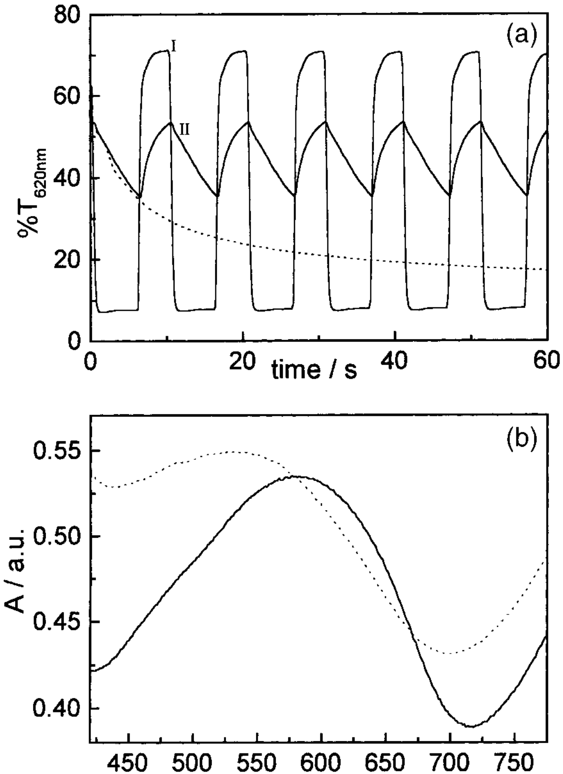

Fig. 5. (a) 1st (I) and the 800th (II) electrochromic cycles of the device by switching the potential between 1.5 and –1.5 V. Dotted lines: Transmittance decay during 60 s after the 800th electrochromic cycle electrochromic. (b) Visible spectra of the dark form of the device at the beginning of the experiment (full line) and after 600 electrochromic cycles (dotted line).

properties, easy construction, sufficiently fast kinetics and high optical contrast between its bleached and coloured forms. In addition, its 'coloured' form absorbs over a wide range of the visible region, giving rise to a smoky-like glass. These properties candidates the device as a component for rear-view mirrors used in automobiles and trucks.

In spite of the improvements obtained by decreasing the potential range used for the electrochromic cycle, work is needed to increase its durability. The crosslinking reactions (probably inside poly(ET2)) could be avoided by employing conductive blends in the construction of the device. Blending conducting polymers with other polymers would preclude crosslinking. If the mixture presents compatibility the insulator polymer chains would occupy the free space between the conducting polymer chains increasing the inter-chain distance. Also, using a flexible-insulating polymer could improve the flexibility of the conducting polymer films. This modification will be the first stage for the construction of an all-polymeric and flexible electrochromic device, which is the objective of work in progress.

Acknowledgments

The authors are grateful to FAPESP/Brazil (Proc. 96/06664-0 and 96/09983-0) and to CNR/Italy for financial support.

References

1. B. Scrosati, *in* 'Applications of Electroactive polymers', edited by B. Scrosati, (Chapman & Hall, London, 1993), chapter 8.
2. M. Gazard, *in* 'Handbook of Conducting Polymers', edited by T.A. Skotheim, vol. 1 (Marcel Dekker, New York, 1986), chapter 19.
3. D. Gonçalves, B. Matvienko and L.O.S. Bulhões, *J. Electroanal. Chem.* **267** (1994) 267.
4. W.A. Gazotti, Jr, R. Faez and M.-A. De Paoli, *J. Electroanal. Chem.* **415** (1996) 107.
5. S. Panero, B. Scrosati, M. Baret, B. Cecchini and E. Masetti, *Solar Energy Mater. Solar Cells* **39** (1995) 239.
6. C. Arbizzani, M. Mastragostino, L. Meneghello, M. Morseli and A. Zanelli, *J. Appl. Electrochem.* **26** (1996) 121.
7. M.-C. Bernard, A.H.-Le Goff and W. Zeng, *Synth. Met.* **85** (1997) 1347.
8. C. Arbizzani, M. Mastragostino, L. Meneghello, X. Andrieu and T. Vicedo, *Mat. Res. Soc. Symp. Proc.* **293** (1993) 169.
9. W.A. Gazotti Jr., M.J.D.M. Jannini. S.I. de Córdoba Torresi and M.-A. De Paoli, *J. Electroanal. Chem.* **440** (1997) 193.
10. M. Mastragostino, *in* 'Applications of Electroactive Polymers', edited by B. Scrosati (Chapman & Hall, London, 1993), chapter 7.
11. E.A.R. Duek, M.-A. De Paoli and M. Mastragostino, *Adv. Mater.* **5** (1993) 650.
12. M.A.B. Gomes, D. Gonçalves, E. C. Pereira de Souza, B. Valla, M. A. Aegerter and L. O. S. Bulhões, *Electrochim. Acta* **37** (1992) 1653.
13. E. Kim, K.-Y. Lee, M.-H. Lee, J.-S. Shin and S. B. Rhee, *Synth. Met.* **85** (1997) 1367.
14. J.C. Gustafsson, O. Inganas and A.M. Andersson, *Synth. Met.* **62** (1994) 17.
15. M.-A. De Paoli, A. Zanelli, M. Mastragostino and A.M. Rocco, *J. Electroanal. Chem.* **435** (1997) 217.
16. G.G. Silva, N.H. Lemes, C.M.N. Polo da Fonseca and M.-A. De Paoli, *Solid State Ionics* **93** (1996) 105.
17. W.A. Gazotti Jr., G. Casalbore-Miceli, A. Geri and M.-A. De Paoli, *Adv. Mater.* **10** (1998) 60.
18. T. Benincori, E. Brenna, F. Sannicolò, G. Zotti, S. Zecchin, G. Schiavon, C. Gatti, and G. Frigerio, submitted to *Chem. Mater.*
19. C. Arbizzani, M. Catellani, M.G. Cerroni and M. Mastragostino, *Synth. Met.* **84** (1997) 249.
20. J.C. Gustafsson, B. Liedberg and O. Inganas, *Solid State Ionics* **69** (1994) 145.
21. J.L. Brédas, *J. Chem. Phys.* **82** (1985) 3808.
22. G. Zotti, M.C. Gallazzi, G. Zerbi and S.V. Meille, *Synth. Met.* **73** (1995) 217.