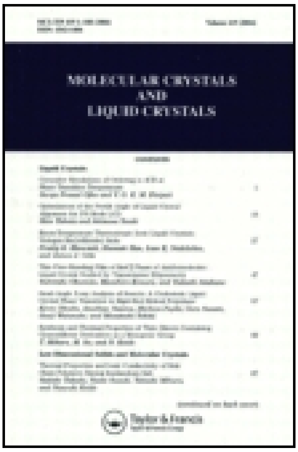


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Conducting Polymers: New Electrochromic Materials for Advanced Optical Devices

Stefania Panero [a] , Stefano Passerini [a] & Bruno Scrosati [a]

[a] Dipartimento di Chimica, Università di Roma 'La Sapienza', 00185, Rome, Italy

Version of record first published: 04 Jun 2010.

To cite this article: Stefania Panero , Stefano Passerini & Bruno Scrosati (1993): Conducting Polymers: New Electrochromic Materials for Advanced Optical Devices, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 97-109

To link to this article: http://dx.doi.org/10.1080/10587259308032182

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 97–109
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CONDUCTING POLYMERS: NEW ELECTROCHROMIC MATERIALS FOR ADVANCED OPTICAL DEVICES

STEFANIA PANERO, STEFANO PASSERINI , BRUNO SCROSATI
Dipartimento di Chimica, Università di Roma 'La Sapienza' 00185 Rome, Italy

Abstract. The basic properties of conducting polymers which can be coloured by reversible electrochemical doping processes, are briefly described. The application of these materials for the development of optical devices of technological importance, such as electrochromic displays and windows, is also illustrated and discussed.

INTRODUCTION

Electrochromism is the phenomenon related to changes in colour induced in selected materials by a reversible electrochemical process. More precisely, electrochromism can be defined as a persistent but reversible optical change produced electrochemically.

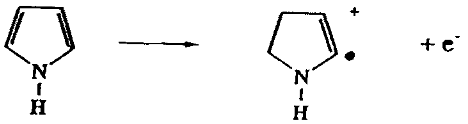
A material which can be reversibly coloured by passing charge through it is defined as an electrochromic material (ECM). Although ECMs can be of different nature, the attention here will be focused on organic conducting polymers. Typical examples are conjugated polymers, such as the heterocyclic polypyrrole (pPy) and polythiophene (pT), polyalinine (PANI), and their derivatives, whose electrical and optical properties may be monitored by reversible electrochemical processes.

The basic principles of electrochromism [1-4], as well as the basic properties of heterocyclic conducting polymers[5-8] , have been extensively treated in various review papers. Here only a few key aspects will be briefly discussed and some recent interesting applications and developments will be reported.

POLYMERIC ELECTROCHROMIC MATERIALS

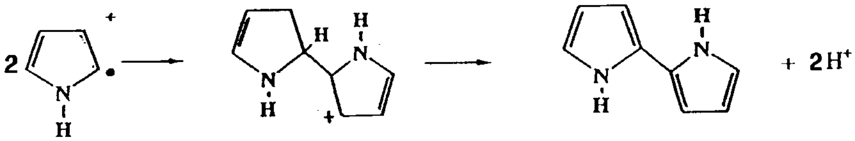
The electrochemical processes which induce changes in the electrical and optical properties in polymers of the heterocyclic and polyaniline type, sometimes designated as doping processes, are essentially oxidation (p-doping) or reduction(n-doping) reactions, involving the removal or the addition of π electrons from the polymer chains followed by ion transport into or out of the polymer matrix to balance the electronic charge[6]. Polymeric ECMS are thus ion-insertion compounds which behave as mixed electronic-ionic conductors.

An important feature of this class of ECMs lies in the fact that their polymerization and doping processes may be driven by a single electrochemical operation which, starting from the monomer, first forms the polymeric chain and then induces its oxidation and deposition in the doped form as a conductive film on a suitable substrate. The polymerization reaction may be basically described as an electrophilic substitution which retains the aromatic structure and proceeds via a radical cation intermediate. For instance, in the case of the hetercoclics say pPy, we have:



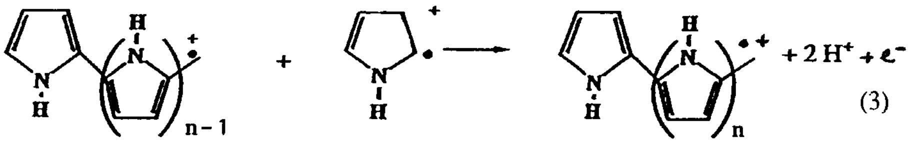
(1)

The coupling occurs at the carbon atoms (generally via α - α' links) which are the most reactive to addition and substitution reactions:



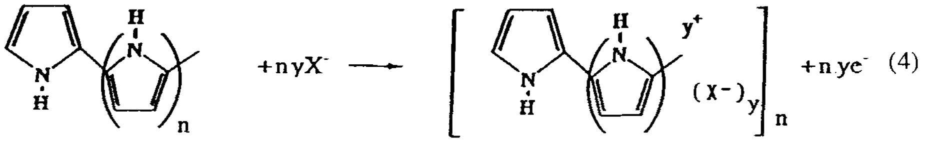
(2)

The polymerization reaction proceeds between the radical cations of the monomer and those of the continuing forming oligomers since the latter, following the growth of the chain length, acquire an oxidation potential progressively lower than that of the monomer :



(3)

The doping process (here of the p-type) takes place with formation of the charged polycation accompanied by diffusion of the generic electrolyte counterion X^-:



(4)

The entire operation can be achieved in a simple electrochemical cell consisting of two (usually planar) electrodes immersed in a solution (generally non aqueous, e.g. an acetonitrile, CH_3CN solution) containing the monomer (e.g. pyrrole, C_4H_5N) and a supporting electrolyte (e.g. $LiClO_4$ or alkylammonium salts, both of which are soluble and highly dissociated in aprotic solvents).

The electrodeposition voltage is specific for any given electropolymerization process and thus upon applying polarization, polymerization takes place, the p-doping of the polymer occurs and, finally, a film of the selected conducting polymer is deposited on the substrate.

The electrochemical polymerization offers several advantages over the chemical one, particularly because it is capable of optimizing the characteristics of the polymer films. In fact, by controlling the charge involved in the electrodeposition process, the thickness of the polymer film may be varied from a few Å to many µm or even mm. Furthermore, by changing the nature of the counterion in solution, the electrical and the physico-chemical properties of the final polymer can be tailored and by varying the value of the electropolymerization current density, the morphology of the polymer can be easily controlled. Finally, different substrates can be used for the electrodeposition process, providing that they have sufficient conductivity to allow the passage of current without inducing substantial ohmic drop. Thus substrates such as indium-tin-oxide (ITO)-coated glasses, which are particularly suitable for the electrochromic applications, can be readily and successfully used.

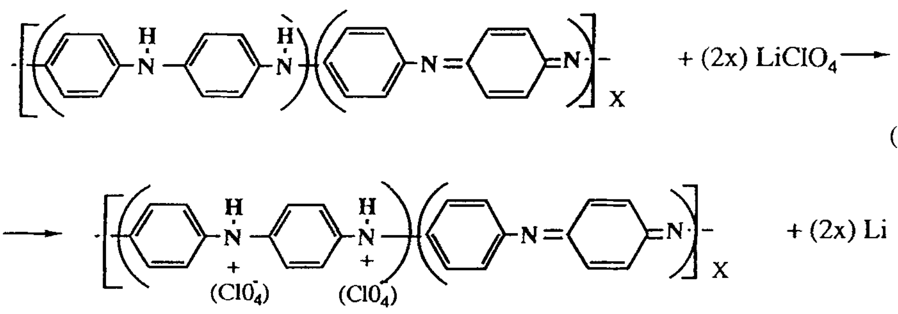
Once deposited as conductive films, the polymers can be repeatedly cycled from the undoped to the doped forms (and vice versa) in electrochemical cells substantially similar to those used for the electropolymerization reactions. Still with the example of polypyrrole, the process can be reversibly driven in an electrochemical cell by polarizing the polymer electrode versus a counter electrode (say Li) in a suitable electrolyte (say, lithium perchlorate in propylene carbonate, $LiClO_4$-PC). Under these circumstance, the p-doping redox reaction (4) can be described by the scheme:

$$(C_4H_5N)_n + (ny)ClO_4^- <==> [(C_4H_5N^{y+})(ClO_4^-)_y]_n + ny(e^-) \qquad (5)$$

which, as previously pointed out, involves the oxidation of polypyrrole with the formation of a positive polycation whose charge is counter balanced by the electrolyte anion (ClO_4^- in this case) diffusing into the polymer matrix. The symbol y represents the ratio between electrolyte ion and polymer repeating unit and it is commonly called the doping level. Other heterocyclic polymers, such as polythiophene, can be similarly treated and the related electrochemical doping process can be indicated as:

$$(C_4H_5S)_n + (ny)\,X^- \Longleftrightarrow [(C_4H_5S^{y+})(X^-)_y]_n + ny(e^-) \qquad (6)$$

Polyaniline can also be prepared electrochemically, e.g. by oxidation of aniline in acid media [7]. The emeraldine base form of this polymer reacts in non aqueous electrolytes, such as the $LiClO_4$-PC solution, with the formation of the conductive emeraldine hydroperchlorate salt:

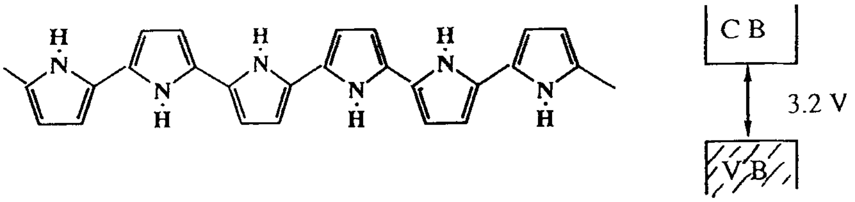


(7)

a process which is relevant in view of the electrochromic applications of polyaniline.

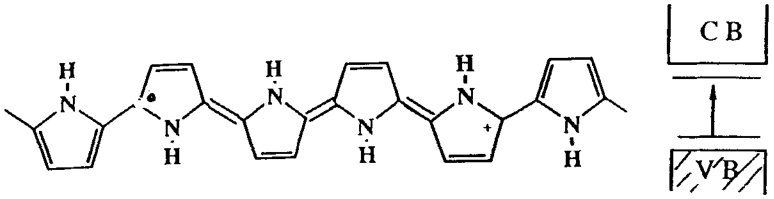
ELECTRICAL AND OPTICAL PROPERTIES OF DOPED POLYMERS

The clarification of the doping mechanism of conducting polymers and of the associated electronic band evolution is of fundamental importance for the comprehension of the operational behaviour of these compounds as electrochromic materials. As an illustrative example, let us consider the p-doping (oxidation) process of polypyrrole. In the undoped state, polypyrrole is a poor electronic conductor with an energy gap Eg of 3.2 eV between the conduction band (CB) and the valence band (VB):



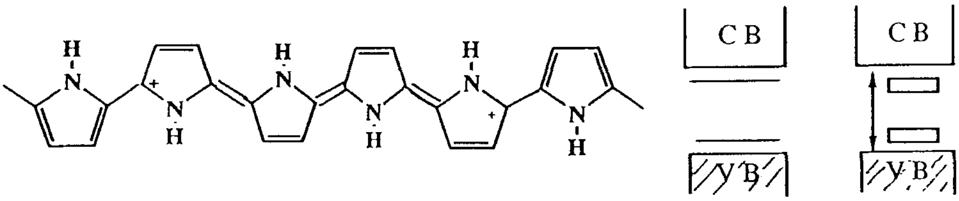
(8)

The initial removal of electrons (following the anodic, p-doping process) leads to the formation of a positive charge localized in the polymer chain (radical cation), accompanied by a lattice distortion which is associated with a relaxation of the aromatic structural geometry of the polymer chain towards a quinoid form. This forms extends over four pyrrolic rings:



(9)

This radical cation (which is partially delocalized over the polymer segment and is stabilized by polarizing the sorrounding medium) is called a *polaron* and it may be energetically described as a half- filled *polaron level* situated at approximately 0.5 eV from the band edges[6,8]. When further electrons are removed from the chain, dications are formed, namely two positive charges localized in the same 'defect site'. This defect has been referred as a ***bipolaron***, defined as a pair of like charges associated with a strong localized lattice distortion, which again extends over four pyrrolic rings:



The bipolarons are energetically described as spinless bipolaron levels (scheme 10a) which are empty and which, at high doping levels, may overlap with the formation of bipolaronic bands (10b). Finally, for polymers with band-gap, Eg values smaller than that of polypyrrole -such as polythiophene- the bipolaronic bands may merge also with the valence and the conduction bands, thus approaching the metallic regime.

A general effect which is associated with the electronic band evolution and which is the basis of the electrochromic activity of conducting polymer is the occurence of bipolaronic states which promotes optical absorption prior to the π–π^* gap transitions. Therefore, by controlling the doping process, it is possible to monitor the optical absorption and thus the colour of the materials. The colour contrast between doped and undoped forms of the polymer depends on the value of the energy gap Eg of the pristine form. Polymers with Eg greater than 3 eV are almost transparent when undoped and highly absorbant in the visible when doped, whereas those with Eg smaller than 3 eV are highly absorbant in the undoped form and slightly coloured in the doped form. Typical cases are illustrated in Table 1. Asan example, polymethylthiophene (pMeT), with Eg = 2.3 eV , is purple in colour and highly absorbant in the visible in its neutral form, while upon doping it assumes a pale blue colour.

TABLE 1-Electrochromic characteristics of some heterocyclic polymers[9]

Polymer	λ/nm $\pi-\pi^*$	Eg/eV	colour undoped	colour doped
poly(pyrrole)	380	3.2	yellow	blue-violet
poly(2,2'-bithiophene)	480	2.6	red	deep-blue
Poly(dithienothiophene)	490	2.5	red	blue
poly(3-methylthiophene	530	2.3	purple	pale-blue
poly(isothionaphtene)	825	1.5	deep-blue	pale-yellow-green

The properties of polyanilines are somewhat different from those of the heterocyclics since the former are unique in the sense that their electrical and optical behaviour depend not only on the oxidation state but also on the protonation and thus on the acidity of the electrolytic medium[7]. Also polyaniline however, basically undergoes a basically electrochemically driven doping process which is associated with a colour change ranging from transparent-yellow to blue.

In summary, a great variety of colour contrast can be attained with conducting polymers and thus these materials are particularly suitable for the realization of a series of versatile optical devices, such as displays and windows. The main parameters which dictate the most appropriate among the various possible candidates are: the electrochromic efficiency (i.e., the ratio of the variation of optical density to the injected charge, measured in $C^{-1}cm^2$), the response time (i.e., the time necessary to switch from one colour state to the other), the operational life (i.e., the number of possible cycles) and the optical memory (i.e. the persistence of the colour in a specified state).

ELECTROCHROMIC DISPLAYS

An electrochromic display, ECD, is mainly an electrochemical cell where the electrochromic electrode is separated from the counter electrode by a suitable electrolytic solution. Figure 1 ilustrates a typical configuration which involves, in sequence, the electrochromic electrode (e.g., a thin polymer film deposited on an ITO-coated glass), the electrolyte and the counter electrode. The ECD works on the basis of the doping process (e.g., reaction (5)): by applying a voltage pulse between the polymer film and the counter electrode, the process can be activated by inducing during the anodic pulse the colour associated to the oxidized (p-doped) form of the polymer and then by switching back to that associated to the undoped form during the cathodic pulse, the cycle being repeated with the pulse frequency.

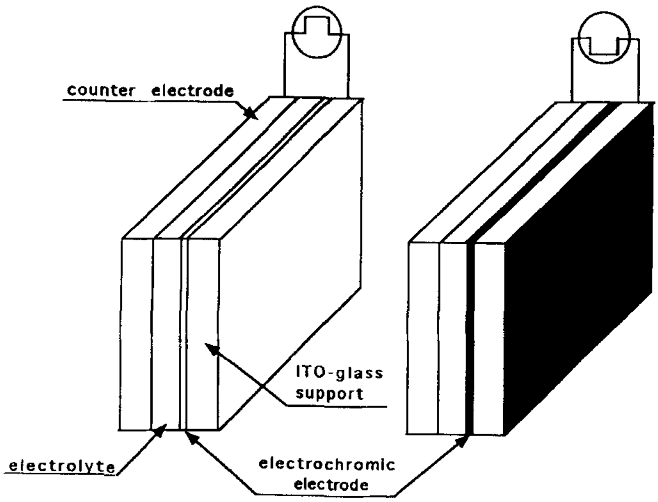


Figure 1 - Schematic configuration of electrochromic devices. In displays the counter electrode is simply any material which assures electrochemical balance. In windows the counter electrode is either optically passive or electrochromic in a complementary way with respect to the primary element.

Since ECDs operate in the diffuse reflectance mode, the main requirement of the counter electrode and of the electrolyte is that of assuring electrochemical balance. Therefore, the counter electrode can be of any material which undergoes reversible electrochemistry (e.g., Li metal in the example case (5)) and the electrolyte any solution which allows transport of the doping anion (e.g., the $LiClO_4$ -PC solution).

It needs be emphasized that ECDs offer over other passive displays (e.g., liquid crystals displays, LCDs) the relevant advantage of having an open circuit memory, since in principle the polymer maintains a given oxidation state (and thus its associated colour) unless the pulse is switched to the reverse polarization. In contrast, the switching response time of ECDs is much slower than that of LCDs, since the former are based on mixed electronic-ionic conductors which involve ion transport throught the polymer structure with attendant diffusion kinetics inevitably slower than those associated with electron movements. However, the emerging display technologies require devices where in the response time can vary from a few hundreds of milliseconds (watches) to a few seconds (information panels) and thus there is a large sector where the ECDs can find their appropriate role also.

A practical example of a polymer-based ECD[10] is based on the following scheme:

$$\text{Li / LiClO-PC / pDTT, ITO-glass} \qquad (11)$$

namely a display based on a poly(dithienothiophene), pDTT, an ECM which, upon applying a pulse voltage presents a sharp colour contrast, namely from blue to red (see Table 1). Figure 2 illustrates the electrical (current density, I) and the optical (percent of transmitted light, TLI) response, following the 1000th voltage pulse.

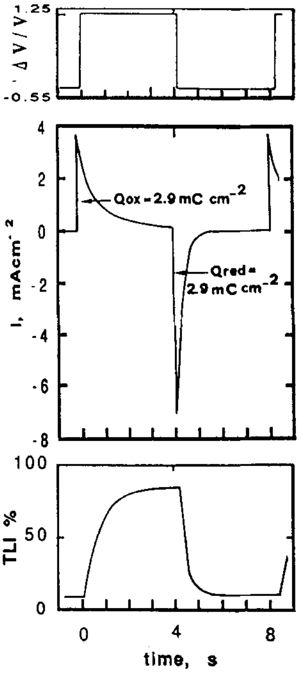


Figure 2- Electrical and optical response of a pDTT-based ECD. Wavelength of maximum absorption, λ_{max} =480 nm, is used for the optical transmittance[10]. ΔV is given with respect to the Li electrode.

It shoud be noted that the ECD has promising behaviour in terms of high coulombic efficiency (Qox/Qred > 0.99), sharp colour contrast (transmittance variation ΔT at λ_{max} from 4 % (red) to 28 %(blue)), good operational life (10^4 cycles), acceptable electrochromic efficiency (120 $C^{-1}cm^2$ at λ_{max}) and response time (of the order of 4 seconds). However, the optical memory, measured by the intensity of the transmitted light of the doped form after the removal of the driving potential, is not satisfactory since it decays about 20% over a period of 8 hours. This is a typical drawback of this entire class of polymeric ECMs due to self-undoping processes, probably induced by solvent and/or electrolyte impurities oxidation[11].

Another promising example of a polymeric ECD is that based on the structure:

$$\text{Pt / KCl in } H_2O \text{ / pPy(DS), ITO-glass} \qquad (12)$$

which uses a dodecylsulphate(DS)-doped polypyrrole as the ECM[12]. There are two interesting aspects to this ECD. The first is that it uses a very simple electrolyte solution. The second is that it uses a polymer film electrode electrodeposited in a solution containing a surfactanct salt (e.g. NaDS) as supporting electrolyte. When this pPy(DS) is placed in a general solution, as in the case of cell (12), the undoping-doping process of the ECM induced by the applied voltage is not the exchange of the DS anion but rather the insertion-deinsertion of the cation (e.g., K^+) since the former remains immobilized in the polymer structure[13]. This is a consequence not only of the large size of the surfactant anion but also of the presence of the polar and unpolar extremety of the molecule: the unpolar end is compatible with the reduced, neutral polymer while the polar end is compatible with the oxidized charged polymer. Such a situation causes the surfactant anionto be immobile thus promoting a doping process with the effect that transport of fast ions stabilizes the response of the overall ECD.

Indeed, ECDs of type (12) have a good colour contrast (ΔT at white light varying from 98% (yellow) to 40% (deep blue)) a long operational life (10^4 cycles) and reproducible behaviour[12,13]. The optical memory is again not satisfactory and this, being a general problem of all the polymeric ECMs, is presently the subject of detailed investigation in various laboratories.

ELECTROCHROMIC WINDOWS.

An ECD which allows electrically driven modulations of light transmission and reflection can be regarded as an electrochromic window, EW. The basic difference with normal ECDs is that in EWs the entire system is in the optical path, this requiring a transparent electrolyte and a counter electrode which is either optically passive (i.e., colorless in both oxidized and reduced states) or electrochromic in a complementary way with respect to the primary ECM. The latter condition implies that if the primary ECM colours anodically, the counter electrode bleaches anodically and vice versa.

EWs are expected to find important applications, for instance, as devices capable of electrically controlling radiant energy transfer and thus of improving energy efficiency in buildings and automobiles[14,15]. This accounts for the large interest presently devoted to EWs and their development, which in turn is directly related to the characterization of efficient counter electrodes.

One choice is to use plain ITO-coated glasses as a readily available, optically passive counter electrode. The assumption[16] is that Li^+ cations can be reversibly inserted or deinserted into the ITO structure while at the same time the anions (say ClO_4^-) dope or undope the polymeric ECM. In this fashion, an EW of the type:

$$\text{glass-ITO/ LiClO}_4\text{-PC/pMeT, ITO-glass} \qquad (13)$$

is characterized by the following overall electrochromic process:

$$\underset{purple}{(MeT)_n} + ITO + nyLiClO_4 <\!\!===\!\!> \underset{pale\ blue}{Li_{ny}ITO + [(MeT)^{+y}(ClO_4^-)]_n} \qquad (14)$$

according to which the EW is switched from the transparent state (pale blue) to the reflectant state (purple) following the alternation of the applied voltage pulse (Figure 3).

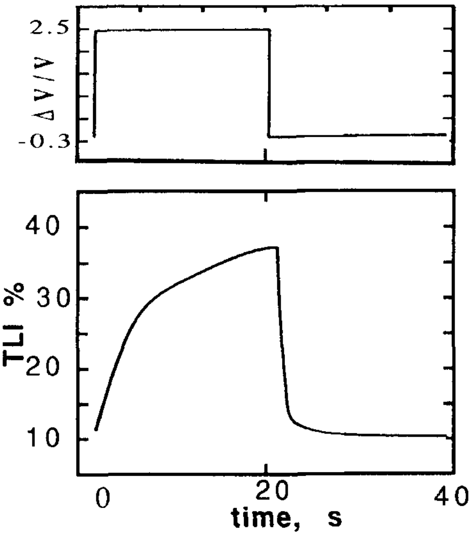


Figure 3- Optical response of a ITO/PMeT type EW evaluated by detecting the transmitted light at 530 nm[16].
ΔV is given with respect to the pMeT electrode.

Note that the response time of this EW (about 20 seconds) is considerably higher than that obseved for the parent polymeric ECDs (about 5 seconds, compare Fig.2) and this is due to the fact that the kinetics of the insertion process in the ITO counter electrode, being much slower than those of the doping process, control the response time of the overall device.

Another type of EW employs lithium-intercalated nickel oxide as improved, optically passive counter electrode. Non-stoichiometric nickel oxide, NiO_z is dark in its pristine state but, upon bleaching by cathodically driven lithium ion insertion (i.e., Li_xNiO_z), it attains a fully transparent state (transmittance ca. 90 % in the entire visible region) for a consistent amount of injected charge and can reversibly exchange a major fraction of this charge while retaining its transparent state[17]. On this basis, an EW of the following structure:

glass-ITO,Li_xNiO_z/ $LiClO_4$-PC/pMeT, ITO-glass (15)

is characterized by the following overall electrochromic process:

$(MeT)_n + nLi_xNiO_z + nyLiClO_4 \Longleftrightarrow nLi_{(x+y)}LiNiO_z + [(MeT)^{+y}(ClO_4^-)]_n$ (16)

purple *pale blue*

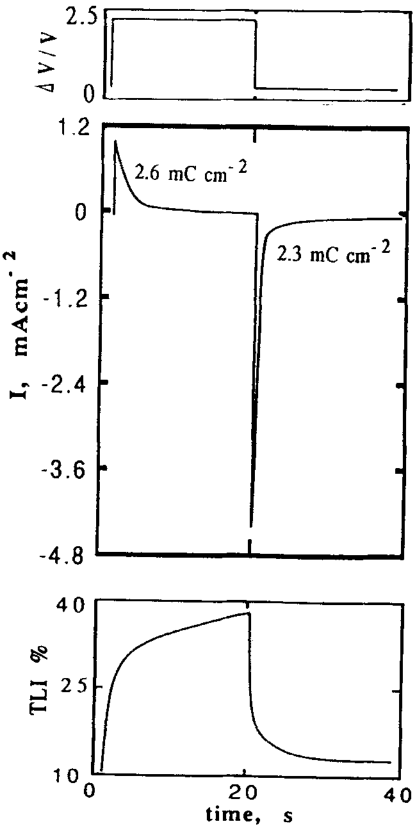


Figure 4.Current and transmittance (at 530 nm) response of the Li_xNiO_z/ pMeT electrochromic window[18]. ΔV is given with respect to the pMeT electrode.

Figure 4 , which illustrates the optical and the current response, reveals that this EW device offers an acceptable change in transmittance (from 10 to 40 %) which is contrasted by a definite difference between the kinetics of the bleaching and colouring processes and by a switching efficiency less than 100%. These limitations are probably associated with the complexity of the Li insertion-dinsertion processes in Li_xNiO_z, which may involve changes of phases and/or slow transition reactions[19].

A final example of EWs considers the use of a polymer ECM, namely polyaniline, pANI, associated in the cited $LiClO_4$-PC solution with a typical inorganic ECM, namely tungsten trioxide, WO_3:

$$\text{glass-ITO,pANI/ LiClO}_4\text{-PC/WO}_3\text{,ITO-glass} \qquad (17)$$

Tungsten trioxide is electrochromically complementary to polyaniline: while the former colours cathodically(following insertion of Li^+ ions),the latter colours anodically (due to doping by the ClO_4^- ions) and thus the EW overall process:

$$\underset{colourless}{(ANI)_n + nWO_3 + nyLiClO_4} \Longleftrightarrow \underset{blue}{nLi_yWO_3} + \underset{dark\ blue}{[(ANI)^{+y}(ClO_4^-)_y]_n} \qquad (18)$$

is accompanied by a colour change from transparent to dark blue, with which is associated a transmittance change from 80% to 30% for an operating life exceeding 10^6 repeated cycles[20]. This performance suggests that the $pANI/WO_3$ EW satisfies the requisites for practical use and thus that polymeric ECMs may indeed be of importance for optical device technology.

ACKNOWLEDGEMENTS

This work has been carried out with the support of Consiglio Nazionale delle Ricerche, Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate. The authors are grateful to Prof. M.Mastragostino for helpful discussions and for providing some of the data quoted in this paper.

REFERENCES

1. W.C.Dautremont-Smith , Displays, 67, January and April 1982.
2. B.W. Faugham and R.S. Crandall, in "Display Devices", J.I.Pankov Ed., Topics in Advanced Physics, Springler, Berlin, 40, 181 (1980).
3. M.Green and Karam Kang, Displays, 166, October 1988.
4. B.Scrosati, Chim.Oggi., 7, 41 (1989)

5. T.A. Skotheim Ed., Handbook of Conducting Polymers, Vols. 1 & 2, Marcel Dekker Inc, New York, (1986)

6. B.Scrosati, Progress In Solid State Chemistry, 18, 1 (1989).

7. A.G.MacDiarmid and M.R. Maxfield, in "Organic Polymers as Electroactive Materials", Electrochemical Science and Technology of Polymers, R.G.Linford Ed., Elsevier Applied Science, London, pag. 67 (1987)

8. J.L.Bredas and G.B.Street, Acc. Chem. Res., 18, 309 (1985)

9. M.Mastragostino, in "Electrochromic Devices", Applications of Electroactive Polymers, B.Scrosati Ed., Chapman & Hall, London, in press.

10. A.Corradini, A.M.Marinangeli, M.Mastragostino, B.Scrosati, Solid State Ionics, 28 & 30, 1738 (1988).

11. M.Mastragostino, A.M.Marinangeli, A.Corradini and C.Arbizzani, Electrochim. Acta, 32, 1589 (1987).

12. M.De Paoli, S.Panero, S.Passerini and B.Scrosati, Adv. Mater. , 2, 480 (1990).

13. M.De Paoli, S.Panero, P.Prosperi and B.Scrosati, Electrochim. Acta, 35, 1145 (1990).

14. D.Rauh, S.F.Cogan,M.Parker, SPIE, vol. 502, Optical Materials Technology for Energy Efficiency and Solar Energy Conversion, III, pag. 38 (1984).

15. J.S.E.M.Svensson, C.G.Granqvist, Solar Energy Mat., 11, 29 (1984).

16. A.Corradini, A.M.Marinangeli, M.Mastragostino, Electrochim.Acta, 35, 1757 (1991).

17. S.Passerini, B.Scrosati, A. Gorenstein J.Electrochem. Soc. 137, 837 (1991)

18. C.Arbizzani, M.Mastragostino, S.Passerini,S.Pileggi, B.Scrosati, Electrochim. Acta, 36, 837 (1991).

19. F. Decker, R. Pileggi, S. Passerini, B. Scrosati J.Electrochem. Soc. 138, 3182 (1991)

20. T.Asaoka, K.Okabayashi, T.Abe, T.Yoshida, 40th ISE Meeting , Kyoto, Japan, Ext. Abs. I,245-246 (1989).