Highly conductive solid polymer electrolyte for smart windows

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A solid-state electrochromic device, which shows excellent performances in terms of colour contrast and response time, has been realized. A solid polymer electrolyte based on a combination of a lithium salt and a chain-extended polyepoxide has been sandwiched between a tungsten oxide electrochromic material (WO_3) and an activated nickel oxide (Li_xNiO) counter-electrode.

(Keywords: polymer electrolyte; smart window; electrochromic device)

INTRODUCTION

Over the last few years, much work has been devoted to the study and development of solid-state devices, such as rechargeable batteries and optical displays, employing solid polymer electrolytes (SPE) as electrolytic membranes. Optical devices, such as photochromic, thermochromic and electrochromic displays, are capable of switching from a condition of maximum transparency to the opposite condition of minimal transmittance following the application of an electrical signal. In particular, electrochromism is a phenomenon related to a persistent and reversible optical change induced electrochemically, whose macroscopic effect is a variation in colour.

These devices are of considerable interest from the viewpoint of energy saving in the field of the building industry (smart windows) and in the automobile industry (anti-dazzling rear-view mirrors). Assembly and characterization of electrochromic displays based on a combination of tungsten oxide and liquid electrolytes are known[1].

Liquid electrolyte devices show a fast response time, owing to their high ionic conductivity, but they lack in other fundamental requirements such as threshold voltage and intrinsic memory. Furthermore, leakage and technological problems have focused the research towards the development of new solid-state electrolytic materials, which would allow one to overcome the operational and manufacturing problems due to the liquid component employment.

Complexes of poly(ethylene oxide) (PEO) and lithium salts have been widely used for this purpose, but their poor ionic conductivity below the phase transition temperature ($T < 65°C$) influences drastically the performance of any device, whose use is restricted to thermoelectrochromic applications, which must be thermally addressed[2,3]. No response time, in fact, can be detected at room temperature.

Amorphous materials, which do not undergo any phase transition over a wide range of temperature, may allow one to improve performance considerably, providing a continuous colour variation under the proper conditions. Besides, the electrochromic behaviour of a display is directly related to the conductivity of the electrolytic membrane and to its temperature dependence: the higher the conductivity, the faster will be the response time.

In particular, for window applications, highly conductive solid polymer electrolytes (SPE) should meet the requirements of transparency, high and homogeneous surface area together with fast and reversible responses.

In a previous investigation we studied comb-shaped poly(vinyl ether) (PVE)–lithium complexes[4,5]. This approach belongs to a widely diffused strategy to obtain polymeric matrices having the same complexing properties as PEO but reduced or no crystallinity, low T_g and high ionic conductivity at room temperature. In PVE structures oligo(ethylene oxide) side chains are attached to an aliphatic, non-active polymer backbone; because of the presence of flexible pendent groups, crystallization phenomena are dramatically reduced and amorphous materials have been obtained. The ionic conductivity (σ) reaches a value of 5×10^{-5} S cm^{-1} at room temperature in the system with five EO units in the side chains, which corresponds to the more flexible, highly conductive material.

Furthermore, the transparency of the membranes has allowed the construction of a solid-state electrochromic device having the following configuration:

$$\text{glass}|\text{ITO}|Li_xNiO|\text{PVE–}LiClO_4|WO_3|\text{ITO}|\text{glass}$$

where ITO is indium tin oxide. The device is capable of operating at room temperature, but its response time (several hundred seconds) is still too high for practical applications[6].

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The modification of polymer chemical structure by the introduction of oxygen atoms in the main chain, apart from in the side chain, should allow substantial improvement of the ionic conductivity and consequently lower the response time.

Following this approach, polyepoxide (PEP) matrices have been synthesized, in which oligo(ethylene oxide) side chains are attached to a PEO-like main chain. The introduction of oxygen atoms along the polymer backbone provides a more flexible system, lowering the T_g in comparison to analogous PVE structures, and consequently enhancing the ionic conductivity. By employing these highly conductive materials in an electrochromic device, fast response time, excellent colour contrast and a good memory effect have been gained.

EXPERIMENTAL

Preparation of polymer–salt membrane

The polyepoxides have been obtained by anionic polymerization of a monoepoxide and a chain-extender diepoxide, whose use allows one to increase the molecular weight, imparting better dimensional stability in comparison to analogous homopolymers. Experimental details concerning the synthesis of epoxide monomers and polymers are reported elsewhere[7,8]. Particular care has been devoted to the purification of the membrane components, mainly with the aim of avoiding the presence of water or other impurities, deleterious for memory retention.

The PEP-lithium salt complexes have been prepared by casting, dissolving the polymer in acetonitrile solution containing the already dissolved lithium salt. The homogeneous solution is poured into a Teflon container, which is placed in an argon forced circulation chamber to remove the solvent slowly. The membranes are then heated to 40°C under vacuum and left overnight. Transparent homogeneous membranes of about 100 μm thickness are obtained, which can be easily handled.

All the above-mentioned operations have been conducted in a dry-box under an argon atmosphere.

Preparation of electrodes

A tungsten oxide (WO_3) film, generally around 1000 Å, and an activated nickel oxide thin film (600–1000 Å) have been deposited by sputtering onto ITO conductive glass. Nickel oxide is activated following a procedure described in detail elsewhere[9,10], which is briefly summarized here. A NiO electrode is charged in an electrochemical cell containing a solution of $LiClO_4$ in propylene carbonate (PC) and a counterelectrode of lithium metal; the cathodic polarization promotes the intercalation of lithium inside the nickel oxide.

Electrochromic device assembly

The solid-state electrochromic device has been assembled in a dry-box (water and oxygen content <10 ppm) by placing into contact a WO_3 film supported on ITO-coated glass, a thin film (100–200 μm thickness) of the polymer electrolyte and the Li_xNiO counterelectrode supported on ITO glass. The display (about 3 cm^2 area) has been lodged in a sealed container and then taken out from the box for characterization.

RESULTS AND DISCUSSION

The polymer electrolyte

A schematic representation of the PEP structure is shown in *Figure 1*. The polyepoxides have been

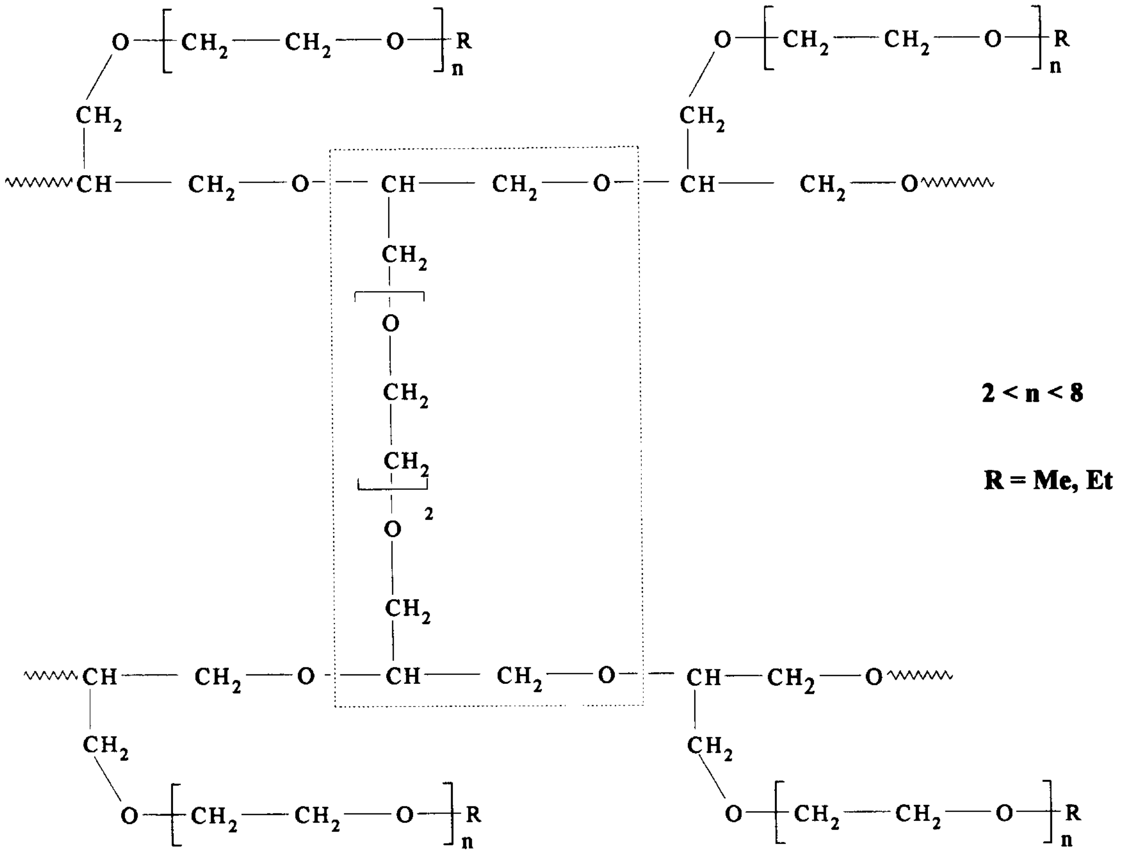

Figure 1 Schematic representation of chain-extended PEP structure

Table 1 Molecular-weight and d.s.c. data of some PEPs and corresponding lithium complexes with $LiClO_4$

n^a	Monoepoxide (mol%)	Diepoxide (mol%)	$M_w{}^b$	T_g (°C)	T_m (°C)	EO/Li	T_g (complex) (°C)	ΔT_g (°C)
3	94	6	240 000	−73	–	20	−43	30
6	80	20	2 533 000	−64	−13	20	−50	14
6	97	3	50 000	−70	−20	20	−49	21
6	85	15	265 000	−69	−20	20	−45	24
6	80	20	2 100 000	−68	−21	20	−52	16
6	87	13	183 000	−69	−21	14	−42	27

[a] *n* is the number of EO units in the monoepoxide
[b] Determined by laser light scattering

synthesized by anionic polymerization of a monoepoxide and a chain-extender diepoxide. Since the adhesive properties of polymers are enhanced as the amount of chain-extender diepoxide increases, the influence of molecular weight on the thermal properties of polymers and on the conductivity of lithium complexes has been investigated.

In *Table 1* the d.s.c. data and molecular weight of PEPs, synthesized with different composition of monoepoxide and diepoxide, are reported. Uncomplexed polymers generally show a higher glass transition temperature as the molecular weight increases; in high-molecular-weight PEPs the presence of a considerable amount of diepoxide should promote the occurrence of dense crosslinking knots, providing a cage and partially ordered structure in which the bulk flexibility of pendent chains is reduced. On the contrary, in low-molecular-weight PEPs the amount of diepoxide is not sufficient to disrupt chain entanglement, and then a highly disordered structure is preserved. This phenomenon leads to a discernible increase, up to 10°C, in the glass transition temperatures of high-molecular-weight PEPs.

When the salt is added to the polymer, a lack of flexibility, together with an increase in the glass transition temperature, is always observed owing to additional crosslinking due to interactions of cations with the solvating groups of the polymer matrix. This phenomenon seems to have a stronger effect on the more flexible system, the low-molecular-weight one, in which greater chain mobility encourages their rearrangement around the cations; as a direct consequence in this latter case ΔT_g values up to 30°C are noticed, at least 15°C higher than those calculated for high-molecular-weight PEPs. Moreover, after complexation high-molecular-weight complexes exhibit a lower glass transition temperature.

All these observations should justify the hypothesis that in chain-extended PEPs, although the increase in molecular weight enhances the T_g of the polymers, on the other hand it reduces the stiffening effect due to chain reorganization in lithium complexes. An interesting observation is that the improvement of dimensional stability is not detrimental for the electrical properties; in fact, membranes based on different molecular-weight PEPs show an improvement in dimensional stability with increasing molecular weight while retaining the same conductivity in all the range of temperatures investigated (see *Figure 2*).

A screening has been carried out to elucidate the influence of lithium salt type on conductivity; $LiClO_4$, $LiBF_4$ and $LiCF_3SO_3$ have been employed and the conductivity behaviour, reported in *Figure 3*, highlights

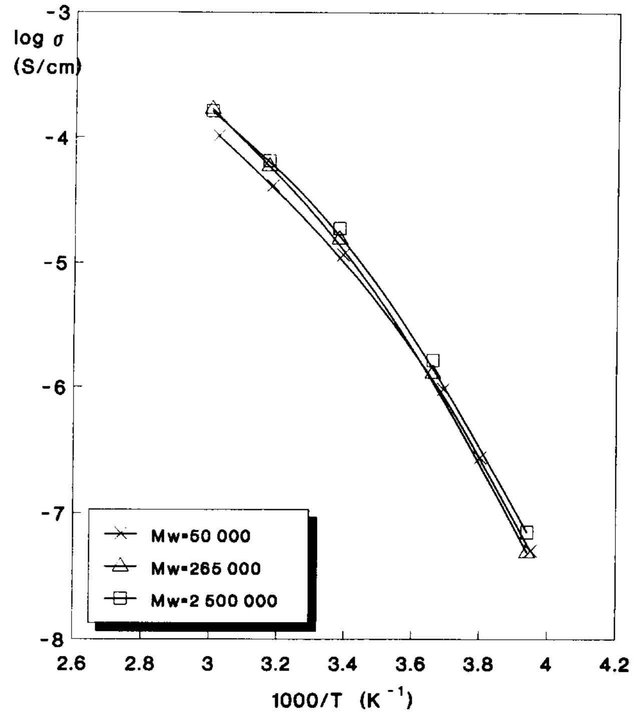

Figure 2 Thermal behaviour of log σ as a function of PEP molecular weight ($EO/LiClO_4=24$, $n=6$)

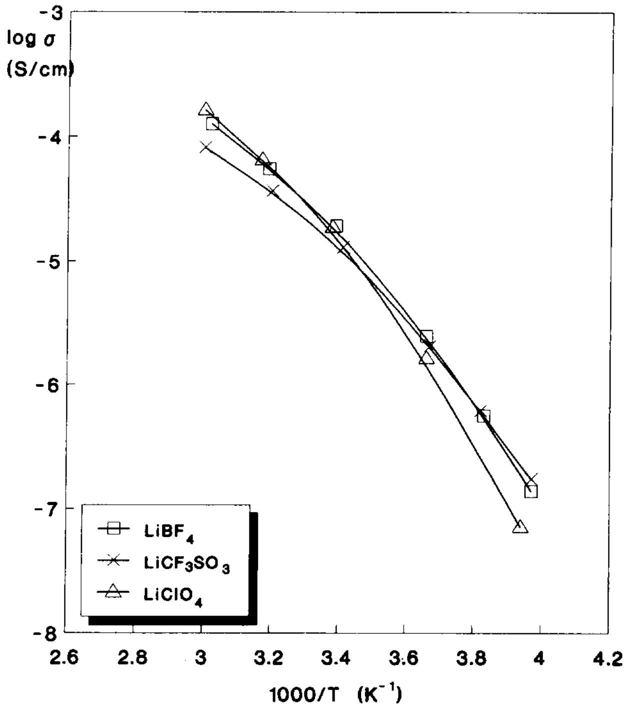

Figure 3 Thermal behaviour of log σ as a function of lithium salt type ($EO/Li=20$)

the negligible influence of this parameter. $LiClO_4$ is chosen for further investigations and an optimum EO/Li = 14 ratio preferred for conductivity tests.

An electrolytic membrane based on PEP seems to constitute a highly versatile system, giving the opportunity to employ different molecular weights and several lithium salts without losing conductivity performances. A wide range of applications could be envisaged for such a system. Work is still necessary to improve the polymerization conditions with the aim of obtaining polymers with reproducible molecular weight for the same composition of monomers.

The effect of side-chain length on conductivity and thermal properties has been explored by synthesizing chain-extended PEPs in which the number of EO units was varied from two to eight in the monoepoxide, keeping the chain extender and the composition ratio (EO/Li = 14) in the lithium complexes fixed. D.s.c. data reported in *Table 2* show that most of the polymers have low T_g, generally lower than comparable PVE, and are fully amorphous above 0°C. When the number of EO units in the side chains becomes greater than five, a melting peak appears besides T_g, due to a certain tendency of longer chains to organize into ordered structures. These in turn disappear after complexation with lithium salt, this phenomenon being salt-concentration-independent. All the lithium complexes are then completely amorphous above T_g.

The conductivity plots, reported in *Figure 4*, clearly confirm the influence of side-chain length as a continuous increase in conductivity is observed by increasing the side-chain length from two to six EO units; six EO units seems to be the critical length above which the introduction of further segments is useless and has a negative effect on conductivity, probably owing to a certain reduction of bulk flexibility. The trend in T_g and thermal analysis indications, in particular the progressive increase of the glass transition temperature in lithium complexes on further increasing the side-chain length, are in agreement with such a hypothesis (see *Table 2*). The glass transition temperature decreases, and consequently the ion mobility increases, as n is raised until 6, which seems to represent the compromise value able to provide adequate segmental mobility of polymer chains without improper tendency to form crystalline phases.

An analogous behaviour has been observed in PVE complexes, but it is worth while to emphasize that PEPs generally show better performances in terms of conductivity for comparable side-chain length and salt concentration. At room temperature almost one order of magnitude is gained, confirming the importance of polymer chemical structure, the modification of which could provide more flexible systems and a better distribution of coordination sites, which in turn could facilitate the transport of ionic species through the matrix.

Table 2 D.s.c. data of some PEP and corresponding complexes with $LiClO_4$

n	Diepoxide (mol%)	T_g (°C)	T_m (°C)	EO/Li	T_g (complex) (°C)
2	3	−77	–	14	−39
2	6	−68	–	14	−38
3	6	−73	–	20	−43
3	6	−73	–	24	−51
4	3	−77	–	14	−49
5	6	−75	−28	14	−49
6	3	−70	−20	20	−49
6	3	−70	−20	14	−44
6	6	−70	−14	14	−45
7	3	−69	−11	14	−40
8	3	−62	6	14	−30

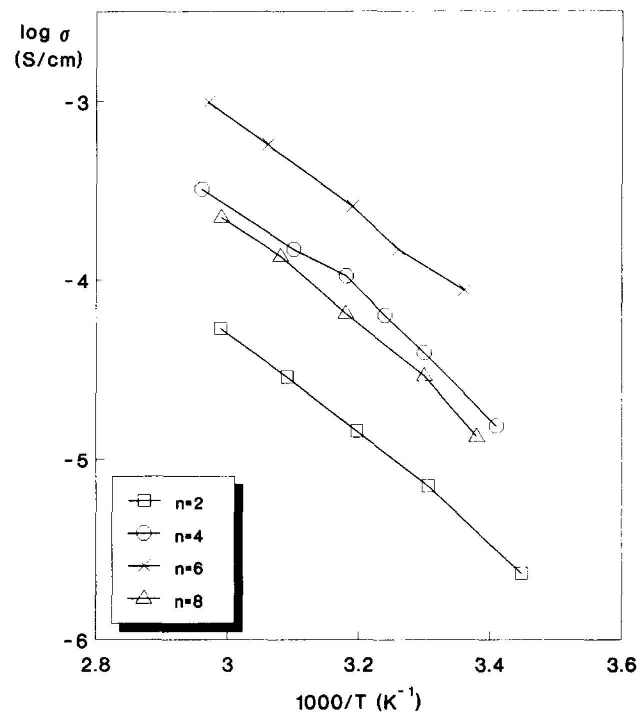

Figure 4 Influence on conductivity (log σ) of the side-chain length in PEP/Li complexes at constant salt concentration (EO/Li = 14)

For electrochromic applications, it is necessary to verify, besides the above-mentioned characterization, the optical properties of the polymer matrix. Transmittance data, detected in a wide range of wavelengths (350–800 nm) and reported in *Figure 5*, confirm the excellent transparency of PEP; the polymer is almost completely transparent as its transmittance is quite close to 90% in all the range of interest, and this condition is preserved even in the presence of the lithium salt.

The electrochromic window

Tungsten oxide (WO_3) is the most widely employed electrochromic material because of its favourable optical properties, reliability and manufacturability[11,12]. Several transition-metal inorganic oxides, capable of reversibly intercalating lithium inside their layered structure, have been investigated as counterelectrode candidates[13-15]. Among these NiO has gained a growing interest in the last few years[16,17].

To act as counterelectrode in an electrochromic device, NiO needs to be activated; it can colour anodically either in its hydrated form, when aqueous electrolytes are present[18,19], or when intercalated with lithium. In the former case the modification of optical properties seems to be associated with hydrogen extraction, while in the latter with insertion of cations into the oxide structure. This activation consists essentially of a pre-intercalation of lithium; this process modifies the optical properties of oxide layers. In the intercalated state, nickel oxide becomes transparent and capable of reversibly donating and retaking lithium, either without losing its transparency

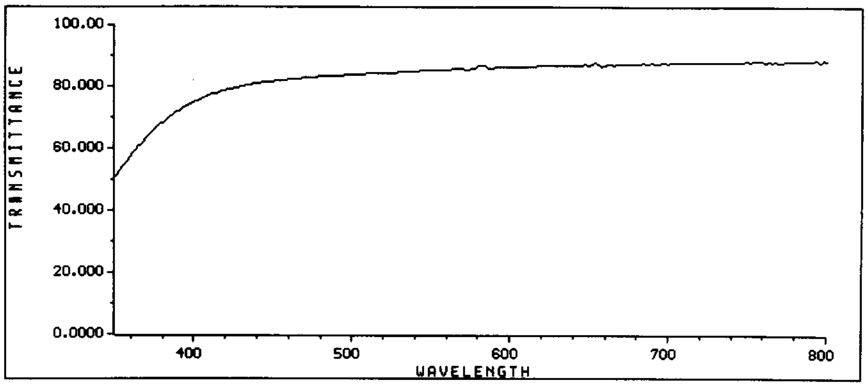

Figure 5 Optical transmittance of a PEP/LiClO$_4$ electrolytic membrane

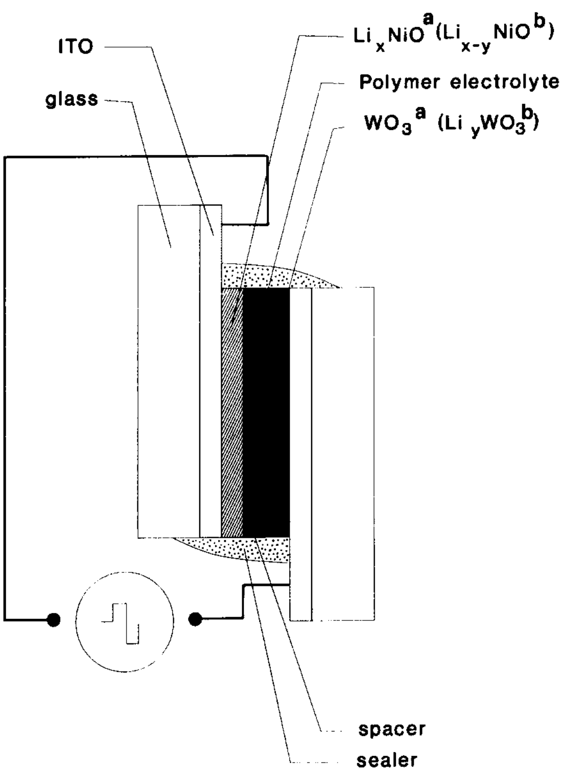

Figure 6 Schematic representation of a solid-state electrochromic window: (a) anodic cycle; (b) cathodic cycle (in parentheses)

or turning into its coloured state with an electrochromic process complementary to the process of WO$_3$. The possibility of NiO undergoing reversible lithium intercalation–deintercalation processes even when an organic liquid or solid electrolyte are present has opened up new opportunitites for electrochromic applications.

The window realized and outlined in *Figure 6* has the following basic configuration:

glass|ITO|Li$_x$NiO|PEP–LiClO$_4$|WO$_3$|ITO|glass

WO$_3$ acting as the main electrochromic electrode and Li$_x$NiO as counterelectrode and lithium reservoir. The corresponding electrochromic process, induced by applying a voltage pulse and involving the transport of lithium ions across the electrodes, is:

$$\underset{\text{transparent}}{\mathrm{Li}_x\mathrm{NiO} + \mathrm{WO}_3} \rightleftharpoons \underset{\text{dark blue}}{\mathrm{Li}_{(x-y)}\mathrm{NiO} + \mathrm{Li}_y\mathrm{WO}_3}$$

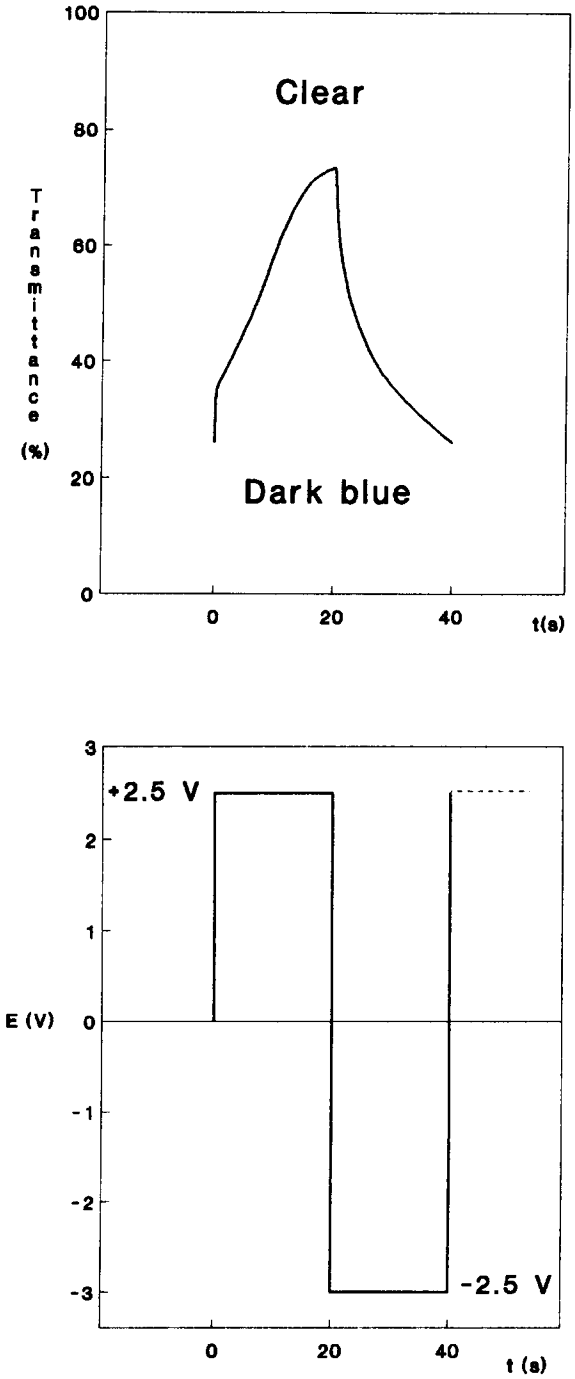

Figure 7 Potentiostatic test performed on a WO$_3$|PEP–LiClO$_4$|Li$_x$NiO window from −2.5 V to +2.5 V

During the negative pulse the window is dark and its transmittance is low (intercalation of WO_3), while during the positive pulse the window turns back to transparent and the transmittance is high (deintercalation of lithium). The process is reversible and it can be repeated many times without losing its efficiency; after one year the window is still able to provide the same performance.

A potentiostatic test carried out on the electrochromic window at room temperature is shown in *Figure 7*. The time interval necessary for the electrochromic processes to take place until completion is generally of the order of tens of seconds, one order of magnitude lower than that observed in an analogous PVE-based device. This time varies with the value of the signal that controls the cell; in the case of a square wave from +2.5 V to −2.5 V, which represents a widely employed potential for practical applications, the change in transmittance between minimum and maximum values, and vice versa, is obtained within a time of approximately 20 s. Correspondingly the optical transmittance changes from 75% in the bleached state to 25–30% in the coloured state. It is worth while to emphasize the considerable optimal transmission in the bleached state. An analogous window employing an amorphous $PEO/LiN(SO_2CF_3)_2$ polymer electrolyte gave 41% transmission in the bleached state[20].

Finally a memory effect of several days has been observed.

CONCLUSIONS

A highly conductive, transparent and adhesive polymer electrolyte, based on the combination of a comb-shaped polyepoxide (PEP) with a lithium salt, has been employed as an electrolytic membrane in the realization of an electrochromic device in which WO_3 is the main electrochromic electrode while an activated nickel oxide (Li_xNiO) acts as counterelectrode.

Colouration and bleaching times of 20 s, at room temperature, have been noticed when a square wave from +2.5 V to −2.5 V is applied; correspondingly the transmittance varies from 20% in the coloured state to almost 80% in the bleached state. The excellent memory characteristics were confirmed by the stability of transparent and dark-blue colours for several days.

Work is in progress in our laboratory to verify the feasibility of an electrochromic device based on a new class of liquid-like conductive solid polymer electrolytes, which should allow the response time to be noticeably improved.

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