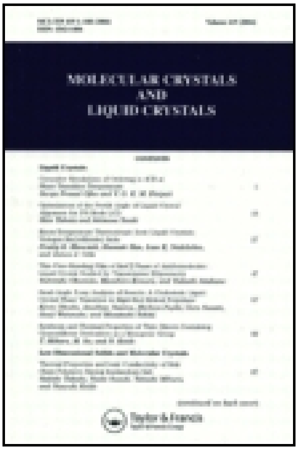

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Ion Conducting Polymers and Related Electrochemical Devices

B. Scrosati [a]

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

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Ion Conducting Polymers and Related Electrochemical Devices

B. SCROSATI
Dipartimento di Chimica, Università di Roma 'La Sapienza', Rome, Italy

SUMMARY

The physico-chemical and electrochemical properties of ion conducting polymers are discussed in terms of ambient temperature ionic conductivity. The applications of these electrolytes in solid-state batteries and electrochromic devices are also illustrated.

Properties of ionic polymers

It is now established that complexes between high-molecular weight PEO and lithium salts (e.g. $LiClO_4$, $LiCF_3SO_3$ and $LiBF_4$) are characterized by an ionic transport and thus may be efficiently used for the realization of advanced electrochemical devices.[1] However, it is also well known that the high conductivity of these materials, often called *'polymer electrolytes'*, is associated to their amorphous phase.[2-4] Consequently, 'conventional' PEO-based polymer electrolytes, reach usefully conductivity values only at temperatures above 80°C. This may not be a serious drawback if the polymer electrolytes are directed to the development of high-rate devices, (such as high-rate batteries) where the necessary heat may be self-provided by internal IR dissipation. However, a temperature of operation above ambient may not be acceptable for a successful application in devices designed for the consumer electronic market. Since polymer-based systems appear particularly suitable for this type of application, polymer electrolytes having improved low-temperature electrical properties are requested.

Various routes can be explored to reach this goal, the most straightforward strategy being the characterization of modified polymer hosts having a lower glass transition temperature (Tg) than linear PEO, in order to develop lithium salt complexes capable of retaining the amorphous condition at room temperature. This can be achieved by using comb-shaped polyethers containing short and active ethylene oxide (EO) side chains attached to a supporting non active polymer backbone. The short, pendant chains assure a high degree of amorphicity to the polymer, while the backbone provides good mechanical properties to its overall structure. This approach has been followed in our laboratory[5] by considering a cross-linked polyether (CPE), having the basic formula illustrated in Figure 1. In this formula n indicates the length of the side active chains and m the length of the crosslinking agent.

This polymer host is then dissolved in acetonitrile, mixed with known amounts of a selected lithium salt (e.g. $LiClO_4$) and the solution casted on a suitable substrate to obtain a polymer electrolyte film of about 50 μm thickness.

It has been found[5] that the best results in terms of conductivity are obtained with complexes having a polymer with $n = 5$ and with an EO/Li composition of 12 (EO/Li = ethylene oxide units/lithium ion ratio). Figure 2 shows that with this configuration, ionic conductivities between 10^{-5} S cm^{-1} and 10^{-4} S cm^{-1} are obtained at 25°C, i.e. values which are several orders of magnitude higher than those offered by electrolytes based on conventional PEO polymer hosts (such as that of PEO-$LiClO_4$ electrolyte, also reported in Figure 2 for comparison purposes). These are encouraging results which indicate that by properly selecting the nature of the polymer host and/or of the polymer electrolyte structure, further successful steps may be achieved in obtaining polymeric membranes having even higher ionic conductivity at ambient temperature. Indeed, it has been recently reported that ionic conductivities of the order 10^{-3} S cm^{-1} may be achieved at room temperature with electrolytes obtained by immobilizing low molecular weight PEO/PPO liquid complexes with $LiClO_4$ in microporous polyethylene membranes[6] or by other still not fully disclosed innovative procedures.[7-9]

Applications of polymer electrolytes

Most commonly, ion conducting polymers have been used as thin-film electrolytes for the development of lithium batteries. Effectively, the feasibility of rechargeable

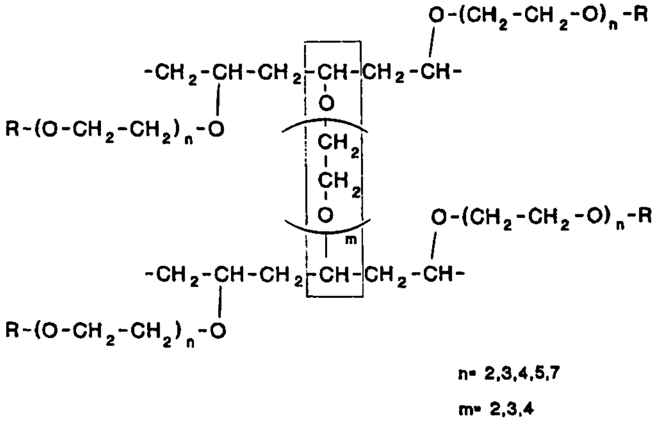

FIGURE 1 Basic formula of cross-linked polyvinylether.

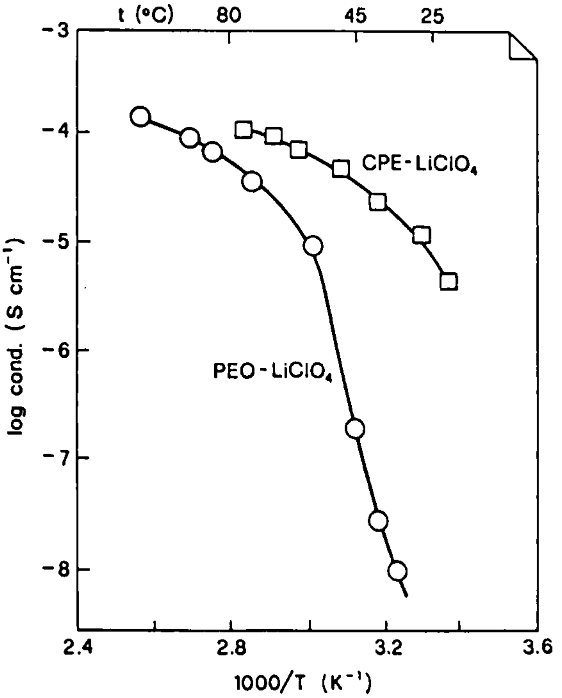

FIGURE 2 Conductivity of the PEO-$LiClO_4$ and of the CPE-$LiClO_4$ polymer electrolytes.

lithium batteries using PEO-based polymer films, has been demonstrated at temperatures of the order of 80 to 100°C.[10-13]

Typically, these batteries have a laminated structure which involves a lithium foil anode, the polymer electrolyte films and a composite cathode. Generally, the composite cathode consists of a homogeneous mixture of the active intercalation compounds, acetylene black and the polymer electrolyte itself. This mixture is casted in the form of a plastic-like film with a procedure similar to that used for the preparation of the electrolyte. As preferred intercalation compounds, TiS_2,[11] V_6O_{13}[9-13] and LiV_3O_8[12] have been used.

Another interesting applications of polymer electrolytes is directed towards the development of electrochromic displays and windows. An electrochromic display (ECD) is mainly an electrochemical cell where the electrochromic electrode (generally an intercalation compound, such as WO_3 or IrO_2) is separated from the counter electrode by a suitable electrolytic solution. A typical configuration involves in sequence the electrochromic electrode (for instance a WO_3 film deposited on an indium tin oxide (ITO) coated conductive glass), a layer of electrolyte and a counter electrode.

By applying a voltage between the WO_3 layer and the counter electrode, the electrochromic process can be promoted, so that to induce colouration by cathodic polarization (insertion of M^+ ions from solution into the WO_3 lattice, in order to form the M_xWO_3 intercalated compound) and reversing to bleaching by anodic polarization (restoration of the pristine WO_3).

ECDs operate in the diffuse reflectance mode and basic requirements are: i) an electrolyte having a good conductivity by the transport of the M^+ intercalation ions and ii) a counter electrode capable to provide the electrochemical balance. The initial development of ECDs implied the use of lithium metal as the counter electrode and a non-aqueous solution of lithium perchlorate in propylene carbonate ($LiClO_4$-PC) as the electrolyte. Using this configuration, ECDs having colouring-bleaching response times of few seconds for a number of cycles exceeding 10^6, have been developed.[14] It has to be emphasized that ECDs offer over other passive displays (e.g. liquid crystals) the relevant advantage of having an open circuit memory, since the M^+ ions (in the above cases Li^+ ions) cannot be deintercalated (and thus the WO_3 film restored to its colorless state) until a reverse, anodic polarization is applied to the device.

Considering the high optical contrast, the unrestricted viewing angle, the memory property and the capability of being constructed in large panels with different colour changes, electrochromic systems may in general find important applications as information displays or as energy controlling devices in buildings and automobiles. The latter function may be performed by an electrochromic window (EW), i.e. an ECD which allows electrochemically driven modulations of light transmissions and reflections. The basic difference with the normal ECDs is that in windows 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 mode with respect to the primary element (e.g. if the primary electrode is cathodic the counter electrode must be anodic and vice versa).

For instance it has been found in our laboratory[15] that activated nickel oxide is electrochromic in a complementary mode respect to tungsten oxide. This is shown by Figures 3 and 4 which illustrate the cyclic voltammetry and the in situ optical transmittance of the two electrodes in the $LiClO_4$-PC electrolyte. The NiO film becomes transparent in the cathodic cycle (Li insertion) and brown in the anodic cycle (Li extraction) while the WO_3 film becomes transparent in the anodic cycle (Li extraction) and blue in the cathodic cycle (Li insertion).

Hence WO_3 and pre-lithiated nickel oxide may be used in conjunction to realize efficient electrochromic windows of the type: glass/ITO/Li_xNiO/lithium electrolyte/ WO_3/ITO/glass. The window operates on the basis of the following process:

$$\underset{\text{(clear)}}{Li_xNiO + WO_3} \leftrightharpoons \underset{\text{(dark)}}{Li_{(x-y)}NiO + Li_yWO_3} \qquad (1)$$

Figure 5 shows the cyclic voltammetry (WO_3 working electrode) and the optical transmistance of a window using the $LiClO_4$-PC solution as a liquid, lithium electrolyte. The transmittance of the two single electrodes is also shown in the figure. It may be clearly noticed the complementary electrochromic behaviour of the two electrodes and the sharp optical contrast of the entire device, which make the selected system as a very promising one for the development of efficient EWs.

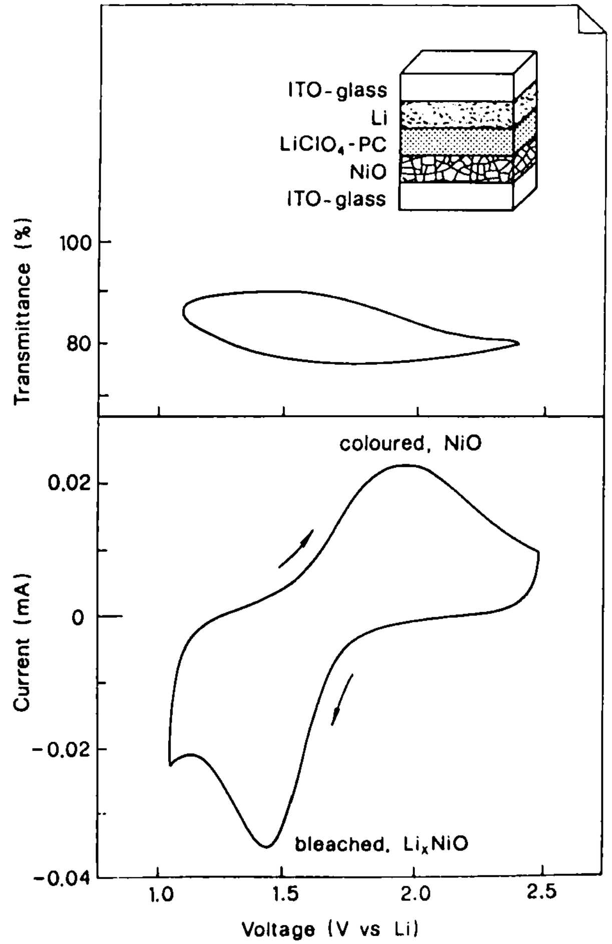

FIGURE 3 Cyclic voltammetry and in situ optical transmittance of the NiO electrode in the $LiClO_4$-PC electrolyte.

However, obvious requirements of reliability and practicity call for the replacement of the liquid electrolyte configuration with an improved design which mainly includes the use of solid or plastic-like electrolytes, possibly in the form of laminated, thin-film polymer layers.

Since process(1) basically implies the transport of Li^+ ions between the two ECMs, the liquid $LiClO_4$-PC solution can be replaced by any electrolyte characterized by Li^+ transport. Promising candidates are polymer electrolytes, i.e. the cited complexes between PEO and lithium salts. However, in this case the performance of the entire solid-state EW may be critically influenced by the thermal dependence of the conductivity of the polymer electrolyte, which, as already mentioned, is reasonably high only in the amorphous state, while at lower temperatures (where the crystalline state is stable) decays to almost negligible values. In fact, this is

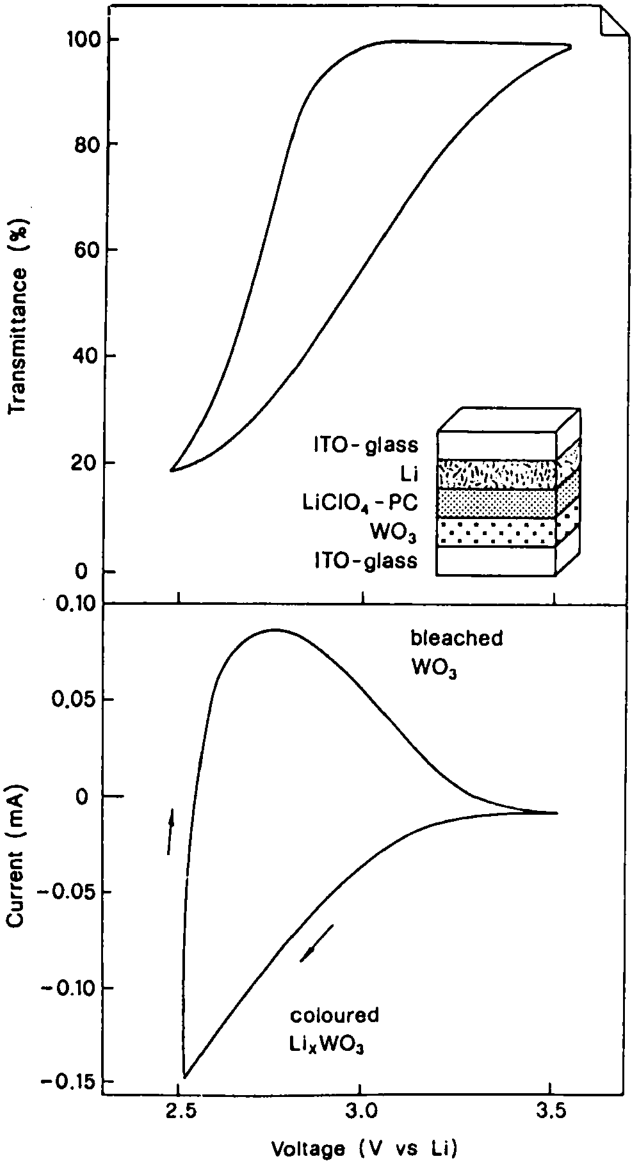

FIGURE 4 Cyclic voltammetry and in situ optical transmittance of the WO_3 electrode in the $LiClO_4$-PC electrolyte.

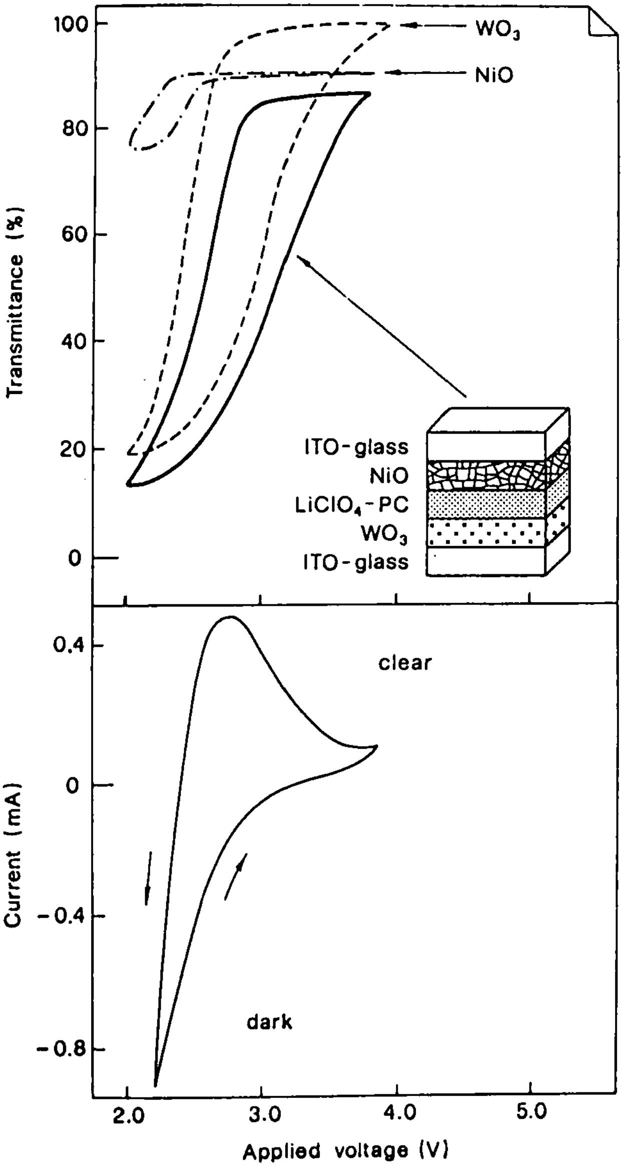

FIGURE 5 Cyclic voltammetry (WO_3 working electrode) and in situ optical transmittance of the $Li_xNiO/LiClO_4$-PC/WO_3 electrochromic window. The optical transmittance of the two single electrodes is also shown in the figure.

clearly revealed by Figure 6 which reports the cyclic voltammetry curves obtained at various temperatures with a Li_xNiO/WO_3 electrochromic window using the PEO-$LiClO_4$ complex as laminated, polymer electrolyte. No response (current practically equal to 0) is obtained at 25°C: the resistance of the electrolyte layer is too high and the entire applied voltage signal is dissipated as ohmic drop. However at 80°C (i.e. beyond the transition temperature), the response is marked and the chromatic contrast vivid.

The behavior of the solid state EW can be substantially improved with the use of modified, highly conductive polymer electrolytes. One example of these is the cited complex between cross linked polyethers (CPE) and lithium perchlorate, which has at room temperature a conductivity various orders of magnitude higher than that of the corresponding PEO-$LiClO_4$ complex (see Figure 2). Therefore, the use of the former should allow the realization of electrochromic windows capable of operating in ambient conditions.

To confirm this, a solid state EW, having the configuration: glass/ITO/Li_xNiO/

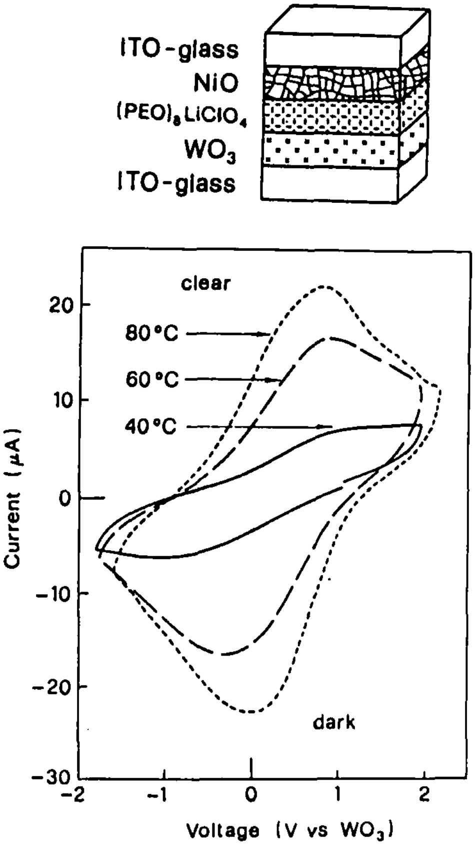

FIGURE 6 Cyclic voltammetry of the $Li_xNiO/PEO\text{-}LiClO_4/WO_3$ solid state electrochromic window at various temperatures.

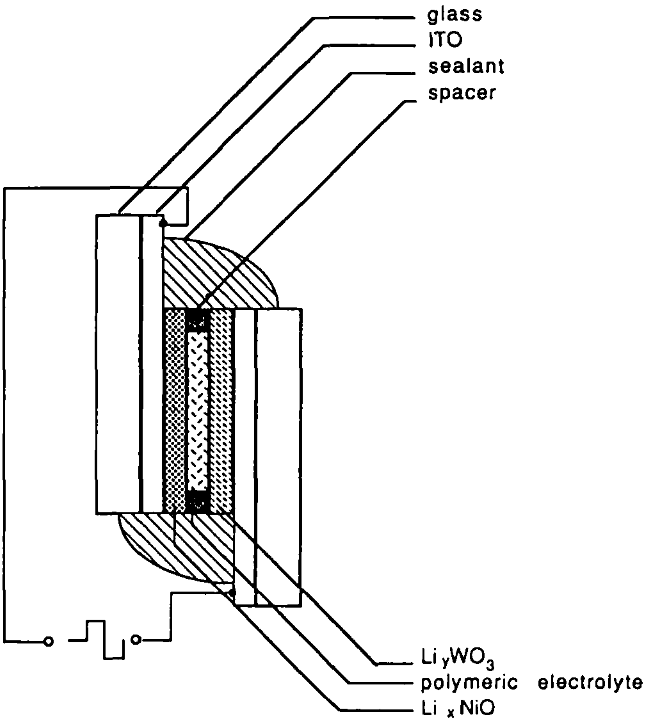

FIGURE 7 Schematic illustration of a solid-state, laminated electrochromic window.

polymer electrolyte/WO_3/ITO/glass (Figure 7), has been realized. The cyclic voltammetry at 25°C of this EW shows well-defined peaks and a manifest colour contrast (Figure 8). In fact, the window is transparent in the anodic cycle (fully intercalated Li_xNiO and pristine WO_3) and reflective in the cathodic cycle (fully intercalated Li_yWO_3 and partly deintercalated $Li_{x-y}NiO$). It may be here useful to remind that a similar window, using the standard $(PEO)_8LiClO_4$ polymer electrolyte, shows no detectable response at the same temperature (compare Figure 6). However, one has to point out that the conductivity of the electrolyte, even if considerably higher than that of standard PEO-$LiClO_4$ electrolytes, is still too low to assure fast response times. Therefore, the use of electrolytes with even higher conductivity at room temperature, i.e. of the order of 10^{-3} S cm^{-1}, should be desirable. As already remarked, various polymer electrolytes having conductivities of this level have been announced and, consequently, the development of high-performance, solid-state electrochromic windows appears now feasible.

Acknowledgments

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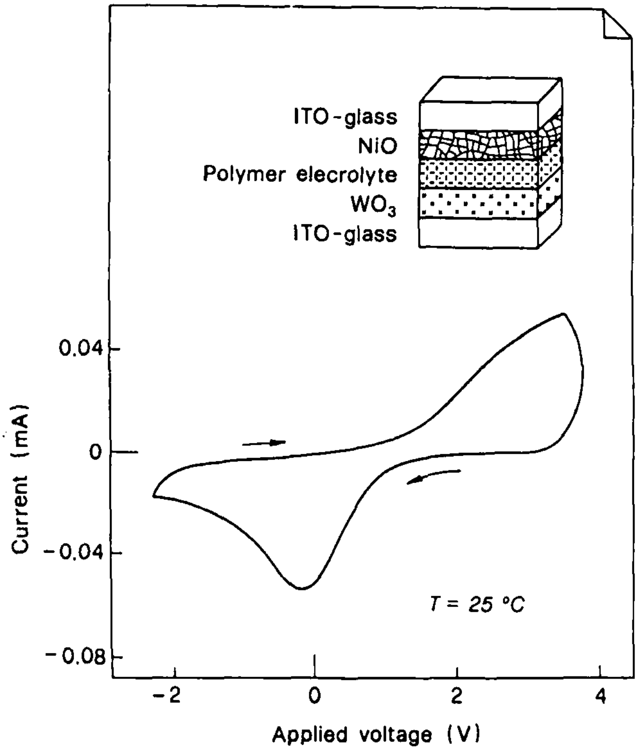

FIGURE 8 Cyclic voltammetry of the $Li_xNiO/CPE\text{-}LiClO_4/WO_3$ solid state electrochromic window at 25°C.

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