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Solid Polyorganodisulfide Electrodes as Ion Storage Layers for Electrochromic Devices

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ABSTRACT

We report on the fabrication and use of new ion storage layers as counter electrodes for completely solid state electrochromic windows. The ion storage layers are transparent composites of a room temperature ion-conducting polymer and an electroactive material based upon the polyorganodisulfide/dithiolate redox couple. Solid state devices consisting of molybdenum doped WO_3 , a polymer ion conductor layer and the new ion storage layers colored rapidly from a pale yellow to a deep blue-green, upon application of 1.2 V d.c. The photopic transmittance changed from 61 to 9%, and the solar transmittance from 45 to 5% during the coloration process, for a typical example. Because the counter electrode does not change optical properties as a function of redox state, problems with color imbalance can be avoided completely. The large number of polyorganodisulfides that may be used for this application allows for flexibility in device design and properties, and the use of solid state components ensures improved stability of windows incorporating this technology.

1. INTRODUCTION

Electrochromic devices known as "smart windows" can be used for the regulation of incident solar energy and glare in buildings, vehicles and aircraft. The world-wide production of flat glass is about 1 billion m^2 per year. In the U.S. alone, glass production is about 470 million m^2 per year (1988), with about 25% for buildings and 11% for automobiles, so the potential for switching applications is very large. Emerging applications for chromogenic materials are automobile mirrors that can automatically regulate glare according to light levels. Prototypes are being tested for automobile sun roofs and visors. Future applications include automobile side and rear windows, architectural glazing and aircraft windows. Chromogenic devices can also be used for large-area information displays in applications where high switching speed is not required, such as for airport display boards. The function of a chromogenic device is to control the flow of light and solar energy through a window, according to an energy management scheme or the desire of the user. This technology can regulate lighting and heating levels for energy load reduction. Substantial savings in lighting and cooling energy consumption and equipment cost may be realized with a significant advantage over existing blinds and drapes.

Although many electrochromic materials themselves are fairly well characterized, optimization of the complete devices has not yet been fully achieved^{1,2}. Fast switching times, good optical properties and stability, the ability to withstand many thousands of cycles and low cost are of primary concern to smart window users. In the invention described herein, a significant improvement in performance for all of these criteria has been achieved by modifying several of the components of the electrochromic device. In particular, we report the use of polyorganodisulfide/dithiolates for counter electrodes in electrochromic devices for the first time. In addition, we have used a modified polyethylene oxide (amorphous PEO) for the ion-conducting layer and as a binder for the counter electrode. This material allows construction of totally solid state devices with improved performance characteristics at room temperature.

2. GENERAL EXPERIMENTAL PROCEDURES

Molybdenum doped tungsten oxide films were deposited potentiostatically from a bath consisting of tungsten and molybdenum metal dissolved in aqueous hydrogen peroxide³. These films were deposited onto 9 ohm/sq. conductive indium-tin oxide (ITO) coated glass electrodes (Donnelly Co. Holland, MI), using a BAS potentiostat/coulometer (model CV-27). The ITO electrodes were ultrasonically cleaned, dipped in ethyl alcohol, dipped in 10-20% sulfuric acid, rinsed in distilled water and dried with nitrogen prior to the deposition. After deposition, the electrodes, approximately 3 x 5 cm in size, were rinsed in distilled water and dried with nitrogen.

works the same with sputtered WO_3 ?

Ion conducting layers were cast onto the coloring electrodes from solutions of high molecular weight amorphous PEO (a-PEO) and lithium triflate (Li:ethylene oxide ratio = 1:20) in acetonitrile (2-4 wt. % solids) and allowed to dry completely. These films were estimated to be less than 10 μm thick.

Ion storage counter electrodes were cast directly onto the dried ion conductor layers from solutions of a-PEO, lithium triflate and the lithium dithiolate salt of the polyorganodisulfide being tested. After drying, another ITO coated glass electrode was placed on top of the ion storage layer, such that the active area of the device was 3 x 3 or 9 cm^2 . The edges were sealed with a hot melt adhesive, and care was taken to prevent contact of the glue with the internal components during the curing. For some experiments, only one layer was deposited on ITO coated glass in order to determine the characteristics of that component individually.

Devices were colored and bleached by application of a controlled potential from a custom d.c. power supply with current regulation. A Cary 14 UV-visible-NIR spectrophotometer was used to measure optical transmittance spectra. In situ spectrophotometry on the WO_3 :Mo electrode was performed using a special quartz cell with a micro-calomel (S.C.E.) reference electrode; a platinum foil counter electrode was used while a potential of -0.7 V vs. S.C.E. was applied to the electrochromic electrode in order to color it.

3. RESULTS AND DISCUSSION

For this work, the electrochromic devices consisted of five layers as shown in Fig. 1: (1) a transparent electronic conductor (indium-tin oxide or ITO) on glass, (2) the electrochromic electrode, consisting of molybdenum doped WO_3 , (3) the ion conductor layer consisting of a polymer electrolyte (4) the ion storage layer, a composite counter electrode comprised of a polymer electrolyte and the dithiolate salt of a polyorganodisulfide and (5) a second transparent electronic conductor on glass.

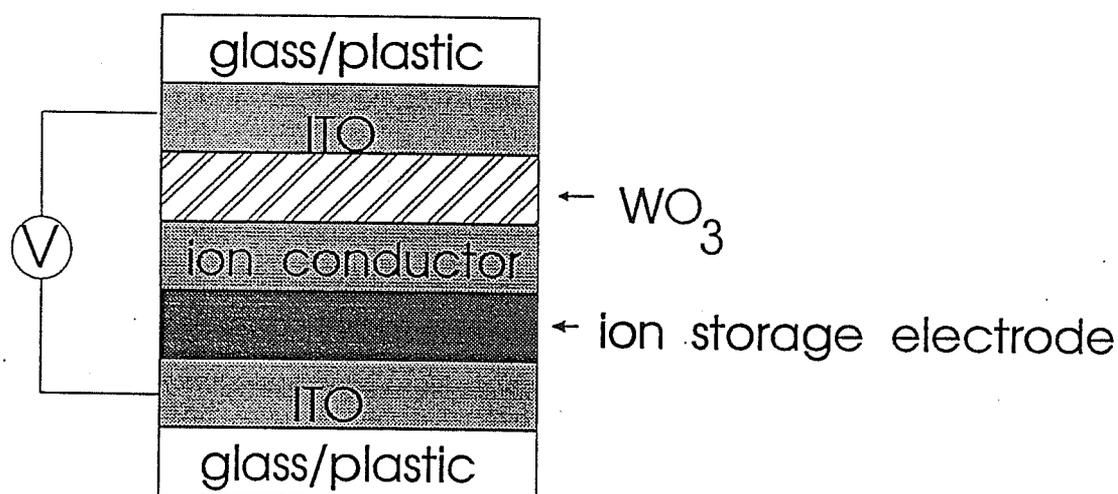


Fig. 1. Construction of the electrochromic devices used in this study.

This construction is similar to a battery, in which a cathode and an anode are separated by an ionically conducting but electronically insulating layer. The indium-tin oxide layers act as current collectors for the device.

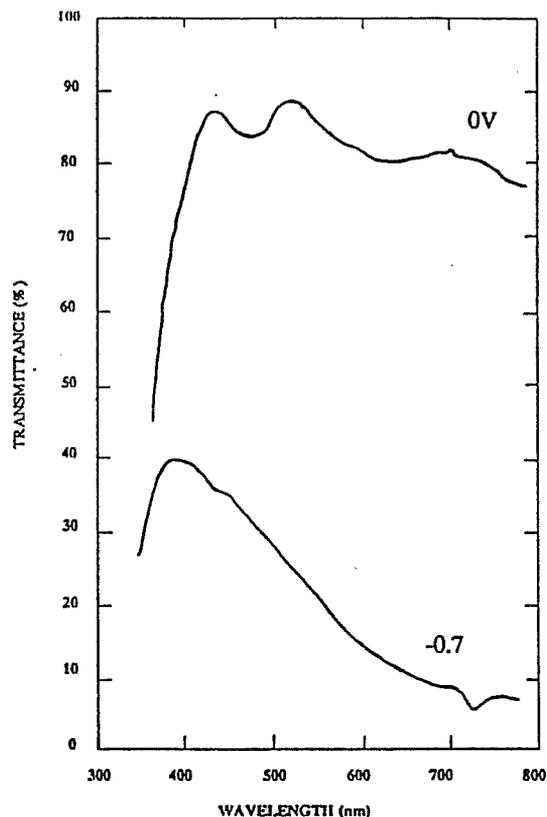


Fig. 2. Normal transmittance for an electrochromic $\text{WO}_3\text{:Mo/ITO/glass}$ electrode in a liquid cell with $0.1 \text{ M H}_2\text{SO}_4$ in the bleached and colored states. The latter was obtained when a voltage of -0.7 vs. S.C.E. was applied to the $\text{WO}_3\text{:Mo}$ electrode, using a platinum foil counter electrode.

The WO_3 used as the electrochromic material for this study intercalates cations upon reduction (application of potential to the device) and deintercalates cations upon oxidation (reversal of the potential). Molybdenum is added to the WO_3 to alter the color from bright blue to gray-blue, but does not participate in the redox process. The visible transmittance spectra for $\text{WO}_3\text{:Mo}$ in both the bleached and the colored state is shown in Fig. 2. The photopic transmittance (T_p) changes from 0.83 to 0.19 when a voltage of -0.7 vs. S.C.E. is applied to the electrochromic electrode in a $0.1 \text{ M H}_2\text{SO}_4$ solution using a Pt foil counter electrode.

The pertinent half-reaction for coloring and bleaching WO_3 is given for lithium ions in equation 1. It should be noted, however, that this reaction is not restricted to Li ions and occurs with other alkali metal cations or protons as well.



In order for the device to function, the counter electrode, or ion storage layer, must undergo the opposite redox process to that of the tungsten oxide electrode. Thus, as the WO_3 is reduced and intercalates cations, the ion storage layer must undergo oxidation and release cations. Upon reversal of the process, the intercalated tungsten oxide compound is reoxidized and releases cations and the ion storage layer is reduced and takes up cations. The counter electrode, then, must also consist of a reversible redox couple. In many cases, this electrode also undergoes a color change upon change of redox state (i.e. it colors as the WO_3 colors and bleaches as the WO_3 bleaches).

In devices where both electrodes undergo color changes simultaneously, it is imperative to match their capacities exactly or the device might not fully bleach. Upon prolonged cycling, parasitic reactions may occur which reduce the capacity of one electrode, even if the electrodes were matched initially. The device then becomes unbalanced and is unable to bleach fully. To avoid this problem, we have chosen the polyorganodisulfide/dithiolate system as the electroactive materials for the counter electrode. These materials, which do not change color as a function of redox state, have been used successfully as highly reversible cathodes in secondary lithium batteries (the solid redox polymerization electrode⁴ or SRPE). Upon reduction, the disulfide linkages in the polymer are broken, and dithiolate salts are produced. Reoxidation causes reformation of the polymer disulfide linkages, and release of cations. Equation 2 shows this process for lithium ions, however other alkali metal ions or protons may also be used.

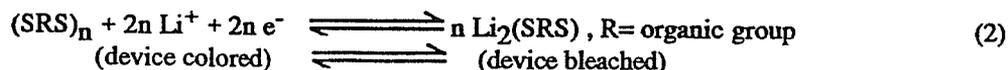


Table 1 shows examples of these materials and some of their physical properties.

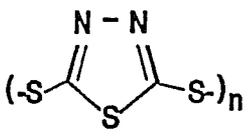
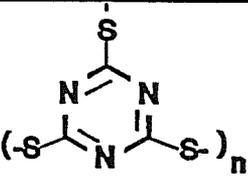
Formula (Notation)	Name of monomer precursor	Physical Properties
$-(\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S})_n$ (X0)	2-mercaptoethyl ether	transparent viscous polymer
 (X1)	2,5 dimercapto- 1,3,4 thiadiazole	off-white to yellow powder. fast redox kinetics at room temperature
 (X5)	trithiocyanuric acid	yellow powder network polymer
$-(\text{SCH}_2\text{CH}_2\text{S})_n$ (X8)	1,2 ethanedithiol	white powder melts at 180° C

Table 1. Organopolydisulfides for batteries and electrochromic windows.

The polyorganodisulfides or organodithiolates used in the SRPEs are inexpensive, easily obtained or synthesized and nontoxic. Furthermore, by changing R groups, it is possible to change the physical and electrochemical characteristics of the compounds, allowing "custom tailoring" of the device to the needs of the user or manufacturer. For example, melt processing may be used with $(\text{SCH}_2\text{CH}_2\text{S})_n$ which is a white powder at room temperature, but melts to a colorless viscous mass at 180 C. Another aliphatic polydisulfide, $(\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S})_n$ is transparent, viscous and colorless at room temperature; it should be possible to make thin films of this material by roll processing. Composite electrodes are readily made by dissolving the dithiolate salts in an appropriate solvent with polymer electrolyte and casting into thin films. Electrodes made in this

fashion are usually colorless or pale yellow. Fig. 3 shows the transmittance spectrum for an ion storage layer containing the lithium dithiolate salt of X1; the integrated photopic transmittance is $T_p = 0.56$.

The large number of usable compounds means tremendous flexibility in device design and characteristics. For this study, we made counter electrodes with the dithiolate salts, and used WO_3 as the electrochromic electrode. It is also possible, however, to start with the organopolydisulfide form in the counter electrode and use an electrochromic material that colors anodically such as NiO, or to assemble a WO_3 device in the colored state, if so desired. Because there is no color change in the ion storage layer it is not necessary to balance its capacity to that of the WO_3 electrode, and insufficient bleaching upon cycling due to the effect of parasitic reactions is no longer a problem. The only requirement, in fact, is that the ion storage capacity be sufficient to allow complete coloring and bleaching for the desired number of cycles (i.e. equal to or greater than the capacity of the WO_3 electrode). This is, in practice, much easier to achieve than the previous requirement for matched electrodes, and thus potentially represents a substantial savings in cost due to simplified device assembly and manufacture.

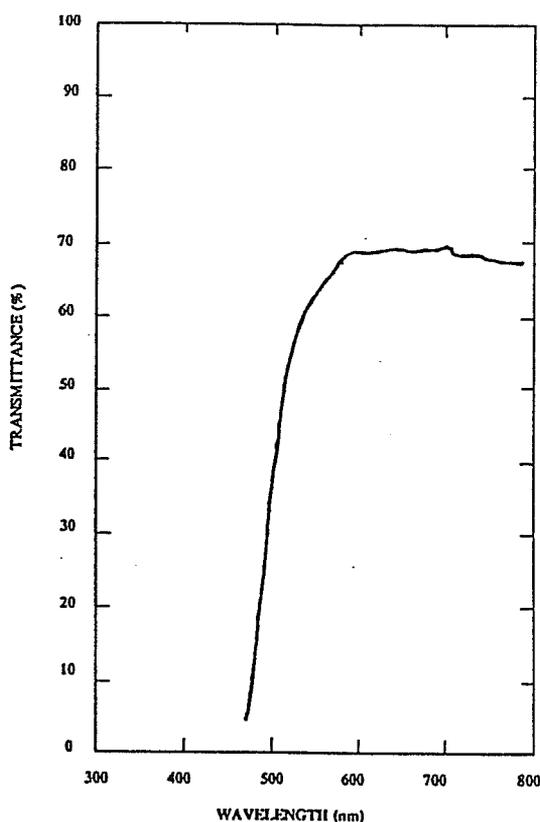


Fig. 3. Spectral optical transmittance of lithium 2,5-dimercapto-1,3,4 thiadiazole salt in a-PEO. Film thickness is approximately $10 \mu\text{m}$. The electrode is faintly yellow to the human eye.

Another major consideration for design of effective electrochromic windows is that of switching speed. Although in the case of large devices ($> 30 \text{ cm}^2$), the electronic conduction of the transparent current collectors can be limiting, the most common cause of sluggish switching is poor ionic conductivity in the electrolyte layer and/or in the counter electrode. Liquids generally have the highest ionic conductivity but may cause problems in electrochromic devices due to sealing difficulties and flow in the vertical position. Solid electrolytes (glasses or polymers), although rigid, usually have low ionic conductivity at room temperature. One exception to this is a class of polymeric materials known as the amorphous polyethylene oxides⁵ (a-PEOs). These have recently been shown to work well as electrolytes in room temperature lithium batteries⁶, but have not been used for electrochromic applications until now. We have used thin films of a-PEO complexed with a lithium salt for the ion conductor (electrolyte) layer and also as an ionically conducting binder for the composite counter electrodes. These

polymers are inexpensive, transparent (Fig. 4), stable, non-toxic and easily fabricated into thin films (10-100 μm) by casting or hot pressing procedures. Most importantly, the conductivity of amorphous PEO/Li salt complexes are sufficiently high at room temperature to allow reliable operation and fast switching of completely solid state experimental windows at room temperature.

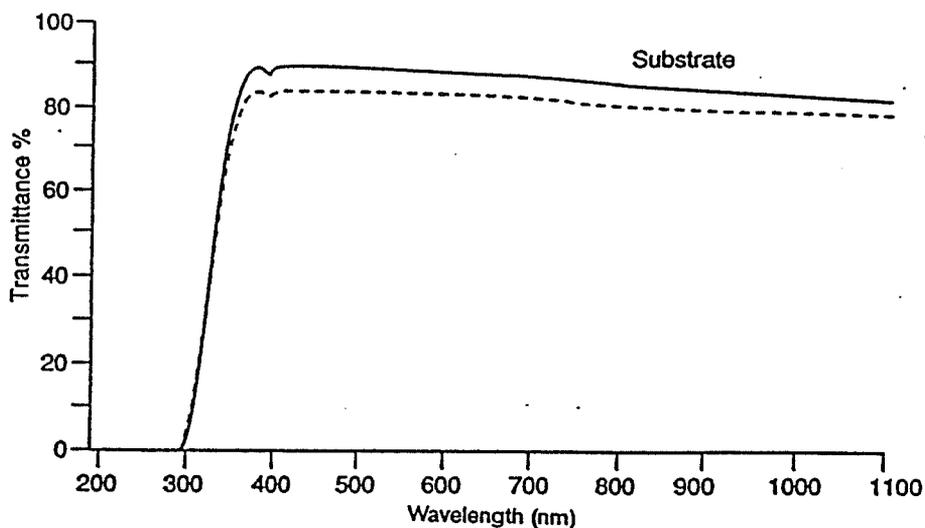


Fig. 4. The optical transmittance of an a-PEO ion conductor layer. The solid line shows the spectrum of the substrate and dotted line that of the a-PEO layer. This material is completely transparent to the human eye.

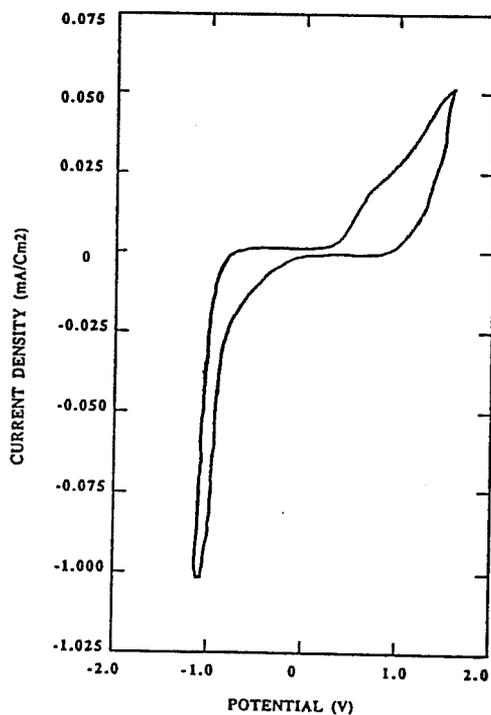


Fig. 5. Current-voltage characteristics of an electrochromic device with a $\text{WO}_3\text{:Mo}$ electrode, an a-PEO ion conductor layer and an ion storage layer containing the lithium dithiolate salt of 2,5-dimercapto-1,3,4-thiadiazole.

We have made several windows using molybdenum doped tungsten oxide and the new ion conducting and ion storage layers described above. In order to determine the potentials needed to achieve coloration and bleaching, current-voltage characteristics of the devices were determined. Fig. 5 shows the profile for a prototype with a ion storage layer containing the lithium dithiolate salt of X1.

When a voltage of about 1.2 V is applied between the $WO_3:Mo$ and counter electrode for this example, current flows and the device rapidly colors to a deep blue-green, indicating that Li ions are intercalating into WO_3 as it is being reduced. Concurrently, the dithiolate salts in the ion storage layer are oxidized to disulfide polymers and release Li ions. When a potential of about -1.0 V is applied to the colored device, rapid and complete bleaching to the original pale yellow occurs, the electrochromic electrode is reoxidized and deintercalates Li, and the counter electrode is depolymerized to the lithium dithiolate salt. Fig. 6 is a schematic showing this process. Switching times for both the coloring and the bleaching processes are less than one minute.

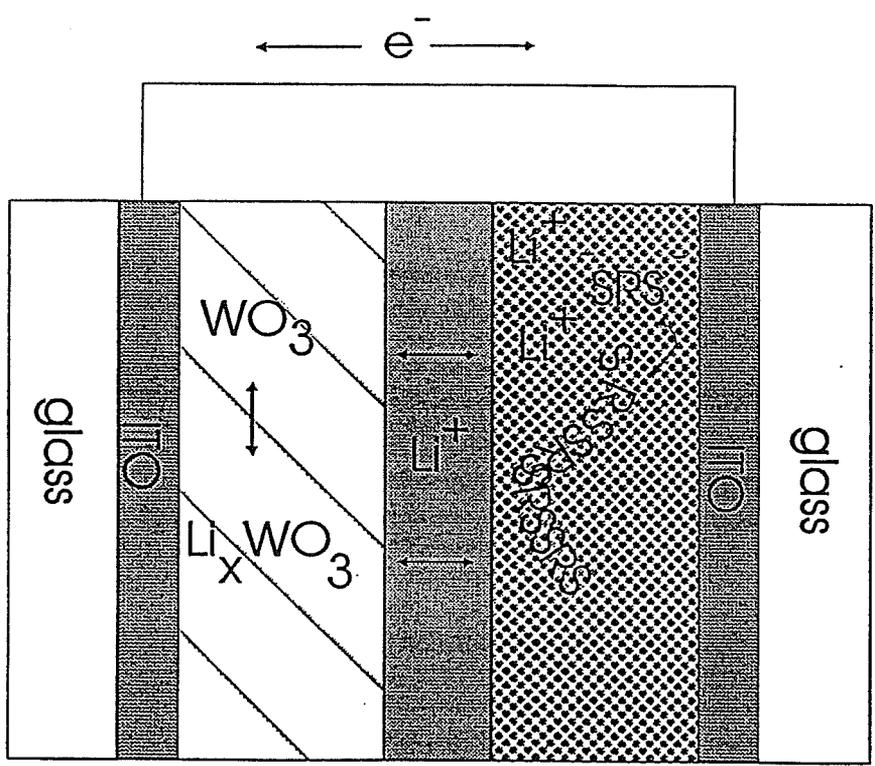


Fig. 6. An electrochromic device using a WO_3 electrode, an a-PEO ion conductor layer and the polymerization electrode as the ion storage layer.

The optical spectra of the device in both the colored and the bleached states are presented in Fig. 7. The photopic transmittance, T_p changed from 0.61 to 0.09 and the solar transmittance, T_s from 0.45 to 0.05, upon coloring (solar properties derived from data not shown in Fig. 7). The optical properties and switching times vary somewhat depending upon the compounds used in the ion storage layer, but the results presented above are fairly typical. The devices remain stable in both the colored and bleached states, and cycle well. A full investigation of the properties of these prototypes with respect to lifetime and cycling is still ongoing, but the early results show distinct improvements in performance over existing windows.

repeatable?
how many cycles?
temperature cycling?

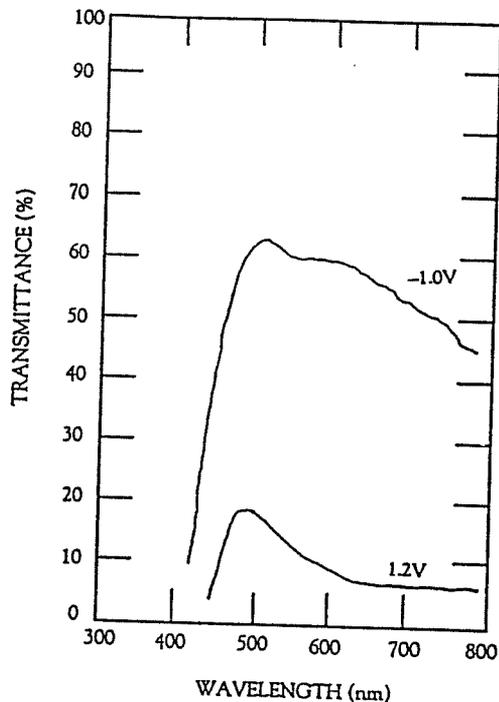


Fig. 7. The optical transmittance of an electrochromic device with a $WO_3:Mo$ electrode, an a-PEO ion conductor layer, and an ion storage layer containing the lithium dithiolate salt of X1, in the colored and the bleached state.

4. SUMMARY

We have described the invention of a new ion conductor and ion storage layers for electrochromic devices. The use of these new components allow construction of a stable, completely solid state window with excellent optical properties and switching times. Because the new ion storage layer does not change color as a function of redox state, there is no need to match the capacity to that of the WO_3 electrode. This greatly simplifies the assembly process, and thus represents a potential savings in manufacturing cost. The organodithiolate or polydisulfide materials used in the ion storage layer are inexpensive, non toxic and, in many cases, already commercially available or are easily synthesized. The wide range of compounds that may be used in the ion storage layer allow for flexibility in the manufacturing of components and device assembly as well. Use of a new polymer electrolyte that has high ionic conductivity at room temperature allows the device to be assembled from completely solid state components and ensures good mechanical stability and reliability. Tests on prototypes show some of the best performances in terms of switching times and optical properties for any electrochromic windows to date.

5. ACKNOWLEDGMENTS

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