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Electrodes**

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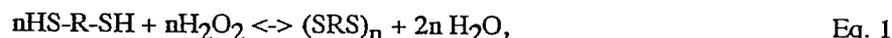
ABSTRACT

The use of polyorganodisulfides as optically passive counter-electrodes in a variety of electrochromic devices are discussed. Characteristic data is presented for electrochromic devices using proton, and lithium coloration ions with polyethylene oxide electrolyte and polydimercaptothiadiazole positive electrodes. Solid state devices consisting of molybdenum doped WO_3 , amorphous polyethylene oxide electrolyte (a-PEO), and a polyorganodisulfide counter-electrode 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. Also, our experiments with polyimidazole are detailed. This family of compounds due to its unique electrical and ion conduction properties allow a single composite ion storage and ion conductor electrode to be made, simplifying the device construction. Devices made from this family of compounds color to deep blue-gray upon application of 1.2-1.5 V. Bleaching occurs at -0.4 to -0.5V. The photopic transmittance changed from 55 to 9%, and the solar transmittance from 34 to 4% during coloration. Both coloration and bleaching are quite rapid.

1. INTRODUCTION

The tremendous demand for switchable window systems for glazing in a variety of applications such as buildings, automobiles and aircraft windows has inspired fundamental and technical breakthroughs in non-aqueous and solid-state electrochromic technology^{1,2}. Still, ongoing refinement of electrochromic device components continues to challenge the researchers in the field. Advanced glazing systems must demonstrate strong improvements in terms of stability, cycle life and ease of fabrication. In this vein, a good deal of effort has been directed towards non-proton, lithium electrochromic systems². Several inorganic metal oxide ion conductors have been made with varying success, with weakness in either ion conductivity, poor temperature range, mechanical properties or processability. Alternatively, relative ease of matching can be realized through the use of solid polymer electrolytes such as amorphous polyethylene oxide (a-PEO). Since their inception by Armand³ solid polymer lithium systems have captured the interest of numerous researchers. Much of the early work on solid polymer electrolytes was done in the temperature range of 60 to 100 C, where polyethylene oxide has suitable ionic conductivity. Since then, a number of groups have reported solid polymer electrolytes with acceptable conductivity at ambient temperature⁴, significantly broadening the scope of applications for solid polymer electrolytes.

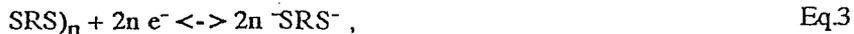
The approach in our laboratory has included the use of solid polymer electrolytes in combination with polymeric organodisulfides and/or polythiols. These materials are termed solid redox polymerization electrodes (SRPE's) to reflect the dynamic process of polymerization/ depolymerization that occurs as these electrodes are oxidized and reduced. Considerable success has come from the use of SRPE's in lithium-polymer batteries. Chemical synthesis of the polymers is easily accomplished by oxidation of di- or tri-mercaptans by an appropriate oxidant as shown in equation 1,



where R is an organic group such as ethyl, phenyl, etc. The synthesis of a number of such polymers has been described in our battery work⁵⁻⁷. The polymers are very inexpensive (\$3-4/lb.), are non-toxic, and biodegradable. Among the advantages of the polymeric organodisulfides is the tremendous chemical flexibility in altering the physical, chemical, and electrochemical properties of the polymers through synthetic means. In addition to moderation of properties through the choice of the organic group R, copolymers are easily generated through oxidation of a mixture of mercaptans,

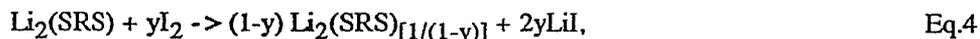


or through reaction of the polymers in the solid state⁸. The redox process for SRPE's can be represented by equation 3,



for a simple linear polyorganodisulfide. The polymerization/depolymerization of polyorganodisulfides and polythiols can be represented schematically as shown in Fig. 1.

If the redox process for the polyorganodisulfides proceeds in a linear fashion, the average molecular weight of the polymer is a function of the percent oxidation of the monomer as described below,



and as shown for polydimercaptothiadiazole, X1 in Fig. 2.

Clearly, the average molecular weight is fairly low until oxidation of the monomer is greater than 85%. The mechanism for assembly/disassembly of the polymer in the positive electrode has not yet been established. The formation of dimeric anions, $\text{ } ^-\text{SRS}^- - 2e^- \leftrightarrow \text{RSSRS}^-$, appear to play an important role. The presence of dimeric anions is evidenced in the discharge curves for battery based, Li/PEO/SRPE cells by a slight drop in the discharge voltage at approximately 50% of the discharged capacity⁵⁻⁷. If reduction of the polymer proceeds by snipping discrete units off the ends of the polymer chain, i.e. removal of monomer, dimer, or trimer end groups, high molecular weight polymer could persist up to 50% reduction of the polymer (Fig. 3). However, the average composition would still follow Fig. 1. This effect tends to stabilize the mechanical properties of the film. For the case of polythiols (Fig. 1b), the molecular weight of the polymer is not affected by the redox process.

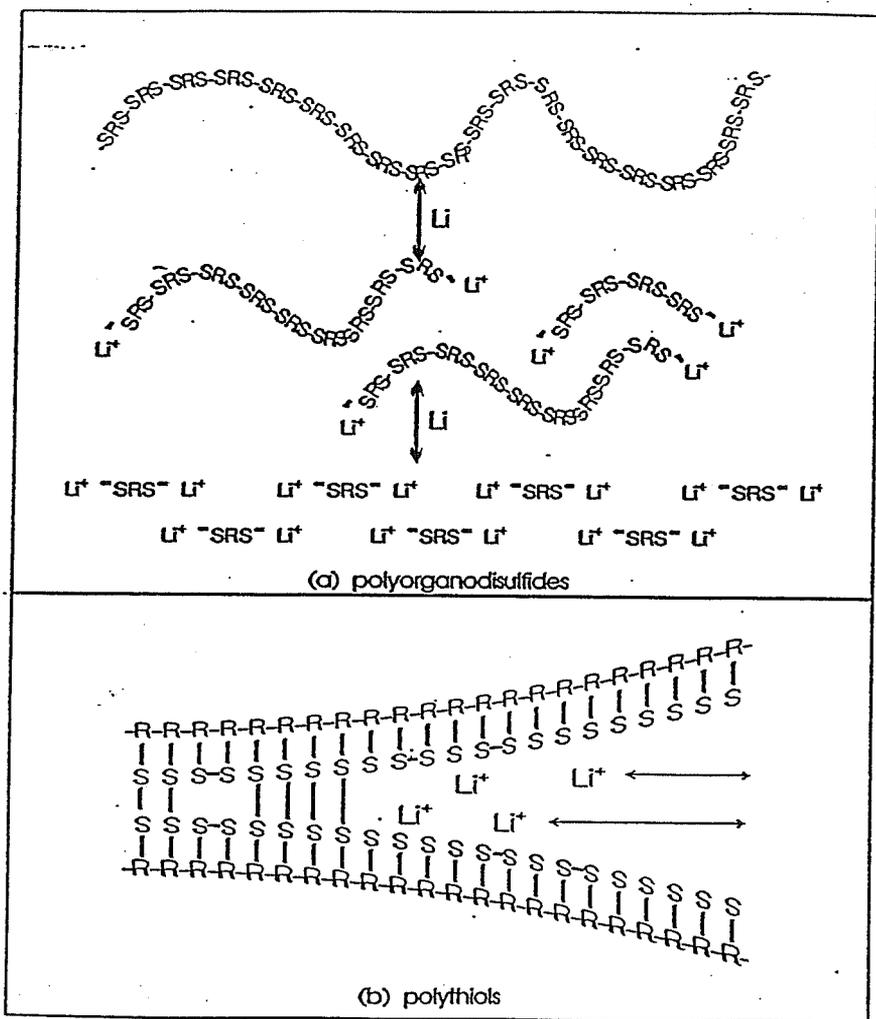
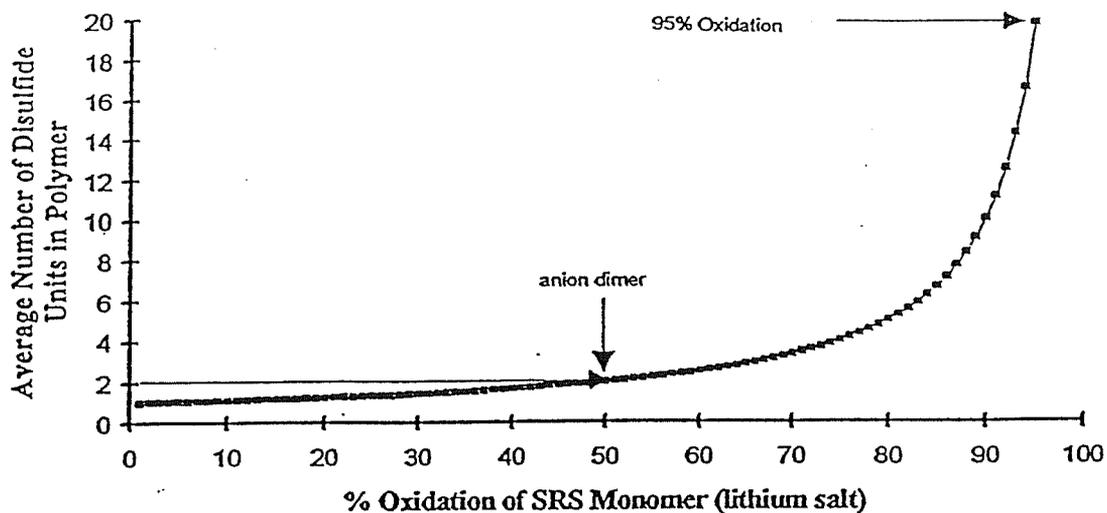
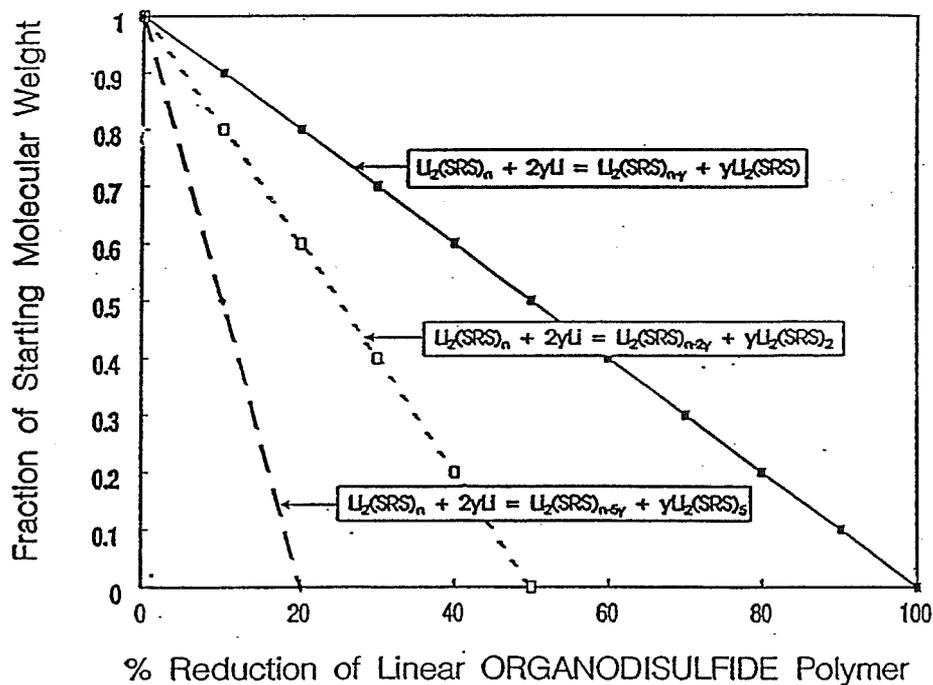


Fig. 1. Idealized redox behavior of (a) organodithiolates and (b) polythiols.



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Fig. 2. Average molecular weight for linear polymerization of dithiolate anions as a function of % oxidation of anions.

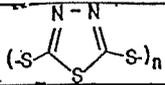
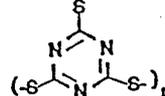


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Fig. 3. Relative change in molecular weight of polymer chains if redox scission of disulfide bonds removes discrete units from the ends of the polymer chains.

For the SRPE's where R is a small organic group such as CH_2CH_2 , the equivalent weight of the polymer can be as low as 46 grams/equivalent making these materials attractive for use in electrochromic windows (Table 1). Furthermore, a number of polyorganodisulfides and their corresponding thiolate salts are essentially transparent in the visible spectrum. Accordingly, polyorganodisulfides can function as transparent, optically passive, counter electrodes in electrochromic devices.

TABLE 1

ID	SRPE	Description	E. W. equiv/g	mAh/g	mAh/cc	V _{nom} vs. Li	Wh/kg	Wh/l
Li	Lithium		7	3,829	2,045	0		
X0	$(\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S})_n$	clear, viscous liquid	76	353	564	2	646	885
X1		pale yellow powder	74	362	652	3	993	1,483
X5		pale, yellow powder	58	462	739	3	1,237	1,629
X8	$(\text{SCH}_2\text{CH}_2\text{S})_n$	white powder	46	583	932	2	1,012	1,281

1.1. Use of SRPE's in Electrochromic Devices

Electrochromic devices can be used for the regulation of incident solar energy and glare in buildings, vehicles, and aircraft. The worldwide production of flat glass is about 1 billion m^2 per year, so the potential for switching applications is very large. A schematic representation of a typical 5-layer solid-state electrochromic device is shown in Fig. 4.

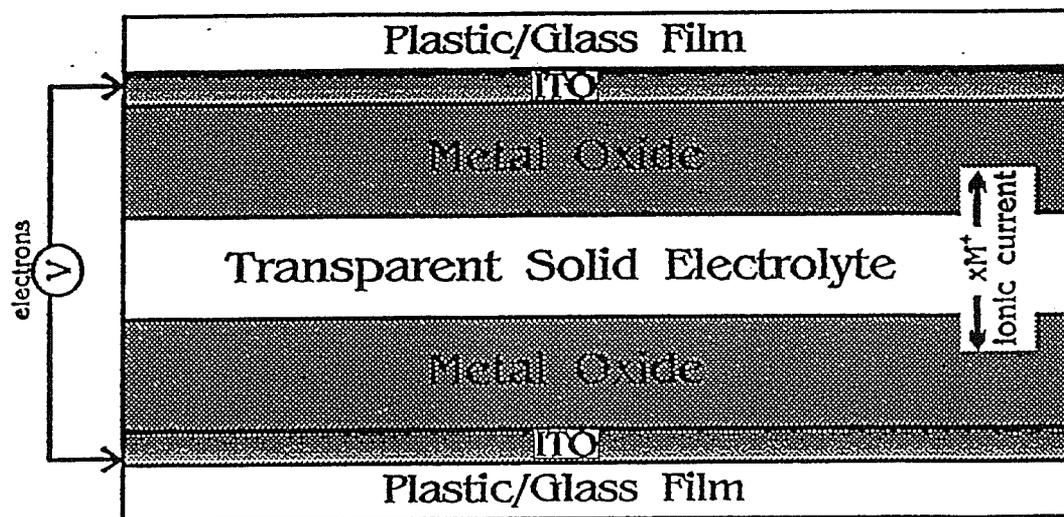
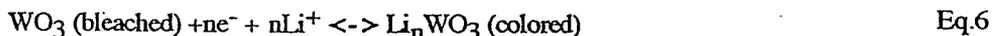


Fig. 4. Schematic representation of solid-state electrochromic device consisting of transparent indium-doped tin oxide (ITO) current collectors, solid polymer ion conductor, metal oxide electrochromic and ion storage layers.

In a typical device, metal oxide insertion (or intercalation) electrodes are chosen such that coloration of the electrochromic electrode occurs upon application of a sufficient voltage bias across the cell. An example is, one of the electrodes colors upon oxidation while the other electrode is usually passive upon reduction; similarly upon application of a sufficient reverse bias, complementary bleaching of the two electrodes occurs. However, upon prolonged cycling, parasitic reactions may reduce the capacity of one electrode, even if the electrodes were matched initially. The device then becomes unbalanced and is unable to bleach fully. One way to avoid this problem is to use an optically passive ion storage electrode that undergoes redox without

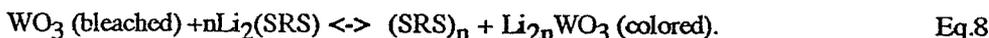
an associated color change. Since the majority of the known electrochromic electrodes reversibly insert (or intercalate) cations, a suitable redox electrode would possess electroactive anions such as the organothioliates. We have been granted a patent covering devices made using these materials¹⁰. The pertinent half-reaction for coloring and bleaching WO_3 can be represented as,



and for the SRPE,



giving a cell reaction for the electrochromic device as:



In the case of an optically passive SRPE, the capacity need not be matched to the electrochromic electrode, but rather would be formulated with excess capacity. A diagram of such a device is shown in Fig. 5.

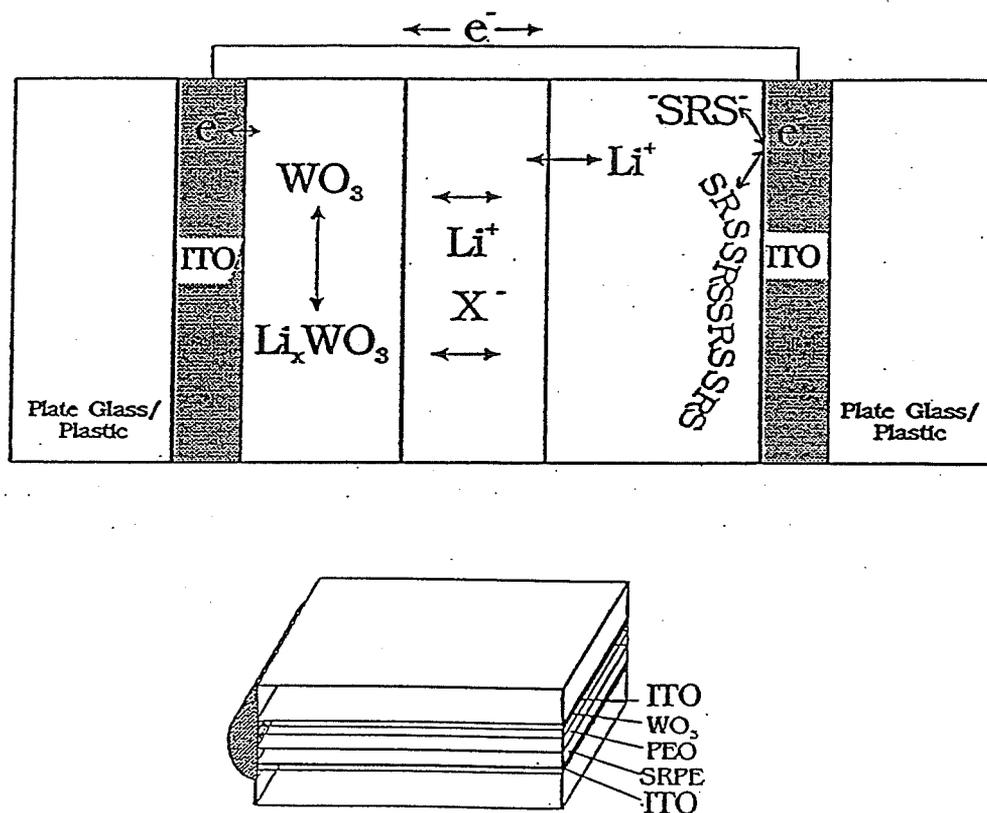


Fig. 5. Solid-state electrochromic device based on solid redox polymerization electrodes. Coloring/bleaching reaction occurs only at metal oxide electrode; SRPE is optically passive and functions only as redox active ion storage electrode.

Since the polyorganodisulfides are not electronically conductive, the redox reaction must take place in the vicinity of the transparent current collector. Fortunately, the amount of charge needed to reversibly color and bleach many electrochromic electrodes is quite small, in the range of 25 to 40 mC/cm^2 , and can be achieved with polyorganodisulfides in the absence of conductive additives. This is also possible because the electrolyte layer is much thinner than in lithium polymer batteries. In batteries, carbon is added to the electrolyte to increase electrical conductivity for charge capacities up to 2-3 C/cm^2 .

2. EXPERIMENTAL

2.1 WO₃/a-PEO/SRPE and WO₃/composite SRPE Electrochromics:

Molybdenum doped tungsten oxide films were deposited potentiostatically from a bath consisting of tungsten and molybdenum metal dissolved in aqueous hydrogen peroxide onto conductive indium-tin oxide (ITO) coated glass electrodes (Donnelly Co. Holland, MI), using a BAS potentiostat/ coulometer (model CV-27). Other methods can be used to make these electrodes including reactive sputtering, e-beam evaporation and sol-gel deposition. We have experimented with substrates made by all methods. The best substrate in terms of optical properties and rapid switching is those made potentiostatically, the next best are made by reactive e-beam evaporation, followed by sputtering. The least durable are the sol-gel deposited coatings, although these may be improved in the future. 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. Ion conducting layers were cast onto the coloring electrodes from solutions of high molecular weight amorphous 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 microns thick. For the composite SRPE devices the ion conductor layer was unnecessary. Ion storage counter electrodes were cast directly onto the dried ion conductor layers from solutions of amorphous PEO (a-PEO), lithium triflate and the lithium dithiolate salt of the polyorganodisulfide being tested. Upon drying of the SRPE films, the polymer electrodes were either colorless or pale yellow, depending on the choice of thiolate salt. Electrochromic cells were assembled as shown in Fig. 5. 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 cm or 9 cm². 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. Devices were colored and bleached by application of a controlled potential from a custom D.C. power supply with current regulation. A Cary 14 and a Perkin-Elmer Lambda 9 UV-Vis-NIR spectrophotometer were used to take optical transmittance spectra. WO₃ 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 WO₃ to alter the color from bright blue to gray-blue, but does not participate in the redox process. In-situ spectrophotometry on the WO₃:Mo electrode was performed using a special quartz cell with a micro-calomel 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

3.1 WO₃/a-PEO/(X1)SRPE Cells:

The solid-state cyclic voltammogram for polydimercaptothiadiazole (X1) is shown in Fig. 6. The CV exhibits the chemically reversible and kinetically quasi-reversible behavior characteristic to organodisulfides^{11,12} and polyorganodisulfides. In fact, polydimercaptothiadiazole exhibits the fastest electrode kinetics of any of the organodisulfides or polyorganodisulfides examined so far.

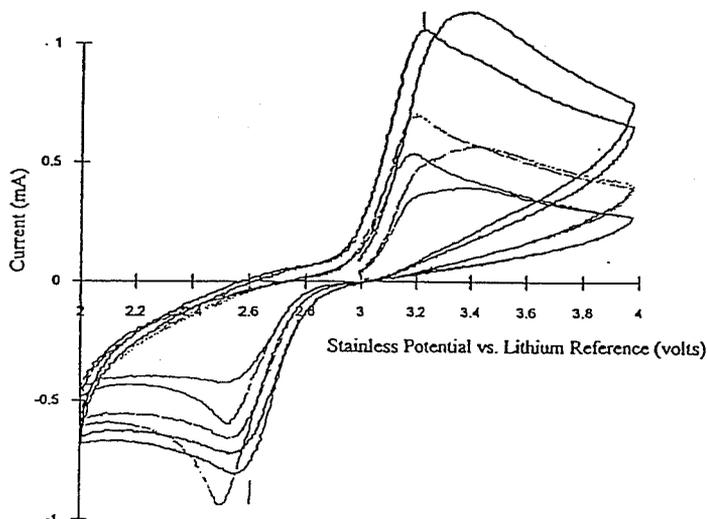


Fig. 6. Solid-state cyclic voltammogram of polydimercaptothiadiazole in amorphous PEO electrolyte at 88 C. A 30 micron lithium foil reference and counter electrodes were used in the solid-state cell.

Amorphous PEO electrolytes were found to have good dimensional stability and excellent optical properties. The optical transmittance of an a-PEO electrolyte is shown in Fig. 7. The electrolyte films appear completely transparent to the human eye. The spectral properties of an SRPE/a-PEO film is shown in Fig. 8; the electrode is faintly yellow to the human eye. Tungsten oxide, WO_3 , intercalates cations upon reduction (application of potential to the device) and deintercalates cations upon oxidation (reversal of the potential) as described in equation 6. The visible transmittance spectra for $WO_3:Mo$ in both the bleached and the colored state is shown in Fig. 9. The photopic transmittance (T_p) changes from 83 to 19% when a voltage of -0.7 vs. S.C.E. is applied to the electrochromic electrode in a 0.1 M H_2SO_4 electrolyte.

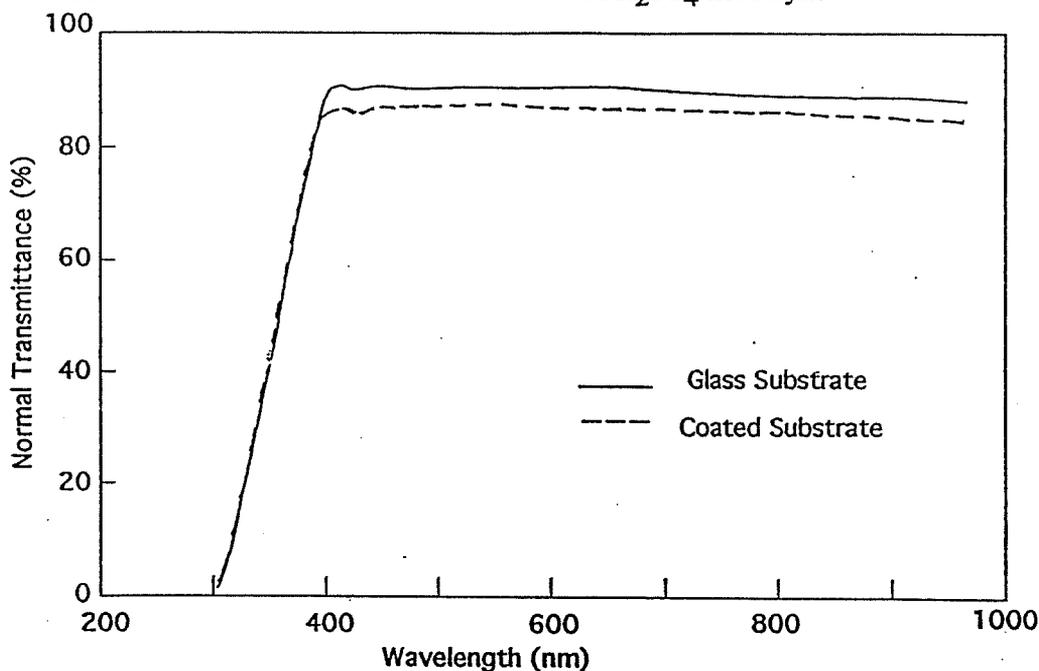


Fig. 7. Spectral normal transmittance of an a-PEO electrolyte layer. The solid line shows the spectrum of the substrate and dotted line that of the a-PEO layer.

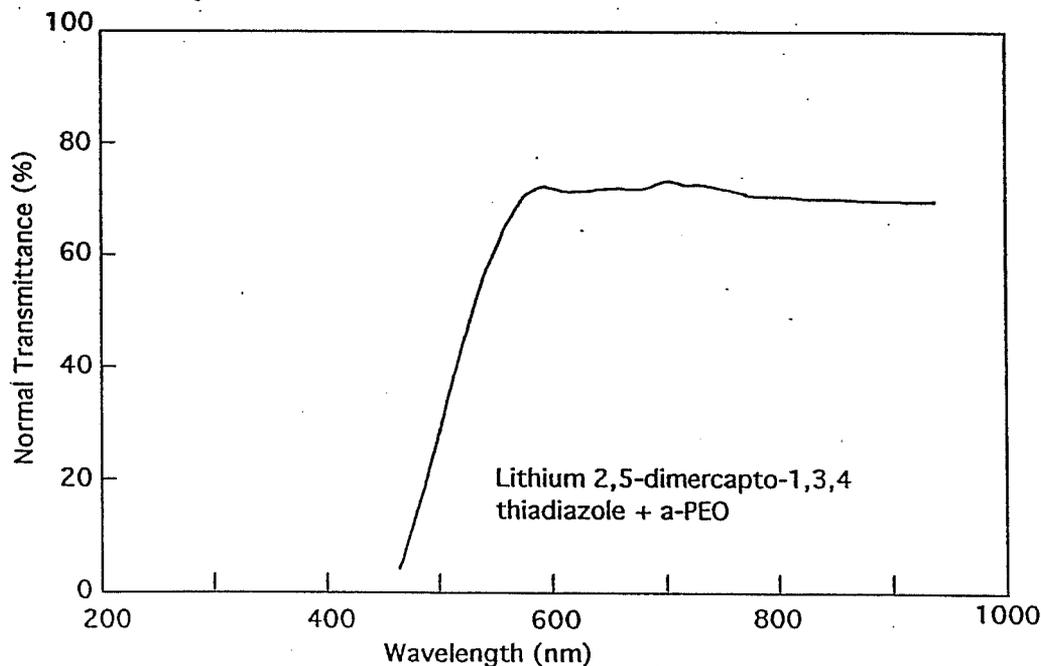


Fig. 8. Spectral normal transmittance of lithium 2,5-dimercapto-1,3,4 thiadiazole salt in a-PEO. Film thickness is approximately 10 microns. The electrode is light yellow in color.

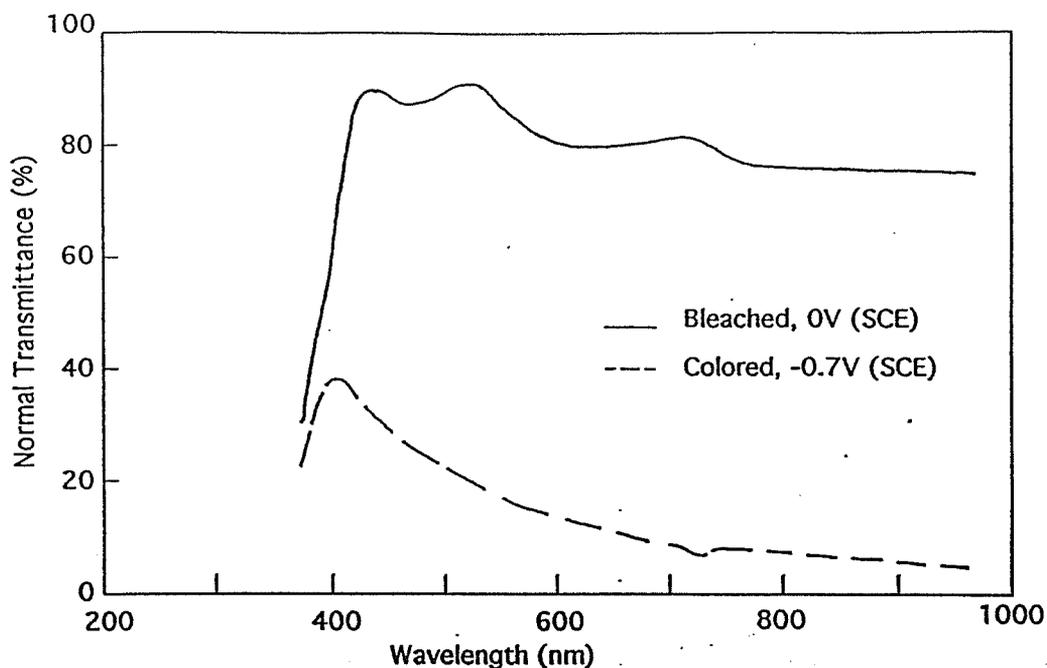
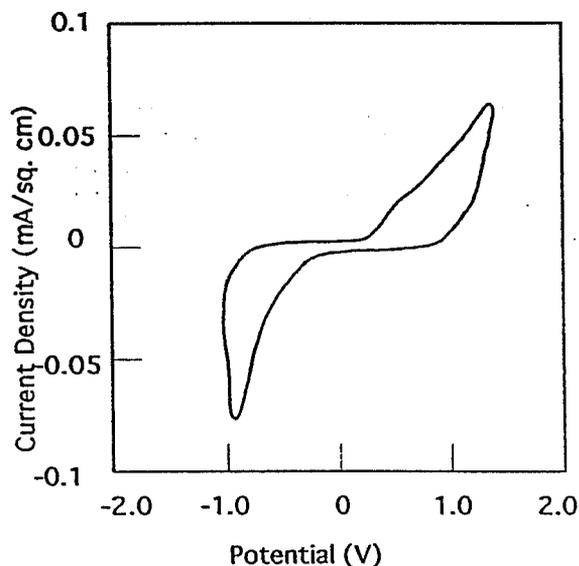


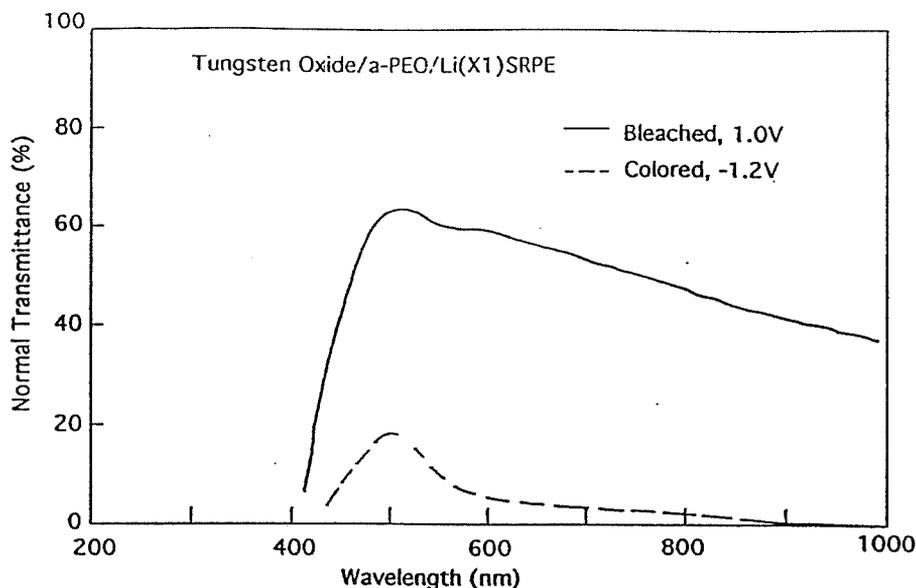
Fig. 9. Spectral normal transmittance for an electrochromic $\text{WO}_3\text{:Mo/ITO/glass}$ electrode in a liquid cell ($0.1 \text{ M H}_2\text{SO}_4$) in the bleached and colored states. Coloration occurs at a voltage of -0.7 volts vs. S.C.E.

The current-voltage characteristic of a $\text{ITO/WO}_3\text{/a-PEO/SRPE/ITO}$ device is shown in Fig. 10. When a voltage of about 1.3 V is applied between the $\text{WO}_3\text{:Mo}$ 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. Switching times for both the coloring and the bleaching processes are less than one minute.



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Fig. 10. Current-voltage characteristics of an electrochromic device with a $\text{WO}_3\text{:Mo}$ electrode, a-PEO solid electrolyte, and ion storage later containing the lithium dithiolate salt of 2,5-dimercapto-1,3,4 thiadiazole.



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Fig. 11. Optical transmittance of electrochromic device having a $WO_3:Mo$ electrode, a-PEO solid electrolyte, and ion storage layer containing the lithium dithiolate salt of 2,5-dimercapto-1,3,4 thiadiazole.

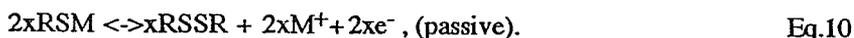
The optical spectra of the device in both the colored and the bleached states are presented in Fig. 11. The photopic transmittance, T_p changed from 61 to 9% and the solar transmittance, T_s from 45 to 5%, upon coloring. The optical properties and switching times vary somewhat depending upon the compounds 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; laboratory cells have demonstrated a few thousand switching cycles thus far.

3.2. $WO_3/a\text{-PEO}+(Z1)SRPE$ Cells:

This electrochromic device combines both the ion storage and ion conductor electrode in the electrochromic device. This layer uses a reversible mercaptan or organothioliolate electrode and an electrochromic film. We currently have a patent pending on this device construction and use of mercaptans and organothioliolate compounds as ion storage layers¹³. The key elements of a window device using this system are an electrochromic material serving as the optical switching material, which can be electro-colored by the dual passage of ions (H^+ , Li^+ , Na^+ , K^+ , Ag^+ , OH^- , F^- , O^{2-} , etc.) and electrons; a reversible redox material from the mercaptan or organothioliolate compound families serving as both an electrolyte and ion storage medium; and conductor layers serving as pathways for electron flow. The redox material can be a mercaptan or organothioliolate salt in a solid polymer electrolyte (Examples are: 2-mercapto-1-methyl imidazole in polyethylene oxide or lithium salt of dimercapto-thiadiazole in polyethylene oxide and lithium triflate). Upon coloring of this device, the mercaptan or organothioliolate dimerizes to form disulfide compounds and the cation and electron, for example, move into the coloring electrode. Upon bleaching of the device, scission of the disulfides occur to give back the original mercaptan or organothioliolate. In operation, the electrochromic film is switched from transparent to colored and reversed by ion transfer. The reversible reactions in tungsten oxide and a generalized mercaptan are:

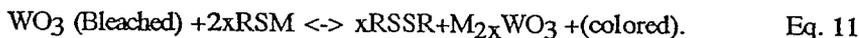


and for the mercaptan,



Where $M = H, Li, \text{ etc.}, R = \text{Organic Group}$.

Giving the cell reaction for the electrochromic device as:



A typical device which may be constructed using this composite electrode is shown in an Fig. 12. Here is shown a pair of transparent conducting films, an electrochromic film, and a reversible ion storage layer (mercaptan or organothiolate). Figure 13 shows the minimum structure where the electrochromic is dispersed into the composite ion storage layer. Optical switching data is shown in Fig. 14 for a device with a structure in Fig. 12. A tungsten oxide device made from one of these polymers had properties of $T_p = 55-6\%$ and $T_s = 34-4\%$, coloring at -1.2 V d.c.. The device using the ion conductor as a separate layer could also use the organothiolate and mercaptan ion storage material (as shown in Fig. 5). The current-voltage response for this composite device is shown in Fig. 15. Devices using mercaptans or organothiolates appear to have very good potential for large-area applications. Improvements in the optical response can be made by chemical modification.

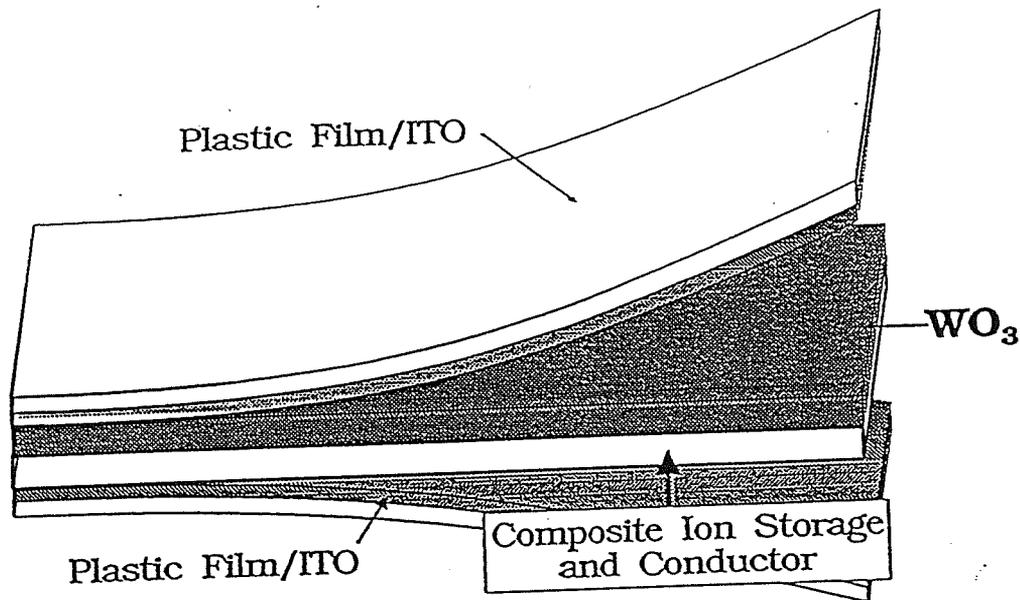
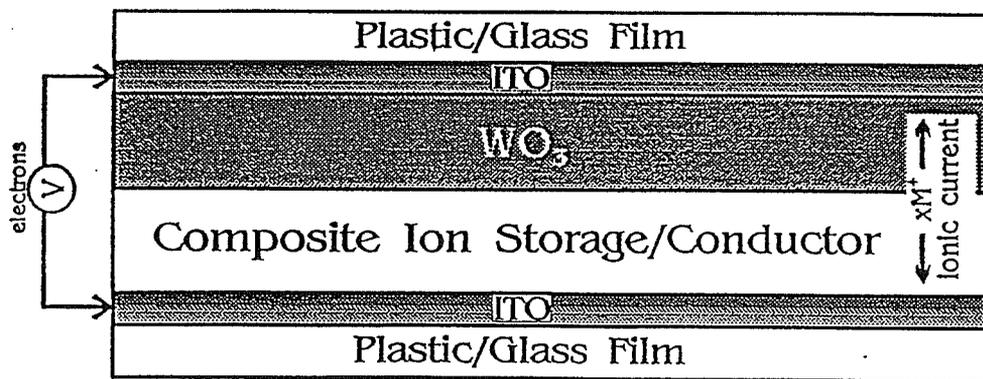
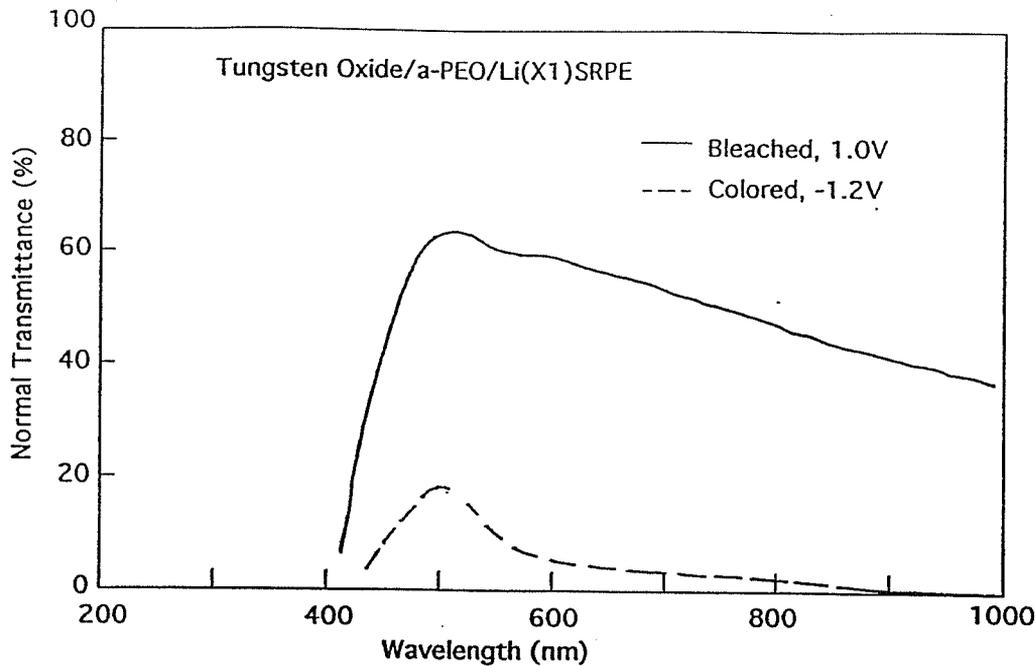


Fig. 12. A flexible electrochromic device configuration. Shown are a pair of conducting films on a plastic film, one coated with a layer of tungsten oxide. These films are laminated together with a composite ion storage layer.



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Fig. 13. A cross-section of the minimum device structure showing electronic and ionic currents.



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Fig. 14. The spectral optical response for a device consisting of ITO/WO₃/a-PEO and imadazole complex/ITO. This device colors from light gray to deep blue-gray.

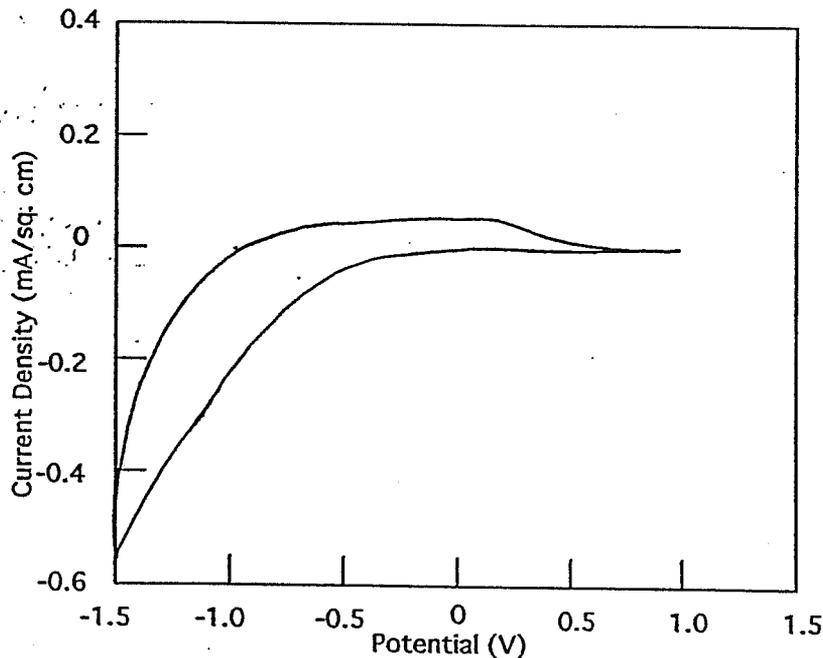


Fig. 15. The current-voltage response for a ITO/WO₃/a-PEO and imadazole complex/ITO electrochromic device, cycled at 20 mV/s. The device size is 4 x 3 cm.

4. CONCLUSIONS

Polyorganodisulfide and polyimidazole electrodes have unique advantages as passive counter electrodes for electrochromic devices. The polymers are easily synthesized, have great chemical flexibility, are inexpensive, and possess very low equivalent weights. Polyorganodisulfide electrodes function well as ion-storage electrodes in solid polymer electrochromic devices. Amorphous PEO appears to be a good electrolyte for this solid-state device, exhibiting adequate ionic conductivity at room temperature and good mechanical stability. The use of a-PEO electrolytes and SRPE ion-storage electrodes 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 electrodes. This greatly simplifies the assembly process, and thus represents a potential saving in manufacturing cost. We will continue to develop these materials in our future studies.

5. ACKNOWLEDGEMENTS

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