Solid State Electrochromic Switchable Window Glazings

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NOTICE

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Abstract

Multilayer, solid state electrochromic coatings based on a-WO$_3$ (amorphous WO$_3$) have been tested. A typical coating on glass consists of indium-tin oxide (520 nm), WO$_3$ (410 nm), MgF$_2$ (170 nm) and gold (15 nm) all deposited by vacuum evaporation. Optical spectra and solar weighted, integrated transmission values are given for the component films and complete multilayer devices. Electrical characteristics and electrooptic responses are reported. Devices with MgF$_2$ layers deposited at low pressures have high internal resistances and exhibit long term optical memories suitable for diurnal switching. The replacement of the gold electrode layer with an indium-tin oxide layer greatly increases the transmittance of the electrochromic coating stack (from solar weighted transmission of 22% to 53%). Electrochromic coatings have promise for solar gain control windows, but further improvements in optical and electrical efficiencies are needed.

Introduction

Multilayer, solid state electrochromic coatings are being evaluated for possible application in windows for solar heated and energy efficient buildings[1]. The potential of electronic control over solar gain and daylighting levels offers several obvious advantages over mechanical shades and shutters. Other environmentally actuated transmission control mechanisms such as thermochromic and photochromic glasses, polymers, and coatings provide much less opportunity for optimization of daylighting or solar gain strategies than does an electronically actuated mechanism.

A practical electrochromic coating must satisfy several criteria. It must be effective, efficient, durable, and economical. To be effective the coating must admit a large fraction of the radiation when desired and block a large fraction when necessary. The maximum transmission should probably be in excess of 50% for most applications, and the coating should be able to reduce the transmission by at least 90% (corresponding to a change in optical density, Δ O.D. = 1) to be effective in solar gain and daylighting control. The optical switching must be fast enough for the application. In order to control glare in daylighting applications, a switching speed of ~1 O.D./min or faster may be required, but many solar applications could tolerate much slower switching, ~0.05 O.D./min. An efficient electrochromic coating should require little electrical energy for operation. In some solar applications, switching may be diurnal, and an optical memory of several hours could reduce the overall energy consumption. In daylighting applications, more frequent switching is expected and a shorter memory may be preferred as it is usually associated with a faster switching speed and higher electrooptic efficiency (the change in optical density for a unit area per amount of charge transported, Δ O.D. cm^2/mC). An electrooptic efficiency of 1 O.D. change with 1 cm^2/charge transfer at ~5V applied potential corresponds to ~0.3 Wh/m^2 per complete switching cycle. In a solar application, the solar energy being controlled by this switching operation may exceed 6,000 Wh/m^2. A diurnally switched coating would have to endure about 11,000 cycles in 30 years. A daylighting control film may experience 200,000 cycles over the same period. The coating could be placed on the interglazing surface of a sealed, insulating window to protect it from weathering and abrasion. Finally, for the coating to be considered economical, it should be cost competitive with other options such as awnings, venetian blinds, etc. These generally cost many dollars per square foot (over a 30 year period), whereas multilayer coatings can now be mass-produced on architectural glass by vacuum deposition at a cost of less than $21.50/m^2 ($2/ft^2), so long as the materials involved are not precious (gold, silver, iridium, etc.).

Solid state, multilayer electrochromic coatings based upon a-WO$_3$ were first reported by Deb in 1974[2] and proposed for use in solar windows by Deb in 1977[3]. Coatings of this original configuration (Fig. 1) appear to have many of the necessary features for solar and daylighting applications. It is the purpose of the ongoing research to examine the feasibility of such use after optimizing their performance for solar applications. This paper reports results obtained in the first year's efforts.

Experimental Procedures

Multilayer devices such as shown in Fig. 1 were fabricated by thermal evaporation of the individual layers sequentially in a liquid nitrogen trapped, diffusion pumped system

(Varian 3118 vacuum coater). Three separate, well shielded tungsten or tantalum boats were used to evaporate the component layers. A quartz crystal monitor was located coplanar with the substrate 38 cm above the evaporation sources. Post deposition film thicknesses were measured with a mechanical stylus thickness gauge (Tencor Alpha-Step).
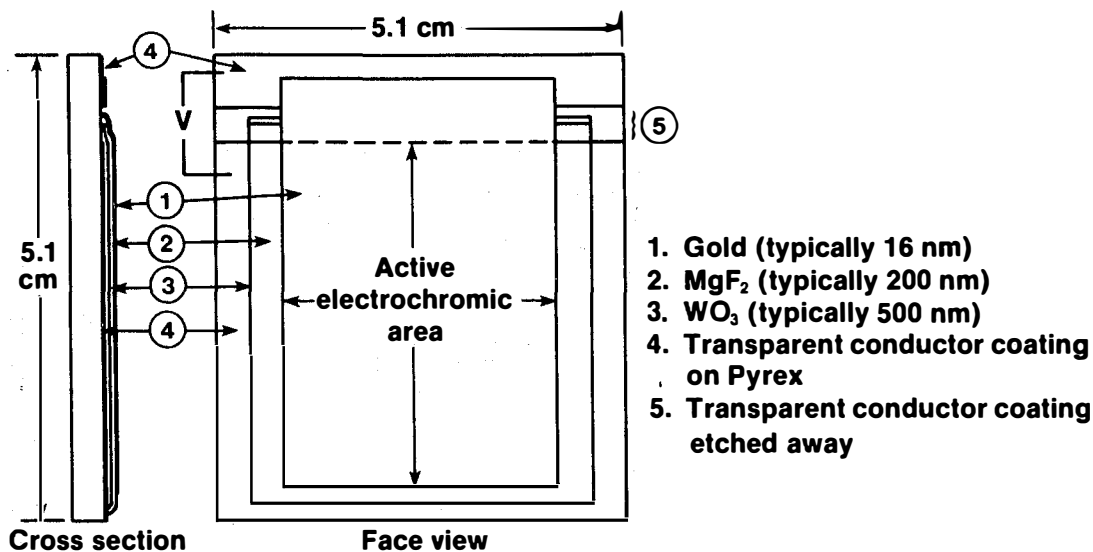
5.1 cm

5.1 cm

V

Active electrochromic area

1. **Gold (typically 16 nm)**
2. **MgF$_2$ (typically 200 nm)**
3. **WO$_3$ (typically 500 nm)**
4. **Transparent conductor coating on Pyrex**
5. **Transparent conductor coating etched away**

Cross section   **Face view**

Fig. 1. Solid state electrochromic test device configuration (typical active area ~12 cm^2).

Evaporation conditions are listed in Table 1. High partial pressures (up to 133 Pa) were maintained during the deposition of WO$_3$ by the use of a metering valve and were measured by a capacitance manometer (MKS Baratron). Either pure oxygen or pure water vapor could be admitted at controlled partial pressures during the evaporation.

Table 1. Typical Characteristics of Electrochromic Test Devices

Cell	Layers	Thickness (nm)	Dep. Rate (nm/s)	Temp. ($^{\circ}$C)	Press. (Pa) $\times 10^{-3}$	T_{SOL} (%)	R (Ω)	E-O Eff. (cm^2/C)
35-4	Pyrex (5 mm)					19	10.7	8.6 (color)
	SnO$_2$:F	380	NA	NA				23 (bleach)
	WO$_3$	490	.56	25	133. (O$_2$)			
	MgF$_2$	100	.24	25	2.7			
	Au	20	.10	25	1.3			
38A	Soda Lime (3 mm)					22	200	26 (color)
	ITO	520	NA	NA	NA			9.8 (bleach)
	WO$_3$	410	.68	25	26.7(O$_2$)			
	MgF$_2$	170	.24	25	1.3			
	Au	15	.25	25	1.2			
47-7	Soda Lime (3 mm)					53	75	NA
	ITO	450	NA	NA	NA			
	WO$_3$	500	1.27	25	26.7			
	MgF$_2$	100	.48	25	1.3			
	ITO	215	3.67	25	133. (O$_2$)			
					533. (AR)			

*T_{SOL} - AM 1.5 solar weighted transmittance in transparent state
 R - Electrical resistance at ~ 0V in transparent state
 E-O Eff. - Electrooptic efficiency = change of O.D. with charge transport per unit area at the reference O.D. of 0.1 and wavelength 633 nm
 NA - Not available.

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Optical measurements were made in a Perkin-Elmer 340 spectrophotometer interfaced with an LSI-II minicomputer. Solar weighted values of transmission were obtained by integration of the spectrum in the wavelength range of 200 to 2200 nm with weighting factors appropriate for an air mass 1.5 solar spectrum (ANSI/ASTM Standard E-903). Electrical measurements were generally made with the sample mounted in the spectrophotometer and optically monitored with a monochromatic 633 nm beam.

Substrate cleaning was found to be a critical step in the procedure of preparing large area electrochromic coatings. The cleaning procedure with the highest level of success to date includes: mechanical cleaning with detergent; rinse in deionized water; etch in a solution of sulfuric acid and hydrogen peroxide (1:1 by volume); rinse in deionized water; rinse in isopropyl alcohol; and vapor degrease in isopropyl alcohol vapor just prior to mounting in vacuum chamber.

Results

Optical Measurements

The optical transmission of typical component layers and complete multilayer devices were recorded. Figure 2 shows typical spectra along with solar weighted transmissions for the device design originally reported by Deb. Notice that the thin gold electrode layer drastically reduces the device transmission. Thinner gold films, while significantly more transparent, would still introduce unacceptable losses in transmission, would provide precarious electrical contacts, and ultimately may be too expensive in a practical electrochromic device.
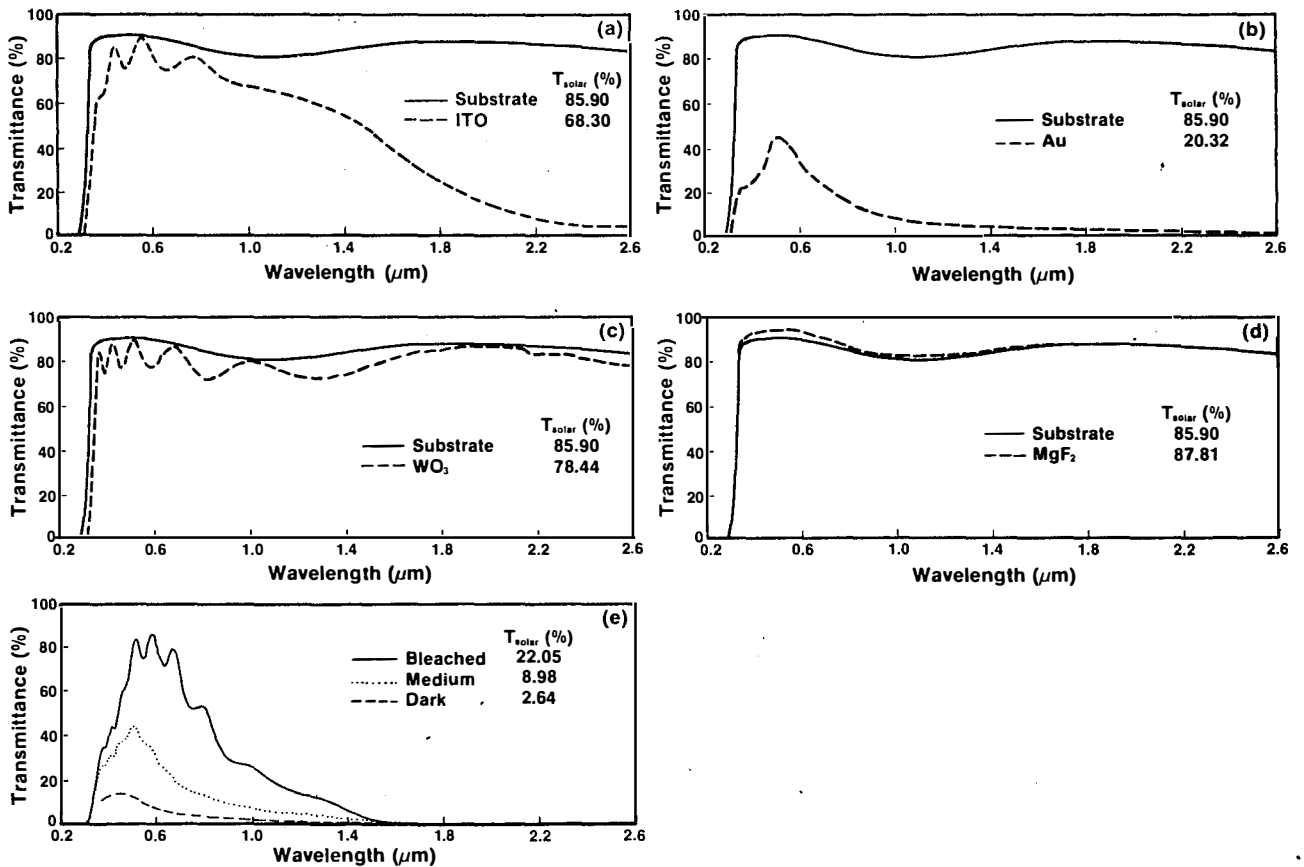

Fig. 2. Optical spectra of component films and completed electrochromic devices: (a) soda lime glass substrate and indium-tin oxide (ITO) coated substrate, (b) substrate with 14.5 nm Au, (c) substrate with 500 nm WO$_3$, (d) substrate with 100 nm MgF$_2$, (e) cell #38A.

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Attempts were made to prepare devices with transparent, conductive indium-tin oxide top electrodes deposited by reactive sputter deposition from a 90 wt % In:10 wt % Sn target. To ensure maximum transparency and conductivity of the ITO, it is common practice to deposit these coatings on substrates heated or post-baked to relatively high temperatures (typically 350°)[4]. However, the a-WO$_3$ undergoes irreversible changes above 135°C. Since these changes reduce its electrochromic performance, our ITO coatings were deposited at room temperature. Figure 3 shows a typical transmission spectrum of a device with such a top electrode (215 nm thick, 160 Ω/□). Even though the ITO is far less than optimum, it demonstrates the marked improvement in optical properties which may be possible. Further work is required to improve the electrical and optical characteristics of this top electrode. The ITO in Fig. 3 is insufficiently conductive to permit efficient and uniform electrochromic operation.
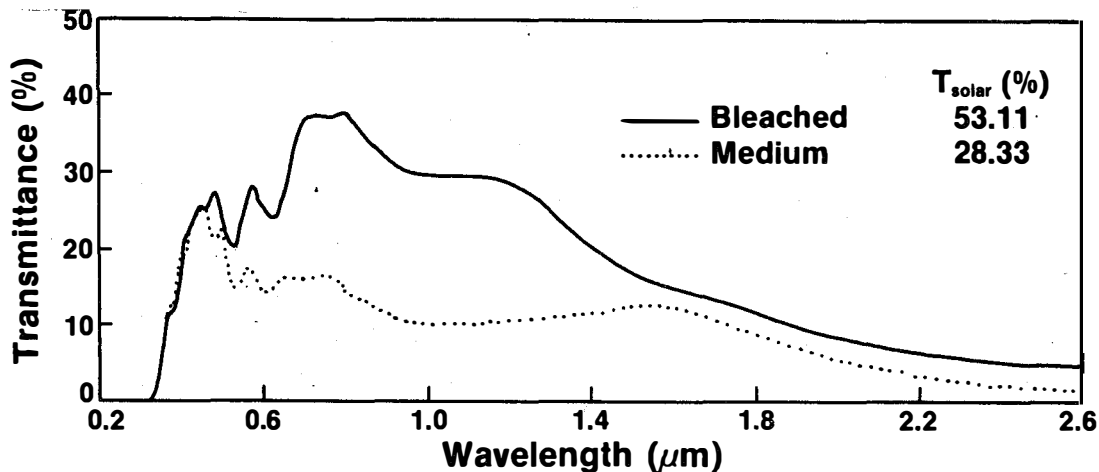

Fig. 3. Optical spectra of cell #47-7. An ITO top electrode coating was used on this cell instead of a gold film.

Electrical Measurements

The current/voltage (I/V) characteristics were measured while monitoring transmission of the sample at 633 nm. Figure 4 shows the response of a typical device to square wave, constant current excitation. Figure 5 shows I/V curves and coloration response under triangular wave voltage excitation for the same device. Notice that the resistances of our test devices are considerably higher than others have reported[6]. The high resistance has been obtained by use of a relatively thick layer of MgF$_2$ deposited at 1.3×10^{-3} Pa. Devices fabricated under such conditions exhibit good optical memory with spontaneous bleaching time constants ~20 hours (unless they contain defect "short circuits").

The colored electrochromic device exhibits an emf much like a solid state battery, and bleaches as it spontaneously discharges through an external load resistor. Figure 6 shows typical results. There is strong evidence that the discharge characteristics, the optical memory time constant and the electrooptical efficiencies in these devices are adversely affected by occasional "short circuit" defects through the devices. Sometimes finished devices draw large currents, but fail to show electrochromic activity. Localized Joule heating identifies the location of the defect, and when it is excised by scribing a small circle around it through the gold electrode, the remaining area functions normally. Occasionally several such areas are found in a 17-cm^2-area device. Such defects are far more prevalent in devices fabricated on SnO$_2$:F coated glass than on ITO coated glass, and in both cases may be dependent on substrate cleaning care. Even in devices which appear to behave well, there is evidence that defects may be limiting performance. In one experiment, a cell with a ~1/2 hour memory decay constant was deeply colored and then part of the gold electrode area was carefully removed by rubbing with a dry cotton swab. The swabbed area, electrically disconnected from the remainder of the device, maintained its coloration for more than 24 hours while the rest of the device spontaneously bleached in less than 1 hour. We do not yet know the nature, nor the causes of such defects.
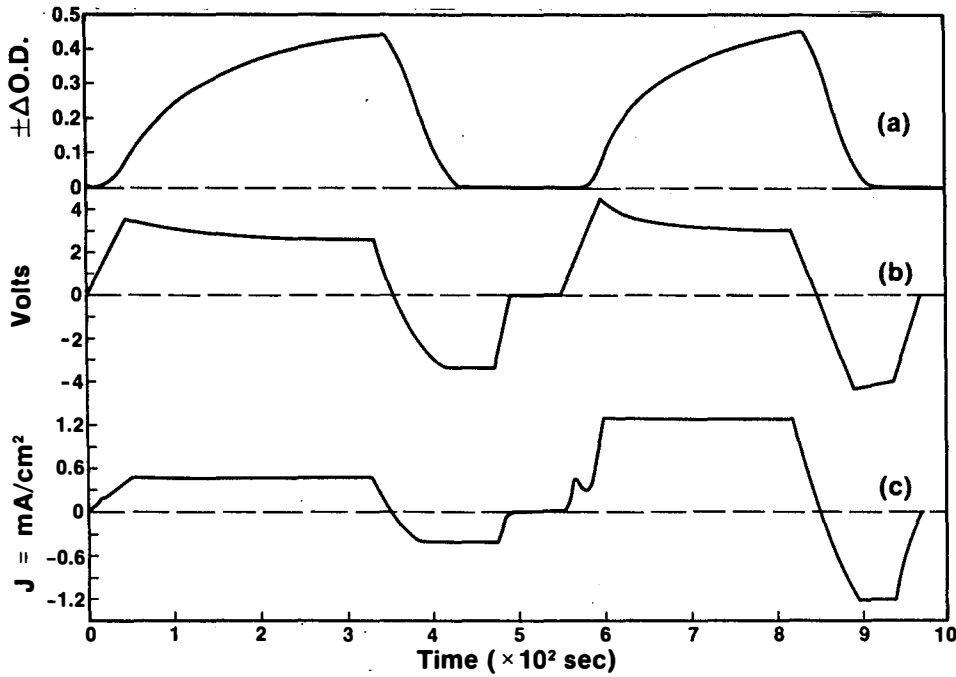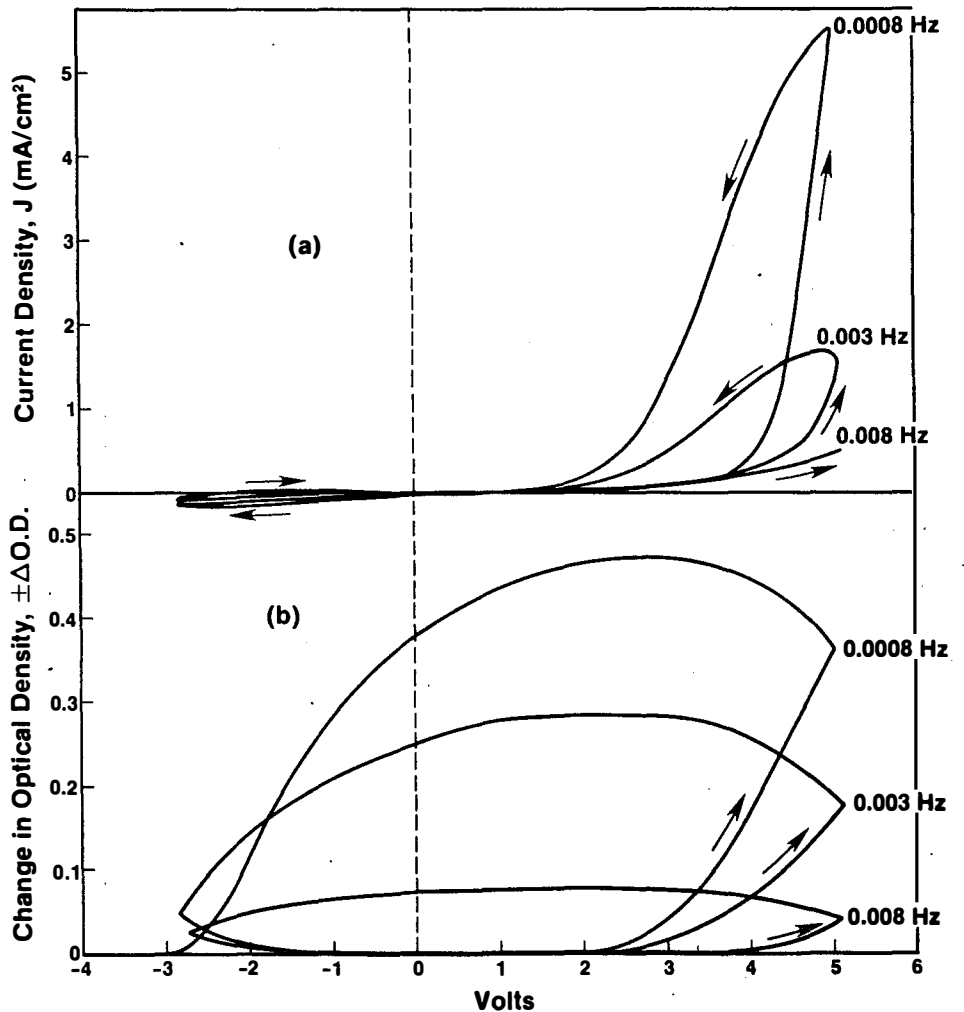
Fig. 4.

Electrooptic behavior of cell #35-4:
(a) change in optical density with constant current coloration and bleaching
(b) voltage across cell
(c) imposed current density.

Fig. 5.

Response of cell #35-4 under triangular wave voltage excitation:
(a) current vs. voltage
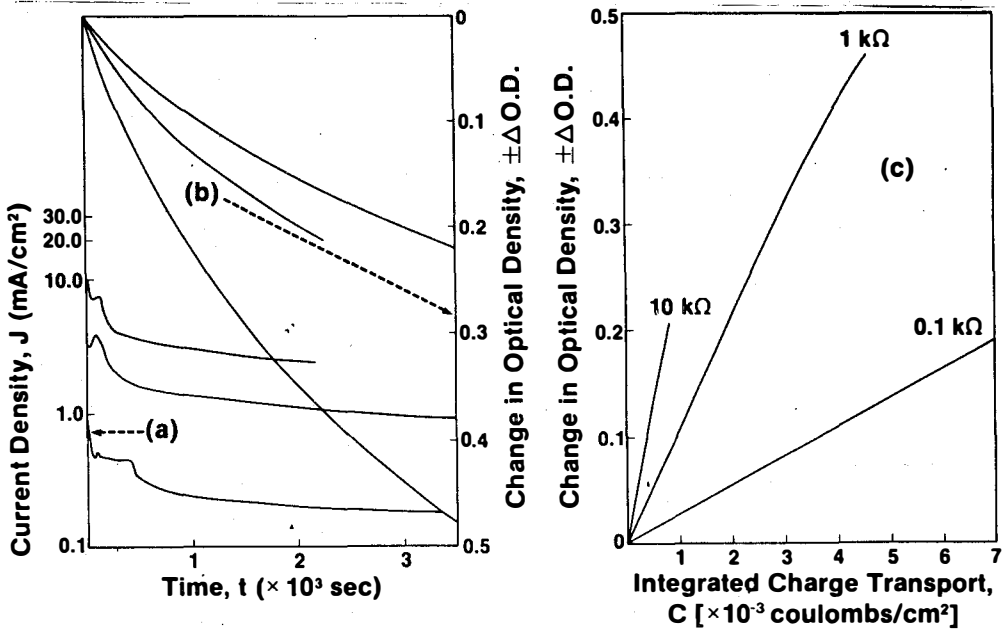(b) coloration vs. voltage (optical measurement at 633 nm wavelength).

Fig. 6. Spontaneous decoloration of cell #38A through externally attached load resistors:
(a) electrical currents
(b) optical densities
(c) optical density vs. integrated charge during spontaneous decoloration.

Keeping in mind that defects may be dominating the behavior, it is still instructive to calculate the device electrooptical efficiency. Fig. 7 shows measured optical densities (633 nm) vs. integrated current densities for two devices. The rate of change in O.D. is a measure of efficiency. The values characteristic of our devices are considerably lower than has been reported elsewhere for liquid electrolyte cells[5] and for some solid state devices with fast response[6]. Long term memory effect appears to be associated with high MgF_2 resistance which is also associated with low electrooptic efficiencies. By altering the conditions of the MgF_2 deposition, an optimum balance of efficiency and memory may be obtained[6].
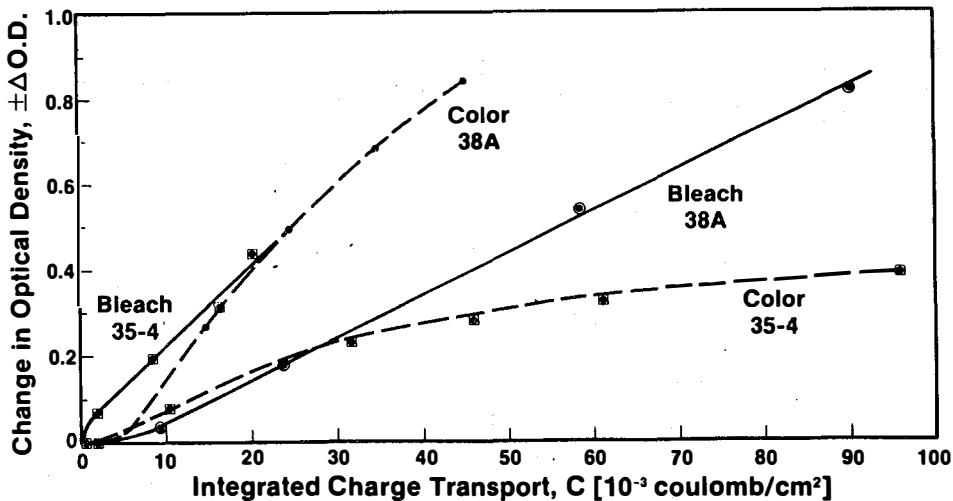

Fig. 7. Optical densities vs. integrated charge transport in cells #38A and #35-4.

Discussion

Solid state electrochromic devices of relatively large areas can be fabricated with acceptable electrooptical efficiencies and long-term optical memories. However, alternative, more highly transparent electrode materials will have to be developed to replace the thin gold layer. It is possible to use reactive sputtering to produce workable ITO electrodes on the a-WO$_3$ devices at room temperature without compromising the electrochromic behavior. However, such ITO coatings have poor conductive and far from optimum transmittance. Both the electrical conductivity and the optical transmittance of ITO are strong functions of deposition temperature[7]; major improvements should be possible by performing the deposition at a compromise temperature slightly above 100°C.

The durability of solid state electrochromic devices such as these have been variously appraised in the technical literature[6,8,9]. Similar devices are reported to gain oxygen during coloration and to lose hydrogen gas during bleaching in (humid) air[8]. Bubbles of evolved gas are reported to form under the electrode films and to cause their disruption and device failure under some circumstances, particularly when high charging or discharging rates are used[9]. This agrees with our own experimental evidence in which the electrode films failed within ~2 seconds upon application of high voltages, typically 30-40 volts. The apparent interaction of such devices with atmospheric water vapor and the presumed dependence of the electrochromic process upon water vapor casts serious doubts on the practicality of any such coating in a window application.

On the other hand, Deneuville and coworkers[6] have concluded that a properly fabricated device based on a-WO$_3$ and MgF$_2$ uses only internal water and need not degrade with time. Other workers have also reported long life, solid state electrochromic devices which showed no signs of electrode degradation nor loss of efficiency during cyclic testing[10]. We have not seen electrode degradation except in devices which required abnormally high voltages and currents. These devices undoubtedly contained localized "short circuit" defects.

Conclusions

Thin film, multilayer electrochromic coatings have been produced with suitable properties for use in passive solar window applications. An open circuit, optical memory of greater than 24 hours has been achieved at the cost of somewhat reduced coloration efficiency. The electrochromic devices require considerable optimization. In particular, a more highly transparent top electrode film is required to replace the semitransparent gold films used in the typical test devices. Preliminary experiments showed that indium-tin oxide could be used for this purpose, but that a sheet resistance much less than 160 Ω/□ was needed. Further optimization of the ionic conductor layer (MgF$_2$ in our samples) is required to improve electrooptic efficiency.

Acknowledgments

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