

All-Solid-State Complementary Electrochromic Windows Based on the Oxymethylene-Linked Polyoxyethylene Complexed with LiClO₄

MIN-HUI CUI,¹ JUN-SHI GUO,² HONG-QUAN XIE,² ZHENG-HUA WU,³ SI-CHOU QIU³

¹ Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

² Department of Chemistry, Huazhong University of Science & Technology, Wuhan 430074, People's Republic of China

³ Department of Solid State Electronics, Huazhong University of Science & Technology, Wuhan 430074, People's Republic of China

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ABSTRACT: Oxymethylene-linked polyoxyethylene complexed with LiClO₄ at a Li/EO molar ratio of 0.05 has a conductivity of $4.7 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 25°C and a transmittancy of 90%. It is a promising electrolyte for an all-solid-state complementary electrochromic window using WO₃ and NiO_x. The modulation depth of the window exceeds 50% from 700 nm to 900 nm. The electrochromic ability of the window increases with temperature and lithium salt concentration and the window also exhibits good storage property under open circuit. Current and optical responses of the window as well as the electrochromic process are also discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1739–1744, 1997

Key words: oxymethylene-linked polyoxyethylene; polymer electrolyte; all-solid-state; electrochromic window; tungsten oxide; nickel oxide

INTRODUCTION

As a kind of light modulation process, electrochromism has attracted extensive attention due to its good perceived content, memory effect, and low switching voltage. An electrochromic device has excellent characteristics of display and/or optical modulation compared with other systems using liquid crystals, such as no angular dependence and continuously variable density of coloration, and it can be utilized in large-area light-controllable windows whose transmittance could be controlled by changing the applied voltage. Electrochromic windows allow the degree of illumination to be adjusted according to the environment by

changing the switching voltage, and are of great interest for many applications,¹ for instance for architectural glazing for energy control ("smart windows"), sun roofs of automobiles, antiglare rear view mirrors, and displays.

Generally speaking, the transmissive electrochromic device has a five-layer structure: TC/EC/EL/CE/TC, where TC, EC, EL, and CE represent the transparent conducting layer, electrochromic layer, electrolyte layer, and counterelectrode layer, respectively. Indium tin oxide (ITO) or SnO₂ have been used as TCs. Many insertion materials, e.g., transition metal oxides, exhibit electrochromic properties when deposited in thin films. Their optical properties can be modified by electrochemical insertion of protons or alkali cations stored in the electrolyte layer. Among these oxides, WO₃, MoO₃, and V₂O₅ are cathodic coloring oxides, and NiO_x, IrO₂, and Rh₂O₃ are anodic

Correspondence to: Min-Hui Cui.

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coloring oxides.² Although liquid electrolytes have higher conductivity than solid, their disadvantages, such as corrosion and leakage, limit their application. Deb³ fabricated an all-solid-state device using the recently found superionic conductors of the type RbAg_4I_5 . Devices of the type $\text{SnO}_2\text{-WO}_3\text{-RbAg}_4\text{I}_5\text{-Ag}$ have been fabricated. The coloration mechanism may be the formation of a silver tungsten bronze by the diffusion of Ag^+ ions from the RbAg_4I_5 into the WO_3 film during coloration and reverse process during the bleaching mode. These devices are extremely unstable because of their sensitivity to moisture and because the Ag can corrode in solid-state electrochemical reactions. In recent years, solid polymer electrolytes have been widely studied. Their use in electrochromic devices is suitable since they can be fabricated as thin films, and they do not present the problem of leakage encountered with liquid electrolytes. The solid polymer electrolyte used in the electrochromic window should have the following properties⁴: (1) high ionic conductivity, $10^{-3} \text{ S} \cdot \text{cm}^{-1}$; (2) electrochemical stability; (3) transparency; and (4) elasticity. Baudry et al.⁵ composed an electrochromic window using WO_3 as the electrochromic material, V_2O_5 , as counterelectrode, and poly(ethylene oxide)–lithium salt complexes as electrolyte. Potentiostatic cycling of the complete transmissive cell yielded a transmission variation from 41 to 13% at 633 nm with a response time of 10 s at room temperature.

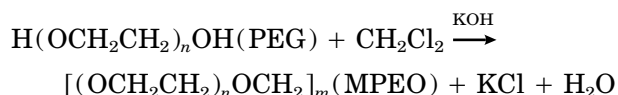
In this work, all-solid-state complementary window— WO_3 and NiO_x color or bleach simultaneously—built using WO_3 as electrochromic material, NiO_x as counterelectrode, and oxymethylene-linked polyoxyethylene/ LiClO_4 complex as electrolyte have been investigated. NiO_x has been selected as a counterelectrode because it can undergo a reversible lithium intercalation–deintercalation process, which is accompanied by a net electrochromic effect, and it can strengthen the contrast between the bleaching and coloring states of the windows.

EXPERIMENTAL

Preparation of Polymer Electrolyte⁶

To a mixture of 10 g KOH powder and 100 mL CH_2Cl_2 , 25 g liquid polyethylene glycol ($M_w = 600$) was slowly added during stirring. Additional amounts (5 g) of KOH powder were added at 0.5, 1.5, and 3.0 h from the beginning of the

reaction. The reaction was carried out at room temperature during stirring for 20 h. Then the reaction mixture was poured into an evaporating dish to vaporize most of the unreacted CH_2Cl_2 . The residue was dissolved in toluene and the solution decanted from the salt sediment. The crude product was precipitated out by adding petroleum ether (b.p. 90–120°C) to the solution. After drying under an i.r. lamp and in vacuum, oxymethylene-linked polyethylene oxide (abbreviated as MPEO) was obtained. The main reaction is described thus



MPEO was dissolved in acetonitrile to which a certain amount of ethanolic solution of LiClO_4 was added during stirring. The mixture was evaporated and the complex formed was vacuum dried. The complex (MPEO-LiClO_4) was hot-pressed in a die into pellets (~ 2 mm thick and 14 mm in diameter), sandwiched between two thin aluminum discs at 80°C, and then kept in a vacuum desiccator containing fresh P_2O_5 for at least 2 days. A.C. conductivity was measured at different temperatures with a DDS-II A conductometer using copper disc electrodes operated at a frequency of 1100–1200 Hz.

Preparation of Electrochromic Layers

The WO_3 layer was made by electron-beam evaporation. Analytical WO_3 powder was compacted into a 10-mm diameter cylinder, and the cylinder was placed in a graphite crucible and used as an evaporation source. The substrate was ITO conducting glass of 4 cm^2 surface ($200\Omega/\square$), and its transparency was 90%. Glass temperature was 80°C, evaporation rate was 8 nm/min, and evaporation time was 15 min.

The NiO_x layer was DC-sputtered on ITO conducting glass. Purity of the nickel target was 99.99%. Pressure of the sputter system was 10^{-3} Pa, and oxygen pressure was 5 Pa. Sputter voltage and current were 1000 V and 5–8 mA, respectively. Sputter rate was 0.5 nm/min, and the film thickness was ~ 450 nm. Analysis of samples indicate that the film was composed of NiO , Ni_2O_3 , etc.

Constitution of Electrochromic Window

The schematic structure of the window is shown in Figure 1. After placing the polymer electrolyte

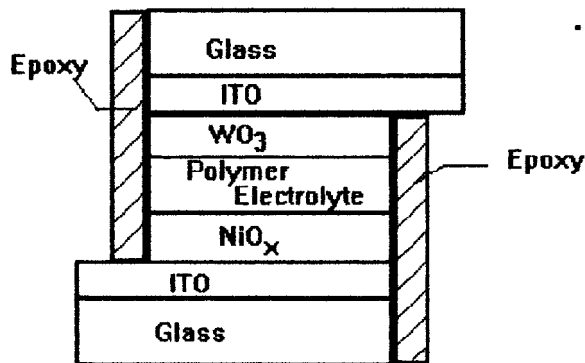


Figure 1 Schematic configuration of the all-solid-state window investigated in this work.

onto the WO₃ of a half-cell (WO₃/ITO/glass), the other half-cell (NiO_x/ITO/glass) was pressed against the polymer electrolyte at 85–90°C in a vacuum system. The thickness of polymer film was 10⁻¹ μm order of magnitude. An epoxy resin was used to seal the edge of the window, providing more mechanical strength, and reducing the rate of moisture absorption from the atmosphere.

UV-visible absorption spectra of the windows were obtained with a Shimadzu UV-240 spectrophotometer.

RESULTS AND DISCUSSION

Conductivities of MPEO/LiClO₄ Complexes

Arrhenius plots of the conductivities of MPEO/LiClO₄ complexes with different molar ratios of Li/EO are presented in Figure 2. The conductivity of the polymer complex increases with increasing molar ratio of Li/EO in the range studied. At 25°C, the conductivity of the MPEO/LiClO₄ complex at a Li/EO molar ratio of 0.05 reaches 4.7 × 10⁻⁴ S·cm⁻¹, a high value for ionic conductive polymers. So, the polymer electrolyte with a 0.05 molar ratio of Li/EO was used in fabricating the electrochromic window.

Transmittance Spectrum

If a polymer electrolyte is used in a transmissive electrochromic window, it should have high transmission. Otherwise, the electrolyte will affect the color contrast. The transmittance spectrum of MPEO/LiClO₄ complex at a Li/EO molar ratio of 0.05 is demonstrated in Figure 3. From 400 to 900 nm, the transmittancy of MPEO/LiClO₄ complex reaches 90%, indicating that the electrolyte has

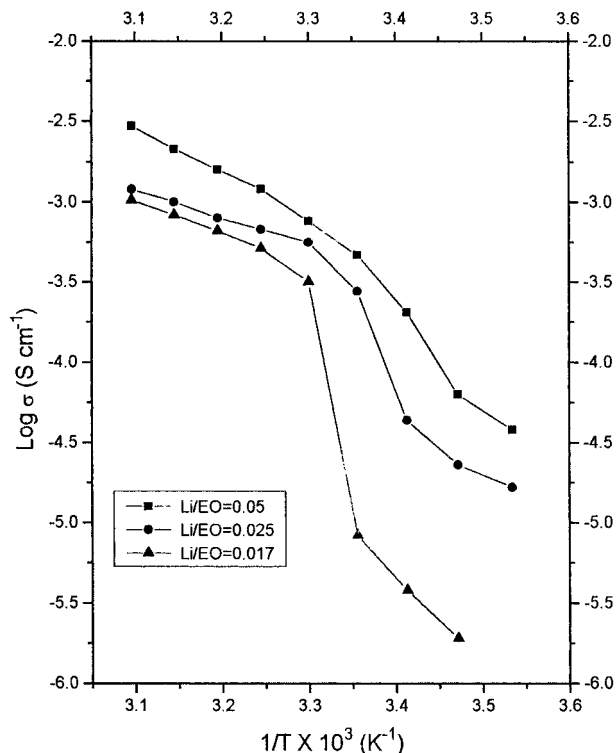


Figure 2 Arrhenius conductivity plots of MPEO/LiClO₄ complexes.

high transmission and could be used in an electrochromic window.

Figure 4 indicates the transmittance spectra of

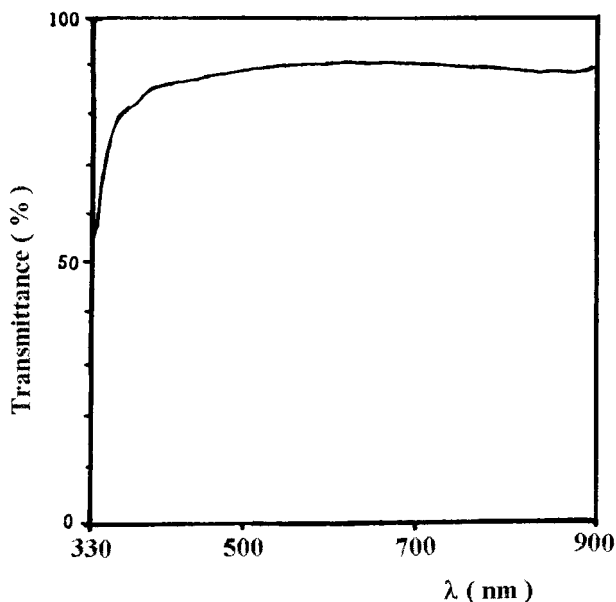


Figure 3 Transmittance spectrum of MPEO/LiClO₄ complex ($n_{Li}/n_{EO} = 0.05$) with glass as substrate.

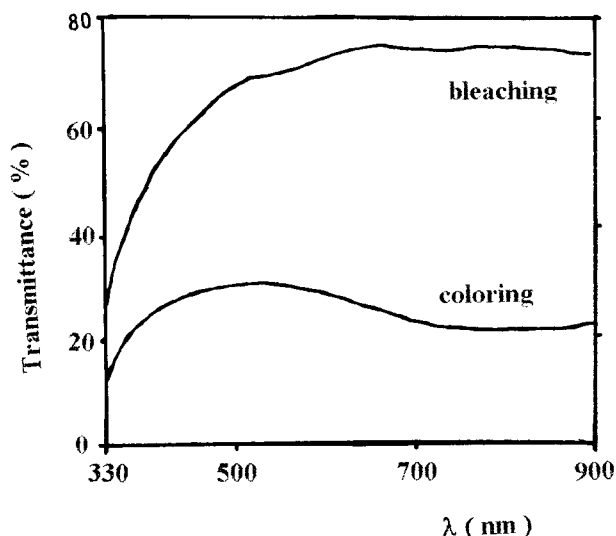


Figure 4 Transmittance spectra of the electrochromic window in the coloring and bleaching states.

our electrochromic windows in the coloring and bleaching states: The coloring or bleaching voltage was 1.5 V and the coloring or bleaching time was 60 s. From 700 to 900 nm, the modulation depth of the window exceeds 50%. In the bleaching state, transmittance decreases gradually with decreasing wavelength; for the coloring state, the transmittance shows a peak value at 500 nm and is $\sim 30\%$.

Current and Optical Responses of the Electrochromic Window

When a voltage of ± 1.5 V is applied across the two electrodes of the window, the resulting changes of current (I) and transmittance are shown in Figure 5. The bleaching current changes rapidly with time; the coloring current changes were slow. There exist obvious differences between the peak values of the coloring process (1.7 mA) and bleaching process (5.5 mA); the reason is not yet known.

Figure 5(b) shows the optical response of the window studied. During the coloring process, the change of transmittance is slower than that of the bleaching process. This corresponds to the current response. By carefully comparing Figure 5(a) and (b), we find that the optical response is slower than the current response, this indicates the formation/elimination of color centers lags behind the injection/ejection of lithium ions. Figure 5(b) shows that the coloring and bleaching times are ~ 30 and 10 s, respectively.

Effects of Temperature and Lithium Salt Concentration on the Electric Charge Transfer

Figure 6 illustrates the effects of temperature and lithium salt concentration on the total electric charge transfer (Q). Figure 6(a) shows that Q increases with increasing temperature in the range of temperature measured. The resistance of ITO has no obvious change in this temperature range. The conductivity of the polymer electrolyte increases with increasing temperature, as shown in Figure 2, thus quickening the migration rate of the lithium ions, thus causing the increase of Q .

Figure 6(b) shows that lithium salt concentration also affects the total electric charge transfer. Q increases with increasing molar ratio of Li/EO, which means that the increase of lithium salt concentration in the range studied can enhance the electrochromic ability. This can be explained thus:

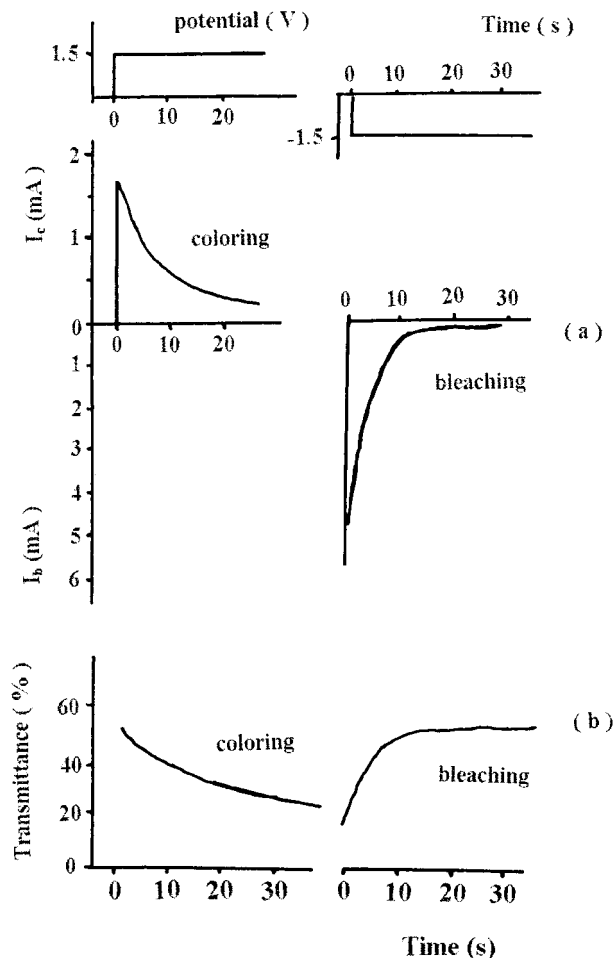


Figure 5 1.5-V potentiostatic tests for the current (a) and optical (b) responses during the coloring and bleaching processes.

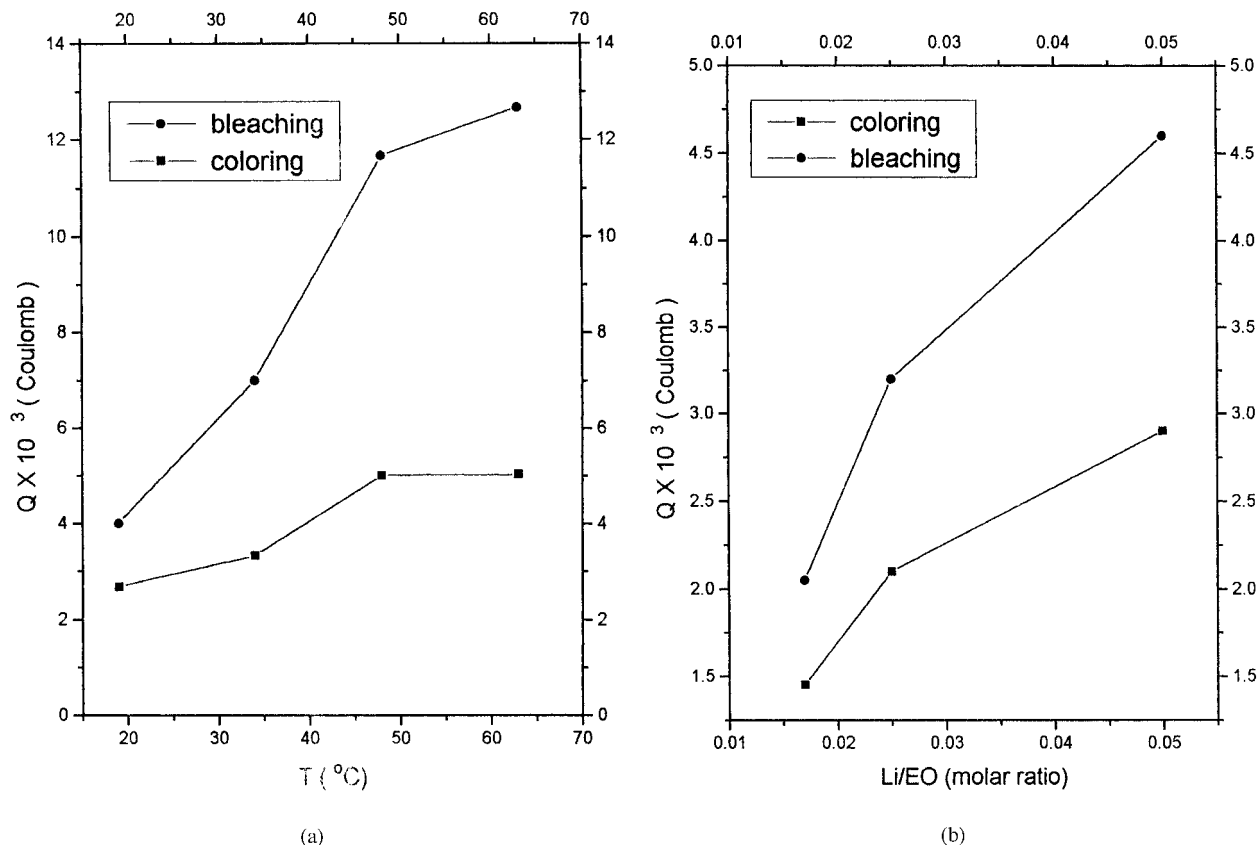
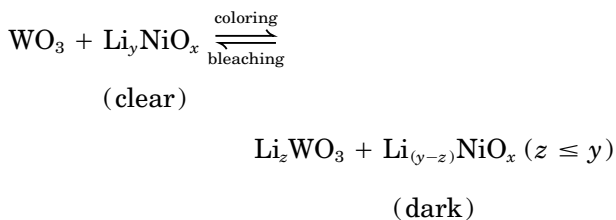


Figure 6 Temperature dependence (a) and lithium salt concentration dependence (b) of the total electric charge transfer for a period of 10 s immediately following a 1.5-V potential step.

the conductivity of the polymer electrolyte increases with the increasing lithium salt concentration, as shown in Figure 2. So under the external electric field, the migration of lithium ions occurs easily to carry on, which strengthens the electrochromic ability of the windows.

Electrochromic Process of the Electrochromic Window

The electrochromic process of the complementary window based on WO₃, NiO_x, and MPEO/LiClO₄ complex can be expressed by the following reaction⁷:



During the cathodic scan, the window is dark and the transmittance decays, while in the following scan the window becomes clear and the transmittance rises. This behavior, reproducible for many cycles, can be indicated by the diagrammatic sketch shown in Figure 7.

Storage Property and Stability

One of the advantages of electrochromic windows over liquid crystal displays is the storage property of the window in an open circuit. The window studied here shows good storage property under open circuit. After 7 days, the transmittance of the coloring state has no obvious rise. The long-term stability of the window, however, needs to be further investigated. After a thousand cycles, some bubbles appeared in the window. These bubbles may be attributed to residual water in the polymer electrolyte.⁸ Since water dissociates at ~ 1.2 V, the residual water in the polymer electrolyte may eventually electrolyze and release H₂

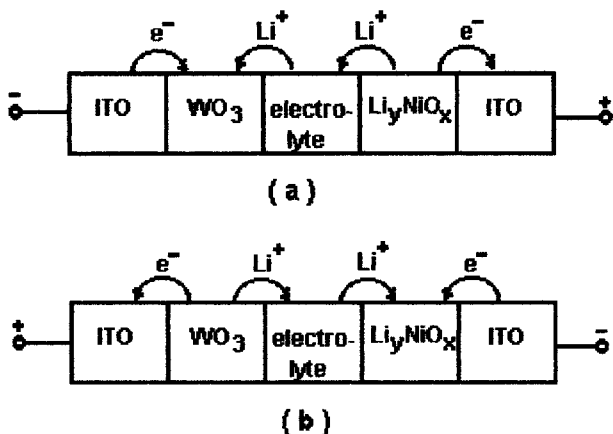


Figure 7 Electrochromic processes of the electrochromic window. (a) coloring, (b) bleaching.

bubbles at the applied voltage used in our window (-1.5 – $+1.5$ V). Preparing the polymer electrolyte and assembling the window in a water-free environment might eliminate this kind of deterioration.

CONCLUSION

Solid polymer electrolyte with high ionic conductivity at room temperature can be used to fabricate all-solid-state electrochromic windows. Transmittancy of the LiClO_4 complex of MPEO is

$\sim 90\%$. All-solid-state complementary electrochromic windows based on WO_3 , NiO_x , and a MPEO/ LiClO_4 complex have a modulation depth of 50% from 700 to 900 nm. Environment temperature and lithium salt concentration can affect the electrochromic ability of the window. Optical response of the window indicates that the coloring and bleaching time are 30 s and 10 s, respectively. The window also exhibits good storage properties under open circuit, but some bubbles appear in the window after a thousand cycles. The electrochromic process of the window is related to the injection/ejection of lithium ions stored in the polymer electrolyte.

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