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All solid-state electrochromic window of Prussian Blue and electrodeposited WO_3 film with PMMA gel electrolyte

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An all solid-state electrochromic window employing Prussian Blue and electrodeposited WO_3 film with PMMA gel electrolyte has been fabricated. The electrochromic window shows excellent electrochromism and memory characteristics. The W 4f core level of the WO_3 film at different levels of coloration has been investigated using XPS. W 4f peaks become broader after coloration.

Intensified research efforts to develop electrochromic devices have spread worldwide in recent years.[1–13] The focus of these research programs is on large area window applications. For such applications, all solid-state electrochromic devices have unique advantages (such as reliability and safety) when compared to conventional liquid-based devices. Lithium-based devices have attracted increasing attention because of their environmental stability. Most lithium-based solid polymer electrolytes are a mixture of $LiClO_4$ and various polymers, such as polyethylene oxide (PEO) and polyacrylonitrile (PAN), and inorganic ion conductors with high conductivity.[2–13] However, the conductivity of the solid polymer electrolyte, of the order of 10^{-9}–10^{-5} S cm^{-1} at room temperature, is still too low for practical applications, for which a conductivity $>10^{-4}$ S cm^{-1} at room temperature is required to minimized the ohmic drop across the electrochromic window. The gelled electrolyte alternative, consisting of a solid phase in which a conventional non-aqueous electrolyte is immobilized by a polymer matrix, offers liquid-like values for the conductivity. By varying the amount of added polymer, the viscosity of the gel may be altered to provide mechanical properties similar to that of the solid polymer, while maintaining liquid-like electrical behavior.[14,15] The common preparation techniques for WO_3 films such as vacuum evaporation, sputtering or chemical vapor deposition (CVD) are expensive and it is difficult to form large area films. The electrodeposition method is probably the most economical method for making the films in addition to its relative ease in forming large area films.[16–19] Here, we report the fabrication of an all solid-state electrochromic window using Prussian Blue and WO_3 films with a PMMA gel electrolyte that has high conductivity (10^{-3} S cm^{-1}) at room temperature.

Experimental

Preparation of WO_3 film

The anode was a Pt plate and the cathode was ITO quartz glass. The cathodic electrodeposition was performed at a constant current density of 200 μA cm^{-2} in 0.5 M Na_2WO_4 aqueous solution (pH = 7) at room temperature.[13] The resulting WO_3 film was subjected to heat treatment at 400 °C for 3 h. The films were uniform, adhesive and transparent. X-Ray diffraction analysis showed that the films were amorphous.

Preparation of Prussian Blue film

Prussian Blue film on the ITO quartz glass was electrochemically deposited under galvanostatic conditions from a 1 : 1 mixture of 10 mM $FeCl_3$ and 10 mM $K_3[Fe(CN)_6]$ aqueous solution at a current density of 5 μA cm^{-2}.

The PMMA gel electrolyte was obtained by immobilizing an appropriate solution in a PMMA matrix. The following composition of electrolyte (mass ratio) was used: 25% PMMA, 35% propylene carbonate (PC), 40% ethylene carbonate (EC), 5% $LiClO_4$. The electrolyte mixture was dissolved in tetrahydrofuran (THF). The electrolyte solution was cast onto the WO_3 film and pressed together with a Prussian Blue counter electrode. After 3 days of gelation the edges of the device were sealed with epoxy.

In order to examine the conductive behavior of the PMMA gel electrolyte, electrochemical measurements were performed with a three-electrode measurement system in PC solution containing 1 M $LiClO_4$ or in PMMA gel electrolyte. A silver wire and platinum were used as pseudo-reference and counter electrodes, respectively. The ac impedance measurements of the conductivity of a polymer gel were carried out in the frequency range 0.1–100 kHz using a PARC Model 378 measurement system by casting the electrolyte between two stainless foil electrodes separated by a 0.3 mm thick spacer. The amplitude of the ac voltage is kept as small as possible to minimize disturbances in the system under investigation. In our case, the amplitude was 5 mV. The changes in UV–VIS absorption spectra for the coloring and bleaching states were measured *in situ* with a UV–VIS spectrophotometer. The X-ray photoelectron spectra (XPS) of the trioxide tungsten film were recorded on a JPS-90SX photoelectron spectrometer (Nihon Denhi) using monochromatized Mg-K (1253.6 eV) radiation. The instrumental resolution was *ca.* 0.6 eV measured as full-width at half-maximum (FWHM) of the C 1s line of graphite. The samples were maintained at room temperature and at a pressure of *ca.* 2×10^{-10} Torr throughout the investigation.

Results and Discussion

When the THF was evaporated at room temperature, a free-standing electrolyte film was formed, having a transparent, elastomeric appearance. The temperature dependence of the conductivity of the PMMA gel electrolyte is shown in Fig. 1. The curvature of the data points of the PMMA gel electrolyte in the Arrhenius plots is characteristic for amorphous polymer electrolytes. X-Ray analysis also confirms that the polymer gel electrolyte is amorphous. The results are due to ion transfer in the polymer gel electrolyte owing to diffusion of the lithium ion. From the slope of straight line, the activation energy (E_a) of the ionic conduction can be calculated according to eqn. (1)

$$\sigma = \sigma_0 \exp(-E_a/kT) \qquad (1)$$

where k is Boltzmann's constant and T is temperature. The

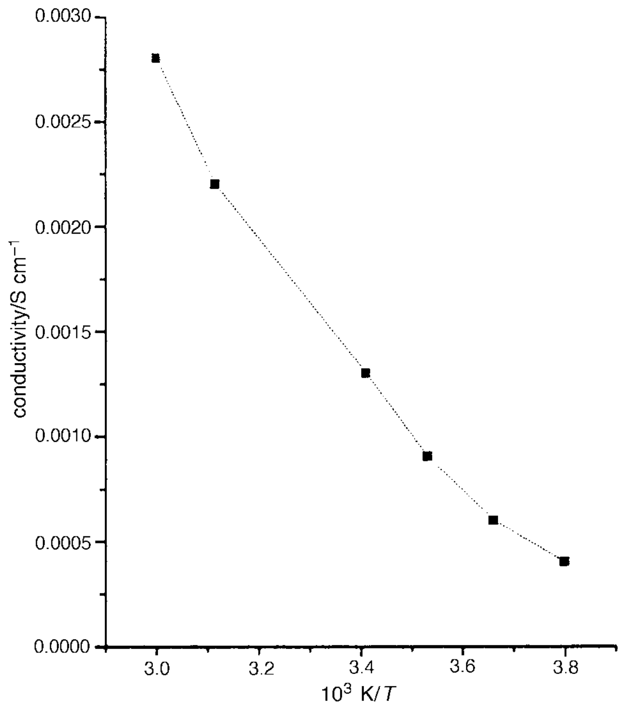

Fig. 1 Temperature dependence of the conductivity of the PMMA gel electrolyte

activation energy, E_a, for the polymer gel electrolyte was 16.9 kJ mol^{-1}.

Fig. 2 shows the conductivity of the polymer gel electrolyte as a function of gelation time at room temperature. The conductivity decreases and reaches a stable value of 0.0014 S cm^{-1} after three days of gelation. In comparison, the conductivity of a PC solution with 1 M $LiClO_4$ was 0.008 S cm^{-1}. The relatively high conductivity of the PMMA gel electrolyte indicates that it will not substantially increase the internal resistance of the device which is flexible, retains its shape, and does not exhibit any significant loss in conductivity after extended exposure to air.

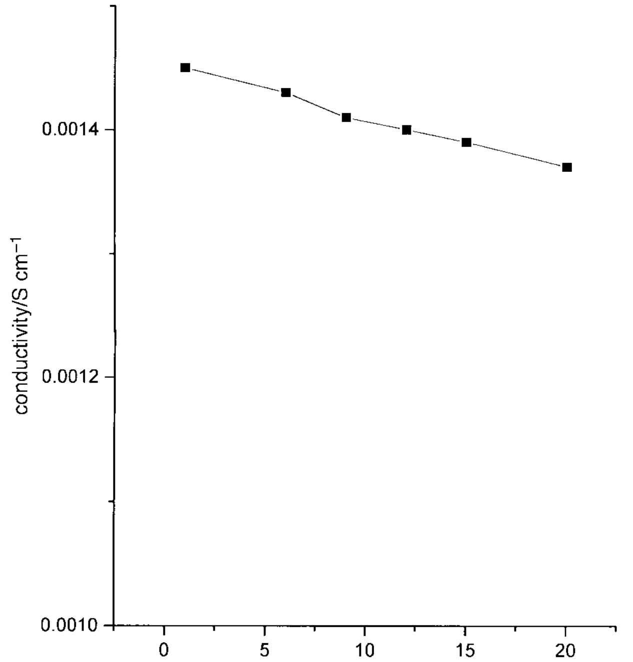

Fig. 2 Gelation time dependence of the conductivity of the PMMA gel electrolyte at room temperature

The cyclic voltammetric behavior of the Prussian Blue film is shown in Fig. 3. The cyclic voltammogram of the Prussian Blue film in the PMMA gel electrolyte is essentially similar in shape and current amplitude to that in solution. Further, the cyclic voltammograms of WO_3 films in PMMA gel electrolyte are also similar in shape and current amplitude to that in solution. These facts mean that the kinetic parameters concerning the charge transport processes within the WO_3 film and the Prussian Blue film and at the interface of ITO surface/film in the PMMA gel electrolyte are similar to those in solution. Thus, it is obvious that the electrochromic characteristics in PMMA gel electrolyte are similar to those in solution.

A reversible color change between blue and colorless was observed when an appropriate voltage was applied repeatedly to the electrochromic window. A difference in the absorbance between the coloring and bleaching states was clearly found. The electrochromic characteristics were consequently evaluated with the transmittance change. Fig. 4 shows the plot of absorbance change, ΔA, *vs.* the amount of charge injected into the electrochromic window, and a linear relationship between the absorbance change and the amount of charge is established. The coloration efficiency of the electrochromic window is defined as the change in absorbance per unit charge injected per unit area of the active electrode. The slope of the straight

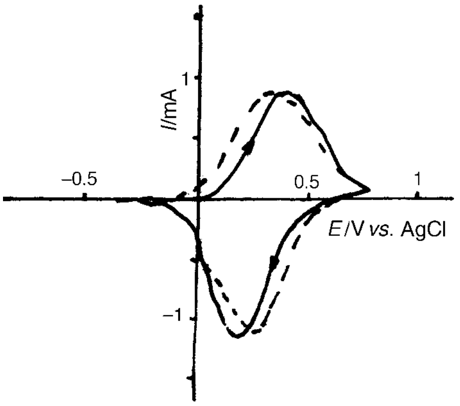

Fig. 3 Cyclic voltammogram of Prussian blue in PMMA gel electrolyte (solid line) and in PC solution (broken line). Sweep rate 10 mV s^{-1}.

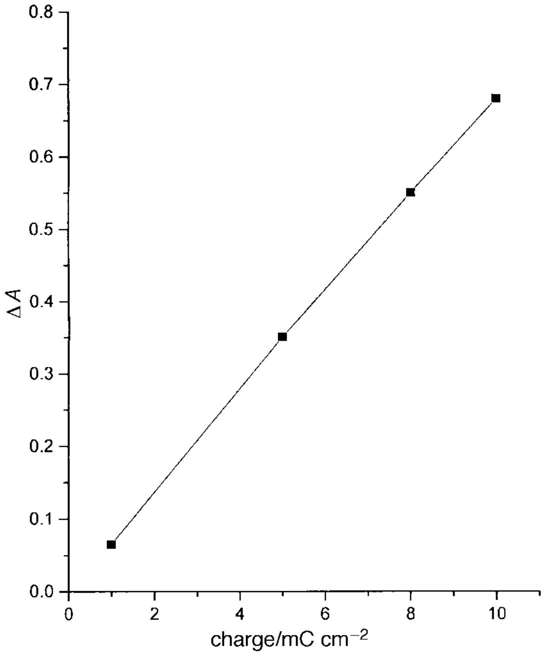

Fig. 4 Absorbance change at 650 nm *vs.* the amount of charge injected into the electrochromic window

line is the coloration efficiency of the window and is found to be 75 cm^2 C^{-1}. This efficiency is higher than that reported by other workers (68 cm^2 C^{-1}).[4]

Fig. 5 shows the absorbance change, ΔA, of the electrochromic window of Prussian Blue and of a WO_3 particulate film at 650 nm. A reversible color change between blue and colorless was observed when a square-wave potential between -0.5 and 1 V was applied repeatedly to the electrochromic window. The transmittance response lost only $<10\%$ of the initial magnitude even after potential stepping for 5×10^4 cycles. The rates of the color change are estimated in terms of ΔA between 0 and 0.9 and the rates of coloring and bleaching were 60 and 30 s, respectively. The blue color of the oxidized form of Prussian Blue and the reduced form WO_3 film remained substantially unchanged even after standing the electrochromic window at open circuit state over a period of more than a week. The transmittance of the electrochromic window at open circuit changed by only 1% per day.

The electrochromic process of the WO_3 has been explained on the basis of the double injection of a positive monovalent ion and an electron to form a colored tungsten bronze,[20,21] eqn. (2), M = H or Li.

$$xM^+ + xe^- + WO_3 \rightleftharpoons M_xWO_3 \qquad (2)$$

The XPS survey scan analyses of the electrodeposited WO_3 surface are shown in Fig. 6. In the XPS spectrum [curve (*a*)] of the electrodeposited WO_3 film, the peaks corresponding to $4f_{7/2}$ and $4f_{5/2}$ are observed at 35.8 and 37.9 eV, respectively. They are in good agreement with those of tungsten (VI) trioxide powder. Therefore, it is evident that the tungsten in the electrodeposited film is present as W^{VI}. The XPS spectra [curve (*b*) and (*c*)] of the WO_3 films with different levels of coloration, *i.e.*, weak and strong coloration states, were obtained. The most pronounced change in Li_xWO_3 is that W 4f peaks became broader with an increasing injected charge. A likely explanation might be due to the presence of different final states, screened by a number of W 5d electrons. W^{VI}, W^V and W^{IV} have $4f^{12}5d^0$, $4f^{12}5d^1$ and $4f^{12}5d^2$ configurations, respectively. The outer electron of the W^{IV} is further out than in W^{VI} or W^V. The outer electronic screening effect of the W^{IV} is larger than in W^{VI} or W^V. The binding energies (E_b) lie in the order $E_b(W^{IV}) < E_b(W^V) < E_b(W^{VI})$.

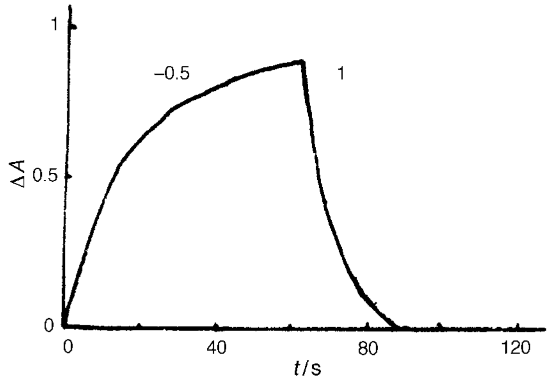

Fig. 5 Absorbance change of the electrochromic window at 650 nm

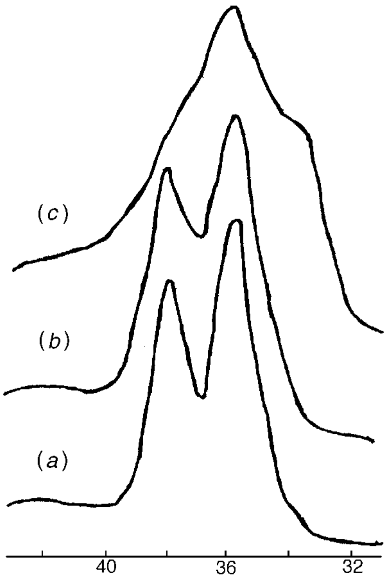

Fig. 6 Comparison of W 4f core level XPS spectra of WO_3 with different levels of coloration: (*a*) bleaching; (*b*) weak coloration; (*c*) coloration

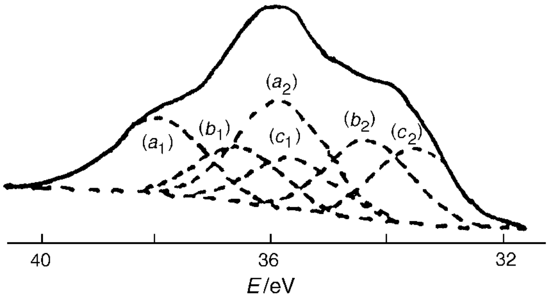

Fig. 7 Fitting spectra of WO_3 film after coloration: (a_1) and (a_2) are W^{6+} 4f spectra; (b_1) and (b_2) are W^{5+} 4f spectra; (c_1) and (c_2) are W^{4+} 4f spectrum

In the weak coloration film, the peaks corresponding to $4f_{7/2}$ and $4f_{5/2}$ are observed at 35.6 and 37.7 eV, respectively. The energy levels are lower than those corresponding to W^{VI} (before coloration). Redox reactions take place between W^{VI} and W^V in the bleaching–coloration process. With an increasing injection of lithium, the W 4f peaks become broader. This indicates that the tungsten in the coloration film may be present in the mixed valences of W^{VI}, W^V and W^{IV}. Curve fitting analysis (Fig. 7) of W 4f shows that tungsten in the coloration film consists of 0.42 W^{VI}, 0.3 W^V and 0.28 W^{IV}. The coloration level is directly proportional to the amount of W^{5+} and W^{4+}, which corresponds to the amount of injected lithium.

In summary, an all solid-state electrochromic display device with a PMMA gel electrolyte has been fabricated. A reversible color change between blue and colorless after cycling more than 5×10^4 times is observed. The W 4f core level of WO_3 films at different levels of coloration have been investigated using XPS. W 4f peaks become broader after coloration. PMMA is readily available and inexpensive and therefore will be of interest for the development of inexpensive electrochromic devices.

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