All-Solid-State Electrochromic Device of Electrodeposited WO₃ and Prussian Blue Film with PVC Gel Electrolyte

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ABSTRACT: An all-solid-state electrochromic device (SED) employing electrodeposited WO_3 and prussian blue film with poly(vinyl chloride) (PVC) gel electrolyte that has high conductivity (10^{-3} S/cm) at room temperature has been fabricated. The SED has been found to have excellent electrochromism and memory characteristics. A reversible color change between blue and colorless was observed when an appropriate potential was applied repeatedly to the electrochromic display device. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1955–1958, 1998

Key words: electrochromic device; polymer gel electrolyte; WO₃; prussian blue

INTRODUCTION

Intensified research efforts to develop electrochromic devices have spread worldwide in recent years.^{1–7} The focus of these research programs is on large-area window applications. For such applications, an all-solid-state electrochromic device have unique advantages (such as reliability and safety) when compared to conventional liquidbased devices. Lithium-based devices have attracted increasing attention because of their environmental stability. Most lithium-based solid polymer electrolytes are a mixture of LiClO₄ and various polymers, such as polyethylene oxides (PEO),⁸⁻¹² oxymethylene polyoxyethylene (OMPE).⁴ However, the conductivity of the solid polymer electrolyte on the order of 10^{-9} to 10^{-5} s/cm at room temperature is still too low for practical applications, for which a conductivity greater than 10^{-4} S/cm at room temperature is required to minimized the ohmic drop across the SED. The commonly prepared techniques for electrochromic

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film, such as molecular beam epitaxy or chemical vapor deposition (CVD), are expensive, and it is difficult to form large area films. The electrodeposition and sol-gel method is probably the most economical method for making the films, in addition to its relative ease, in forming large-area films. The fabrication of an all-solid-state electrochromic device using electrodeposited WO₃ and prussian blue film with a poly(vinyl chloride) (PVC) gel electrolyte that has high conductivity (10^{-3} S/cm) at room temperature is reported here.

EXPERIMENTAL

Preparation of WO₃ Film

WO₃ film on the ITO glass was electrochemically deposited under glavanostatic conditions in 0.5 mol/L Na₂WO₄ aqueous solution (pH = 7) at a constant current density of 200 μ Acm⁻² at room temperature. The resulting WO₃ film was subjected to heat treatment at 400°C for 3 h. The films were uniform, adhesive, and transparent. The qualitative X-ray photoelectron spectroscopy (XPS) survey scan analysis of the WO₃ surface was shown in Figure 1. The survey scan informa-

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Figure 1 XPS scan spectra (a) and (b) of the WO_3 surface.

tion is useful, particularly in the identification of the elements present at the film surface. The spectra exhibits the spin-orbit-split $4f_{5/2}$ [Fig. 1(a)] components and [Fig. 1(b)] $4f_{7/2}$, separated by about 2.2 eV. They are in good agreement with those of tungsten(VI) trioxide power. Therefore, it is evident that the tungsten in the film is present in the 6-valent state.

Preparation of Prussian Blue Film

Prussian blue film on the ITO glasses was electrochemically deposited under glavanostatic conditions of an equivolume mixture of 10 mmol/L FeCl₃ and 10 mmol/L K₃[Fe(CN)₆] aqueous solution at a current density of 5 μ Acm⁻².

The polymer gel electrolyte was obtained by immobilizing an appropriate solution in a PVC matrix. The following composition of a electrolyte (in weight ratio) was used: 15% PVC, 40% propylene carbonate (PC), 40% ethylene carbonate (EC), and 5% LiClO₄. The mixture of the electrolyte was dissolved in tetrahydrofuran (THF). The electrolyte solution was cast onto the WO₃ particulate film and pressed together with a prussian blue counter electrode. After 3 days of gelation, the edges of the device were sealed with epoxy.

The alternating current (AC) impedance measurements of the conductivity of a polymer gel were carried out in the frequency range from 0.1 to 100 kHz. Changes in UV–visible (UV–VIS) absorption spectra for the coloring and bleaching states were measured with a UV–vis spectrophotometer.

RESULTS AND DISCUSSION

When the THF was evaporated at room temperature, a free-standing electrolyte film was formed. The following scheme illustrates the formation of the new solid electrolytes. The Li salt-solvate I formed when the Li salt is dissolved in the EC–PC solvent mixture is immobilized in the PVC polymer host by electrostatic forces between the solvate and the polymer, as shown in II, as follows:

$$LiX + EC/PC \Longrightarrow Li^{+}[(PC)x(EC)y]X^{-}(I)$$

$$PVC$$

$$\Longrightarrow -(CH_{2}CHCI)_{n}^{-}$$

$$|$$

$$Li^{+}[(PC)x(EC)y]X^{-}(II)$$

The temperature dependence of the conductivity of the gel electrolyte is shown in Figure 2. The curvature of the data of the polymer 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 obviously to the ion transfer in the polymer gel electrolyte due to the diffusion of the lithium ion. From the slope of straight line, the activation energy (E_a) of the



Figure 2 The temperature dependence of the conductivity of polymer gel electrolyte.



Figure 3 The gelation time dependence of the conductivity of the polymer gel electrolyte.

ionic conduction can be calculated according to the following equation:

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

where k is Boltsmann constant, and T is temperature. The activation energy E_a for the polymer gel electrolyte was 15.3 kJ/mol.

Figure 3 shows the conductivity of the polymer gel electrolyte as a function of gelation time. The conductivity decreases and reaches a stable value of 0.0023 s/cm after 3 days of gelation. In comparison, the conductivity of a PC solution with 1 mol/L LiClO₄ was 0.008 s/cm. The relatively high conductivity of PVC 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 conducting after extended to air.

A reversible color change between blue and colorless was observed when an appropriate voltage was applied repeatedly to the solid-state electrochromic device (SED). The difference in the absorbance between the coloring and bleaching states was clearly found. The electrochromic characteristics were consequently evaluated with the transmittance change at 700 nm. Figure 4 shows the plot of optical density change versus the amount of charge injected into the electrochromic display device. The linear relationship between optical density and the amount of charge is established. Light transmittance at 700 nm reached 10% of the bleaching state when the amount of charge of 15 mC cm⁻² was injected into the electrochromic device for coloration. The coloring efficiency of the SED is found to be 74 cm²/C from the straight line. This efficiency is closer than that reported by other workers (70 cm²/C).¹³

Figure 5 shows the optical density change of electrochromic display device of prussian blue and WO₃ particulate film at 700 nm. A reversible color change between blue and colorless was observed when a square wave potential between 2 and -2 V was applied repeatedly to the SED. The transmittance response only lost less than 2% of initial magnitude even after the potential stepping of 1000 cycles. The electrochromic responses became lower with a decrease of the applied potential. The blue color of the oxidized form of prussian blue and the reduced form WO_3 film remained substantially uncharged even after standing the electrochromic display device at open circuit state over a period of more than 1 week.

In summary, an all-solid-state electrochromic device employing electrodeposited WO₃ and prus-



Figure 4 The relationship plot of optical density change versus the amount of charge injected into the electrochromic display device.



Figure 5 The optical density change of electrochromic display device at 700 nm: solid line, 2V; broken line, 1V.

sian blue film with PVC gel electrolyte that has high conductivity (10^{-3} S/cm) at room temperature has been fabricated. The SED has been found to have excellent electrochromism and memory characteristics. A reversible color change between blue and colorless was observed when an appropriate potential was applied repeatedly to the electrochromic display device. A reversible color change between blue and colorless with cycling more than 1000 times is observed. This project was supported by the National Natural Science Foundation of China.

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