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Electrochromic Film Derived from Cathodic Deposition of Polyoxometalates

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Much attention has recently been given to the electrochromic materials, because of their possible application to the flat panel display systems [1–7]. The material changes its light absorbing properties under the influence of an externally applied electric field and returns to its original state by reversing the polarity of the externally applied electric field. Amorphous WO_3 (a-WO_3) film prepared by vacuum evaporation of WO_3 is known to exhibit the electrochromic properties and improvements in response time and reliability of the display have been continued [8–11]. The electrochromic phenomena in a-WO_3 films can be expressed by the following reaction

$$WO_3\ (\text{colorless}) + XM^+ + Xe^- \rightleftharpoons M_xWO_3\ (\text{blue})$$

where M^+ is a proton or metal ion. The formula exhibits the formation of pseudo-tungsten bronze by the double injection of a positive ion and an electron.

We wish to report an electrochromic film prepared by heating polyoxometalates deposited cathodically on a base electrode, in particular $K_{0.33}WO_{3.165}$ film on the transparent indium–tin oxide (ITO) electrode. By this method, a relatively thin display is feasible compared to the electrochromic cell based on $H_3PW_2O_{40}$ heteropolyacid which is both an electrochromic material and an ionic conductor [12, 13], because the thin film of $H_3PW_{12}O_{40}$ could not be obtained by either electrochemical deposition or vacuum evaporation. The method is very simple, compared to the a-WO_3 preparation, and has the advantage of not using vacuum evaporation.

Experimental

CH_3CN was dried over 5A molecular sieves and then purified by distillation over P_2O_5. Propylene carbonate was stored over 5A molecular sieves for 24 h and purified by three distillations. Tetrakis(butylammonium)decatungstate $[NBu_4]_4[W_{10}O_{32}]$ was prepared by adding the solution (at 80 °C) containing 2.4 g tetrabutylammonium perchlorate in 1000 ml water adjusted to pH 2 with $HClO_4$ into the solution (at 80 °C) containing 3.0 g $Na_2WO_4 \cdot 2H_2O$ in 1000 ml water adjusted to pH 2. The yellow precipitate was filtered off, washed with hot water, ethanol, and diethylether successively, and recrystallized from CH_3CN and acetone, once for each. Tetrabutylammonium salts of $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$ or $[BW_{12}O_{40}]^{5-}$ were prepared by mixing NBu_4Br and $H_3PW_{12}O_{40}$, $H_4SiW_{12}P_{40}$, or $K_5BW_{12}O_{40}$ [14] in water. The precipitates were recrystallized from CH_3CN. All other reagents were at least analytical grade and used as supplied.

Cathodic deposition of polyoxometalate film onto a transparent ITO electrode (I-type 10 Ω/sq Matsuzaki-Sinku Co.) was carried out in CH_3CN containing 5 mM tetrabutylammonium salts of polyoxometalates and 10 mM $KClO_4$ under potentiostatic conditions of −0.8 V, −1.0 V, −1.2 V and −1.0 V *vs.* Ag for $[W_{10}O_{32}]^{4-}$, $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$, respectively. The strip (30 mm × 9 mm) of the blue ITO electrode was removed from the solution vertically with a rate of 4 cm/min and heated in an electric furnace with the programmed heating rate of 100 °C/h from room temperature to 400 °C for $[W_{10}O_{32}]^{4-}$, 530 °C ($[PW_{12}O_{40}]^{3-}$), 550 °C ($[SiW_{12}O_{40}]^{4-}$), and 450 °C ($[BW_{12}O_{40}]^{5-}$) followed by 0.5, 2, 2, and 2 h of calcination at that temperature, respectively. The resulting electrode was then cooled gradually to room temperature.

The atomic ratio K/W in the tungstate films was determined by X-ray fluorescence analysis (Horiba MESA 1130 spectrophotometer). Potentiostatic measurements were carried out in a rectangular glass cell (10 × 10 × 4 mm) with the total volume of the solution being 3 ml. Ag and Pt wires were used as quasi-reference and counter electrodes, respectively. Cyclic voltammograms were recorded with a combination of Nikko Keisoku Model DPGS-1 + NPS-2 + NFG-3 instruments. The electronic absorption and infrared (IR in KBr pellet) spectra were recorded on Hitachi-33- and 260-10 spectrophotometers, respectively. Thermogravimetric analysis was carried out using a Rigaku thermoflex TG-DSC.

Results and Dicussion

Potentiostatic reduction of $[W_{10}O_{32}]^{4-}$ at −0.8 V *vs.* Ag ($U_{Ag} = -0.8$ V) in CH_3CN brought about the deposition of the blue film on the ITO electrode. There was no significant formation of other reduction products. Figure 1 shows the electronic absorption and IR spectra for the blue film

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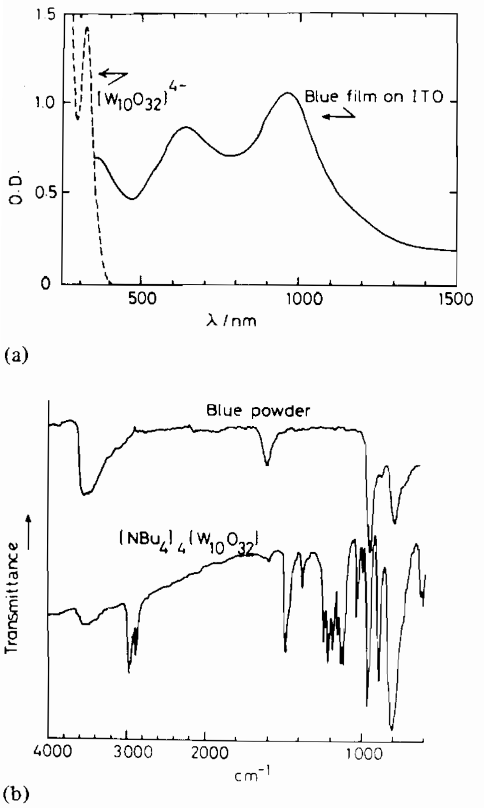

Fig. 1. (a) Electronic absorption and (b) IR spectra for the blue film and $[NBu_4]_4[W_{10}O_{32}]$. The two curves in (a) are obtained with the blue film (17 mC cm^{-2}) deposited on the ITO electrode and the solution (10 mm thickness) containing 0.1 mM $[NBu_4]_4[W_{10}O_{32}]$ and 10 mM $KClO_4$ in CH_3CN, respectively.

and starting material $[NBu_4]_4[W_{10}O_{32}]$. The visible absorption spectrum of the blue film exhibits absorption maxima at 630 and 960 nm, suggesting the formation of the protonated two-electron reduction species $[H_2W_{10}O_{32}]^{4-}$, since $[H_2W_{10}O_{32}]^{4-}$ showed λ_{max} = 630 and 945 nm in CH_3CN [15, 16]. The red shift of the intervalence-charge-transfer band (λ_{max} = 960 nm) may be ascribed to the adsorption on the ITO surface. The adsorbed blue species could be removed from the electrode by weak acid (pH 2) and the resulting blue solution faded in the presence of oxygen due to oxidation to $[W_{10}O_{32}]^{4-}$ exhibiting $\lambda_{max} = 320$ nm ($\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) [17]. Thus, we could estimate the total amount of decatungstate deposited on the electrode. Coulometric analysis indicated a linear relationship between the total amounts of the electrons consumed by the reduction and the amounts of $[W_{10}O_{32}]^{4-}$ deposited on the ITO surface with a slope of 1.9 (=electrons/$[W_{10}O_{32}]^{4-}$), providing that the blue film on the ITO electrode consists of the two-electron reduction species of $[W_{10}O_{32}]^{4-}$. As shown in Fig. 1b, the IR spectrum of the blue film exhibits no significant absorption bands around 3000, 1500, and 1300–1100 cm^{-1} due to $[NBu_4]^+$. Furthermore, X-ray fluorescence analysis of the blue film gave us the atomic ratio of K/W = 0.495. Therefore, from these results, the blue film can be assigned to the mixture of $K_4[H_2W_{10}O_{32}]$ and $K_5[HW_{10}O_{32}]$. It must be recalled that the electrochemical reduction of polyoxometalates in aqueous media (for example, $[BW_{12}O_{40}]^{5-}$) resulted in an increase of the solution pH and that the protonated reduction species is prone to be adsorbed on to the metal oxide surface [14]. Therefore, the proton of the two-electron reduction species $[H_2W_{10}O_{32}]^{4-}$ or $[HW_{10}O_{32}]^{5-}$ originates from the dissociation of the water contaminated in CH_3CN, as supported by the IR absorption band at 3500 cm^{-1} (Fig. 1b). The electrochemical reduction of $[W_{10}O_{32}]^{4-}$ at $U_{Ag} \leqslant -1.0$ V or $U_{Ag} \geqslant -0.6$ V was avoided because of the lack of uniformity of the blue film.

Thermal decomposition of the film deposited on the ITO electrode at 400 °C yielded the electrochromic film. As shown in Fig. 2a, X-ray diffraction showed that $K_{0.33}WO_{3.165}$ crystals are already formed below 800 °C, at 400 °C: Although the pattern was obtained on $K_{0.33}WO_{3.165}$, prepared by the reaction of WO_3 with K_2CO_3 at 800 °C [18], the light yellow film specimen prepared by the present method showed an identical pattern. Furthermore, there was no significant difference in the IR spectrum pattern between the materials prepared by the two methods. Figure 2b shows thermograms of the deposited decatungstate powder which was scrubbed out from the ITO electrode: there is a loss of water in the range 70–200 °C and a decomposition to $K_{0.33}WO_{3.165}$ at the range 380–410 °C.

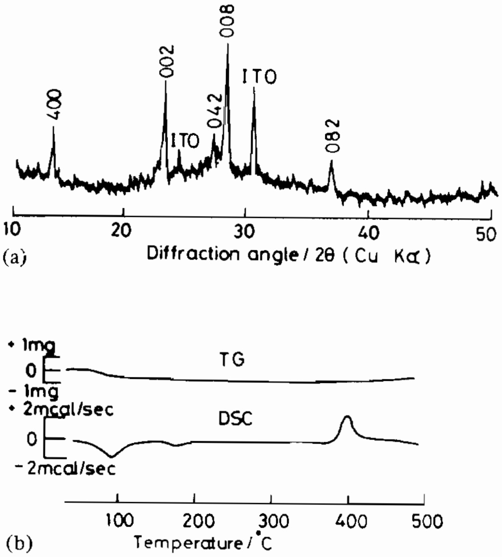

Fig. 2. (a) X-ray diffraction pattern of $K_{0.33}WO_{3.165}$ and (b) thermogram (TG and DSC) curves of the decatungstate deposited cathodically.

Cyclic voltammograms could be obtained in propylene carbonate, using 1 M $LiClO_4$ as electrolyte. Figure 3a shows a typical curve for the electrochromic film as a working electrode. Upon subjecting the working electrode to an initial cathodic scan, a reduction peak was observed around $U_{Ag} = -0.6$ V and resulted in the appearance of a distinct blue color which became darker at the range of more reductive potential. Upon subjecting the electrochromic working electrode to a subsequent anodic scan, a corresponding oxidation peak was observed at $U_{Ag} = -0.4$ V resulting in a bleaching and a complete removal of the blue color at $U_{Ag} = +1.0$ V. There was no significant change in the shape and peak currents during the repeated scan of 2.0 mV/s at the range $-1.0 \sim +1.0$. The change of the absorption spectrum of the film (about 10 μm thickness) is shown in Fig. 3b, where broad intervalence-charge-transfer bands at the range of the near infrared wavelength appear under the cathodic scan. Since the electrochemical reduction of polyoxometalates in protic solvents occurs with an accompanying protonation [14], we propose that the reductive coloration of $K_{0.33}WO_{3.165}$ accompanies the protonation due to the presence of a small quantity of water in the crystal lattice or electrolyte (eqn. (1)) and that a resultant OH^- is in the equilibrium of eqn. 2, although we have at present no information on the crystal structure of $K_{0.33}WO_{3.165}$ which is ESR-silent at 77 K. However, we cannot preclude the possibility of the direct transport of Li^+ from the electrolyte (eqn. (3)).

$$K_{0.33}WO_{3.165} + e^- + H_2O \rightleftharpoons K_{0.33}HWO_{3.165} + {}^-OH \quad (1)$$

$$Li^+ + OH^- \rightleftharpoons LiOH \quad (2)$$

$$K_{0.33}WO_{3.165} + e^- + Li^+ \rightleftharpoons LiK_{0.33}WO_{3.165} \quad (3)$$

The electrochemical reversibility of the electrochromism was investigated by monitoring changes in the absorbance at 850 nm as a function of applied potential. Figure 4 summarizes the electrochemical cycling characteristics of the electrochromic cell as a function of varying potentiostatic charge/discharge voltages. A preliminary cell demonstrated an excellent reversibility in excess of 10^4 cycles and for the frequency of 0.1 Hz under $U_{Ag} = \pm 1.5$ V.

In applying the present system to the electrochromic device, we constructed the semi-solid state device as shown in Fig. 5. The cell consists of a two-electrode system. The electrolyte is Al_2O_3 powder (Merck, GC 70-230 mesh) immersed by the propylene carbonate solution containing 1 M $LiClO_4$. With 1 Hz cycle the $K_{0.33}WO_{3.165}$-coated ITO electrode colored when the ITO electrode was biased 3 V negative

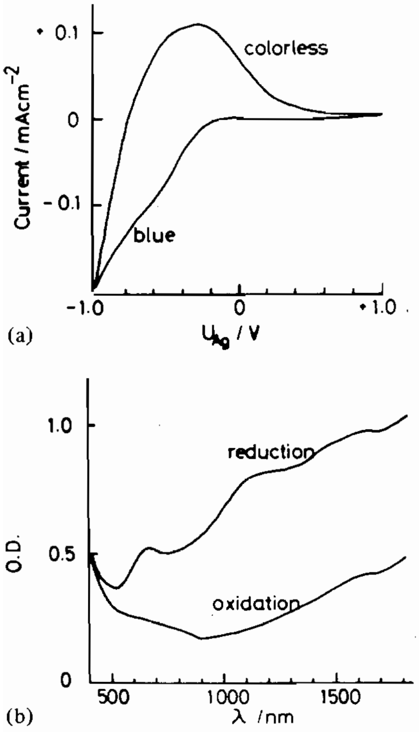

Fig. 3. (a) Cyclic voltammogram and (b) absorption spectra of a $K_{0.33}WO_{3.165}$ ($d \approx 10$ μm)-modified ITO electrode.

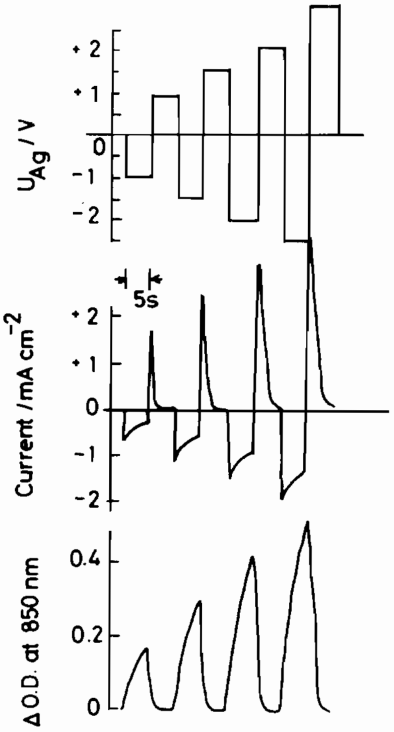

Fig. 4. Cycling characteristics of $K_{0.33}WO_{3.165}$ ($d \approx 10$ μm)-modified ITO electrode.

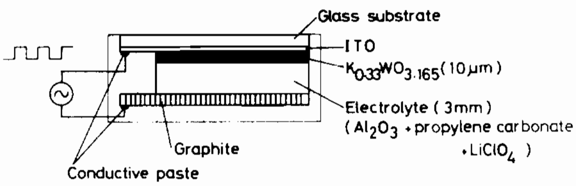

Fig. 5. Schematic configuration (in cross-section) of $K_{0.33}WO_{3.165}$-based electrochromic device.

with respect to the graphite counter electrode; it bleached when the ITO was 3.0 V positive. The electrochromic device based upon the electrochemically reversible $K_{0.33}WO_{3.165}$ would greatly benefit from the incorporation of the electrolyte within Al_2O_3 fine powder.

Preparation of the electrochromic film could be extended to Keggin typed polyoxometalates such as $[PW_{12}O_{49}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{5-}$. The optima for the preparations of these electrochromic film electrodes were described in 'Experimental'. Although there seemed to be no significant changes in the absorption spectra of the colored electrochromic films among starting polyoxotungstates, the apparent coloration under the cathodic bias decreased in this order

$$[W_{10}O_{32}]^{4-} > [PW_{12}O_{40}]^{3-} > [SiW_{12}O_{40}]^{4-} > [BW_{12}O_{40}]^{5-}.$$

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