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Effect of W^{VI}–OH Group on Electrochromism of Polyoxotungstate Film

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We have reported the electrochromism of polyoxotungstate $K_{0.33}WO_{3.165}$ polycrystalline prepared by decomposition (at 400 ℃) of the decatungstate film deposited cathodically on the indium–tin oxide (ITO) electrode [1]. It has been proposed that the process occurs according to the following reactions [1]

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

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

where H_2O exists in the crystal lattice or propylene carbonate (PC) electrolyte as contamination and donates H^+ on the reductive coloration of $K_{0.33}WO_{3.165}$. The property of the $K_{0.33}WO_{3.165}$-based electrochromic cell appears to be favorably comparable with the more developed amorphous WO_3(a-WO_3)–liquid electrolyte system [1]. It is well-known that $K_{0.33}WO_{3.165}$ can also be prepared by thermal reaction of WO_3 and K_2CO_3 in the ratio of 6:1 (molecule) at a much higher temperature (at 800 ℃) [2]. Unfortunately, the crystal structure of $K_{0.33}WO_{3.165}$ is still unknown due to difficulty in growing a single crystal, although the crystal lattice has been assumed to have a hexagonal system [2].

We have found that the polycrystalline form of $K_{0.33}WO_{3.165}$ is easily evaporated in vacuum compared with WO_3 and the resulting film exhibits the electrochromic property in the amorphous state. This paper describes that heat treatment of the evaporated film of $K_{0.33}WO_{3.165}$ causes a shift in the potential of the cathodic coloration reaction to the positive side due to a decrease in the W^{VI}–OH groups, in addition to a change in the amount of the porosity in the film and that the annealing of the amorphous $K_{0.33}WO_{3.165}$ film at 150 ℃ for 4 h causes a drastic improvement of the electrochromic property.

Experimental

$K_{0.33}WO_{3.165}$ was prepared by reacting WO_3 with K_2CO_3 in the ratio of 6:1 (molecule) at 800 ℃ for 20 h [2]. The films were prepared by vacuum evaporation of $K_{0.33}WO_{3.165}$ from electrically heated tungsten boats onto unheated ITO-coated glasses (10Ω/sq. Matsuzaki-Sinku Co.) at 4–5 $\times 10^{-5}$ Torr. The deposition rate of 80 Å/s was used. Annealing of the sample was done in an electric furnace at constant temperature. The film thickness of $K_{0.33}WO_{3.165}$ was measured by a spherical drill method. The thickness and area of the film were 2–3 μm and 9 × 40 mm^2, respectively.

The electrochemical measurements were made with a three-electrode system with a potentiostat (Hokuto Denko Co., HA-301) which was supplied with voltage from a function generator (Nikko Keisoku, NFG-3). The evaporated $K_{0.33}WO_{3.165}$ film electrode, Ag wire and Pt plate (1 cm^2) were used as working, pseudo-reference and counter electrodes, respectively. The electrolytes were PC solutions containing 1 M $LiClO_4$. All electric potentials (U_{Ag}) were with reference to Ag. PC was stored for 24 h over 5 Å molecular sieves and purified by distillation. For measurements of infrared spectra, $K_{0.33}WO_{3.165}$ was grown on KBr pellets by vacuum evaporation and supplied as samples. The absorption spectra were obtained with a Hitachi Model 330 spectrometer. Infrared spectra were taken with a Hitachi 260-10 IR spectrometer.

Results and Discussion

The films, as deposited, were slightly blue due to a small broad absorption centered at 900 nm. All of the films, on standing in the air, were bleached. The absorption spectral change of the film at U_{Ag} = –0.6 V (reduction) and +1.2 V (oxidation) in the electrochemical cell is given in Fig. 1. A very broad

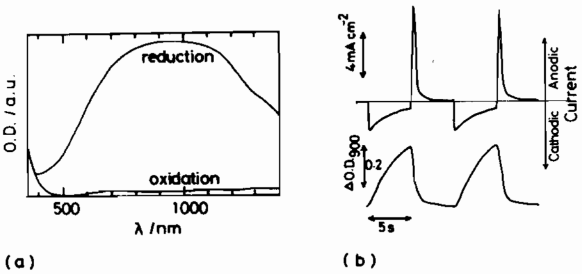

Fig. 1. Absorption spectral change (a) of the evaporated $K_{0.33}WO_{3.165}$ film (d ≈ 2 μm) electrode and (b) current (upper) and absorbance at 900 nm (lower) time transients of the film electrode during repetitive potential steps between U_{ag} = –0.6 V (5 s) and +1.2 V (5 s).

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asymmetric absorption band develops with λ_{max} = 900 nm (1.4 eV), probably due to the intervalence charge-transfer [1, 3, 4]. The absorbance at 900 nm was proportional to the total amount of charge consumed by the reduction. Thus, the absorption coefficient at 900 nm was estimated to be 1.2×10^6 coulomb^{-1} cm, assuming that the current efficiency for the blue form formation was 100%. The bands are apparently an intensification of absorption which was present in the film as deposited. The absorption spectrum upon reduction was similar to that for a-WO_3, suggesting a similarity of structure between evaporated films of $K_{0.33}WO_{3.165}$ and WO_3. It must be recalled that the intervalence–charge-transfer transition appeared extensively at the range of 1000–2000 nm in the polycrystalline state of $K_{0.33}WO_{3.165}$ [1]. The shift of the optical transition to a lower energy in the polycrystalline state supports that the evaporated film is amorphous, since the optical transition in a-WO_3 shifts to lower energy when the film is crystallized [5]. The electrochromic reversibility was investigated by monitoring changes in the relative absorption of an initially 1 mV He/Ne laser beam (633 nm) after being passed directly under $U_{Ag} = -0.6$ and +1.2 V through the electrochemical cell with a thickness of 10 mm. The electrochromic reversibility depended strongly upon the annealing (heating temperature and time) of the evaporated $K_{0.33}WO_{3.165}$ film. The sample annealed at 150 °C for 4 h or at 200 °C for 2 h exhibited the best electrochromism. As shown in Fig. 2 samples obtained by different heating times (t_{150}) at 150 °C give different variations of the absorbance at 633 nm if the repetition of the potential step between $U_{ag} = -0.6$ V (5 s) and +1.2 V (5s), was continued for a longer period: for the sample of t_{150} = 4 h the coloration rate under the 5-s reduction at $U_{Ag} = -0.6$ V increases with repeated cycling and the bleaching under the 5 s oxidation at U_{Ag} = 1.2 V occurs almost completely. The behavior is observed over 10^4 cycles. On the other hand, for the sample of t_{150} = 0, 3, or 6 h, the coloration rate decreases with repeated cycling although the bleaching seems to occur nearly completely. We could not observe any X-ray diffraction patterns arising from the evaporated films. Furthermore, the heat treatment of $K_{0.33}WO_{3.165}$ powder at 150 °C brought about no significant change in the X-ray diffraction patterns. In conjunction with the shift of the optical transition of the intervalence transition to higher energy in the evaporated film, these results indicate that the evaporated $K_{0.33}$-$WO_{3.165}$ films are amorphous and the structure of polyoxotungstate hardly changes during annealing at 150 °C.

Cyclic voltammograms of the films obtained for the various t_{150} values are shown in Fig. 3. The sample of t_{150} = 0 indicates that the cathodic current associated with coloration starts at $U_{Ag} = -0.2$ V and the anodic current associated with bleaching peaks at $U_{Ag} = -0.3$ V. The first scan exhibits the cathodic current peak around $U_{Ag} = -0.6$ V. A similar cyclic voltammogram was obtained for the polycrystalline $K_{0.33}WO_{3.165}$ which was prepared by thermal decomposition of the decatungstate deposited cathodically [1]. However the latter exhibited no significant change in the cyclic voltammograms during repeated cycling at the range of $U_{Ag} = +1.0 \sim -1.0$ V. On the other hand, as shown in Fig. 3, the electrochromic current for the sample of t_{150} = 0 decreases on cycling

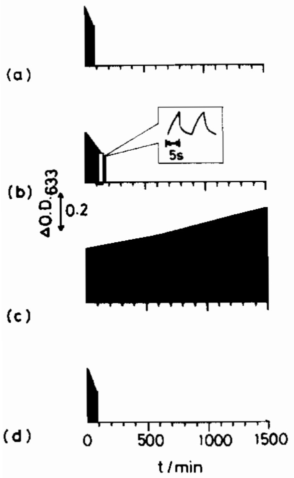

Fig. 2. Variation of the color change for the cycling (U_{Ag} = −0.6 V (5 s) and +1.2 V (5 s)) continued for long period. (a) (b) (c) and (d) indicate results for the sample of t_{150} = 0, 3 h, 4 h, and 6 h, respectively.

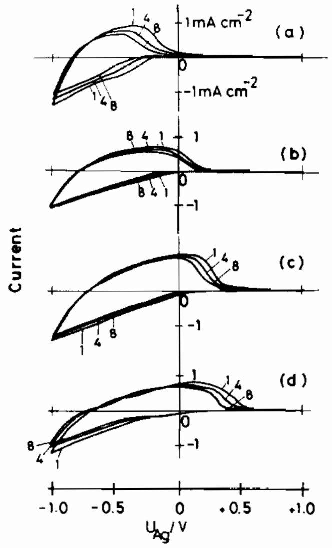

Fig. 3. Changes of currents during continuous cycling (U_{Ag} = −1.0 ~ +1.0 V, 20 mV s^{-1}) for the samples t_{150} = 0 (a), 3 h (b), 4 h (c), and 6 h (d). The numbers in the figures indicate voltammograms recorded at different cycles of first, 4th, and 8th.

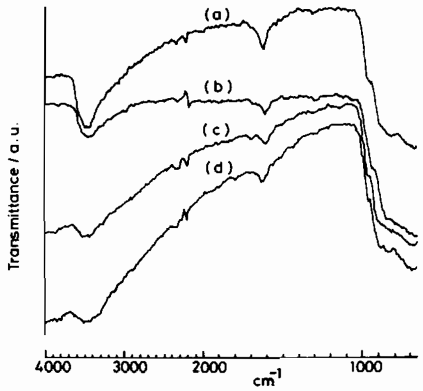

Fig. 4. IR spectra of $K_{0.33}WO_{3.165}$ evaporated on KBr. The spectra are shown for the pellets of t_{150} = 0 (a), 3 h (b), 4 h (c), and 6 h (d).

under the potential-scan rate of 20 mV s^{-1} and the potential of zero current of the cathodic reaction in the range of $U_{Ag} = 1.0 \sim -1.0$ moves gradually to more negative potentials. The same feature of the *V–I* curves is observed for other samples but the curves for the sample of t_{150} = 4 h exhibit larger currents and a small shift of the potential for the cathodic reaction to the negative side on repeated cycling, leading to constancy of the *V–I* curve during continuous cycling after 8 cycles. Furthermore, one should notice that the sample of t_{150} = 0 gives a large current at the first cycle, as well as the t_{150} = 4 h sample, and that the voltage of zero cathodic current at the first cycle shifts to more positive voltages with an increase of t_{150}, attaining $U_{Ag} \approx +0.2$ V for the sample of t_{150} = 4 or 6 h.

IR spectra for the $K_{0.33}WO_{3.165}$ films of various t_{150} values are shown in Fig. 4. The broad peak at 3400 cm^{-1} has been assigned to O–H stretching at the W–OH group or H_2O and the peak at 1600 cm^{-1} to the H–O–H bending [6]. The peak at 3400 cm^{-1} decreases with an increase of t_{150} and reaches nearly constant intensity for $t_{150} \geqslant 4$ h. This is in good agreement with the positive shift of the potential of zero cathodic current at the first cycle on the increase of t_{150} (Fig. 3). On the other hand, the decrease of the peak at 1600 cm^{-1} upon the increase of t_{150} is likely to be depressed significantly for $t_{150} \geqslant 3$ h. In conjunction with the fact that thermogravimetric analysis of the $K_{0.33}WO_{3.165}$ powder gave no observable desorption of the lattice water at a temperature below 300 °C, the potential shift of the cathodic current to the positive direction upon the increase of t_{150} can be associated with a decrease in the concentration of W^{VI}–OH groups of the polyoxotungstate rather than the physisorbed water, although we have no structural information of the a-$K_{0.33}WO_{3.165}$ film. The decrease of the W^{VI}–OH groups of the polyoxotungstate gives a decrease in the negative charges on nonprotonated anions and results in a shift of the initial reduction potential to a more positive direction due to electrostatic consideration. Similar behavior has been reported for the electrochemical reduction of Keggin polyoxotungstic acids where the initial reduction potentials of $[XW_{12}O_{40}]^{n-}$ (X = P, Si, and B) become more positive with decreasing *n* [7]. Furthermore, this behavior could also be expected as a result of a variation of the potential drop in the Helmholtz double layer between oxide semiconductors and aqueous electrolyte, which has the form of the Nernst equation for pH dependence [8]. The conclusion supports the assumption proposed for the a-WO_3 film [9–12]: the hydroxylated surface layer of the a-WO_3 film, which will be produced by the hydroxylation or hydrolysis in air containing humidity, shifts the potential for the cathodic reaction to the negative side. Thus, the potential shift for the cathodic reaction on repeated cycling to the negative side (Fig. 3) may be explained by the increase of the W^{VI}–OH groups in the a-$K_{0.33}WO_{3.165}$ film on the cycling, which results from hydrolysis with the contaminated water in the electrolyte. An increase of the W^{VI}–OH groups in the polyoxotungstate film during repeated cycling loses the electrochromic coloration density under the same applied potentials ($U_{Ag} = -0.6$ and 1.2 V) as shown in Fig. 2(a), (b) and (d).

Larger currents for the sample of t_{150} = 4 h (Fig. 3(c)) may be attributed to an increase in the porosity of the film as discussed for the a-WO_3 system [9]. If the cycling was continued for long periods, the electrochromic coloration density increased with time (Fig. 2(c)). This phenomenon seems to reflect the effect of the physisorbed water from the contaminated water in PC similar to the behavior shown in the a-WO_3 film where a larger content of physisorbed water contributes to a faster electrochemical coloration due to larger currents but not to the potential shift of the cathodic reaction [9, 11]. Thus, the large amount of porosity in the film leads to the increase in the content of physisorbed water during repeated cycling rather than the hydration of the polyoxotungstate, and makes the diffusion process of hydrogen or lithium ions faster (eqns. (1) and (2)). Then, the film will become a better ionic conductor. A large current at the first cycle for the sample of t_{150} = 0 (Fig. 3(a)) may be ascribed to a large amount of physisorbed water (Fig. 4(a)). In this case, a small amount of the porosity will let the film suffer from hydration during repeated cycling and result in a decrease of the coloration density (Fig. 2(a)).

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