

A NEW AND SIMPLE METHOD FOR MANUFACTURING ELECTRO- CHROMIC TUNGSTEN OXIDE FILMS

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A new and simple method for the preparation of electrochromic tungsten oxide film is presented. This novel approach can be realized by introducing a nanoporous textured polyacrylic acid (PAA) layer between tungsten oxide layer and indium tin oxide (ITO) one by dip-coating process. Homogeneous film with a thickness of about 0.8 μm is made by single dipping a PAA-coated ITO glass in the $\text{WO}_3\text{-NH}_4\text{OH}$ solution and shows an X-ray amorphous structure. During the cathodic and anodic processes by chronopotentiometry, the present films exhibit highly reversible electrochemical insertion of lithium ions; the corresponding inserted charge of 12.5 mC/cm^2 gives rise to a marked blue color yielding the change in optical density (ΔOD) of 0.65 at 550 nm and a coloration efficiency (η) of 51.8 cm^2/C .

Keywords: Electrochromism; polyacrylic acid; tungsten oxide

1. INTRODUCTION

Electrochromic coatings have been extensively investigated due to their potential application in a broad range of devices including smart windows and flat panel displays [1–4]. Various kinds of inorganic or

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organic materials for electrochromism have been proposed and their coloration properties have been studied in relation to their application for electrochromic devices. Among them, W oxide becomes one of the most promising materials for electrochromic devices because of its advantages of a good perceived contrast, memory effect and low switching voltage. Therefore several techniques have been used to prepare W oxide films, such as sputtering, evaporation, chemical vapor deposition, electrodeposition, and sol-gel method [5]. Recently, the last method has attracted much attention since this approach allows not only for the formation of oxides using relatively low temperature, much higher deposition rates and low-cost coating technique compared to other techniques but also for a large-area electrochromic coating.

In order to obtain a suitable coating solution by the sol-gel method, such parameters as temperature, nature and concentration of electrolyte (acid and base), nature of the solvent, and type of precursor material should be adjusted during hydrolysis and polycondensation processes [6]. Furthermore, some of starting materials in the sol-gel method are alkoxyates which are more or less expensive and do not afford satisfactory coating results if directly dissolved in typical solvent. In this context, a conventional sol-gel approach for electrochromic coating seems to be complicated and impractical.

The modified sol-gel methods [7, 8] concerning electrochromic W oxide film have been proposed, where the peroxotungstic species obtained by reacting W metal with aqueous H_2O_2 were used as a source of coating solution. These methods, however, call for some several steps to obtain a proper coating solution, and the viscosity of coating solution should be controlled upon mixing the intermediate of peroxotungstic acid or ester powder with water or alcohol. Therefore, it is considered that a more efficient preparative method with easier route toward electrochromic W oxide film is being required in order to fabricate a low-costable large-area electrochromic coating.

Here we report the preparation of W oxide film by a new and simple method in which a polyacrylic acid (PAA) layer is introduced as a buffer layer before making W oxide film. Electrochromic phenomena are examined by chronopotentiometry and UV-Vis-NIR spectrophotometry. To our knowledge, the present method is the first example of producing electrochromic W oxide film by incorporating

inorganic oxy-anions into a nanoporous textured polymer layer and provides an easily fabricable way for a large-area electrochromic coating.

2. EXPERIMENTAL

2.1. Preparation of Coating Solutions

The coating solution for polyacrylic acid (PAA) was prepared by dissolving the PAA powder in absolute ethanol (EtOH). To make 1% PAA solution, 3g of PAA (Aldrich, average molecular weight = 450,000) was dissolved in 300 ml of EtOH at room temperature, which was stirred for 1 day in order to obtain a transparent clear solution. The coating solution for tungsten oxide (WO_3) film was prepared by dissolving 21g of WO_3 powder (99+ %, Aldrich) in 60 ml of NH_4OH (30% solution in H_2O , Aldrich) at 100°C for 4h; then 240 ml of H_2O was added. The solution was further stirred at room temperature for 1 day, and was finally filtered in order to remove the undissolved WO_3 powder.

2.2. Film Preparation

The ITO glass ($10\Omega/\square$, Samsung) with $10 \times 10 \text{ cm}^2$ size was rinsed with ethanol and distilled water, then dried with air blowing just before coating. The ITO glass was first dipped into the 1% PAA-EtOH solution and withdrawn vertically at 30 mm/sec, then dried at room temperature. After this step, the ITO glass with a PAA layer was dipped into the $\text{WO}_3\text{-NH}_4\text{OH}$ solution and withdrawn vertically at 30 mm/sec. The coated film was dried at 100°C in an oven for 5 min, where the glass was tilted with respect to the vertical line to obtain a homogeneous film. Before using the film in lithium electrolyte, proton and electron were electrochemically injected/extracted into/from the as-prepared film in 1N HCl electrolyte under a charge density of $\sim 10 \text{ mC/cm}^2$ to induce polycondensation; a Pt wire was used as counter electrode. This electrochemically treated film was heated in the deintercalated state at 60°C for 1 hr under vacuum to remove the weakly adsorbed water contaminating the film surface. In order to

achieve electrochemical and optical measurements, the $10 \times 10 \text{ cm}^2$ film was cut into appropriate small pieces.

2.3. Preparation of Hydrophobic Lithium Electrolyte

Hydrophobic Li ion electrolyte was prepared by dissolving lithium bis-trifluoromethanesulfonimide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, 3M, abbreviated as LiTFSI) in hydrophobic 1-ethyl-3-methylimidazolium bis-trifluoromethanesulfonimide (1, 3- $\text{C}_3\text{H}_3\text{N}(\text{CH}_3)\text{N}(\text{C}_2\text{H}_5)[(\text{CF}_3\text{SO}_2)_2\text{N}]$, which was first prepared by Graetzl *et al.* [9] abbreviated as 1, 3-EtMeImTFSI), in which the composition of the electrolyte by weight ratio of LiTFSI : 1, 3-EtMeImTFSI was 10 : 90.

2.4. Film Characterizations

X-ray diffraction measurements were carried out using $\text{CuK}\alpha$ radiation to investigate the film structure. Scanning Electron Microscopy (SEM), JEOL JSM-840A apparatus, was used to determine the film thickness and composition.

2.5. Electrochemical and Spectrophotometric Measurements

Chronopotentiometric experiments were performed with a computer-controlled potentiostat/galvanostat (TACUSSEL, PGS 201 T model) for the electrochemical cell of Pt / LiTFSI + 1, 3-EtMeImTFSI / WO_3 -PAA-ITO. All the measurements were advantageously performed at room temperature in air owing to the hydrophobic character of the lithium electrolyte. The electrochemical lithium insertion/deinsertion was processed under the charge density of 12.5 mC/cm^2 , which was repeated automatically. Optical properties of the colored and bleached state were investigated in the wavelength range between 300 nm and 2000 nm using a UV-Vis-NIR spectrophotometer (Varian Cary 2415 Spectrophotometer equipped with DS-15 Data Station).

3. RESULTS AND DISCUSSION

The chemical species in the dissolution of inorganic material in aqueous solution and its dissolved chemical species depend on the pH

of the solution and the oxidation state of the metal cation M^{z+10} . High-valent cations with $z > 4$ gives oxy-anions $[MO_n]^{(2n-z)-}$ at high pH. The oxidation state of tungsten in WO_3 is hexavalent; therefore, the tungsten oxy-anions of $[WO_n]^{(2n-z)-}$ can be formed at high pH domain. According to the voltage equilibrium-pH diagram¹¹ WO_4^{2-} species are easily formed at the pH domain higher than 7.

It is found that the utilization of a PAA layer provides a unique opportunity to prepare W oxide coating. Though PAA is an electronic-nonconducting polymer, the W oxide layer formed on such an electrically insulating PAA layer exhibits electrochromic property, which implies that the PAA layer may have a nanoporous textured matrix in order to carry electrons between ITO and W oxide layer.

For the as-prepared WO_3 -PAA-ITO film and the proton and electron injected one, X-ray diffraction analysis has been performed. The X-ray diffraction diagrams, reported on Figure 1, show not only

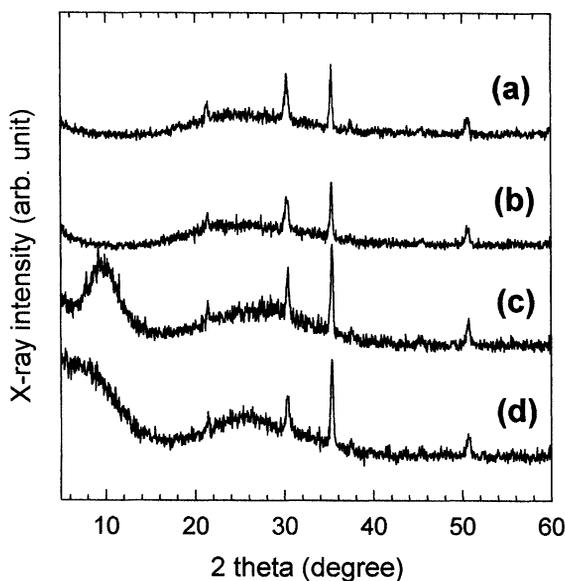


FIGURE 1 X-ray diffraction diagram for the ITO film (a); the PAA-coated ITO film (b); the as-prepared WO_3 -PAA-ITO film (c); the colored film after injection of $Q=10$ mC/cm^2 in 1 N HCl (d).

the expected narrow peaks corresponding to well crystallized ITO, but also a broad peak, observed for low angle, which accounts for the amorphous structure of the W oxide layer.

In order to determine the sample thickness, SEM analysis is carried out for the cross sectioned area. Figure 2 shows the WO₃-PAA film coated on the ITO layer. The average film thickness is determined to be about 0.8 μm and 0.3 μm for the WO₃-PAA layer and the ITO one, respectively. According to elemental analysis by energy dispersive mode with 15 kV, WO₃-PAA layer has tungsten and oxygen with small amount of carbon, and ITO one has indium, tin and oxygen.

To study the electrochromic property of the present WO₃-PAA-ITO film, the change of potential for the electrochemical cell with the Pt anode and the WO₃ cathode assembly is monitored with time at room temperature by chronopotentiometry, where the charge of 12.5 mC/cm² is inserted and extracted automatically over 100 cycles. Figure 3 shows the $E=f(t)$ diagram for the electrochemical cell with Pt/LiTFSI + 1, 3-EtMeImTFSI/WO₃-PAA-ITO. One coloration and one subsequent bleaching phenomenon constitute a cycle. During the cathodic process, the WO₃ electrode gets colored with a deep blue color. It is

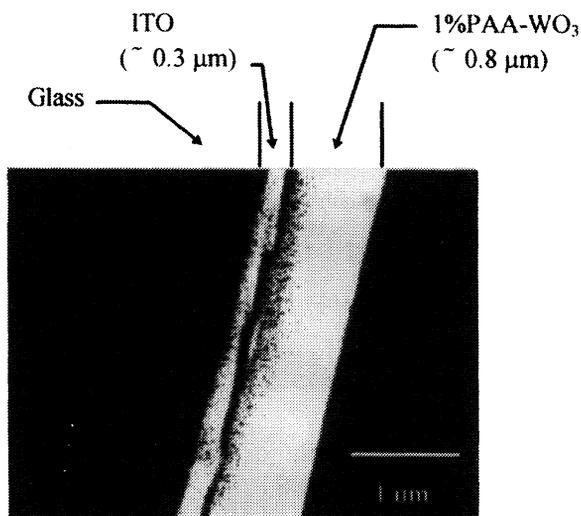


FIGURE 2 Cross sectioned SEM photograph for the WO₃-PAA-ITO film on glass.

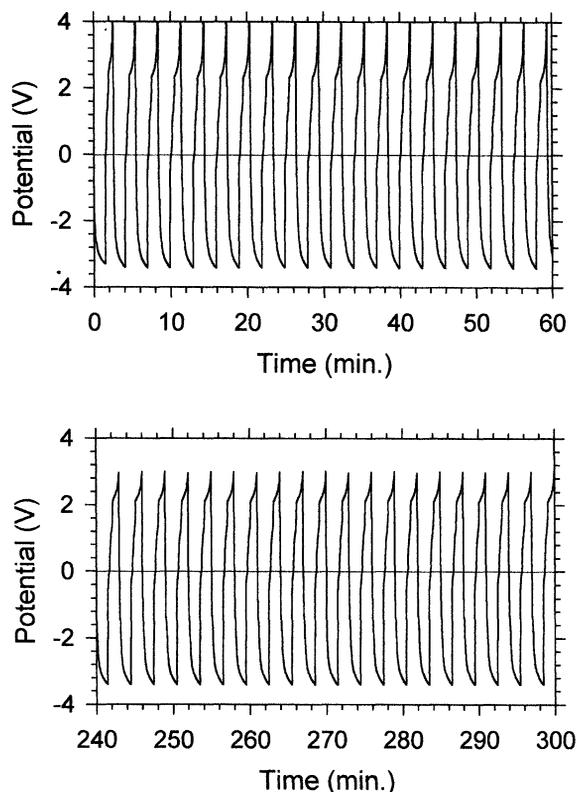


FIGURE 3 $E(V) = f(t)$ cycling diagram of the cell with Pt/LiTFSI + 1, 3-EtMeIm TFSI / WO_3 -PAA-ITO during 0 to 20 cycles (top) and 80 to 100 cycles (bottom), where each cathodic and anodic process is carried out at constant current of 0.5 mA for 150 sec (corresponding to $Q = 12.5 \text{ mC/cm}^2$).

found that the present WO_3 films exhibit reversible electrochemical and electrochromic cycling behaviors.

Figure 4(a) shows the UV-Vis-NIR spectra for the bleached state of the WO_3 -PAA-ITO film together with the ITO and PAA-ITO films as a reference. The spectrum of the well crystallized ITO film shows little spectral interferences, which accounts for the small film thickness. The PAA-ITO structure shows no spectral interference because of the nanoporous structure of the PAA thin film. On the other hand, the spectrum of the X-ray amorphous WO_3 -PAA-ITO film exhibits many

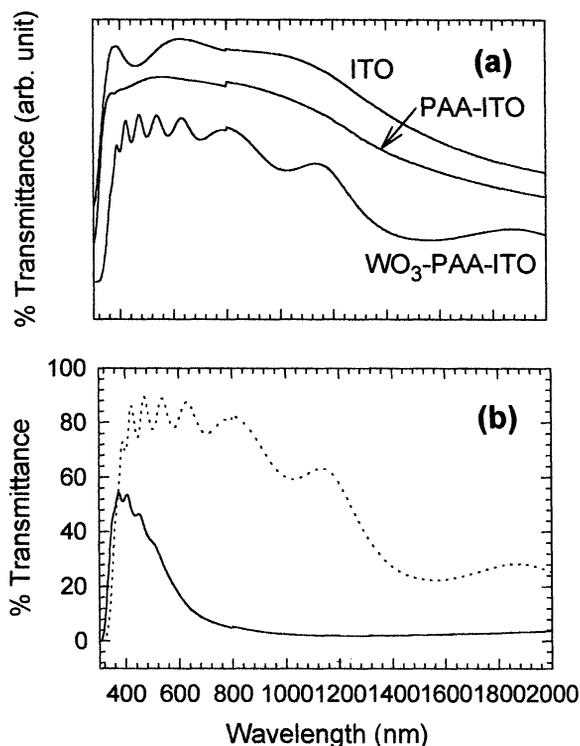


FIGURE 4 Comparison of spectral interferences among the ITO film, the PAA film coated on ITO, and the WO₃ films coated on PAA-ITO (a) and the UV-Vis-NIR spectra of colored state (—) and bleached one (...) for the WO₃-PAA-ITO film after 100 cycles of inserting and extracting charge of $Q = 12.5 \text{ mC/cm}^2$ (b).

spectral interferences due to the dense WO₃ layer and large thickness. In Figure 4(b), the colored and bleached spectra are obtained after 100 cycles of inserting and extracting charge of $Q = 12.5 \text{ mC/cm}^2$ by chronopotentiometry; the transmittance (%) is determined to be 19.47 for the colored state while the bleached state has a transmittance (%) of 86.30. The change in optical density ($\Delta OD = OD_{\text{color}} - OD_{\text{bleach}} = \ln [T_{\text{bleach}}/T_{\text{color}}]$, where OD is defined as $\log T^-$) at 550 nm is determined to be 0.65, and the coloration efficiency ($\eta = \Delta OD/Q$) is estimated to be $51.8 \text{ cm}^2/\text{C}$. It is found that there is no destructive problem in surface adhesion and optical property of the WO₃-PAA-ITO film during cathodic and anodic processes.

4. CONCLUSIONS

Electrochromic W oxide coating has been developed using a new concept of introducing a nanoporous textured PAA layer on ITO-coated glass. The resulting film obtained by dip-coating method shows reversible transparent-to-dark blue color change in a hydrophobic lithium electrolyte. We believe that the present technique is highly promising and can be advantageously extended to other materials.

We will report separately a detailed investigation of the W oxide amorphous phase using vibrational spectroscopic techniques, and also the electrochromic properties of the electrochromic device (ECD) constructed with counter electrode, hydrophobic Li electrolyte and WO₃-PAA-ITO electrode.

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