



# Electrochromic device application of tungsten oxide film with polymer electrolytes



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## ABSTRACT

We have compared tungsten chloride, peroxotungstic acid and acetylated peroxotungstic acid precursors in terms of their efficiency to prepare tungsten oxide thin films in our recent work. Therein, our results indicated the superiority of tungsten hexachloride over the others, in the sense that the formation of the film requires shorter deposition time of film and lower potential of deposition, when the former is of choice. Moreover, these films allow a higher extent of ion intercalation/deintercalation, resulting in superior electrochromic performance. Encouraged by these results, we turned our attention to the preparation of electrochromic devices wherein both liquid and solid Nafion functioned as the electrolytic layer. Our results primarily indicate that these devices offer a large optical modulation (i.e., the color of the device switches from dark blue to a fully transparent state with the applied potential) in liquid Nafion electrolyte. More importantly, the use of liquid Nafion in conjunction with its solid form functioned as a kind of network between layers, by facilitating intercalation/deintercalation of ions. If the full EC device is desired to be fabricated, electrochromic properties of the device can be effortlessly modulated by adding ion storage layer or altering the material of EC layer. Overall, we report that this configuration presents an easy and expeditious way of preparing electrochromic devices.

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## 1. Introduction

Electrochromism refers to the reversible change of color of thin films due to a small change in the voltage. This is important for smart windows and display applications [1–3]. The color change takes place because of intercalation and deintercalation of ions, which is controlled by voltage applied between transparent conductive oxide (TCO) layers [2,4]. The simplest solid electrochromic (EC) device consists of three layers: TCO, EC active layer and electrolyte. EC active layer and electrolyte are the most crucial parts of the solid EC device. Therefore, researchers have studied these parts extensively for a long time. Tungsten oxide has been one of the most widely studied materials for the EC active layer [5]. Tungsten oxide films are an ideal choice because they can show different types of chromogenism due to their multifunctional properties, which have a broad spectrum of applications in electrochromic devices and also the ability to be switched continuously between two different optical states [6–9]. Generally, lithium- and proton-based electrolytes are used for EC devices. There are several coating techniques of tungsten oxide, e.g.,

sol-gel [10,11], electrodeposition [12], chemical vapor deposition [13], and sputtering [5,14]. The electrodeposition technique, which is a simple, inexpensive, and an efficient method for producing thin films at room temperature, has been studied extensively. With this method, the thickness of the films can be controlled after calibration, and thin films can be coated uniformly on any shape [15–17]. Precursor materials for depositing tungsten oxide-based electrochromic films have been prepared by numerous methods based on the electrodeposition technique. Tungsten metal powder, sodium tungstanate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) starting materials are often used for electrodeposition. Sodium tungstanate starting material is usually preferred for electrodeposition by colloidal tungstic acid (ITA) and acetylated peroxotungstic acid with several preparation steps [18]. Tungsten hexachloride ( $\text{WCl}_6$ ) starting material has been employed for synthesizing tungsten oxide-based electrochromic films using the sol-gel technique [11,19]. From our literature survey we found that tungsten hexachloride precursor has not been used for depositing tungsten oxide-based electrochromic films by using the electrodeposition technique. With this precursor, the electrodeposition coating process is very rapid and requires lower initial potential. The films are deposited in relatively shorter time, less effortlessly.

In this study,  $\text{WCl}_6$  precursor is employed using the electrodeposition technique. The optical, electrochemical and structural

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properties of the deposited films were examined in both liquid and solid Nafion electrolytes. We fabricated all solid electrochromic devices using tungsten oxide active electrochromic layers prepared by tungsten chloride precursor and Nafion electrolytes. The use of a polymer electrolyte, in contrast to commonly used liquid electrolytes, allows integration of the electrode into fully solid-state devices. In this paper, we describe the fabrication and evaluation of a prototype solid-state electrochromic device based on a four-layer sandwich structure with the following configuration: ITO/ $\text{WO}_3$ /Nafion/ITO.

## 2. Experimental procedures

Indium tin oxide (ITO) coated glasses were used as substrates. Prior to the deposition of film on ITO glass substrates, the glass substrates were cleaned ultrasonically in deionized water and ethanol successively and dried at room temperature. 2 g of  $\text{WCl}_6$  were dissolved in 20 ml of ethanol. Then, in order to fully dissolve the tungsten hexachloride in ethanol, hydrogen peroxide was added to the solution. The color of the solution turned from blue to white when hydrogen peroxide was added. The stability of the solution depends on the amount of hydrogen peroxide. The prepared solution was aged for one week before deposition. The electrodeposition process was carried out at a constant current. The as-deposited glass substrate was placed in a water and ethanol mixture for 2 h, and then it was left to dry for 24 h and annealed at 100 °C for 2 h. The EC device was fabricated by the electrodeposited tungsten oxide layer using both liquid and solid Nafion electrolytes. The thicknesses of the electrodeposited films were 140–190 nm. Nafion membrane electrolyte is the most promising candidate for fuel cells because it has transportation, residential, and portable applications. Membrane electrodes contain an important element required for chemical production of electricity: a proton exchange membrane providing proton transport. A solution of Nafion, in a mixture of lower aliphatic alcohols and 10% water was furnished by Aldrich Chemical. Nafion is used in commercial applications as a membrane in electrochemical processes. Nafion has high

hydrogen conductivity and its optical properties make it a good candidate for use in the EC device. It can be easily laminated by drying to obtain uniform and transparent membranes. In addition, it works at temperatures up to almost 200 °C.

In this study, proton-conducting membranes, in films and liquid, were used as electrolytes for the EC devices. Finally, all-solid-state devices were fabricated by assembling another ITO glass slide on the thick Nafion film layers using a few drops of the concentrated Nafion solution as glue.

Electrochemical experiments were performed by utilizing an Arbin battery testing system (Arbin Instruments) and an in situ spectrophotometer to examine the electrochemical and optical behavior of the coated films. Thicknesses of the films were measured by a Dektak 150 model profilometer. A JEOL 6320 FV FE-SEM was used to examine the microstructure and the surface morphology of the films deposited on ITO substrates. INCA energy dispersive spectroscopy (EDS) attached to scanning electron microscopy (SEM) was used for elemental analysis. Electrochemical impedance spectroscopy (EIS) was performed in three-electrode system by using Parstat 2263 model potentiostat.

## 3. Results and discussion

The microstructures of the tungsten oxide films, which were deposited with  $\text{WCl}_6$  precursor on ITO, are illustrated in Fig. 1. SEM and EDS analyses confirmed that the films electrodeposited on ITO was uniform on a macro scale and composed of tungsten oxide (identified by microanalysis). Many fine spherical structures, along with small cracks, are formed over the surface of tungsten oxide films. It is believed that amorphous tungsten oxide films deposited with  $\text{WCl}_6$  have high residual stresses and therefore the cracks observed from the micrograph are due to their brittle structure. The tungsten oxide spherical structures may form agglomerates. These spherical structures have a mean radius of 770 nm, as illustrated in Fig. 1. The radius of the spherical structure changes from 550 to 835 nm. Chemical analysis of the films was conducted by EDS as represented in Table 1. EDS results were taken

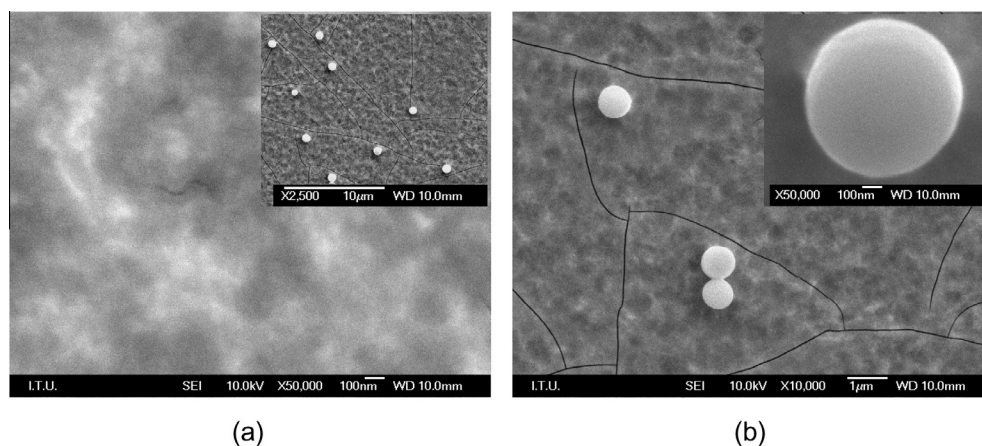


Fig. 1. SEM images of electrodeposited tungsten oxide films with tungsten hexachloride precursor on ITO (a) low-magnification, (b) high-magnification.

Table 1

Chemical composition of tungsten oxide films on ITO substrate.

Spectrum	O (%at.)	W (%at.)	Na (%at.)	Mg (%at.)	Al (%at.)	Ca (%at.)	In (%at.)	Sn (%at.)
Overall	69.18	14.23	2.18	1.31	0.79	4.02	7.40	0.89
Spot area	73.24	17.90	1.09	0.59	0.48	1.51	4.35	0.85
Flat area	70.49	12.90	2.74	1.01	0.83	4.24	7.80	
Substrate	45.92		5.27	1.94	0.81	5.56	5.99	0.47

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