Lithiation of WO₃ films by evaporation method for all-solid-state electrochromic devices

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Lithium (Li) electrolyte plays an important role in the electrochromic devices (ECDs), however, there are few studies on the matching between Li content and electrochromic layer in all-solid-state ECDs. In this work, lithiation WO₃ films with different Li thickness were prepared by evaporation method to investigate the effect of Li thickness on the optical properties of WO₃ films. Meanwhile, the Li storage capacity of WO₃ in liquid electrolyte was calculated. The results showed that the optimal thickness of Li for 450 nm WO₃ film prepared by evaporation was 42 nm. All-solid-state ECD glass/ITO/NiO/ZrO₂/Li/WO₃/ITO with optimal Li thickness exhibited large optical transmittance modulation (64.9% at 680 nm and 52.5% at 550 nm), high coloration efficiency (CE, 106.6 cm²/C at 550 nm) and superior cycle stability (98% retention of the maximum optical modulation after 4000 cycles). This work provides a new idea for the design and preparation of all-solid state ECDs.

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1. Introduction

Energy shortage is an increasingly serious issue in recent years. In addition to the exploration and utilization of alternative energy, effective energy saving measures are also crucial to solve the issue properly. The rapid development of building industry leads to a sharp increase in energy consumption. Smart windows technology, including electrochromism [1], thermochromism [2] and photochromism [3], is an efficacious energy conservation means which is conductive to reduce the energy consumption of artificial lighting and air conditioning [4]. Among them, electrochromic window has attracted great interests because of its active control and large optical modulation.

Conventional electrochromic devices (ECDs) are composed of five layers, embodying two transparent conductive layers, an electrochromic layer, an ion conductor layer (electrolyte layer) and an ion storage layer [5]. The commonly used electrolytes are divided into three types: liquid, gel and inorganic solid electrolyte. The all-solid-state ECDs employing inorganic solid electrolyte are the most promising due to their advantages of safety, continuous production and potential commercial applications [6]. Tungsten oxide [7,8] (WO₃) and nickel oxide [9,10] (NiO) are widely studied as the electrochromic and ion storage layer. Given the limited optical modulation and relative low transmittance of NiO, as well as the deterioration of ECD under long-term cycle, the current researches are mainly focused on improving the performance of NiO and exploring the degradation mechanism. For example, Zhu et al. reported a new type of ion storage layer LiₓNiOₓ deposited by magnetron sputtering using a LiNOₓ target, and LiₓNiOₓ-based all-solid-state ECDs were prepared. The ECDs exhibited excellent electrochromic performance with an optical modulation of 72.8% at wavelength of 550 nm, which could be attributed to the gradient distribution of Li element in the LiₓNiOₓ layer [11]. Wang et al. prepared lithium-doping (LiNiOₓ) and lithium-aluminum codoping nickel oxide (Al-LiNiOₓ) films, and the results showed lithium-aluminum co-doping could improve the transmittance, optical modulation and cycle stability simultaneously. The transmittance of the ECD ITO/WO₃/LiNbO₃/Al-LiNiOₓ/ITO in bleached state reached 74.5% and the transmittance contrast was 44% at 550 nm [4]. Dong et al. explored the cation-trapping of all-solid-state ECD glass/ITO/WO₃/LiTaO₃/NiO/ITO during the cycle, and the results indicated that the degradation of the ECD was related to the uncovering Li-trapping and morphology evolution of the NiO layer [12].

Electrolyte ions play an important role in the ECDs, but there are few studies with respect to the content of electrolyte ions and their matching with electrochromic layer in the ECDs. Because it is
difficult to quantify the ions content in the electrolyte layer, which may be an important parameter that is easy to be ignored. When the content of electrolyte ions is insufficient, the optical modulation of the ECDs may be limited. While excessive electrolyte ions usually form a thicker electrolyte layer, which may have an adverse impact on the performance of the ECDs, such as the response rates. It is also inefficient and high-cost to prepare a thicker electrolyte layer. Wen et al. believed that when \( x \) exceeded 0.65 in \( \text{Li}_x\text{WO}_3 \), significant ion trapping would occur during ion insertion \cite{13}. However, this value should be related to the microstructure and morphology of \( \text{WO}_3 \), as it has been reported that the microstructure and morphology would affect the capacity and active sites of \( \text{WO}_3 \) \cite{14-16}. Porqueras et al. reported their study on efficiency of Li doping on \( \text{WO}_3 \) films, but they did not applied the result to the ECDs \cite{17}.

Herein, Li with different thicknesses are deposited on the \( \text{WO}_3 \) thin films and then extracted in liquid electrolyte to investigate the actual extracted Li thickness and its effect on the transmittance of \( \text{WO}_3 \) films. For comparison, the Li capacity of \( \text{WO}_3 \) films in the liquid electrolyte is also calculated, which is represented by thickness. The results show that the Li capacity of \( \text{WO}_3 \) films with thickness of 450 nm is approximately 42 nm, which is the optimal Li thickness. All-solid-state ECD glass/ITO/\( \text{NiO}/\text{ZrO}_2/\text{Li/} \text{WO}_3/\text{ITO} \) with optimal Li thickness is prepared based on the above experiment, which exhibits superior electrochemical performance.

2. Experimental section

2.1. Fabrication of \( \text{WO}_3, \text{NiO, ZrO}_2 \) and ITO films

The \( \text{WO}_3, \text{NiO} \) and \( \text{ZrO}_2 \) films were prepared on the commercial ITO coated glass (\( 1 \times 4 \) cm\(^2\), 8 \( \Omega \)/square) and ITO films were prepared on glass by e-beam evaporation method using \( \text{WO}_3 \) particles (99.99%), \( \text{NiO} \) particles (99.9%), \( \text{ZrO}_2 \) particles (99.99%) and low density ITO particles (99.99%) with diameter of 1–3 nm, respectively. Before deposition, the glass and ITO coated glass substrates were washed by ultrasonic in deionized water, acetone and ethanol. The chamber was pumped down to \( 6 \times 10^{-4} \text{ Pa} \) before the preparation and the distance from substrates to targets was 30 cm. The substrate holder was kept rotating to guarantee the uniformity of the films. The thicknesses of \( \text{WO}_3, \text{NiO, ZrO}_2 \) and ITO films were 450, 170, 100 and 180 nm, respectively.

2.2. Fabrication of Li/\( \text{WO}_3 \) films

Li was deposited on as-prepared \( \text{WO}_3 \) films by resistive heating evaporation. The target lithium sheets (99.99%) were placed on a Molybdenum (Mo) boat and the distance between Mo boat and \( \text{WO}_3 \) films was 30 cm. The thickness of Li, measured by quartz crystal thickness monitor, ranged from 10 to 70 nm in increments of 5 nm.

2.3. Preparation of all-solid-state ECD

The all-solid-state ECD glass/ITO/\( \text{NiO}/\text{ZrO}_2/\text{Li/} \text{WO}_3/\text{ITO} \) was deposited continuously in a multi-target e-beam and resistive evaporation system without breaking the vacuum. The chamber was evacuated below \( 6 \times 10^{-4} \text{ Pa} \) and the target was pre-evaporated for about 20 nm before each deposition. The holder was rotated at a constant speed to make sure the layers were homogeneous. The \( \text{ZrO}_2 \) layer was used as the ion conductor layer to conduct the ions and block the electrons. \cite{18} The ECD was annealed at 250 °C in air atmosphere after fabrication. The detailed parameters were listed in Table 1.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Power source</th>
<th>Pressure (Pa)</th>
<th>Deposition rate (nm•min(^{-1}))</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NiO} )</td>
<td>e-beam</td>
<td>( 2 \times 10^{-3} )</td>
<td>5</td>
<td>170</td>
</tr>
<tr>
<td>( \text{ZrO}_2 )</td>
<td>e-beam</td>
<td>( 6 \times 10^{-3} )</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Li</td>
<td>resistance</td>
<td>( 8 \times 10^{-4} )</td>
<td>3</td>
<td>42</td>
</tr>
<tr>
<td>( \text{WO}_3 )</td>
<td>e-beam</td>
<td>( 8 \times 10^{-4} )</td>
<td>12</td>
<td>450</td>
</tr>
<tr>
<td>ITO</td>
<td>e-beam</td>
<td>( 2 \times 10^{-3} )</td>
<td>4</td>
<td>180</td>
</tr>
</tbody>
</table>

2.4. Characterizations

The crystal structure of \( \text{WO}_3, \text{Li/} \text{WO}_3, \text{NiO and ZrO}_2 \) films on ITO coated glass and ITO film on glass substrate were measured by X-ray diffractometry (XRD, PANalytical B. V. Model X’pert Pro) with a Cu-Ka radiation and a grazing angle of 1.0°. The morphology of the films were characterized by Raman spectra (Horiba Jobin Yvon LabRAM) and Atomic Force Microscopy (AFM, Bruker, Dimension Fastscan). The cross sectional morphology of the ECD was obtained by scanning electron microscopy (SEM, Zeiss supra 55).

The electrochemical properties of the films and the ECD were characterized by CHI 660E electrochemical workstation. \( \text{WO}_3 \) and \( \text{Li/WO}_3 \) films were measured in the liquid electrolyte using a three-electrode system, in which the films, Pt wire, Ag wire and 1 M LiClO\(_4\)-PC (propylene carbonate) were employed as the working electrode, counter electrode, reference electrode and electrolyte, respectively. Chronoamperometry (CA) measurements were performed at 0.8 V for extraction and −0.8 V for insertion with a duration of 30 s. The ECD was tested with a two-electrode system, using the top ITO layer close to \( \text{WO}_3 \) as working electrode and the bottom ITO layer as reference and counter electrode. Cyclic voltammetry (CV) was carried out at a scan rate of 0.1 V/s from −2.5 V to 2.5 V. CA measurements were performed at ±2.5 V with durations of 30 s and 120 s. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 0.1 Hz to 1 MHz. The optical transmittance spectra of the samples were monitored in situ by Vis-NIR fiber optic spectrometer (MAYA 2000-Pro, Ocean Optics) in the range of 400–1050 nm.

3. Results and discussion

3.1. Effect of Li content on \( \text{WO}_3 \) films

Li with different thickness is deposited on the \( \text{WO}_3 \) films to investigate the influence of Li thickness on the optical properties and structure of \( \text{WO}_3 \). XRD patterns of Li/\( \text{WO}_3 \) and \( \text{WO}_3 \) films are presented in Fig. S1. Both Li/\( \text{WO}_3 \) and \( \text{WO}_3 \) films are amorphous, \cite{19} indicating that lithiation does not change the crystallinity of \( \text{WO}_3 \) films. Fig. 1a shows the digital photos of Li/\( \text{WO}_3 \) films with different Li thickness, it can be seen that the colors of \( \text{WO}_3 \) films change from transparent to light blue, dark blue and blue-black with the increase of Li from 0 to 30 nm. The visual appearance to the naked eyes is almost unchanged when the thickness of deposited Li exceeds 30 nm. The corresponding transmittance spectra are exhibited in Fig. 1b, from which one can find that Li injection has a great effect on the transmittance of \( \text{WO}_3 \) films in the near infrared range. As Li content increases, the infrared transmittance of Li/\( \text{WO}_3 \) films decreases rapidly until the Li thickness
reaches 25 nm. However, in the short wave band (380–600 nm), the transmittance has been decreasing slowly. Fig. 1c records the transmittance of LiWO₃ films at 550 nm. The LiWO₃ films maintain a transmittance of approximately 6.5% when the Li thickness exceeds 45 nm, indicating that fully coloration could be achieved by injecting 45 nm Li.

CA measurements are performed in 1 M LiClO₄-PC electrolyte to extract the Li ions from LiWO₃ films. As shown in Fig. 2a, the current densities of all samples are reduced from a large value to nearly zero, which implies the process of extraction of Li from the films. The time required for complete extraction of Li increases from about 2 s to 15 s with Li thickness increasing. The charge densities can be obtained by integral method, as exhibited in Fig. 2b. Here, to compare the extracted Li with the deposited Li clearly, thickness is used to characterize the Li content. Each extracted charge is equivalent to a Li ion, thus, the corresponding extracted Li thicknesses can be calculated according to the following formula:

\[
h = \frac{V}{S} = \frac{m}{\rho \times S} = \frac{n \times M}{\rho \times S}
\] (1)

\[
n = \frac{Q \times 6.24146 \times 10^{18}}{N_A}
\] (2)

**Fig. 1.** (a) Digital photos, (b) transmittance spectra in 350–1050 nm and (c) transmittance at 550 nm of the Li/WO₃ films with different thickness of Li. Li thicknesses are from 10 to 70 nm in increments of 5 nm.

**Fig. 2.** (a) The current densities in the extraction process (0.8 V, 30 s) of Li/WO₃ films with different Li thickness. (b) Extracted charge densities of Li/WO₃ films derived from (a). (c) Comparison of deposited and extracted thicknesses of Li in Li/WO₃ films.
where h, V, S, m, ρ and n are thickness, volume, area, volume density and amount of substance, respectively. Q is quantity of electricity, Nₐ is Avogadro constant, and 6.24146 × 10¹⁸ refers to the amount of electrons per Coulomb. Fig. 2c presents a comparison between the deposited thickness and the extracted thickness of Li. When the deposited thickness is less than 30 nm, the extracted thickness is obviously smaller than the deposited. As the deposited thickness increases, the deviation between them decreases until it exceeds 65 nm. This may be associated to the irreversible trapping of Li ions in the deposition process [20], and the amount of them are limited so the extracted thickness is gradually consistent with the deposited thickness, and the little fluctuations may be caused by the inherent errors of the equipment. However, the deviation appears again with the further increase of deposited thickness, which is possibly due to it is beyond the capacity of WO₃.

As shown in Fig. 2b, the charge densities of bare WO₃ film in the coloring and bleaching process are also calculated, which are 31.61 and 31.51 mC/cm², respectively. The corresponding thicknesses exhibited in Fig. 2c are approximately 42.4 and 42.2 nm. Here, the ratio of Li/W in Li₃WO₃ film is roughly 0.23. The electrochromic performance of the Li/WO₃ film is similar to that of WO₃ film, as presented in Fig. S2.

3.2. Characterization of all-solid-state ECDs

The all-solid-state ECD with structure of glass/ITO/NiO/ZrO₂/Li/WO₃/ITO is designed and fabricated by e-beam and resistive evaporation based on the above results, where the thicknesses of WO₃ and Li are 450 nm and 42 nm, respectively. The as-prepared ECD is dark because itO prepared by evaporation has a low transmittance, thus, the ECD needs to be annealed to obtain a high transmittance. To investigate the crystallinity of each layer, the top ITO, WO₃, ZrO₂ and NiO films are prepared and characterized by XRD after annealed at 250 °C, as shown in Fig. 3a. The top ITO prepared by e-beam evaporation exhibits the same structure as the commercial ITO, with diffraction peaks corresponding to In₂O₃ (JCPDS card No. 65-3170) [21]. In addition to the diffraction peaks of In₂O₃, no other diffraction peaks are observed in the XRD patterns of WO₃ and ZrO₂ films, implying that both WO₃ and ZrO₂ are amorphous, [19] which is beneficial to the electrochromic performance of the ECD [22]. The diffraction peaks of NiO film at 37.3°, 43.4° and 63.0° (corresponding to the (111), (200) and (220) crystal planes of cubic NiO (JCPDS card No. 73-1519) [23]. The Raman spectra indicate that some Ni²⁺ are oxidized to Ni³⁺ after annealing. AFM analyses demonstrate that the films have uniform and dense surfaces, as exhibited in Fig. S3 and F4.

The cross sectional SEM image of the ECD is presented in Fig. 3b. The clearly identified interfaces suggest the great physical and chemical stability of all layers. Strong adhesion between layers, which is essential for the stability of the ECD, can also be noticed [24]. The cross section SEM image shows a five layer structure: ITO, WO₃, ZrO₂, NiO and ITO from top to bottom, where Li does not exist in isolation due to its diffusion into other layers during the deposition process [25]. The corresponding thicknesses of each layer from top to bottom are 180, 450, 100, 170 and 200 nm, respectively.

The electrochemical and electrochromic performances of the ECD are characterized by CV and CA. Fig. 4a shows the CV curves for different cycles. It can be seen that the ECD is gradually activated during the cycle. The area enveloped by CV curves increases, indicating the improvement of the capacity [26], which means that more active ions participate in the electrochromic reaction. Optical properties are the most important index to evaluate the performances of the ECD [27]. The optical transmittance spectra of the ECD in the colored (Tₘ) and bleached state (Tₜ) and optical modulation (ΔT=Tₘ-Tₜ) are displayed in Fig. 4b and c. The corresponding CA curves are presented in Fig. S5, from which the decrease of leakage current with cycling can be observed. The ECD has a small optical modulation before activation, which is in agreement with the CV results. The average transmittance of bleached state (Tₘ-ave) and colored state (Tₜ-ave) in the wavelength of 400–800 nm are 76.1% and 35.2%, respectively. The optical modulation increases significantly in the first 500 cycles and then slowly increases until reaches its maximum of 55.2% after 2700 cycles. The ECD shows a large optical modulation of 64.9% at 680 nm. The Tₘ-ave decreases slightly from 76.1% to 72.3% after 4000 cycles (Fig. 4d), which is related to the ion trapping of WO₃ layer. Fig. 4e presents the digital photos of ECD in bleached and colored state, from which one can see that the ECD is blue-black in colored state and light gray in bleached state. The performance of ECD is recorded as shown in Video. S1.

Fig. 5 shows the CA curves and the corresponding transmittance spectra of the ECD after 4000 cycles, with durations of 30 s and 120 s, respectively. After 4000 cycles, the ECD still exhibits excellent electrochromic performance with an optical modulation at 680 nm reaching 53.7% for 30 s and 63.5% for 120 s, respectively. The ECD with ideal Li thickness demonstrates superior capability of optical modulation and cycle stability.

Response time is one of the most significant performance factors of the ECD, which is defined as the time required to achieve 90% of the maximum optical modulation of the ECD [28]. Fig. 6a lists the response times of bleaching and coloring at wavelength of 550 nm for different cycles, and the detailed curves are presented in Fig. S6. From Fig. 6a one can see that the time needed for the bleaching process is only 6–12 s, and that for the coloring process is 48–54 s. Besides, both the bleaching (tₘ) and coloring times (tₜ) increase slightly with cycling. The electrochemical impedance spectroscopy (EIS) measurements for different cycles are also carried out and shown in Fig. S7. The plots show two semi-
circles in high frequency region, indicating the charge transfer impedance, and an oblique line in low frequency region, which represents the ion diffusion [29]. The equivalent circuit is presented as inset in Fig. S7b. The radius of semicircles in plots gradually increases with cycling, implying the increases of charge transfer impedance, which may affect the response time. A larger slope of the plots observed after 500 cycles implies a faster ion diffusion.

However, the response time has strong link to the optical performance. As Fig. 4d shows, the optical modulation also increases with cycling, thus, it is difficult to quantitatively evaluate the evolution of response time during the cycles. Therefore, a suitable method is adopted to judge the response time, and the formula is as follows,

\[ \Delta t = \frac{\Delta T_{90}}{t} \]  

where \( \Delta T_{90} \) is the 90% of total \( \Delta T \), \( t \) is response time. \( \Delta T_{t} \) represents the change of transmittance per second, larger \( \Delta T_{t} \) indicates faster response speed. The calculated results are exhibited in Fig. 6b. The \( \Delta T_{t} \) of bleaching process decreases with cycling until almost invariable after 2700 cycles, which implies that the bleaching response speed is slowing. While a slight increase of that is observed in the coloring process, indicating the small increase of coloring response speed. The results are consistent with that of the EIS.

Coloration efficiency (CE), defined as the variation of optical density (\( \Delta OD \)) per unit charge density (\( \Delta Q \)) in the coloring or bleaching process, is another vital performance evaluation criteria of the ECD [29]. The formula is as follows,

\[ CE = \frac{\Delta OD}{\Delta Q} = \frac{\log(T_b/T_c)}{\Delta Q} \]  

(4)

where \( T_b \) and \( T_c \) refer to the transmittance of ECD in the bleached and colored state. Fig. 7 shows the CE for different cycles, and the detailed figures are listed in Fig. S6. The CE increases from 71.8 cm²/C to 106.6 cm²/C after 3300 cycles, due to the increase of optical density and decrease of leakage current with cycling. Even after 4000 cycles, when the optical density decreases slightly, the CE value of the ECD still remains as high as 98.1 cm²/C, indicating great energy saving effect. The comparison of electrochromic
performance indexes of various all-solid-state ECDs with previous work are summarized in Table S1, from which one can see that the ECD in this work has superior electrochromic performances.

4. Conclusions

In this study, WO₃ films with different thickness of Li are prepared by evaporation method and the effect of Li thickness on the optical properties and structure of WO₃ is investigated. Lithiation has a greater influence on the transmittance in the near infrared region and part of Li will be trapped into the WO₃ films during the deposition. The results show that 42 nm is the optimal thickness of Li for 450 nm WO₃ film prepared by evaporation. Based on the results, all-solid-state ECD with structure of glass/ITO/NiO/ZrOₓ/Li/WO₃/ITO is designed and fabricated, which exhibits superior electrochromic performance with a maximum optical modulation of 64.9% at 680 nm. The CE of the ECD is as high as 106.6 cm²/C. The ECD has impressive cycle stability up to 4000 cycles with approached to 98% retention of the maximum optical modulation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Wenjie Li: Conceptualization, Methodology, Validation, Software, Writing - original draft. Xiang Zhang: Conceptualization, Formal analysis, Writing - original draft. Xi Chen: Validation, Formal analysis. Yingming Zhao: Resources. Lebin Wang: Visualization. Mingjun Chen: Resources, Visualization. Zitong Li: Visualization. Jiupeng Zhao: Supervision, Project administration, Writing - review & editing. Yao Li: Funding acquisition, Project administration.

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Supplementary materials


References


