

Study on Electrodeposition Process of Molybdenum Doped Vanadium Oxide Electrochromism Films

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Abstract. Molybdenum doped vanadium oxide (Mo doped V₂O₅) xerogel films are prepared by cathodic electrodeposition on indium tin oxide substrate from Mo doped V₂O₅ sol. As an anodic and cathodic coloration electrochromic material, the electrodeposited Mo doped V₂O₅ film presents multi-electrochromic behavior (orange–yellow–green–blue) with an optical modulation of 30–62% in the spectral region 550–800 nm, which can be expected as a result of different film thickness. The electrodeposited process of Mo doped V₂O₅ films is investigated. With the increase of the electrodeposition time, the thickness of the films increases gradually. The thickness of the films increases sharply with the increase of the concentration of the sol. When the film thickness is about 400 nm, the optical modulation range of the film is about 60%.

Introduction

The great interest on the electrochromic effect shown by transition metal oxides, such as V₂O₅ and MoO₃, are due to their possible applications in smart windows, information display, light shutters, variable reflectance mirrors and variable-emittance thermal radiators [1-4]. Among electrochromic transition metal oxides, V₂O₅ shows anodic and cathodic coloration, and the electrochromism of V₂O₅-based films can be considered as a reversible reduction/oxidation process accompanying the double insertion/extraction of Li⁺ ions and electrons [5]. Recently, we described the preparation of Mo doped V₂O₅ films by cathodic electrodeposition at various cathodic potentials from Mo doped V₂O₅ sol and studied their electrochromic mechanism [6,7]. Electrodeposited method is probably the most economical method for making the films in addition to its relative ease in forming large area films. In this article, the electrodeposited process of Mo doped V₂O₅ films was further studied. The effects of electrodeposition time and sol concentration on film thickness were investigated. Moreover, the relationship between film thickness and electrochromic properties was discussed.

Experimental Procedure

Mo doped V₂O₅ sol was formed by sol-gel combined with hydrothermal reaction. Firstly, the peroxy-polymolybdate solution was mixed with 30 mL of V₂O₅ sol to form a mixed sol by stirring for 1 h, and then the sol was kept into autoclaves at 180 °C for 12 h. The molar ratio of Mo to V₂O₅ was 5 mol %. Mo doped V₂O₅ sol laid motionless for two to five days before electrodeposition. By changing the concentration of V₂O₅ sol, different concentrations of Mo doped V₂O₅ sol were prepared. The concentrations of Mo doped V₂O₅ sol were 0.0125, 0.025, 0.050, 0.075 and 0.10 M.

Mo doped V₂O₅ films were prepared by cathodic electrodeposition [6,7]. The film electrodepositions and electrochemical experiments were carried out with an Autolab model PGSTAT30 potentiostat/galvanostat interfaced to a computer. The standard three-electrode arrangement was used. The counter electrode was a platinum sheet with an area of 1 cm². The reference electrode was saturated calomel electrode (SCE). The ITO-coated glass substrates act as the working electrode. Mo doped V₂O₅ films were deposited potentiostatically by applying a fixed potential of -0.3 V vs. SCE for different length of time (10, 30, 60, 120, 240, 600 and 1200 s) from Mo doped V₂O₅ sol with the concentration of 0.05 M. Mo doped V₂O₅ films were also deposited

potentiostatically by applying a fixed potential of -0.3 V vs. SCE for a predetermined length of time (100s) from Mo doped V_2O_5 sol with the different concentrations (0.0125, 0.025, 0.050, 0.075 and 0.10 M). Following deposition, the films were dried in air at room temperature. After heat treatment in air oven at 120 °C for 24 h, the homogeneous yellow films were obtained.

Film thickness was measured with the sectional view of films by scanning electron microscope (Phenom Pro). The electrochromic films were polarized in an electrolytic solution of 0.5 M LiClO₄ (Aldrich) in propylene carbonate (PC) (Aldrich) using chronoamperometry at 1.0, 0.3, -0.3, -0.3 and -1.0V for 30 s, respectively. The optical properties of Mo doped V_2O_5 films were characterized by UV–Visible spectrophotometer (TENSOR-27 model).

Results and Discussion

Effect of electrodeposition time on film thickness and electrochromic property. The maximal transmittance change ΔT_{max} is used to indicate the ability of the optical modulator of the electrochromic materials. Fig. 1 shows the effect of electrodeposition time on film thickness and ΔT_{max} with a specific sol concentration of 0.05 M. Fig. 3 shows the corresponding ex-situ optical transmittance data for Mo doped V_2O_5 films with different electrodeposition time (10, 120 and 1200 s) in different coloration states, which the film was polarized at +1.0, +0.3, -0.3, and -1.0 V, respectively. As can be seen, with the extension of the electrodeposition time (from 10 s to 1200 s), the thickness of the films increases gradually (from about 90 nm to 1050 nm). Moreover, ΔT_{max} for the film with different electrodepositon time is 38–62% in the spectral region 550–800 nm, while ΔT_{max} reach a maximum value of 61% at the electrodeposition time of 120 s with the film thickness of about 400 nm, as shown in Fig. 2.

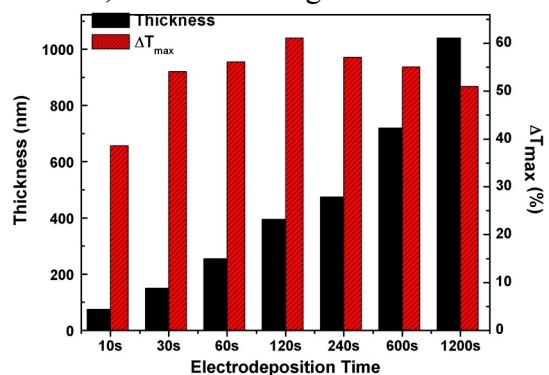


Fig. 1 The effect of deposition time on the thickness and ΔT_{max} of Mo doped V_2O_5 film

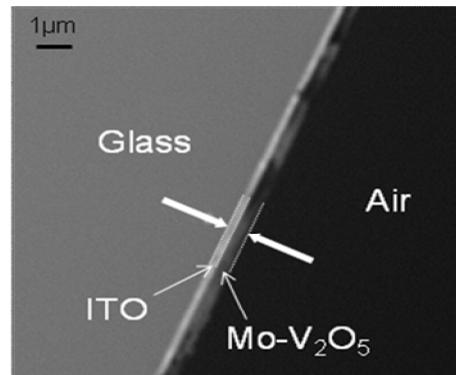


Fig. 2 SEM cross-sectional image of Mo doped V_2O_5 film with deposition time of 120 s

During the process of electrochromism, the film switches from a transmissive, orange red color when oxidized (+1.0 V), to a dark green color (+0.3 V), a deeply absorptive purple/blue color when reduced (-0.3 and -1.0 V), which is in agreement with the blue shift of the corresponding absorbance peaks in the transmittance spectra. The electrochromism of Mo doped V_2O_5 film can be considered as a reversible reduction/oxidation process accompanying the double insertion/extraction of Li⁺ ions and electrons. For as-deposited films, as the thickness of the film increases, the absorption edge has obvious red shift, and the optical band gap becomes narrow. This is attributed to the increase in absorbance for thicker films due to large number of atoms available for the absorption of photon energy [8]. For colored films, Mo doped V_2O_5 films showed increasing the coloring state with increasing the thickness of thin films. For the thin film of 90 nm thickness, the transmittance in the short wave (<500 nm) increased by more than 70%, but the transmittance changes in the visible infrared wave (>500 nm) were about 60%. For the thick film of 1050 nm thickness, the transmittance in the short wave (<500 nm) increased by 30%, but the transmittance changes in the visible infrared wave (>500 nm) were about 50%.

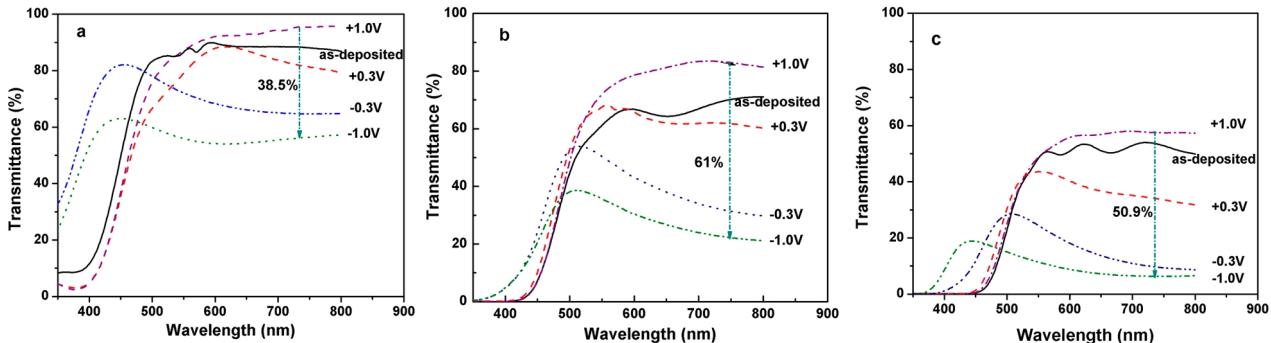


Fig. 3. Transmittance spectra of Mo doped V₂O₅ films with different electrodeposition time in different coloration states (a)10 s , (b)120 s, (c)1200 s. All films were polarized with the potential of +1.0, +0.3, -0.3 and -1.0 V, respectively, with an interval of 30 s in propylene carbonate solution containing 0.5 M LiClO₄.

Effect of sol concentration on film thickness and electrochromic property. Fig. 4 shows the effect of sol concentration on film thickness and ΔT_{\max} with a specific deposition time of 100 s. Fig. 6 shows the corresponding ex-situ optical transmittance data for Mo doped V₂O₅ films with different sol concentration (0.0125, 0.05 and 0.1 M) in different coloration states, which the film was polarized at +1.0, +0.3, -0.3, and -1.0 V, respectively. As can be seen, with the extension of the sol concentration (from 0.0125 M s to 0.1 M), the thickness of the films increases sharply (from about 100 nm to 1500 nm). Moreover, ΔT_{\max} for the film with different sol concentration is 36–62% in the spectral region 550–800 nm, while ΔT_{\max} reach a maximum value of 61.6 % at the sol concentration of 0.05 M with the film thickness of about 400 nm, as shown in Fig. 5.

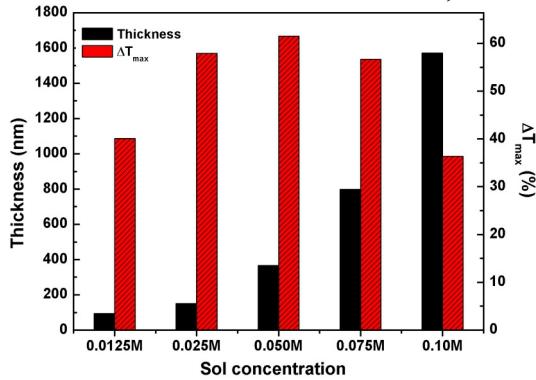


Fig.4 The effect of sol concentration on the thickness and ΔT_{\max} of Mo doped V₂O₅ film

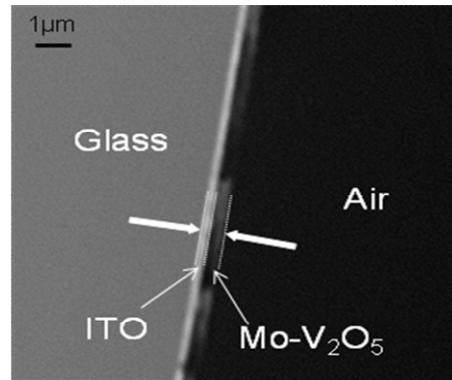


Fig. 5 SEM cross-sectional image of Mo doped V₂O₅ film electrodeposited with sol concentration of 0.05 M

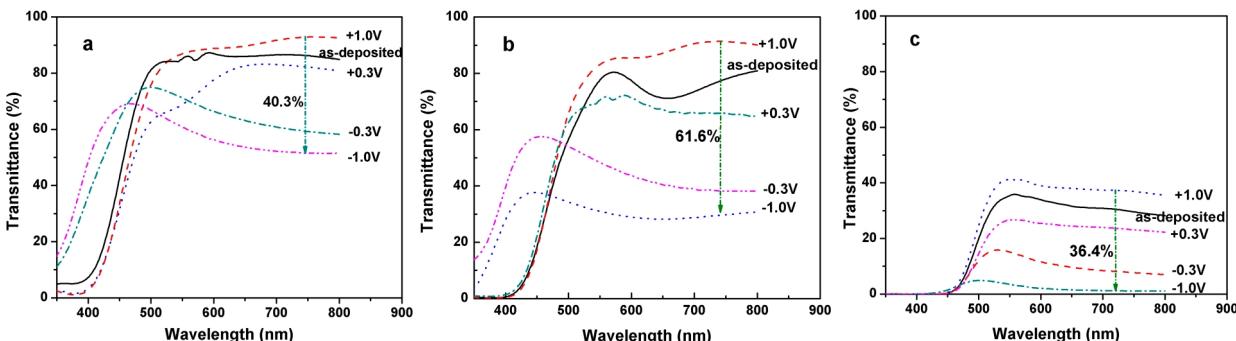


Fig. 6. Transmittance spectra of Mo doped V₂O₅ films with different sol concentration in different coloration states (a)0.0125 M , (b) 0.05 M, (c) 0.1 M. All films were polarized with the potential of +1.0, +0.3, -0.3 and -1.0 V, respectively, with an interval of 30 s in propylene carbonate solution containing 0.5 M LiClO₄.

In order to verify the influence of sol concentration on film thickness, the particle size distribution and median particle size of Mo doped V₂O₅ sol at different molar concentration of 0.0125, 0.025, 0.05, 0.075 and 0.1 M was investigated as shown in Fig. 7. It can be found that the sol particle size decreases with the increase of the sol concentration. According to the theory of Stern's model, when the sol concentration is increased, the concentration of counter-ions in the medium is increased and then the diffusion layer is compressed and thinned, so the sol particle size decreases. The micelles with smaller particle size have a faster migration rate, so the thickness of the film deposited by a larger concentration of the sol is thicker at the same deposition time, which is consistant with the results of Fig.4.

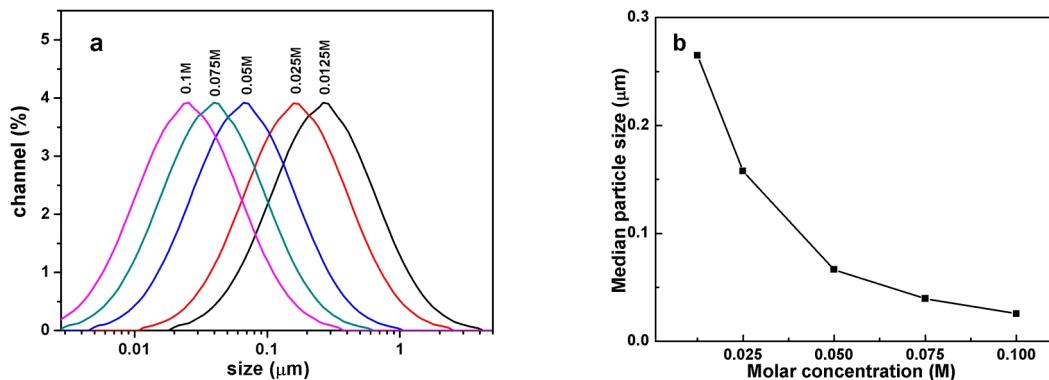


Fig.7. Particle size distribution (a) and median particle size (b) of different concentration Mo doped V₂O₅ sol

Conclusions

Mo doped V₂O₅ films were fabricated by cathodic electrodeposition. The deposition time and concentration of sol have been found to influence directly the optical modulation capability. With the increase of the electrodeposition time, the thickness of the films increases gradually. The thickness of the films increases sharply with the increase of the concentration of the sol. The best film with the thickness about 400 nm exhibited wide optical modulation over 60%. The wide optical modulation of Mo doped V₂O₅ films render them to be a promising application in electrochromic devices.

Acknowledgements

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