

ELECTROCHEMICAL PERFORMANCES OF Li^+ INTERCALATION AND DEINTERCALATION PROCESSES FOR ELECTROCHROMISM OF MoO_3 -DOPED V_2O_5 FILMS PREPARED BY THE SOL-GEL METHOD

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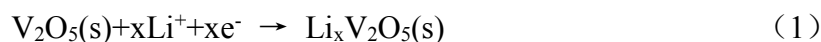
Key words: Electrochromism, MoO_3 -doped V_2O_5 films, Cyclic voltammetry.

Summary: *The MoO_3 -doped V_2O_5 thin films electrode exhibit much enhanced electrochemical performances than the pure V_2O_5 counterpart. 1M nonaqueous solution of LiClO_4 in propylene carbonate (PC) was the electrolyte solution about cyclic voltammetry (CV) of $\text{V}_2\text{O}_5/\text{MoO}_3/\text{ITO}$ glass electrodes at room temperature. With the increasing proportion of MoO_3 doped in V_2O_5 , all the redox peak currents of the five samples increased, suggesting that their electrochemical activity increased with the initial CV cycles. Disappearing of some phase transition peaks also show that the MoO_3 -doped V_2O_5 film makes cyclic stability declining. Compared with the switching speed of films, the coloring and the bleaching times of the MoO_3 -doped V_2O_5 thin films are shorter.*

1 INTRODUCTION

Electrochromism, the reversible change in optical properties when a material is electrochemically oxidized or reduced, has a long history of fundamental and practical interest.^[1,2] Various types of materials and structures, can be used to construct electrochromic devices, according to the specific applications.

Vanadium-based oxides such as V_2O_5 , LiV_3O_8 and V_6O_{13} have aroused great interest due to their high energy density, low price, abundant sources, and good safety performance when used as cathode materials for rechargeable lithium-ion batteries. Moreover, vanadium as transition metal oxides used for electrochemical supercapacitor electrodes possesses significantly higher special capacitances.^[3] As an electrochromic material, vanadium pentoxide (V_2O_5) has its low operating potential, -1 V, and very small amounts of energy to change its coloration state.^[4]



Just like above expression, the electrochromic color of vanadium oxide changes from yellow to green/gray.^[5] What's more, the compound easily undergoes various phase transitions, such as α , ϵ , δ , γ , and ω phases, depending on the degree of Li intercalation (x)^[6] The α -phase $\text{Li}_x\text{V}_2\text{O}_5$ ($x < 0.01$) and ϵ -phase $\text{Li}_x\text{V}_2\text{O}_5$ ($0.35 < x < 0.7$) which the structure of unintercalated V_2O_5 have similar with, but result in weak puckering of V_2O_5 layers. The δ -phase $\text{Li}_x\text{V}_2\text{O}_5$ ($0.7 < x < 1$) has more puckered V_2O_5 layers. When the Li intercalation is more than one, an irreversible structural change to γ -phase $\text{Li}_x\text{V}_2\text{O}_5$ ($1 < x < 2$) occurs. In γ -phase $\text{Li}_x\text{V}_2\text{O}_5$, the layer puckering becomes more pronounced than that in δ -phase $\text{Li}_x\text{V}_2\text{O}_5$. Further intercalation of the third Li into V_2O_5 results in the irreversible formation of ω -phase $\text{Li}_x\text{V}_2\text{O}_5$ ($2 < x < 3$) with a rock salt type structure, where the Li^+ diffusion will be very slow. In addition, this ω -phase rapidly loses the ability to cycle due to a large fraction of lithium ions that cannot be removed.^[7] Vanadium pentoxide prepared by sol-gel method has the advantage of large area production, however, weak physical adhesion strength which it attaches themselves to a transparent current collector (e.g., ITO, FTO) among individual electrochromic nanomaterials may cause the release of active materials, resulting in optical contrast loss in long-term testing.^[8] In this study, we researched the effect of Mo doping on the microstructure and Li^+ intercalations/extractions properties of V_2O_5 films. The pure and Mo-doped V_2O_5 films were prepared by using the sol-gel method, followed by annealing 400°C for 4h in the air. The Mo-doped V_2O_5 thin films electrode exhibit much enhanced electrochemical performances than the pure V_2O_5 counterpart.

2 PREPARATION SECTION

Analytical reagent grade MoO_3 and V_2O_5 powder of various molar concentrations have been taken in an agate mortar and ground well to get a fine powder of the mixed oxide, which is then pelletized. After that the mixed oxide powder which is in the air, was heated to 800°C that rised up 10°C per minute. And then the system was put into 800°C surrounding for 30min. We took it out quickly into the 500mL of cold pure water, at the same time, stired and heated the material rapidly and uniformly for 1h. To obtain the sol precursor, the precipitate was filtered. Then we got sol-gel mixed vanadium oxide which was sealed to avoid light preservation for 7 days. The sol-gel vanadium oxide is stable that no deposition occurs.

Indium-doped tin oxide substrates (ITO, 10~15R/sq, 2cm*3cm) were cleaned ultrasonically in acetone, in absolute alcohol, and then in distilled water, for 20 min each. The cleaned ITO glass substrates were placed into cylindrical vessels.

After finishing all the preparations, the thin films were obtained by sol-gel method on the surface of ITO. The films of 5% MoO_3 , 95% V_2O_5 ; 3% MoO_3 , 97% V_2O_5 ; 2% MoO_3 , 98% V_2O_5 ; 1% MoO_3 , 99% V_2O_5 and 100% V_2O_5 have been used for optical and electrical investigations which ensured that the quality of MoO_3 would be not cover the quality of V_2O_5 . Then they were kept at a temperature of 40°C for drying that the films were not crystallization.

3 RESULTS AND DISCUSSION

The phase structure, surface morphology, and the oxidation state of the thin Mo-doped V_2O_5 films and pure V_2O_5 films was analyzed with the help of X-ray diffractometer (Rigaku D/max-2550). For XRD tests, in order to eliminate the interference of ITO layer, both the Sn-doped V_2O_5 film and pure V_2O_5 film were prepared on bare glass substrate. The XRD with Cu-K α source, was performed a scan of θ -2 θ in the range between 10° and 70° . Figure.1 shows the XRD test curve of each different concentration of the film. The pure V_2O_5 film

shows a single orthorhombic V_2O_5 phase.^[4] For the pure V_2O_5 , there are three peaks located at 20.3° , 21.4° and 41.3° , which correspond to the (001), (101) and (002) directions. In the case of 1% MoO_3 -doped V_2O_5 film, there are no peaks other than those observed for pure V_2O_5 film, indicating that Molybdenum oxide is either amorphous or crystalline with very small crystallites. However, 2-5% MoO_3 -doped V_2O_5 films have different and more peaks. These peaks position is neither MoO_3 ^[9] nor V_2O_5 . At the same time, these are not same with the peaks in other XRD of some doping experiments. The reason for this phenomenon is that the MoO_3 in doped thin films as the solute donor forms solid-solution phases^[10] with V_2O_5 . There are the same location of peaks in this curve between pure V_2O_5 films and 1% MoO_3 -doped V_2O_5 films because in the 1% MoO_3 -doped V_2O_5 films, MoO_3 does not insert into the V_2O_5 crystal and it's rare to check out. Furthermore, about the location of the peaks of 2-5% MoO_3 -doped V_2O_5 films there are not same peaks with the existing literature or XRD alignment card. And the intensity of those peaks rise up following with the increase of dopant concentration.)

Figure.2 is compared the crystallization temperature of different doping concentration of the films. From Figure.2(a) which curve has peaks in XRD spectra of the film was annealed at $65^\circ C$, and the other one was annealed at $60^\circ C$. We can see that crystallization temperature of the pure V_2O_5 thin film is between $60^\circ C$ and $65^\circ C$. The same can be seen in Figure.2(b), the crystal temperature of 1% MoO_3 -doped is between $55^\circ C$ and $60^\circ C$; Figure.2(c), the crystal temperature of 2% MoO_3 -doped is between $50^\circ C$ and $55^\circ C$; Figure.2(d), the crystal temperature of 3% MoO_3 -doped is between $50^\circ C$ and $55^\circ C$; Figure.2(f), the crystal temperature of 5% MoO_3 -doped is between $45^\circ C$ and $50^\circ C$. The conclusion can be obtained, that different mixed ratio has the effects of crystallization temperature about the films. The V_2O_5 films doped with more MoO_3 have the lower the crystallization temperature. The reason for this phenomenon is that the band gap of the films becomes smaller along with the MoO_3 -doped which MoO_3 was inserted into the V_2O_5 crystal. So the crystallization temperature decreased with the amount of doped films increasing. The crystallization temperature of 1% MoO_3 -doped and pure V_2O_5 film declined, but in the 1% MoO_3 -doped V_2O_5 film, MoO_3 did not insert into V_2O_5 crystal because of the pure physical mixing.

Lithium insertion in sol-gel deposited V_2O_5 films was accomplished using cyclic voltammetry (CV). The CV was performed on $V_2O_5/MoO_3/ITO$ glass electrodes in an electrolyte of 1 M $LiClO_4$ with PC at room temperature. Several cycles were required to achieve a steady-state voltammogram in each case. Figure. 3 shows typical cyclic voltammograms (CV) of V_2O_5/MoO_3 in the potential range of $-1.2 \sim 1.5$ V (vs Li/Li^+) at the scan rate of 10mV/s. Over this potential range, the shape of the curves is a typical diffusion-controlled CV of a highly reversible lithium intercalation / deintercalation process. With the increasing proportion of MoO_3 doped in V_2O_5 , all the redox peak currents of the five samples increased, suggesting that their electrochemical activity increased with the initial CV cycles. For the pure V_2O_5 films, two couples of the redox peaks can be observed at Figure. 3. The two well-defined reduction peaks at about $-0.202V$ and $-0.520V$ correspond to the respective α/ϵ and ϵ/δ phase transitions, and the two well-defined oxidation peaks at about $-0.227V$ and -0.072 V correspond to the respective δ/ϵ , and ϵ/α phase transitions.^[10] However, for the MoO_3 -doped V_2O_5 films, two more couples of the redox peaks can be observed at Figure. 3. Their positions are about $-0.75V/0.42V$ and $0.76V/-0.95V$ respectively. The two well-defined reduction peaks at about $-0.219V$ and $-0.513V$ correspond to the respective α/ϵ and ϵ/δ phase transitions, and oxidation peaks about δ/ϵ , and ϵ/α phase transitions move to right with the proportion of MoO_3 in V_2O_5 .

The comparison of oxidation peaks about ϵ/α phase transitions in the pure V_2O_5 film and MoO_3 -doped V_2O_5 film was summarized as Table.1. At the same scan rate, the peaks of ϵ/α phase transitions shifted to right and became higher as the more amount MoO_3 doped in V_2O_5 . With the incorporation of MoO_3 , and the number of phase transitions changed. The number of peaks increasing, the properties of the films are becoming more and more lively with the increasing of mixed concentration. This conclusion of Fig.3 is same with the test results of pure V_2O_5 films and thin MoO_3 -doped V_2O_5 films about cyclic voltammograms. During more electrochemical cycling, all peaks of pure V_2O_5 film doesn't have began to gradually disappear. However, the disappearing of some phase transition peaks about the MoO_3 -doped V_2O_5 films also show that the MoO_3 -doped makes electrochromic cyclical declining.

Fig. 4 shows the chronoamperometric response curves of the pure V_2O_5 films and the thin MoO_3 -doped V_2O_5 films in the potential region of -1.0V to 1.3V. The amplificatory curve on the left of Fig. 4 was current density changing with time under the condition of -1.0V. And the other potential was 1.3V on the right of Fig. 4. Consistent with the switching response results, the films doped with high concentration have faster response, and the different response time of intercalation processes is clearer than deintercalation processes. The incorporation of MoO_3 has changed the structure of V_2O_5 crystal. The atomic radius of Mo is larger than the atomic radius of V. With the increase in MoO_3 , structure of thin films become more and more loose, blocking effect of lithium ion becomes smaller, the channel of lithium ion intercalation /deintercalation becomes much smoother and the resistance of ion migration changes less, then, the films doped with high concentration have faster response^[10]

We took cyclic voltammetric tests of different concentration MoO_3 -doped V_2O_5 films, and the test results obtained: the higher doping concentration is, the lower the cycle performance of thin film. It's same with the former result. So to improve the performance of films effectively, we took the lowest cycle performance of 5% MoO_3 -doped V_2O_5 films to conduct experiments. In order to improve the cycle performance of the thin film, we put them in acetone horizontally at room temperature where the films were put right side up, and the experimental variable was just time. Treatment time were 10min, 30min, 60min, 2h, 4h, 8h, 16h, 24h, 30h, 36h, 42h, 48h. Figure.5 shows the cyclic voltammetric of the original film, acetone treatment confirmed by 10min, 4h, and 16h about 5% MoO_3 -doped V_2O_5 films at 20mV/s. As we can see from the curve, the cyclicity of film which 10min acetone treatment didn't any enhance, while the difference of tenth circle and fiftieth circle CV cycle reduction peak current density of the film that 4h processed is only $5 \times 10^{-4} A/cm^2$. The film that 16h acetone treated has changed the crystal characteristics of the thin film, so CV curve has changed. Analysis in combination with the patterns of any other treatment time, we can draw the conclusion: the cyclical films treated below 1h are not significantly increased, and the cyclical films whose treatment time is from 2h to 8h rised considerably, it leads to the position change of cyclic peak by 16h or more acetone treatment. Fig.6 show the colored and bleached states of 5% MoO_3 -doped V_2O_5 films which is treated by acetone treatment for 4h in the range from 300nm to 1000nm at different voltages in 1M $LiClO_4/PC$ electrolyte. As shown in Fig.6, the film which is added with different voltage does show the same transmittance spectra.

4 TITLE, AUTHORS, AFFILIATION, KEY WORDS

4.1 Title

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4.2 Author

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4.3 Key words

Electrochromism, MoO_3 -doped V_2O_5 films, Cyclic voltammetry.

5 FIGURES

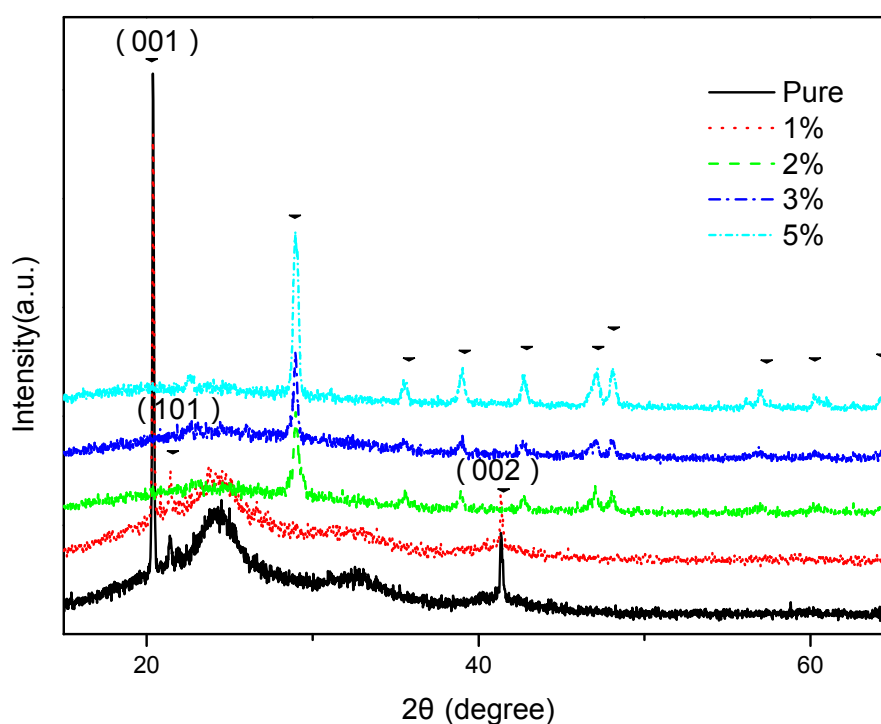


Figure 1: XRD patterns of different concentration of the film

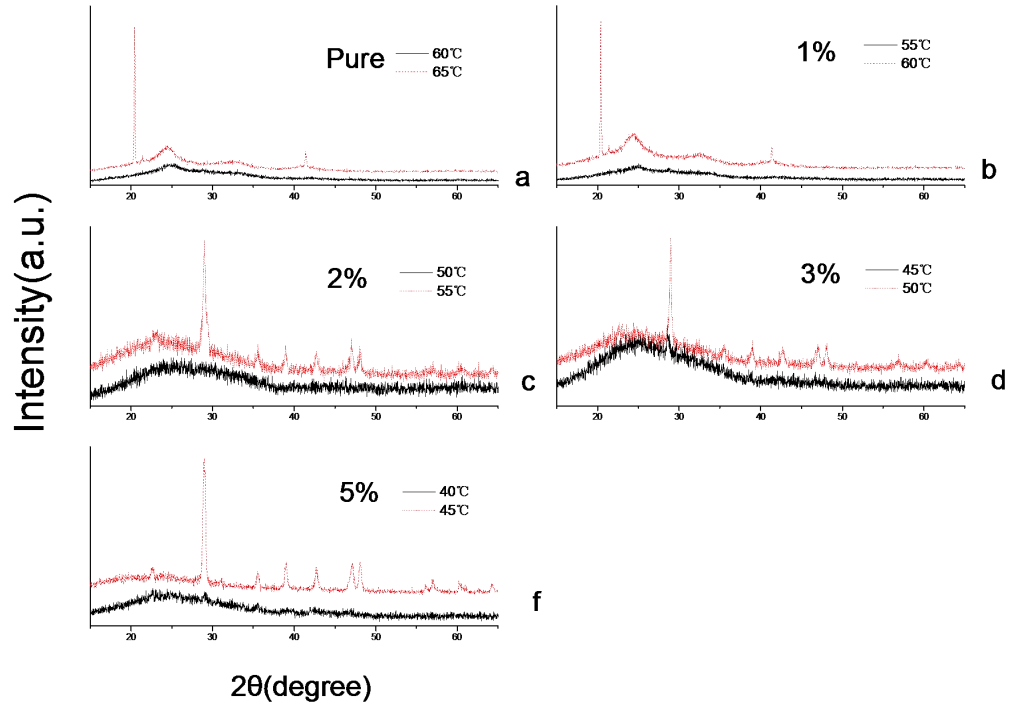


Figure 2: The crystallization temperature of different doping concentration of the films

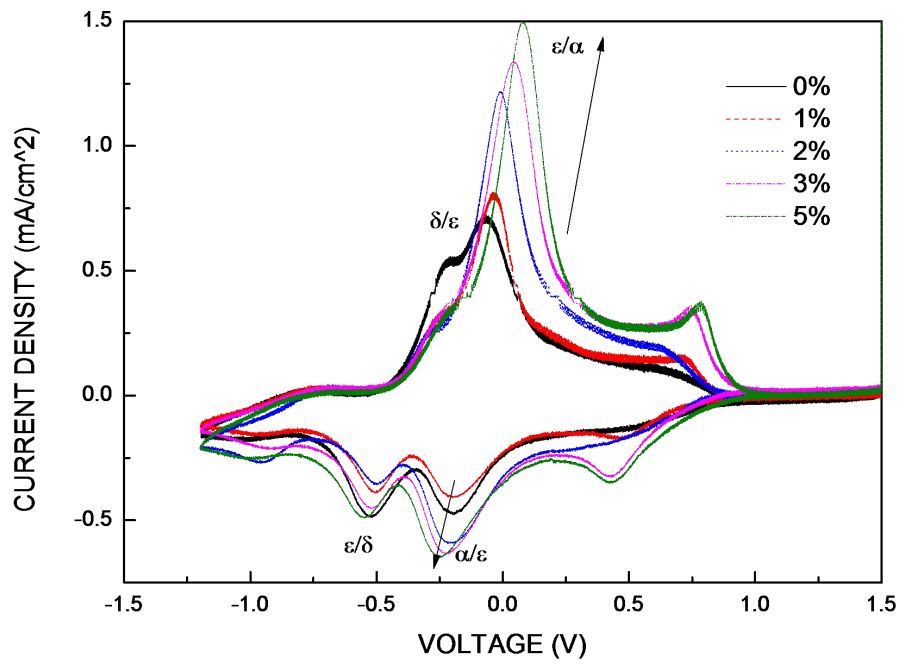


Figure 3: Cyclic voltammograms of V_2O_5 - MoO_3 films

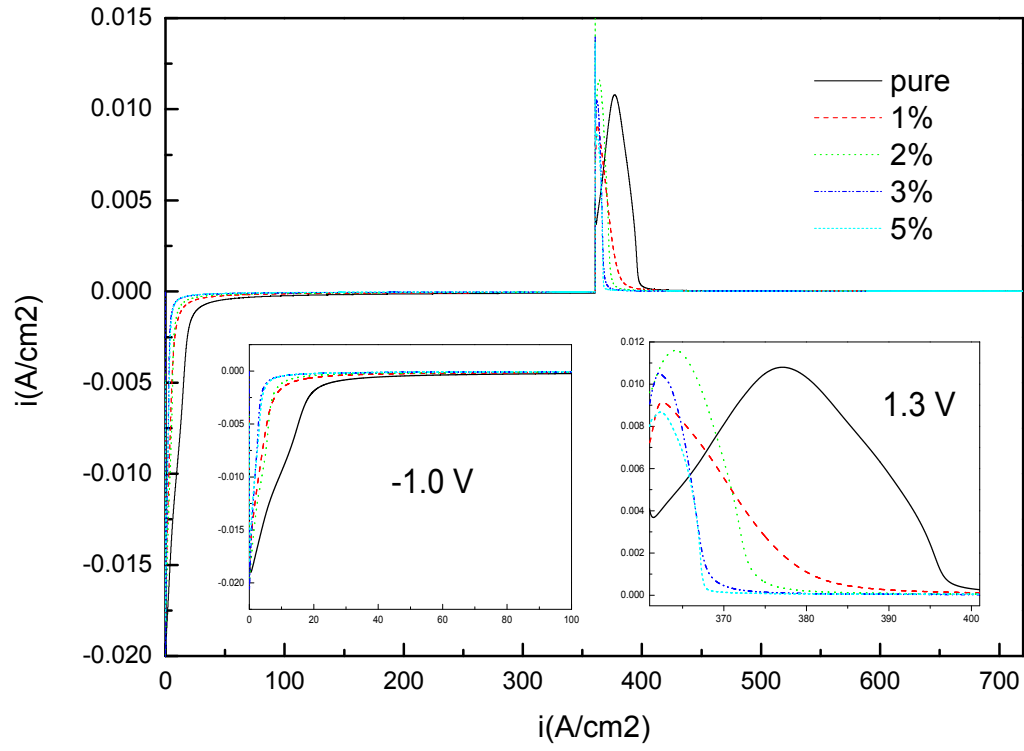


Figure 4: Chronoamperometric response curves different doping concentration of the films. The amplificatory curve on the left is current density changing with time under the condition of -1.0V. And the right one is 1.3V.

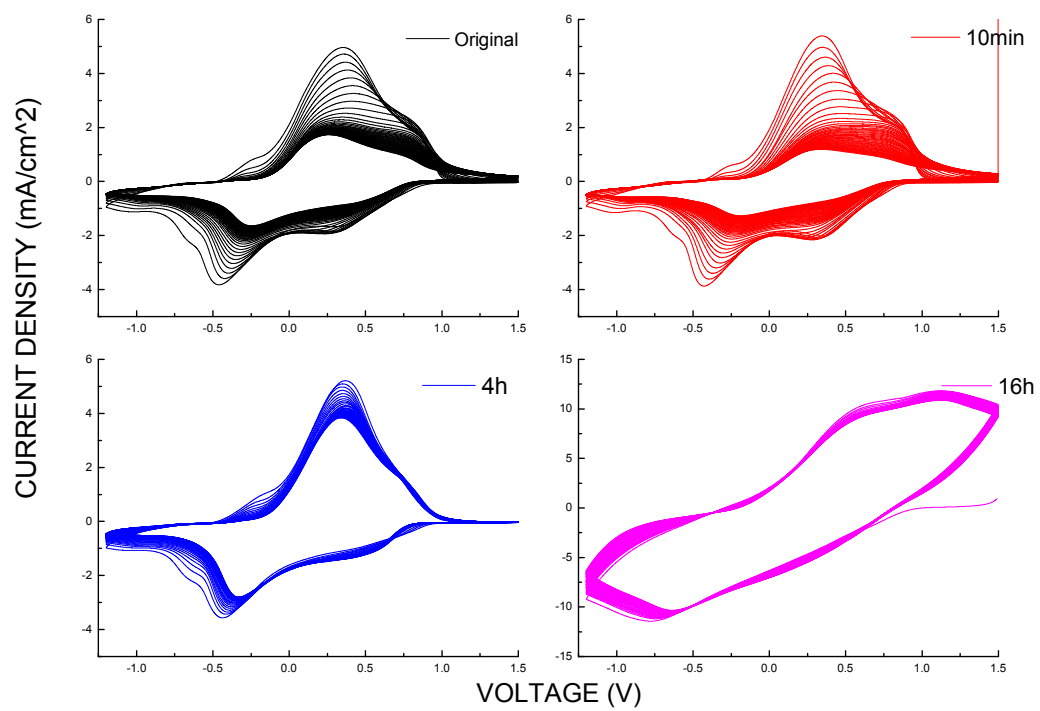
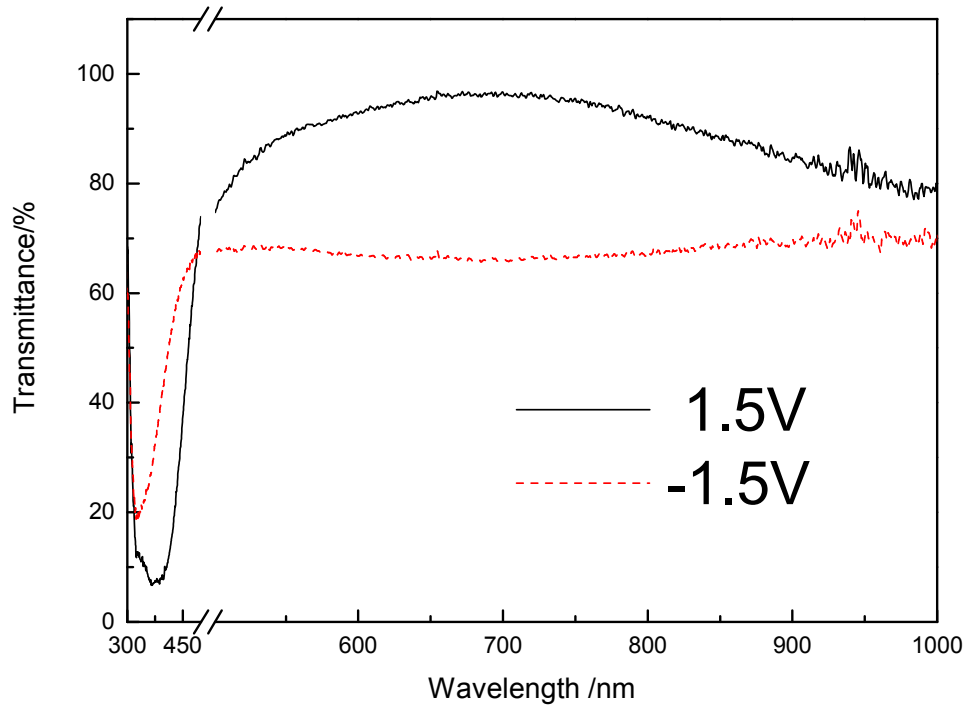


Figure 5: Cyclic voltammetric of the original film, acetone treatment confirmed by 10min, 4h, and 16h about 5% MoO₃-doped V₂O₅ films

Figure 6 : Transmittance spectra of 5% MoO₃-doped V₂O₅ films at different voltages

6 TABLES

The doping concentration of MoO ₃	Oxidation peaks(V)
0%	-0.072
1%	-0.034
2%	-0.009
3%	0.048
5%	0.080

Table 1: Comparison of oxidation peaks about ϵ/α phase transitions in the Pure V₂O₅ Film and MoO₃-Doped V₂O₅ Film

7 CONCLUSIONS

Comparing the cyclic voltammetric of the pure V₂O₅ films and the thin Mo-doped V₂O₅ films, the number of oxidation ϵ/α phase transitions changed with the incorporation of MoO₃. The incorporation of MoO₃ has changed the structure of V₂O₅ crystal. With the increase in MoO₃, the properties of the films are becoming more and more lively, and the films doped with high concentration have faster response. Treated by acetone horizontally at room temperature with different time, the cyclical films obviously increased, and the position of

cyclic peak could change by much acetone treatment.

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