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# Electrochemical Performance of $\text{Li}_x \text{V}_2\text{O}_5$ Nanoporous Films with Heat Treatment in Various Atmospheres

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**Abstract:**  $\text{Li}_x\text{V}_2\text{O}_5$  nano-porous films were prepared by dip-coating vanadium oxide sol onto ITO substrates, utilizing  $\text{V}_2\text{O}_5$  powder,  $\text{LiOH}\cdot\text{H}_2\text{O}$  powder, Benz alcohol, Isopropanol as precursors. X-ray diffraction (XRD) and atomic force microscopy (AFM) were employed to examine the crystallization and surface morphology. The electrochemical behavior of the nano-porous films was investigated by means of cyclic voltammograms (CV) and chronopotentiometry (CP). Results showed that the film annealed in nitrogen atmosphere can stabilize the rate capability and improve the cycling stability.

**Keywords:** Films; Lithium ion batteries; Cathode materials; Sol-Gel;  $\text{Li}_x\text{V}_2\text{O}_5$

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## Introduction

Energy storage technology was incontrovertibly one of the great challenges in modern society that faces environmental and ecological concerns. Lithium ion battery was regarded as one of the most important energy storage technologies due to their extensive applications in a wide range of areas including portable electronic devices, electric vehicles, and implantable medical devices [4,5]. In recent years, porous material as cathode material of lithium-ion batteries had aroused special interest due to its three-dimensional network, which could markedly improved the electrochemical properties. Among these promising materials, nano-porous films have attracted increasing attentions because of their short  $\text{Li}^+$  diffusion paths and large surface areas.

Vanadium oxide was an attractive multifunctional material possessing extensive applications in various

fields [6,7]. It has been discovered that during  $\text{Li}^+$  ion intercalation, vanadium pentoxide possessed high specific electrochemical capacity  $442 \text{ mAh g}^{-1}$  with 3 Lithium ion per  $\text{V}_2\text{O}_5$  unite inserted. Although the  $\text{Li}$ -ion intercalation voltage was lower than that of  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$  was still regarded as one of the most popular cathode candidates for the following advantages: i)  $\text{V}_2\text{O}_5$  provided higher energy and power density than  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ , ii) its fabrication method was easier and more controllable than  $\text{LiMO}_2$  ( $\text{M}=\text{Ni}, \text{Mn}, \text{Co}, \text{Fe}$ ), and iii) it had a higher capacity and better cyclic stability than  $\text{LiMn}_2\text{O}_4$ <sup>8</sup>.

In this paper, nano-porous  $\text{Li}_x\text{V}_2\text{O}_5$  thin films were prepared by dip-coating method using the sol derived from  $\text{V}_2\text{O}_5$  powder. We used AFM and XRD to characterize the surface morphology and crystallinity to study the influence of atmosphere heat treatment on the  $\text{Li}_x\text{V}_2\text{O}_5$  film. Chronopotentiometric (CP) tests and

cyclic voltammograms (CV) were further employed to investigate the electrochemical performance of the films thermal treated at different atmospheres.

## Experimental

$V_2O_5$  powder (A. R., and purity  $\geq 99.6\%$ ) was purchased from Kefeng Ltd.  $LiOH \cdot H_2O$  powder (A.R., and purity  $\geq 99.0\%$ ), benzyl alcohol (A. R., and purity  $\geq 99.0\%$ ), isopropyl alcohol (A. R., and purity  $\geq 99.7\%$ ) were obtained from Sinopharm chemical reagents Co. Ltd.  $Li_xV_2O_5$  sol was prepared via sol-gel method as follows.  $V_2O_5$  powder,  $LiOH \cdot H_2O$  powder, benzyl alcohol and isopropyl alcohol were refluxed at  $110^\circ C$  for 4 hours with a certain mol ratio. After filtration a dark green sol was obtained. Then the sol was centrifuged at 2500 r/min for half an hour and then cooled to room temperature to obtain a limpid sol. The sol was further aged at  $40^\circ C$  for three to five days in a thermostat. The films were deposited onto Indium-Tin Oxide (ITO) conducting glass substrates by dip-coating technique with a rate of  $1.7 \text{ mm} \cdot \text{s}^{-1}$ . The prepared films were annealed in air and nitrogen (purity  $\geq 99.0\%$ ) at  $300^\circ C$  for 3 h at the same temperature rising rate of  $10^\circ C/\text{min}$  to ensure a complete films growth. The ITO conducting glass substrate was both weighed before and after the films deposition. Then the mass of films was obtained by subtraction.

$Li_xV_2O_5$  films were investigated using a standard three-electrode system, using 1M  $LiPF_6$  in the mixed solution of ethylene carbonate (EC), methyl carbonate (EMC) and diethyl ethylene carbonate (DEC) (1:1:1 by vol) as the electrolyte. Lithium foils were used as counter and reference electrodes. Chronopotentiometric (CP) tests were carried out in the voltage range from 4 to 2 V with a current density of  $100 \text{ mA g}^{-1}$ . The CP tests were performed using a Land system (CT2001A). All the electrochemical measurements were carried out in a glove box filled with argon with  $H_2O$  and  $O_2$  content both below 1 ppm. Atomic force microscopy (AFM, XE-100), and X-ray diffraction (XRD, DX-2700) were employed to characterize the micromorphology, surface roughness, crystalline of the films.

## Results and Discussion

Different annealing treatments did demonstrate appreciable influences on surface roughness and crystallization. So we compared the as-prepared films without heat treatment, films heat treated under air atmosphere, and the films heated in nitrogen condition. All the films were examined by AFM and XRD.

The X-ray diffraction patterns of the three films (non-annealed, annealed in nitrogen and air) were compared in Fig. 1. Sol-gel derived film without thermal treat-

ment exhibited only an amorphous phase (Fig. 1(a)), whereas after annealing at temperature higher than  $330^\circ C$ , it exhibited an orthorhombic phase. As can be seen in Fig. 1, film annealed in air at  $300^\circ C$  (Fig. 1(c)) showed sharp diffraction peaks at  $20.26^\circ$  and  $20.32^\circ$ , indicating well-crystallized structure. But the film heated in the  $N_2$  (Fig. 1(b)) showed amorphous and partial starting to crystallize. So it was the presence of oxygen that facilitates the film to crystallize.

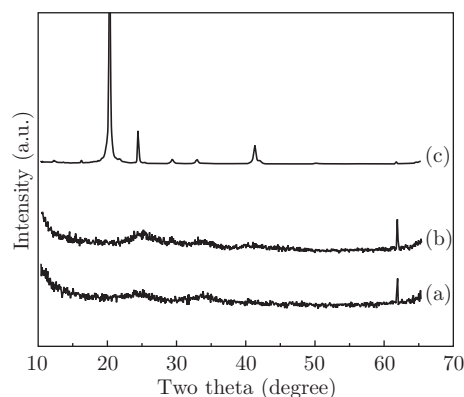


Fig. 1 X-ray diffraction patterns of films non-annealed (a) and annealed in nitrogen (b) and air (c) at  $300^\circ C$ .

**Table 1** The  $R_q$  and  $R_a$  value of three films

	$R_q$ (nm)	$R_a$ (nm)
Film non-annealed	1.132	0.886
Film annealed in air for 3h	1.002	0.816
Film annealed in nitrogen for 3h	0.773	0.597

The surface morphology of the as-prepared sol-gel derived  $Li_xV_2O_5$  films was smooth and featureless. After annealed in different atmospheres, however, the films presented different colors. The films annealed in  $N_2$  turned dark green, while samples treated in air became yellow. This may be because of the oxidation of  $V^{4+}$  ions to  $V^{5+}$  ions during the exposure to air when annealing. AFM patterns of three films (non-annealed, annealed in air and nitrogen) were shown in Fig. 2. The  $R_q$  (root-mean-squared roughness) and  $R_a$  (average roughness) value of three different kinds of films were calculated, and the results were summarized in Table 1. The film non-annealed was the roughest one, while the film annealed in nitrogen was the smoothest one. The roughness of the film annealed in air for 3 h was between them. The organic compounds on the surface of film may burn out during the heat treatment, and then the film became smoother. But the presence of oxygen may facilitate the grain to grow and crystallize during annealing, and then the film annealed in the air became roughness.

Cyclic voltammograms of three kinds of films (non-annealed, annealed in air and nitrogen) were displayed

in Fig. 3. The film which was not annealed had the highest intensity of redox peak of lithium insertion, but the film annealed in nitrogen had the poorest one. Combining with the results of Table 1, it should be noticed that the roughest film had the highest current intensity. As known, roughness is independent of film porosity. So it can be deduced that porous structures such as aerogels are benefit for fast lithium ion intercalation. However, the non-annealed films exhibited bad electrochemical stability, which can be enhanced by

heat-treatment with a little charge intercalation density decrease.

Figure 4 showed a comparison of cyclic stability of the two films with a current density of  $100 \text{ mA g}^{-1}$  for first ten discharge/charge cycles. The film annealed in  $\text{N}_2$  exhibited better cyclic stability. It started with a low discharge capacity of  $54.6 \text{ mAh g}^{-1}$  but increased to  $138.3 \text{ mAh g}^{-1}$  in the second cycle. After decreasing in the following seven cycles, the capacity started to increase in the 8th cycle. The capacity was  $127.8 \text{ mAh}$

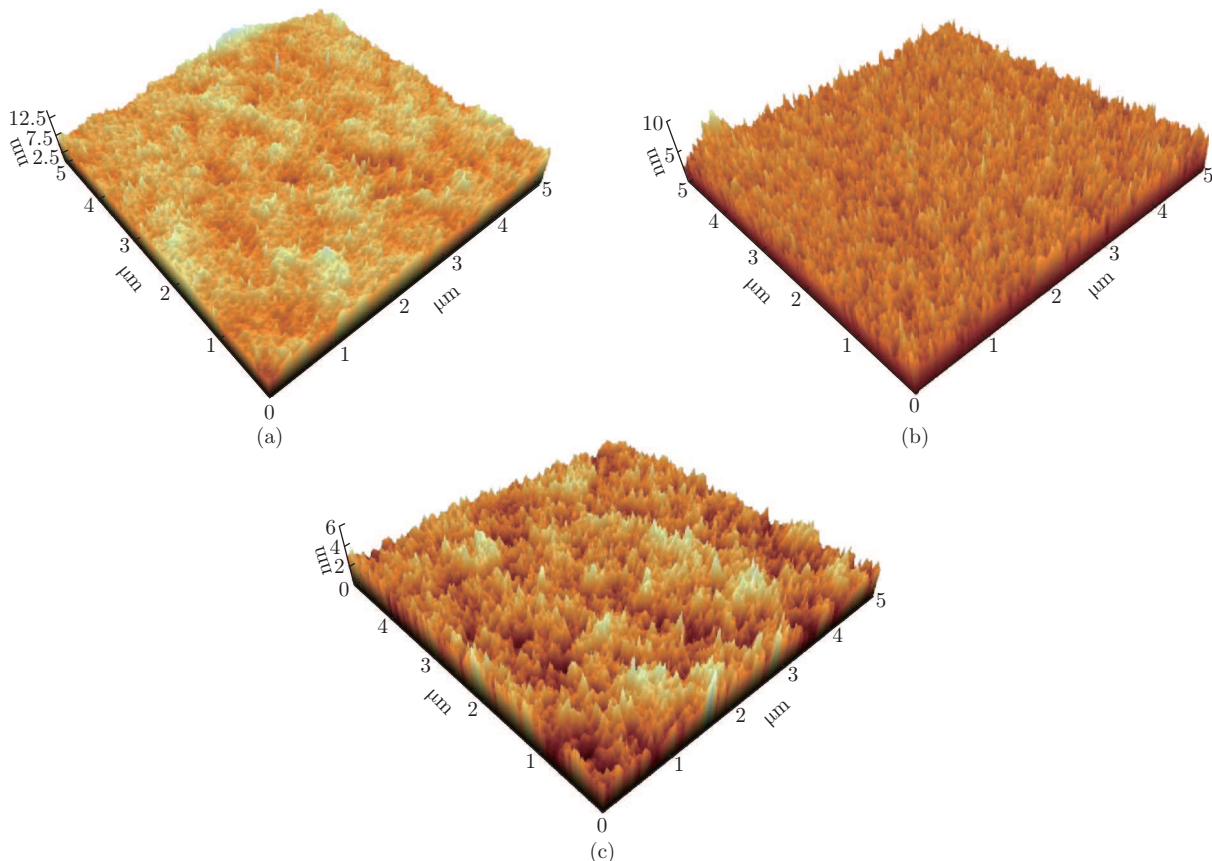


Fig. 2 AFM patterns of films non-annealed (a), annealed in air (b) and nitrogen (c).

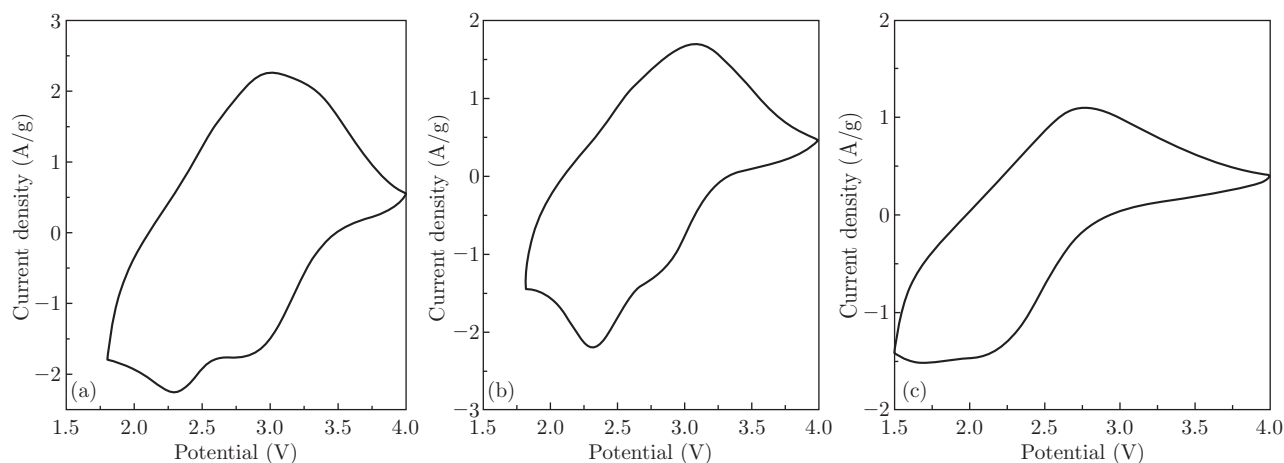


Fig. 3 Cyclic voltammograms of films non-annealed (a), annealed in air (b), annealed in nitrogen (c) at  $5 \text{ mV s}^{-1}$ .

$\text{g}^{-1}$  after 10 cycles, 92.4% of the peak value. The cyclic performance of the film annealed in air was very similar: it started with the capacity of  $51.9 \text{ mAh g}^{-1}$  and was as high as  $148 \text{ mAh g}^{-1}$  in the 2th cycle. But it decayed very fast with the capacity of  $125.7 \text{ mAh g}^{-1}$  after 10 cycles, 84.9% of the peak value. Thus, the crystalline of films can reduce the reversibility charge/discharge capacity. The good cycling stability of film annealed in nitrogen can avoid crystallization and be derived from the surface defects which were  $\text{V}^{4+}$  and oxygen vacancies on the film surface [9]. This was proved by the films colors. The films annealed in  $\text{N}_2$  turned dark green, which represents the existence of lower valance Vanadium, while samples treated in air became yellow, which reveals a higher  $\text{V}^{5+}$  state.

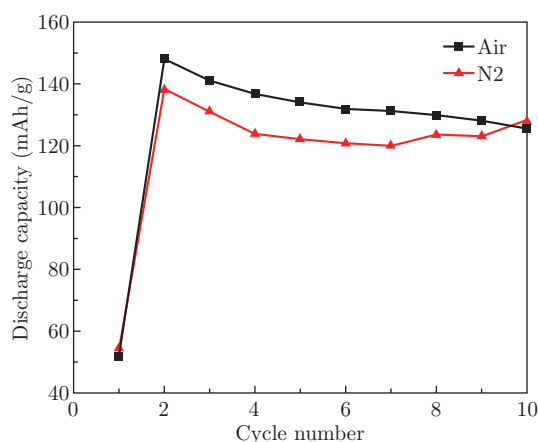


Fig. 4 Li-ion intercalation discharge capacity of films annealed in air and nitrogen. The measurements were carried out in a potential window between 4 and 2 V vs  $\text{Li}/\text{Li}^+$  at a current density of  $100 \text{ mA g}^{-1}$ .

## Conclusion

Air atmosphere treatment facilitates the grain crystallization. After the comparison, the film annealed in  $\text{N}_2$  has low crystallinity than that in air. It is clear that the film annealed in  $\text{N}_2$  possesses good reversibility by maintaining a high charge/discharge capacity, whereas the film annealed in air exhibits severe capac-

ity degradation within 10 cycles. The roughness analysis indicated that porous structure is quite useful for fast Li ion diffusion. And the surface defects and less well packed structure, which has been achieved by heat treatment in  $\text{N}_2$  atmosphere, can accommodate more lithium ions and exhibit better cyclic stability than the well-crystallized film annealed in air.

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