

Short communication

Synthesis and electrochemical properties of V_2O_5 nanostructures prepared via a precipitation process for lithium-ion battery cathodes

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Abstract

One-dimensional (1D) nanostructures of vanadium pentoxide (V_2O_5) have been successfully synthesized via a precipitation process followed by heating in vacuum at 300 °C. The samples have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrochemical testing by techniques such as cyclic voltammetry (CV) and discharge–charge cycling in lithium cells. Average crystal size of these oxides increased from 36 to 83 nm as annealing time was increased from 45 min to 1 h, which also led to a decrease in Brunauer–Emmett–Teller (BET) specific surface area from 41 to 17 m² g⁻¹. Good cyclability and high capacity (>200 mAh g⁻¹) were achieved in the voltage range of 2.0–4.0 V (versus Li metal) at a current rate of 50 mA g⁻¹ by annealing the oxides for 1 h. The increase in crystallinity and higher yield of one-dimensional nanostructure oxides contributed significantly to the improved capacity and enhanced cycle life.

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1. Introduction

Vanadium pentoxide (V_2O_5) is an attractive cathode material in lithium-ion batteries because of its unique features such as high electrochemical activity, high energy density, and high stability towards lithium insertion [1]. The electro-reduction of V_2O_5 can occur in a large potential window between 4.0 and 1.5 V versus Li/Li⁺, where ~3 lithium/mole of V_2O_5 could be theoretically inserted, leading to a theoretical capacity close to 400 mAh g⁻¹ [2]. Since the performance of V_2O_5 cathode heavily depends on its crystallinity and morphology, many studies have been done on modifying the form and structure of V_2O_5 to achieve higher specific capacities and better cyclability [3]. These studies show that crystalline V_2O_5 has a high specific capacity but exhibits a weak cyclability due to a damaged crystal structure during discharge/charge cycles, while amorphous and low crystallinity V_2O_5 allows faster lithium-ion diffusion and displays remarkable cyclability. Deformation associated with

lithium intercalation may be easily relaxed in small crystallites with a high surface area, which also leads to higher ionic conductivity. Therefore, nanocrystalline V_2O_5 might be a good and promising cathode material for lithium-ion batteries [4]. Vanadium pentoxide nanostructures can be obtained by various physical and chemical techniques. The V_2O_5 nanostructures have mostly been prepared by wet processes such as electro-deposition [5], Sol–gel [6], templating against carbon nanotubes [7], and soft chemistry synthesis involving an amine with long alkyl chains as a molecular, structure-directing template [8].

However, synthesis of V_2O_5 one-dimensional nanostructures via a precipitation process followed by heating in vacuum to obtain well-crystallized and fully grown V_2O_5 nanostructures has never been explored for use as lithium-ion battery cathodes. Therefore, in this study, well-crystallized V_2O_5 one-dimensional nanostructures with high surface area (above 40 m² g⁻¹) have been synthesized via a precipitation process followed by heat treatment in vacuum. The electrochemical properties of these V_2O_5 nanostructures will be examined and evaluated for use in lithium-ion battery cathodes. The effect of the cut-off potential on the electrochemical properties will also be investigated.

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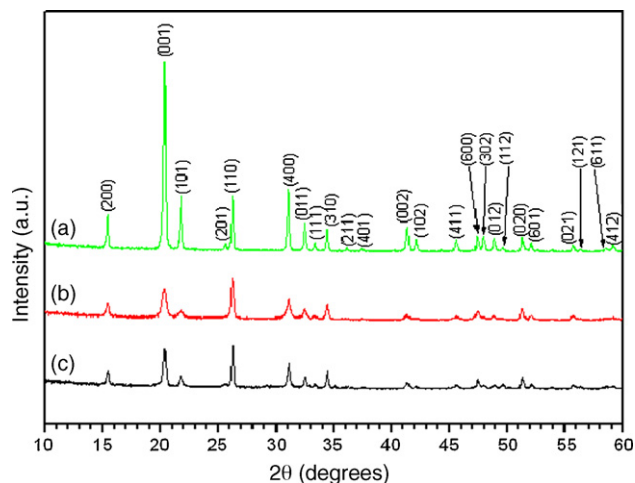


Fig. 1. XRD patterns for (a) commercial V_2O_5 , (b) V_2O_5 annealed for 45 min at 300 °C (sample A), and (c) V_2O_5 annealed for 1 h at 300 °C (sample B).

2. Experimental

A peristaltic pump delivered ammonium hydroxide (NH_4OH) droplet by droplet into a 0.5 M vanadium oxytrichloride ($VOCl_3$) solution. The solution was continuously stirred with a magnetic stirrer throughout the precipitation process. An excess of NH_4OH was used to avoid contamination with chloride. The precipitate was then filtered and washed several times with de-ionized water. Finally, the precipitate was heated

Table 1

Summary of experimental conditions and physical characteristics for the V_2O_5 nanostructures prepared via a precipitation method

Sample ID	A	B
Annealing temperature, T (°C)	300	300
Annealing duration under vacuum, t (min)	45	60
Morphology (from SEM)	Nanoparticles only	Nanoparticles + nanofibers
Average crystal size, D_p (nm)	36	83
Specific surface area, S_{BET} ($m^2 g^{-1}$)	41	17

for a varying duration at 300 °C in the vacuum oven to produce well-crystallized vanadium pentoxide (V_2O_5). Two types of V_2O_5 samples were synthesized via this new approach, differing only in the annealing time in the vacuum oven at 300 °C. One sample was annealed for 45 min (sample A) while another was annealed under the same conditions for 1 h (sample B).

Powder samples were analyzed by X-ray diffraction (XRD), using a diffractometer with $Cu K\alpha$ radiation and a graphite monochromator. Scanning electron microscopy (SEM) was performed using a JEOL JSM 6460A scanning electron microscope. Specific surface areas of the nanostructured particles of V_2O_5 were measured with a Quantachrome Nova 1000 nitrogen gas analyzer using the Brunauer–Emmett–Teller (BET) method.

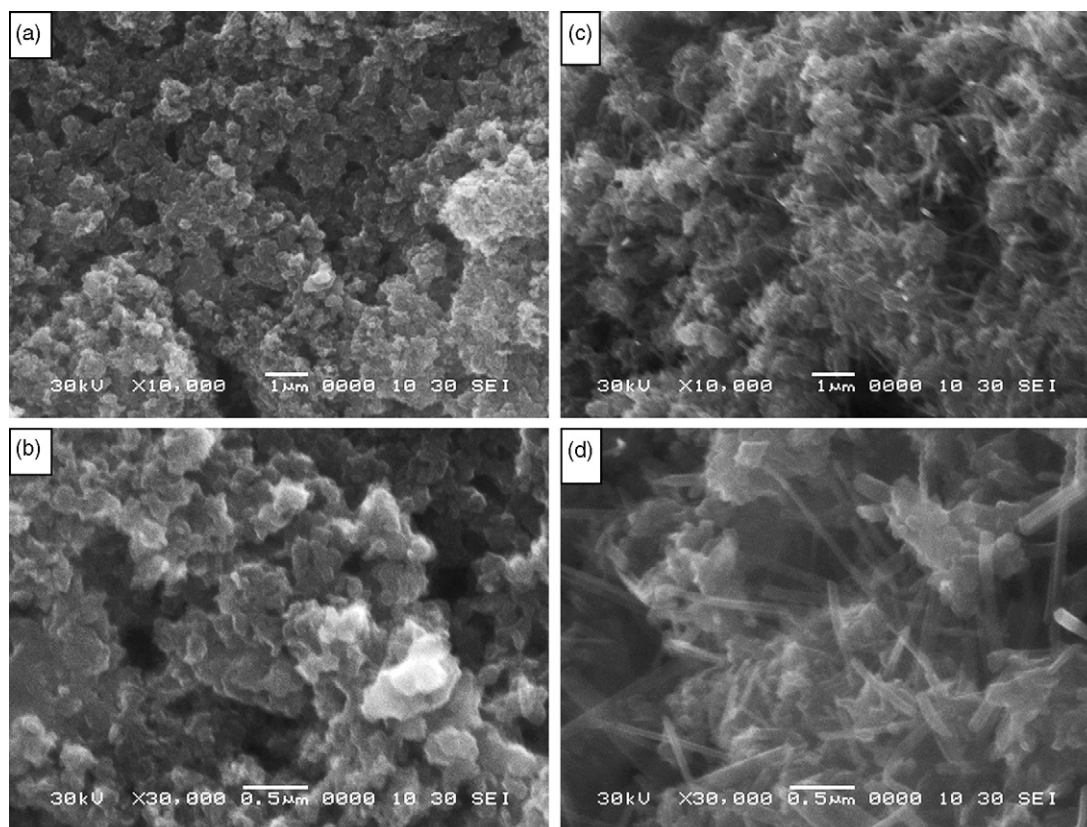


Fig. 2. SEM images of nanostructured V_2O_5 electrodes: (a) and (b) are for V_2O_5 annealed for 45 min at 300 °C (sample A), while (c) and (d) are for V_2O_5 annealed for 1 h at 300 °C (sample B).

The cathode was prepared by mixing V_2O_5 powders with 20 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder in *N*-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry, which was then spread onto aluminium foil. The coated electrodes were dried in a vacuum oven at 110°C for 24 h and then pressed. Electrochemical characterizations were carried out using coin cells (CR 2032) assembled in an argon-filled glove box. Lithium metal was used as the counter and reference electrode. The electrolyte used was 1 M LiPF_6 in a 50:50 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), provided by MERCK KgaA. Subsequently, electrochemical tests were performed by galvanostatically discharging/charging the cells in the range of 1.5–4.0 V at a constant current density of 50 mA g^{-1} via a Neware Battery Tester. Cyclic voltammetry (CV) measurements were performed at a scanning rate of 0.5 mV s^{-1} , using a CHI 660A electrochemical workstation system (CH Instrument, Cordova TN). All tests were performed at room temperature.

3. Results and discussion

Both samples (A and B) were highly crystallized and the peaks positions agree well with those of the commercial V_2O_5 (JCPDS 41-1426) as shown in Fig. 1. From the XRD patterns in Fig. 1, it was estimated that sample A (b) has an average crystal size of 36 nm while sample B (c) has an average crystal size of 83 nm. Meanwhile, as seen from Table 1, it was found that sample A had a higher BET specific surface area of $41\text{ m}^2\text{ g}^{-1}$, compared to $17\text{ m}^2\text{ g}^{-1}$ for sample B. Therefore, the average crystal size is reduced with a longer annealing time, which leads to a higher specific surface area.

Fig. 2 shows scanning electron microscope images of the as-synthesized V_2O_5 one-dimensional nanostructures (samples A and B). Fig. 2(a and b) were SEM images of sample A while Fig. 2(c and d) were SEM images of sample B. From the SEM images, it is very obvious that the oxides have become well-crystallized and that there is a higher yield of nanofibers in sample B compared to the smaller, but also denser, nanoparticles in sample A.

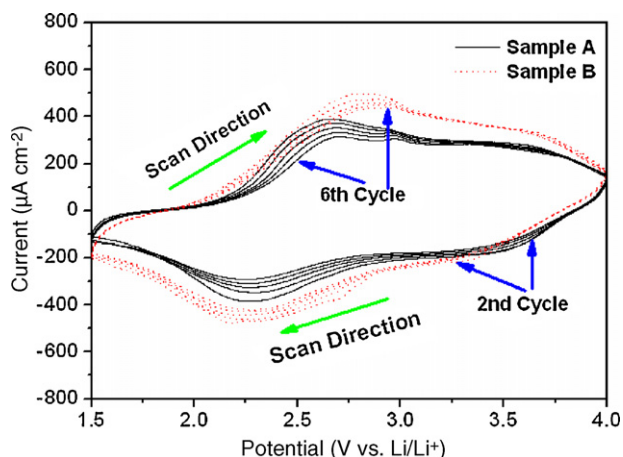


Fig. 3. Cyclic voltammograms of nanostructured V_2O_5 electrodes. The applied scan rate was 0.5 mV s^{-1} .

Cyclic voltammetry was used to analyze the active voltage range for the nanostructured V_2O_5 electrodes (Fig. 3). Well-defined, and almost identical reduction and oxidation peaks occur at 2.3 and 2.8 V, respectively, for both the samples A and B electrodes. However, sample B shows higher kinetics and reac-

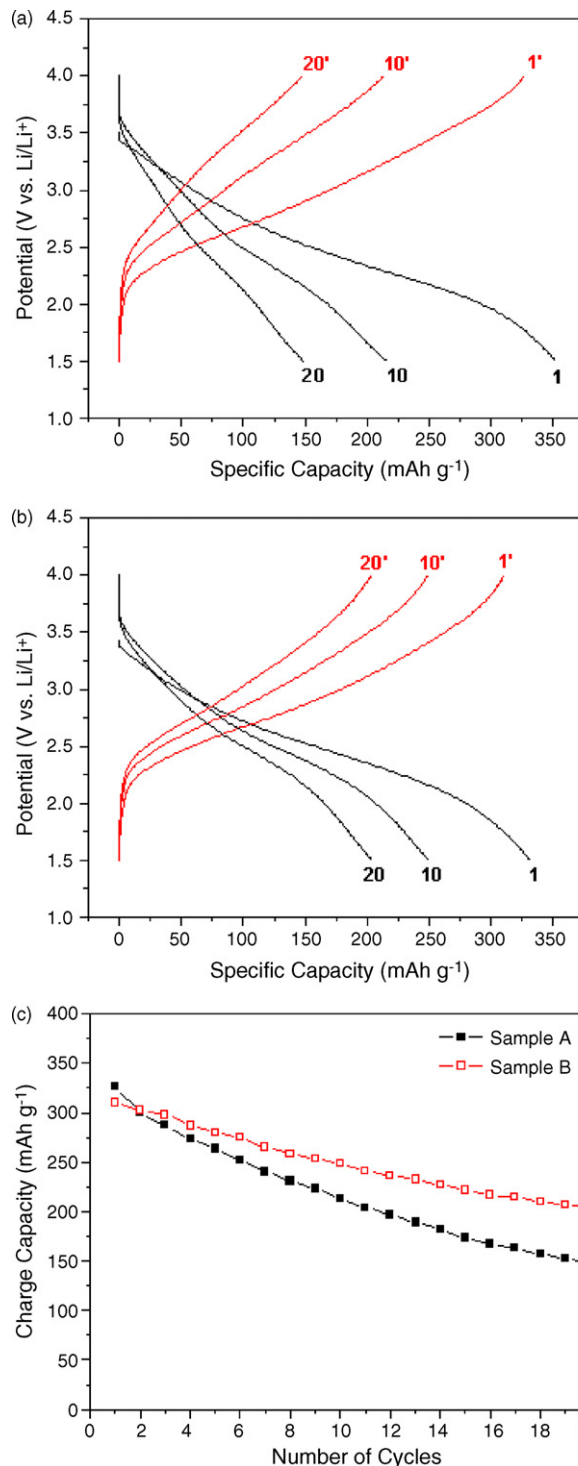


Fig. 4. The 1st, 10th and 20th charge–discharge profiles of nanostructured V_2O_5 electrodes: (a) V_2O_5 annealed for 45 min at 300°C (sample A) and (b) V_2O_5 annealed for 1 h at 300°C (sample B). (c) Charge capacity vs. cycle number for nanostructured V_2O_5 electrodes cycled between 1.5 and 4.0 V at a cycling rate of 50 mA g^{-1} .

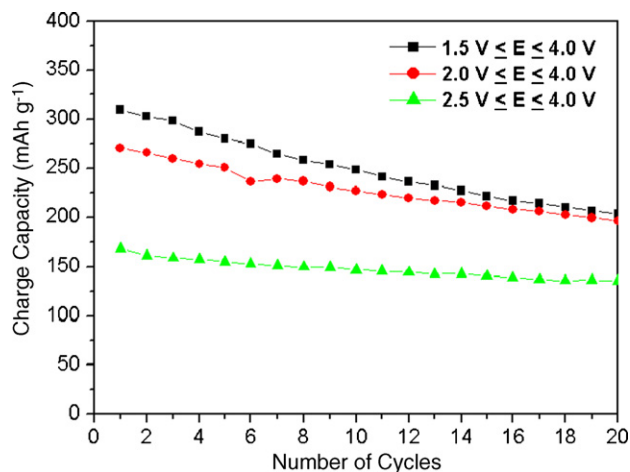


Fig. 5. Cycling behaviour for sample B V_2O_5 electrode at different cut-off voltages: (a) 1.5 V; (b) 2.0 V and (c) 2.5 V. The current density applied was 50 mA g^{-1} .

tivity towards Li^+ insertion and extraction compared to sample A. This may be due to the higher degree of crystallization and the well-grown nanostructure shown by the sample B electrode.

Electrochemical properties for both V_2O_5 samples were examined by galvanostatically discharging/charging in the range of 1.5–4.0 V at a constant current density of 50 mA g^{-1} . Fig. 4 shows that both samples demonstrated an initial charge capacity above 300 mAh g^{-1} , followed by capacity fading after 20 cycles. However, the capacity fading in sample A is more significant, decreasing from 328 to 146 mAh g^{-1} after 20 cycles at a rate of 50 mA g^{-1} . This may be because some vanadium dissolution occurs when the oxide is discharged to 1.5 V [9]. The vanadium dissolution in sample A may be enhanced because the higher specific surface area amplifies this phenomenon. This behaviour is also consistent with a report that amorphous materials dissolve more easily than crystallized ones [10].

Fig. 5 shows the charge capacities for the different potential spans for sample B. From Fig. 4, we already know that the charge capacity for both the samples decreases rapidly with increasing cycle number between 1.5 and 4.0 V. Increasing the cut-off voltage to 2.0 V gave less capacity fading, and there was even better cycling stability when the cut-off voltage was increased to 2.5 V. Although the 136 mAh g^{-1} charge capacity obtained in the latter case is small, it is important to keep in mind that this capacity was obtained with a reduced voltage window (2.5–4.0 V). Besides the possibility of vanadium dissolution when discharging to 1.5 V, the structural changes or damage inflicted upon the one-dimensional nanostructure of the oxides upon cycling in the larger potential span might be another reason for loss in the electroactivity of the material [11–12]. Sample B shows good cyclability and high capacity (200 mAh g^{-1} after 20 cycles) in the voltage range of 2.0–4.0 V at a cycling rate of 50 mA g^{-1} .

4. Conclusions

In this study, we have successfully prepared one-dimensional V_2O_5 nanostructures via a precipitation process followed by heating in vacuum at 300°C . Both the XRD patterns and SEM images reveal that the V_2O_5 crystal sizes were ~ 36 – 83 nm . The as-prepared V_2O_5 nanostructures are well crystallized and give a higher yield of nanofibers with longer annealing in the vacuum oven. However, the longer annealing time leads to a larger crystal size and consequently a lower BET specific surface area. Therefore, the morphology and electrochemical properties of the V_2O_5 nanostructures are strongly influenced by the annealing duration. We have showed that the V_2O_5 nanostructures are electrochemically active towards Li^+ insertion and extraction in the potential window of 1.5–4.0 V. The V_2O_5 nanostructure shows an improved cycle life when the cut-off voltage for discharging is increased from 1.5 to 2.5 V. We strongly believe that the significant capacity loss when discharging to 1.5 V is related to the dissolution of vanadium and the structural changes upon cycling in the larger potential span. Good cyclability and capacity as high as 200 mAh g^{-1} after 20 cycles are achieved in the voltage range of 2.0–4.0 V at a cycling rate of 50 mA g^{-1} when the oxides are annealed for 1 h.

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