



High capacity and excellent cyclability of vanadium (IV) oxide in lithium battery applications

Ning Ding^{a,b}, Xuyong Feng^a, Shuhua Liu^b, Jing Xu^a, Xin Fang^a, Ingo Lieberwirth^b, Chunhua Chen^{a,*}

^a Department of Materials Science and Engineering, University of Science and Technology of China, 96 Jinzai Road, Hefei, Anhui 230026, PR China

^b Max Planck Institute for Polymer Research, Mainz 55128, Germany

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ABSTRACT

A $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ powder with a flaky particle morphology was synthesized via a hydrothermal reduction method. It was characterized by scanning electron microscopy, electron energy loss spectroscopy, and thermogravimetric analysis. As an electrode material for rechargeable lithium batteries, it was used both as a cathode versus lithium anode and as an anode versus LiCoO_2 , LiFePO_4 or $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. The $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ electrode exhibits an extraordinary superiority with high capacity (160 mAh g^{-1}), high energy efficiency (95%), excellent cyclability (142.5 mAh g^{-1} after 500 cycles) and rate capability (100 mAh g^{-1} at 10 C-rate).

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1. Introduction

There are two types of commercial lithium batteries which have been playing important role in nowadays information society. One is primary lithium battery using a lithium-free metal oxide (such as electrolytic MnO_2) as the active material of its cathode and lithium metal as the anode material; the other is secondary lithium battery using a lithium-containing metal oxide (such as LiCoO_2) as the active material of its cathode and a carbonaceous anode (such as graphite). The latter was first commercialized by Sony in 1991 [1,2] and has been widely used in portable electronics. Both MnO_2 and delithiated LiCoO_2 can provide vacancies to allow the intercalation of lithium ions into the host, but the structure of MnO_2 undergoes an irreversible variation during lithiation while lithium ions can only be partially extracted from lithiated MnO_2 in the following charge process [3]. Therefore, MnO_2/Li is only used as a primary battery. In contrast to MnO_2 , vanadium oxides (VO_x) are good host materials for the reversible lithium intercalation and extraction. In addition, the wide range of oxidation states of vanadium from +2 to +5 may accommodate multi-electron transfer processes in applications. Therefore, vanadium oxides have the potential to be used in rechargeable lithium batteries and to provide higher specific capacities than the common one-electron-transfer cathode materials, such as LiCoO_2 , LiMn_2O_4 and LiFePO_4 . In fact, several VO_x compounds V_2O_5 , $\text{VO}_2(\text{B})$, V_6O_{13} and LiV_3O_8 have been reported in literature on their syntheses and potential applications for lithium ion batteries [4–7]. Usually, nanoscaled particle size is

necessary to achieve good electrochemical performance. For example, Chan et al. [8] reported that V_2O_5 nanoribbon shows a characteristic of ultrafast Li diffusion and probably can be used at a super high power rate (360 C). In this communication, we report the synthesis and characterization of a new vanadium oxide powder, $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$, with a flaky particle morphology. It shows superior performance with high capacity, high energy efficiency and extremely excellent cyclability.

2. Experimental

A $\text{VO}_x \cdot n\text{H}_2\text{O}$ powder was synthesized via a hydrothermal method. Safety precaution should be taken because the use of vanadium compounds is hazardous and vanadium is a P-listed toxic material. Ammonium metavanadate (2.5 mmol) was added in a mixed solution made from 10 ml ethanol and 3 ml 2 M nitric acid, and a suspension was obtained. The suspension was then transferred into a 15 ml Teflon-lined autoclave, which was then kept at 180 °C for 24 h. Consequently, a precipitate was produced after the hydrothermal process. It was filtrated and washed with deionized water, and then dried at 50 °C in a vacuum dry-box. Its morphology and crystal structure were characterized by scanning electron microscopy (LEO 1530 Gemini) and powder X-ray diffraction (Philips X'Pert Pro Super diffractometer with $\text{Cu K}\alpha$ radiation). The oxidation state of V in the obtained $\text{VO}_x \cdot n\text{H}_2\text{O}$ sample was analyzed by electron energy loss spectroscopy (Zeiss 912 microscope operated at 120 kV with an in-column omega energy filter). The amount of water in $\text{VO}_x \cdot n\text{H}_2\text{O}$ was determined by thermogravimetric analysis (Shimadzu TA-50).

* Corresponding author. Tel.: +86 551 360 6971; fax: +86 551 360 1592.
E-mail address: cchchen@ustc.edu.cn (C. Chen).

The electrochemical characteristic of the $\text{VO}_x \cdot n\text{H}_2\text{O}$ powder was evaluated in coin cells (CR2032 size) with $\text{VO}_x \cdot n\text{H}_2\text{O}$ as the active material of its positive electrode, which consisted of $\text{VO}_x \cdot n\text{H}_2\text{O}$, carbon black and poly(vinylene difluoride) in the weight ratio of 7:2:1. The mixture was milled by hand in a mortar with 1-methyl-2-pyrrolidone (NMP) as a solvent, then the slurry was pasted on Cu foil as a current collector, finally was dried for 2 h in the dry box at 70 °C. The mass of loading active material was about 5 mg. Coin cells were assembled in an argon-filled glove box (MBraun Labmaster 130) with Li metal (Wuhan Qilaje Tech. Co., Ltd) as a counter electrode and 1 M LiPF_6 /ethylene carbonate-diethyl carbonate (w/w = 1:1) as the electrolyte (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd). Galvanostatic cycling of the cells was carried out on a multi-channel battery test system (NEWARE BTS-610).

3. Results and discussion

The SEM image of the vanadium oxide powder (Fig. 1a) shows that the synthesized powder consists of flaky particles of micrometers in width. XRD pattern indicates that it has a monoclinic structure (JCPDS 76-0674) with lattice constants $a = 8.986$, $b = 5.752$, $c = 4.412$ Å and $\beta = 93.9^\circ$. The EEL spectrum (Fig. 1b) of V L-edge for the $\text{VO}_x \cdot n\text{H}_2\text{O}$ exhibits two distinct white lines with the maximum peaks at 519.3 (L_3 , corresponding to four $2p^{3/2} \rightarrow 3d^{3/2}3d^{5/2}$) and 525.7 eV (L_2 , corresponding to two $2p^{1/2} \rightarrow 3d^{3/2}$), respec-

tively, and the peaks at high energy loss correspond to the O K-edge [9,10]. By comparing the absolute energy position of the white-lines and their intensity ratio (L_3/L_2), the valence of V in the $\text{VO}_x \cdot n\text{H}_2\text{O}$ powder is easily determined as +4, indicating that the precursor ammonium metavanadate has been reduced by ethanol during the hydrothermal process. In fact, V_2O_5 can be reduced by ethanol even at the room temperature [11,12]. Also, the amount of hydrated water, i.e. n in $\text{VO}_2 \cdot n\text{H}_2\text{O}$, can be calculated as 0.43 from its TGA curve (not shown here).

The cyclic voltammogram of the $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ (or VO(F) for short) electrode exhibits three reduction peaks at 2.78, 2.6 and 2.5 V vs. Li^+/Li (Fig. 2a). Combined with the voltage profile of this cell (Fig. 2b), a few electrochemical reaction steps can be distinguished at different discharged states and can be written as following: (1) at the beginning of discharge, 0.1 mol lithium ions intercalate into VO(F) to form $\text{Li}_{0.1}\text{VO(F)}$, corresponding to the peak at 2.78 V; (2) then, another 0.1 mol lithium ions further intercalate into $\text{Li}_{0.1}\text{VO(F)}$ to form $\text{Li}_{0.2}\text{VO(F)}$, corresponding to the peak at 2.6 V; (3) at the end of discharge, $\text{Li}_{0.2}\text{VO(F)}$ is finally transformed into $\text{Li}_{0.5}\text{VO(F)}$, corresponding to the peak at 2.5 V. Because two sloping ranges and one plateau can be clearly seen in the voltage profile, the first two processes at the higher voltage can be attributed to one-phase solid-solution transitions, i.e. $\text{VO(F)} + x\text{Li} = \text{Li}_x\text{VO(F)}$ ($x = 0-0.1$) and $\text{Li}_{0.1}\text{VO(F)} + y\text{Li} = \text{Li}_{0.1+y}\text{VO(F)}$ ($y = 0-0.1$) and the last process corresponds to a two-phase transition between $\text{Li}_{0.2}\text{VO(F)}$ and $\text{Li}_{0.5}\text{VO(F)}$, i.e. $\text{Li}_{0.2}\text{VO(F)} + 0.3\text{Li} = \text{Li}_{0.5}\text{VO(F)}$. In addition, by integrating the voltage profile, the energy efficiency of VO(F) is 95%, which is much higher than those of other transition metal oxides, such as CoO (54.6%) [13] and RuO_2 (54.9%) [14]. Thus, $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ is a highly efficient host material for lithium storage, which is beneficial for energy saving in applications.

The cycling performance of VO(F) between 2 and 3 V (Fig. 2c) gives a very stable capacity of 162 mAh g^{-1} for at least 80 cycles, which is superior to other nanostructured VO_x reported in literature [15–18]. Furthermore, VO(F) shows excellent rate capability in that it can still retain 100 mAh g^{-1} at 10 C (Fig. 2d). After the high C rate test, the VO(F)/Li cell can recover at least 96% of its initial capacity. It still retains 142.5 mAh g^{-1} (88.3%) at 1 C rate after subsequent 230 cycles.

According to Dahn et al. [19–22], vanadium oxide shows the best thermal stability among almost all electrodes for lithium batteries. We expect that our VO(F) should have similar good thermal stability as VO_2 . Considering the source of active lithium, the use of VO(F) as the cathode in secondary lithium cells has to couple with metallic lithium as the anode, which may be stabilized by coating a solid electrolyte [23]. Thus, owing to its excellent rate performance, long lifespan and high safety, the use of $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ to replace LiCoO_2 (or LiMn_2O_4 and LiFePO_4) is a potential route to design safe, high performance secondary lithium batteries for many applications.

On the other hand, as the potential of $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ is less than 3 V vs. Li^+/Li , it can also be used as an anode material. It has been reported that vanadium oxides are good candidate of anode materials for aqueous lithium batteries, which can fundamentally resolve the safety problems of lithium batteries [24–27]. Therefore, we couple VO(F) with different cathode materials to tune their open-cell voltages and examine the possibility of being further used for aqueous batteries. Three cathode materials are chosen, i.e. LiFePO_4 , LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Their discharge voltage plateaus are found at 3.5, 3.9 and 4.8 V (voltage profiles not shown here), respectively. The cyclic voltammograms of VO(F) cells coupled with three cathode materials are shown in Fig. 3a–c with the main reduction peaks at 0.7, 1.2 and 2 V, respectively. For the theoretical decomposition electrode potential difference of water is 1.23 V, the cycling performances of the $\text{LiFePO}_4/\text{VO(F)}$ and $\text{LiCoO}_2/\text{VO(F)}$ cells are further studied. The cells exhibit good

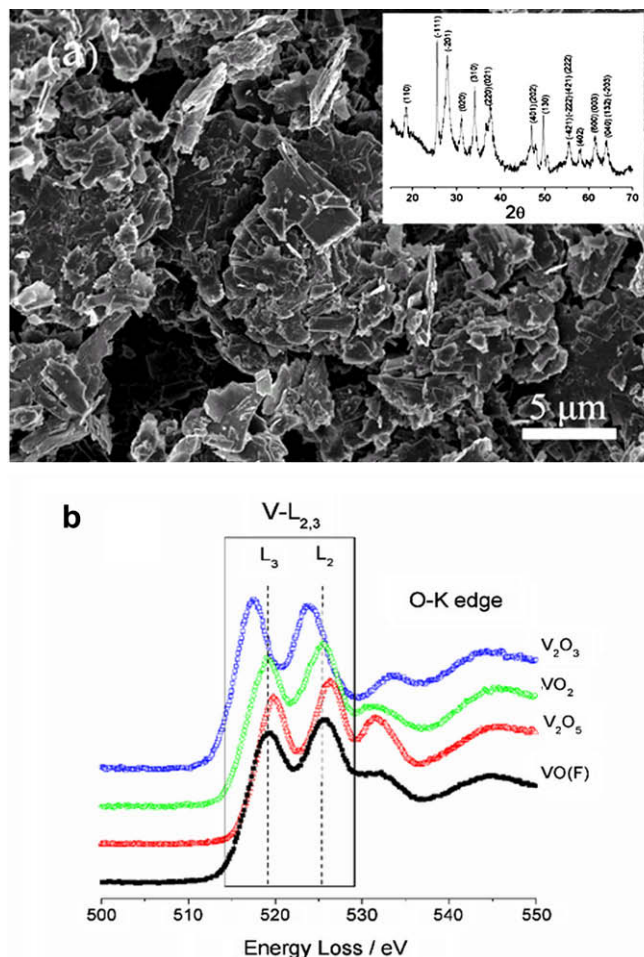


Fig. 1. (a) Field-emission SEM image (with XRD pattern in the inset) and (b) EEL spectrum of a flaky $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ powder. The EEL spectra of reference samples (V_2O_3 , VO_2 and V_2O_5) are also given.

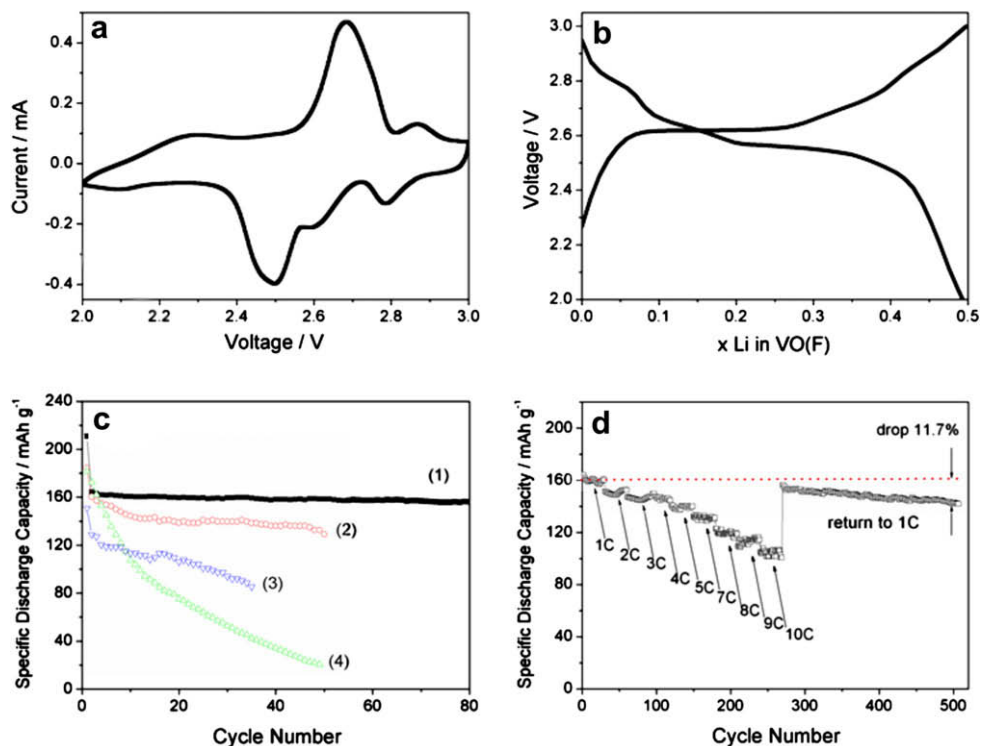


Fig. 2. (a) Cyclic voltammogram and (b) charge–discharge voltage profile of a VO(F)/Li cell; (c) The cycling performance of (1) VO(F) between 2 and 3 V vs. Li^+/Li , (2) VO_2 (B) nanorods (2–3.2 V) [16], (3) V_2O_5 submicron spheres (1.8–3.8 V) [17] and (4) VO_x nanotubes (1.4–3.9 V) [18]. (d) C-rate retention and cycle life test of the VO(F)/Li cell.

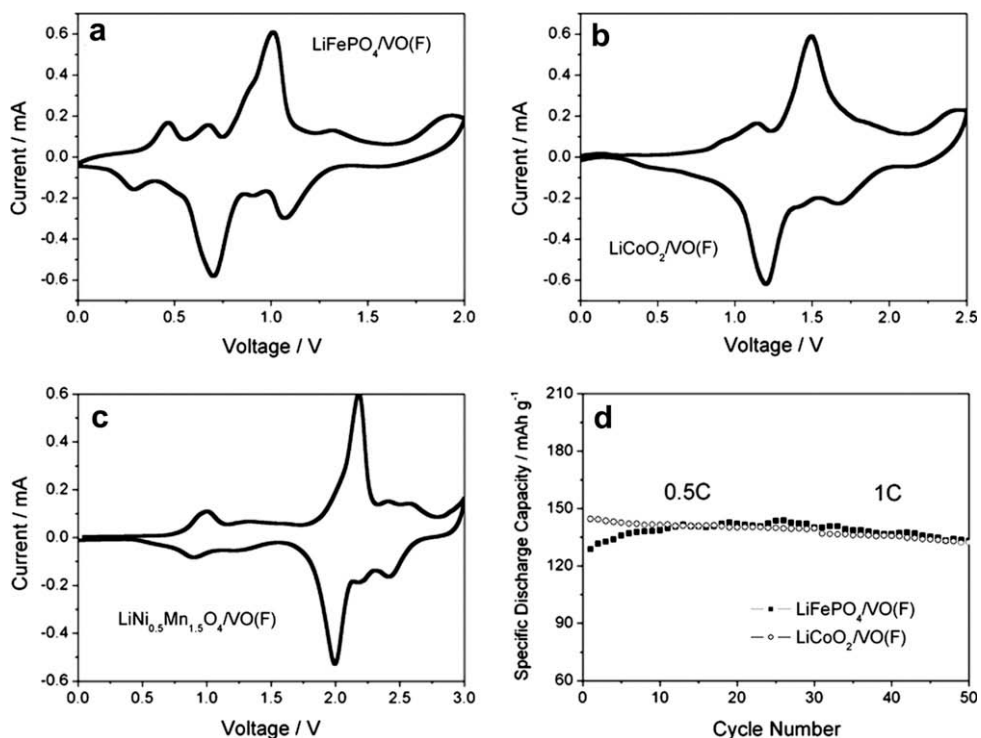


Fig. 3. Cyclic voltammograms of the cells: (a) $\text{LiFePO}_4/\text{VO(F)}$, (b) $\text{LiCoO}_2/\text{VO(F)}$ and (c) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{VO(F)}$. (d) The cycling performance of $\text{LiFePO}_4/\text{VO(F)}$ and $\text{LiCoO}_2/\text{VO(F)}$ cells in the voltage windows of 0–1.5 V and 0–2.5 V, respectively, with 1 M LiPF_6 /ethylene carbonate–diethyl carbonate as the electrolyte.

capacity retention during cycling (Fig. 3d). These results obtained in organic electrolyte provide an exciting prospect for the aqueous lithium batteries. Future work will be focused on the performance of $\text{LiFePO}_4/\text{VO(F)}$ and $\text{LiCoO}_2/\text{VO(F)}$ cells with aqueous electrolytes.

4. Conclusions

We have synthesized a $\text{VO}_2 \cdot 0.43\text{H}_2\text{O}$ powder with a flaky particle morphology via a hydrothermal method. It exhibits a

significant superiority with high capacity (about 160 mAh g⁻¹), high energy efficiency (95%), excellent cyclability (retaining 142.5 mAh g⁻¹ after 500 cycles) and rate capability (100 mAh g⁻¹ at 10 C). We believe that VO₂ · 0.43H₂O can be considered as a potential cathode material to design safe and high energy density batteries for EV/HEV.

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