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Novel sodium intercalated $(NH_4)_2V_6O_{16}$ platelets: High performance cathode materials for lithium-ion battery

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A B S T R A C T

A simple and versatile method for preparation of novel sodium intercalated $(NH_4)_2V_6O_{16}$ is developed via a simple hydrothermal route. It is found that ammonium sodium vanadium bronze displays higher discharge capacity and better rate cyclic stability than ammonium vanadium bronze as lithium-ion battery cathode material because of smaller charge transfer resistance, which would favor superior discharge capacity and rate performance.

1. Introduction

With fossil fuels depletion, global warming and environmental pollution, increasing attention has been paid to develop and use renewable clean energy to lessen green house gas emissions. Lithium-ion batteries with high energy density, low cost and long cycle life are the ideal power source for electric vehicles, which has great significance for lessening greenhouse gas emissions and alleviating the energy crisis. But the energy density, security and cost of lithium-ion battery should be further enhanced [1].

Vanadium oxides and bronzes offer the advantages for being cheap, easy to synthesize, abundance in the earth and high-energy density, and thus has attracted much interest [2–10]. Vanadium oxide bronzes are a wide range of crystalline structures with mixed valence networks $[V_xO_y]$ containing the V^{5+}—V^{4+} or V^{4+}—V^{3+} couples whose electrical balance of the ionocovalent network is directly linked to the amount of inserted or intercalated elements—alkalis, alkaline earths or metals [11]. Compared with vanadium oxides, the advantages of vanadium bronzes as lithium-ion battery electrode materials are as follows. Metal ions would stabilize the crystal lattice, increase the diffusion rate of lithium ion and increase electric conductivity. In addition, it is possible to find new lithium-ion battery electrode materials with high capacity and good cyclic stability for the complicated crystalline structures of vanadium bronzes.

Recently, various ammonium vanadium oxide nano-structures have been receiving a great deal of attention as lithium-ion battery cathode materials, for example, $NH_4V_4O_{10}$ nano-belts [12,13], $(NH_4)_2V_6O_{16}$ nano-rods [14], $NH_4V_3O_8{\cdot}0.2H_2O$ flakes [15] and $NH_4V_3O_8$ nano-rods [16]. Also, $Na_2V_6O_{16}{\cdot}xH_2O$ nanowires were used as Li inserting material for lithium-ion battery [17]. The CV curves of all these single ammonium and sodium vanadium oxides are characteristic of multi-pairs of oxidation and reduction peaks. Furthermore, their discharge cures also display several discharge platforms, which resulted in limits to practical application. It would be very important to find novel crystalline and cheap sodium and ammonium vanadium bronze with high capacity and good cyclic stability and fewer discharge platforms as cathode materials for lithium-ion battery. However, few attentions were paid to prepare bi or multi-cations vanadium bronze, such as ammonium and sodium bi-cation vanadium bronze.

Herein, we controllably fabricated sodium intercalated $(NH_4)_2V_6O_{16}$ via the intercalation of Na^+. When they were tested as cathode materials for lithium-ion battery, the ammonium sodium vanadium bronze exhibited higher discharge capacity and better cyclic stability than ammonium vanadium bronze.

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2. Materials and methods

Ammonium sodium vanadium bronze was prepared via a simple hydrothermal method. 1.28 g oxalic acid and 0.21 g $NaNO_3$ was dissolved in 30 ml deionized water, and then 0.59 g ammonium metavanadate (NH_4VO_3) was added into the solution under stirring at room temperature for 2 h. After that the mixture was transferred into a 50-ml Teflon-lined stainless autoclave, sealed, kept at 200 °C for 90 h and cooled to room temperature. Ammonium vanadium bronze was prepared under the identical condition without $NaNO_3$.

The morphology of products was observed by Hitachi S-4800 field emission scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded on a diffractometer (Co Kα, PANalytical, X'Pert). X-ray photoelectron spectroscopy (XPS) measurements were performed with an Escalab 250 spectrometer. Thermal analysis measurements were performed using a Netzsch Sta449C analyzer. Energy dispersive spectroscopy (EDS) measurement is also performed with Hitachi S-4800 field emission scanning electron microscope.

The as-synthesized materials were tested as the cathode materials for lithium-ion battery. The composite positive electrodes were consisted of the active material, conductive material (acetylene black) and binder (PVDF) in a weight ratio of 7/2/1. The Li metal was used as the counter electrode. The electrolyte was 1 M $LiPF_6$ in a 1/1/1 (volume ratio) mixture of ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC). The cells were charged and discharged between a 2.0 and 3.4 V voltage limit at different discharge rate. A Land CT2001A battery tester was used to measure the electrode activities at room temperature.

The electrochemical impedance measurements were carried out by Zahner IM6 using a 5 mV acoscillation amplitude which was applied over the frequency of 5 MHz to 0.1 Hz frequency ranges. The equivalent circuit was fitted by the Zman 2.0 software of the Zahner IM6 electrochemical workstation. The cells were discharged and charged for 1 cycle, and then were kept at the open-circuit condition for 2 h before performing impedance tests. Cyclic voltammetry (CV) experiments were performed with a Chi660c electrochemical workstation at a scan rate of 1 mV s^{-1}.

3. Results and discussion

SEM observations show that the ammonium vanadium bronze was micro-platelets as well as the ammonium sodium vanadium bronze prepared with $NaNO_3$ in Fig. 1a and b, respectively. X-ray diffraction (XRD) pattern displays that both the ammonium vanadium bronze and ammonium sodium vanadium bronze have the same crystalline structure to $HNaV_6O_{16}{\cdot}4H_2O$ (Fig. 2a and b). So both the ammonium vanadium bronze and ammonium sodium vanadium bronze may be expressed as $(NH_4)_2V_6O_{16}$ and $(NH_4)_xNa_yV_6O_{16}$, respectively.

X-ray photoelectron spectroscopy (XPS) was performed to identify elemental composition of ammonium sodium vanadium bronze. The results show that the surface of ammonium sodium vanadium bronze is composed of N, Na, V and O. Fig. 3 shows that the binding energy of N1s is at 401.4 eV, which is ascribed to NH_4^+ [18]. The binding energy of Na1s is at 1071.4 eV ascribed to Na^+. The XPS spectra of the O1s region for ammonium sodium vanadium bronze is composed of three peaks at 530.0, 531.4 and 532.9 eV, corresponding to O^{2-}, C=O and C—O(H), respectively [19]. The V2p3/2 peak is composed of two peaks at 517.4 and 515.9 eV corresponding to V (V) and V (IV), respectively [20]. The average oxidation number for V is +4.74 calculated from X-ray photoelectron Spectroscopy (XPS) data. TG curve (Fig. 4) shows

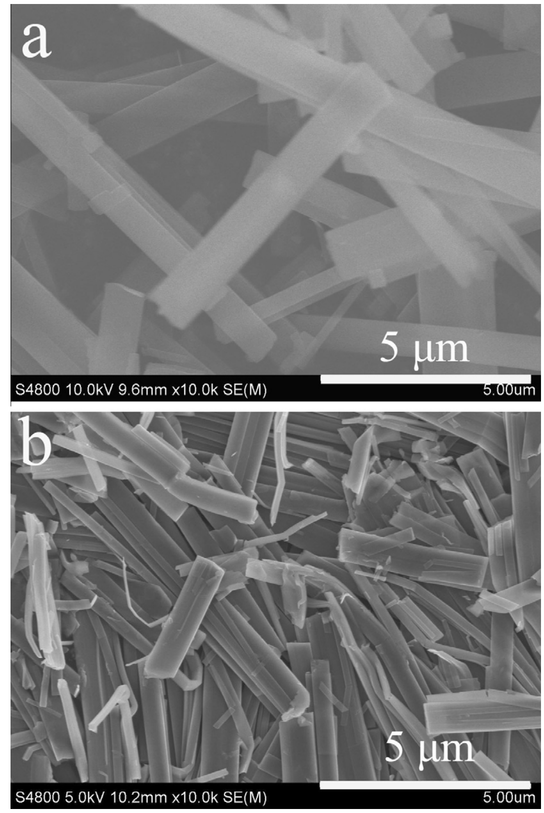

Fig. 1. SEM images of ammonium vanadium bronze (a) and ammonium sodium vanadium bronze (b).

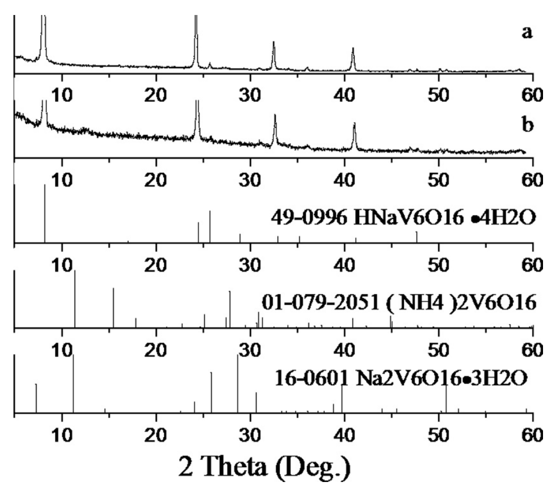

Fig. 2. Wide-angle powder XRD patterns of ammonium vanadium bronze (a) and ammonium sodium vanadium bronze (b).

that there is the weight loss of 2.18% between 280 and 400 °C, due to the release of NH_3. EDS results show that the molar ratio of V to Na is 1:0.12. Based on the above analysis, the formula of ammonium sodium vanadium bronze can be expressed as $(NH_4)_{0.71}Na_{0.72}V_6O_{16}$.

Both the ammonium vanadium bronze and ammonium sodium vanadium bronze were tested as cathode material for lithium-ion battery at a current density of 750 mA g^{-1}. The first, second and final charge–discharge profiles of the ammonium sodium vanadium bronze and ammonium vanadium bronze/Li cell are shown in Fig. 5a and b, respectively. They have similar discharge curves,