



Short communication

Flower-like $(\text{NH}_4)_{0.83}\text{Na}_{0.43}\text{V}_4\text{O}_{10}\cdot 0.26\text{H}_2\text{O}$ nano-structure for stable lithium battery electrodes

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ABSTRACT

3D flower-like $(\text{NH}_4)_{0.83}\text{Na}_{0.43}\text{V}_4\text{O}_{10}\cdot 0.26\text{H}_2\text{O}$ vanadium bronze nano-platelet clusters are prepared via a facile hydrothermal method. The thickness of the nano-platelet is around 50 nm and the length ranged up to several micrometers. When used as positive electrode in rechargeable lithium battery, this material exhibits good cycle stability at different discharge rates (0.18–0.67C rate) and voltage limits (1.5–3.4 V and 2.0–3.4 V). The improvement the electrochemical properties of the $(\text{NH}_4)_{0.83}\text{Na}_{0.43}\text{V}_4\text{O}_{10}\cdot 0.26\text{H}_2\text{O}$ might be attributed to the change of the lattice parameters due to the co-intercalation of the superstoichiometric cations (Na^+ and NH_4^+).

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1. Introduction

Vanadium oxide (V_2O_5) has attracted much interest as rechargeable lithium battery electrode materials, owing to its high energy density [1]. However, the un-reversible structure change that took place when more than one lithium was discharged [2], low electronic conductivity and Li^+ diffusivity have restricted its practical application [3]. To increase conductivity and stabilize the host lattice, transition metal ions were introduced to improve the electrochemical properties [4–7]. It was reported that 3D V_2O_5 nano-structures exhibited higher capacity and better cycle stability than its 1D and 2D nano-structure counterpart [1]. Though various 1D nano-architectures of single metal vanadates or vanadium bronzes were reported [8], little attention has been paid to fabricate 3D multi-cations vanadium bronzes nano-structures. Recently, we found that the intercalation of two kinds of cations (such as Na^+ and NH_4^+) could induce structural transformation of the vanadium bronzes and thus gave rise to novel crystalline structures with well-defined morphologies [9]. Herein, we fabricated another type of 3D flower-like sodium ammonium vanadium bronze $(\text{NH}_4)_{0.83}\text{Na}_{0.43}\text{V}_4\text{O}_{10}\cdot 0.26\text{H}_2\text{O}$ nano-platelet clusters via the intercalation of bi-cations. When used as positive electrode materials of lithium batteries, it exhibited good cycle stability at different dis-

charge rates (0.18–0.67C) and voltage limits. This facile method can be extended to prepare series of multi-cation intercalated vanadium bronzes.

2. Experimental

The $(\text{NH}_4)_{0.83}\text{Na}_{0.43}\text{V}_4\text{O}_{10}\cdot 0.26\text{H}_2\text{O}$ nano-platelet clusters were prepared via a simple hydrothermal method. 1.28 g oxalic acid and 0.21 g NaNO_3 were 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 180 °C for 6 h and cooled to room temperature. The product was filtered, washed with deionized water and dried at 60 °C for 12 h.

Scanning electron microscopy (SEM) was performed on a Shimadzu SS-550 instrument working at 15 keV. Transmission electron microscopy (TEM) was carried out on a Philips Tecnai F20 electron microscopy instrument. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max-2500 diffractometer using $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurements and Auger electron spectroscopy (AES) were performed with a Kratos Axis Ultra DLD spectrometer. Infrared data was recorded on a Bruker Vector 22 spectrometer. N, Na and V element analyses were performed with a Vanio-EL analyzer, Solaar S2 atomic absorption spectroscopy (AAS) and IRIS Intrepid II inductive coupled plasma emission spectrometer (ICP), respectively. Thermal analysis measurements were performed using a Rigaku TG-DTA analyzer. 1.7 mg

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sample was heated from room temperature to 800 °C with a rate of 10 °C min⁻¹ under a flow of air.

The as-synthesized material was tested as the cathode materials of lithium battery. The composite positive electrodes consisted of the active material, conductive material (carbon) and binder (PVDF) in a weight ratio of 75/15/10. The Li metal was used as the counter electrode. The electrolyte was 1 M LiPF₆ in a 3:1:1 (volume ratio) mixture of ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC). The cells were charged and discharged between 1.5 and 3.4 V (or 2.0–3.4 V) voltage limit at a different discharge rates. A Land CT2001A battery tester was used to measure the electrode activities at room temperature.

3. Results and discussion

SEM observations of the micro-flower-like particles demonstrate that they were consisted of many superimposed nano-platelets from 5 to 10 μm wide and 50 nm thick (Fig. 1a and b). The feather was also confirmed by the TEM image (Fig. 1c). The selected area electron diffraction (SAED) pattern measured from one nano-platelet indicated that the nano-platelet was single crystalline (Fig. 1d).

X-ray diffraction (XRD) pattern demonstrates that the as-prepared material had similar crystalline structure to NH₄V₄O₁₀ (monoclinic, #PDF 31-75) (Fig. 2a). The *d*₀₀₁ interlayer distance was 9.77 Å, while that of NH₄V₄O₁₀ was 9.60 Å (#PDF 31-75), and the possible reason might be attributed to the intercalation of Na⁺. The lattice parameters of the obtained sodium ammonium vanadate were refined and indexed by the software Jade 5.0. The refined lattice constants (*a*, *b*, *c* and β) were (11.70 Å, 3.70 Å, 9.73 Å and 102.4°), while those of NH₄V₄O₁₀ (#PDF 31-75) were (11.71 Å, 3.66 Å, 9.72 Å and 101.0°).

The band at 1406 cm⁻¹ in FT-IR spectrum (Fig. 2b) confirms the existence of NH₄⁺ in the material [10]. While the bands at 3434 and 1625 cm⁻¹ reveal that it contained water [11]. Auger electron spectroscopy further confirms that sodium existed in the form of intercalated Na⁺ because of the signal appeared at 495.6 eV (Fig. 2c) [12]. The average oxidation state of V was 4.71 calculated from X-ray photoelectron spectroscopy data. Element analysis (EA), atom absorption spectroscopy, inductively coupled plasma spectroscopy were used to analyze the content of the elements of N (2.71% by EA), Na (2.29% by AAS) and V (47.50% by ICP), respectively. TG curve (Fig. 2d) shows that there was the weight loss of 4.38% between 208 and 361 °C, due to the release of H₂O and NH₃. The weight of NH₃ was calculated to be 3.30% based on EA result and thus the weight of H₂O was 1.08%. Based on the above analysis, the formula of the as-synthesized material can be expressed as (NH₄)_{0.83}Na_{0.43}V₄O₁₀·0.26H₂O. It was reported that non-stoichiometric amounts of alkalis could be inserted within tunnels of vanadium bronze with mixed valence networks (V_xO_y) via electrical balance [13]. In our case the superstoichiometric cations (Na⁺ and NH₄⁺) could exist in the layers or tunnels of the NH₄V₄O₁₀ structure.

The sodium ammonium vanadium bronze was tested in lithium battery as cathode material. The initial and final discharge profiles and corresponding cyclic performance were displayed in Fig. 3. The initial discharge capacity was 165.5 mAh g⁻¹ in the range of 2.0–3.4 V (0.27C rate) in Fig. 3a. The discharge capacity was 157.4 mAh g⁻¹ after 49th cycle (Fig. 3b), corresponding to 95.1% of the electrode capacity of initial cycle, exhibiting good cycle stability. When further increasing the discharge rate to 0.67C, the initial and final (50th) discharge capacity is decreased to 148.9 and 133.7 mAh g⁻¹ (Fig. 3c and d), respectively. The decay of capacity was about 10.2%. Extra experiments were also performed to test

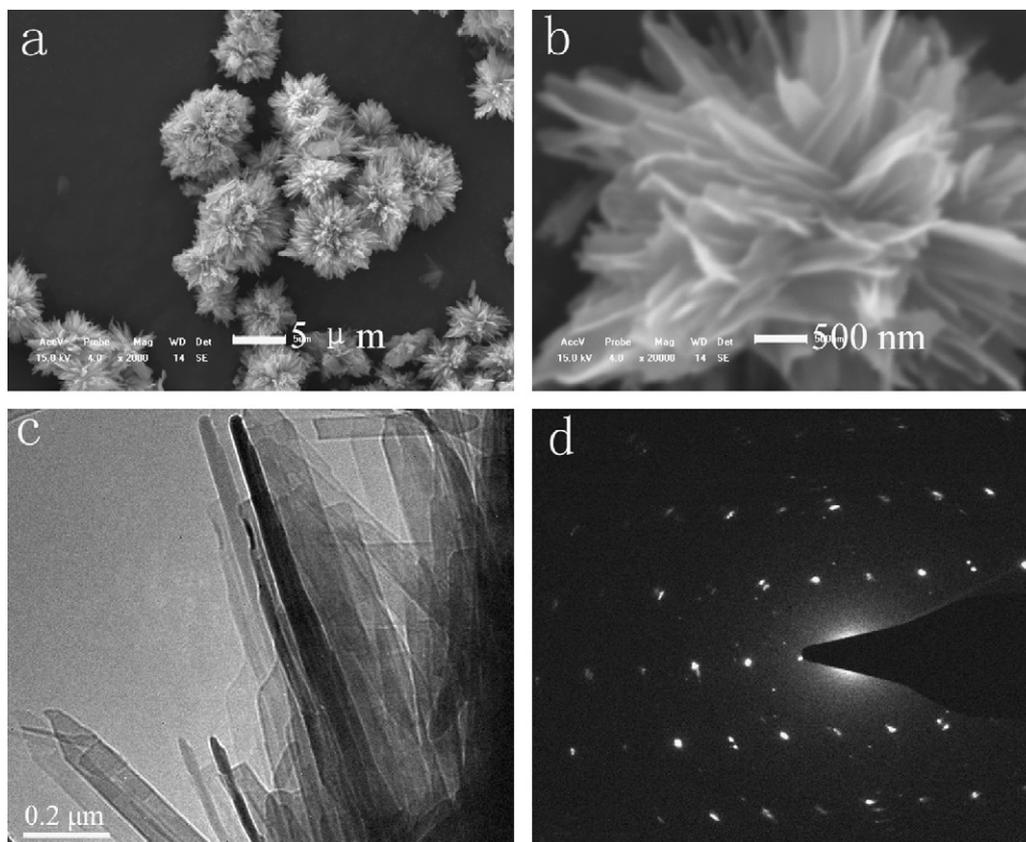


Fig. 1. SEM images of sodium ammonium vanadium bronze nano-platelet clusters (a, b), its TEM image (c) and the selected area electron diffraction (SAED) (d).

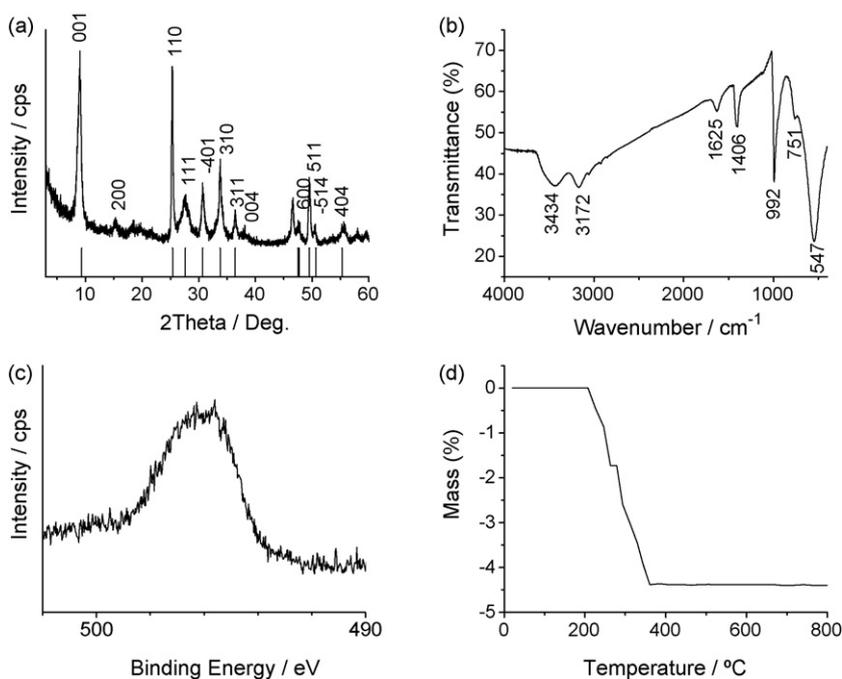


Fig. 2. Wide-angle powder XRD pattern (the vertical lines denoted as the indexed data) (a), FT-IR (b), Na KLL Auger emission spectrum (c) and TG curve (d) of sodium ammonium vanadium bronze.

the material at different discharge rate in the range of 1.5–3.4 V. As displayed in Fig. 3e and f, the initial and final (50th) discharge capacity was 225.7 and 245.3 mAh g⁻¹ at 0.18C rate. The corresponding cyclic performance of the cells exhibited no decay in capacity. When the cell was discharged at 0.57C rate, the initial and final (50th) discharge capacity was decreased to 225.5 and 220.8 mAh g⁻¹ (Fig. 3g and h), corresponding to about 95.1% of the initial electrode capacity. On the whole, the sodium ammonium vanadium bronze exhibited good cycle stability at discharge rates between 0.18 and 0.67C. It was demonstrated that NH₄V₄O₁₀ nanobelts exhibited unfavorable cycle stability [14], and the improved electrochemical properties of the (NH₄)_{0.83}Na_{0.43}V₄O₁₀·0.26H₂O might

be attributed to the change of the lattice parameters due to the co-intercalation of the superstoichiometric cations (Na⁺ and NH₄⁺).

4. Conclusion

Novel sodium ammonium vanadium bronze (NH₄)_{0.83}Na_{0.43}V₄O₁₀·0.26H₂O nano-structures were fabricated from cheap reagent at a large scale via a facile template-free method. It exhibited good cycle stability at different discharge rate as positive electrode material. This facile method and novel structured flower-like sodium ammonium bronze would be significant to the fields of materials synthesis and energy storage of lithium battery.

Acknowledgments

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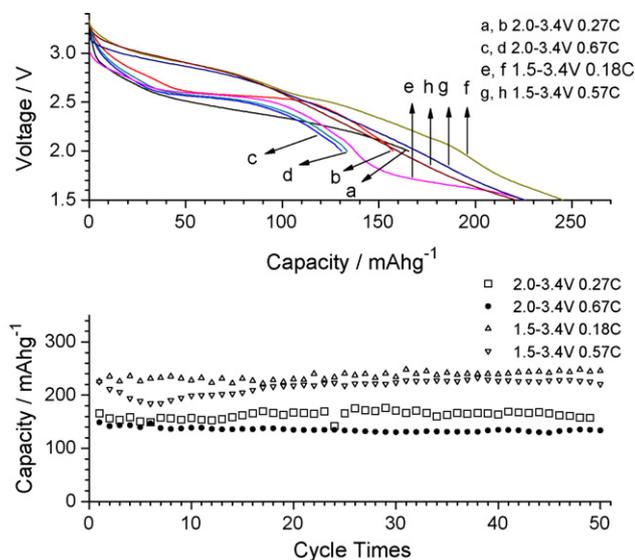


Fig. 3. The initial and final discharge profiles of the sodium ammonium vanadium bronzes/Li cell (a, b) 2.0–3.4 V (0.27C rate), (c, d) 2.0–3.4 V (0.67C rate), (e, f) 1.5–3.4 V (0.18C rate) and (g, h) 1.5–3.4 V (0.57C) and corresponding cyclic performance (below).