Facile synthesis of graphite nitrate-like ammonium vanadium bronzes and their graphene composites for sodium-ion battery cathodes

Hailong Fei, a,b Huan Li, a Zhiwei Li, a Wenjing Feng, a Xin Liu a and Mingdeng Wei a*

A simple and versatile method for preparation of new crystalline graphite nitrate-like ammonium vanadium bronze (NH₄)₀.₁₉V₂O₅·0.₄₄H₂O nano-microstructures is developed via a simple hydrothermal route following heat treatment. (NH₄)₀.₁₉V₂O₅·0.₄₄H₂O platelets are tested as a novel high-energy cathode material for sodium-ion batteries. The enhancement of electrochemical performance for a (NH₄)₀.₁₉V₂O₅·0.₄₄H₂O platelet electrode is offered by addition of graphene and using graphite nitrate-like ammonium vanadium bronze microflowers. A graphene-based graphite nitrate-like vanadium bronze microflower composite shows a higher discharge capacity of 208.9 A h g⁻¹ for the second cycle in a 1.5–3.4 V voltage limit at a discharge current density of 20 mA g⁻¹. The reversible capacity of 141.5 A h g⁻¹ remained after 40 cycles.

1. Introduction

Nowadays, there is a remarkable demand for rechargeable batteries with reversible and efficient electrochemical energy storage and conversion in the field of portable electronic consumer devices, electric vehicles, and large-scale electricity storage in smart and intelligent grids. The sodium-ion battery is one of the promising rechargeable batteries owing to its widely abundant and low cost sodium resources. The current concerns are leading to increasing interest in low cost, high safety electrode materials for sodium-ion batteries with a long cycle life and high energy-density. Nowadays researchers in growing numbers are paying more attention to the electrochemical properties of various electrode materials, for example a Nason-type structured Naᵥ₂(V₅O₁₅)ₓₙ,y layered Naᵥ₂FePO₄F and olivine Na(Fe, Mn)PO₄, Naᵥ₂Mn₉O₁₈ nanowires, Naᵥ₂[Feₓ/₂-Mn₁₋ₓ]O₂, Prussian blue analogues, amorphous phosphorus–carbon composites, and organic sodium-ion batteries.

Vanadium oxides and bronzes offer the advantages of being cheap, easy to synthesize, widely available on the earth and having high-energy density. Therefore, they have attracted great interest in energy conversion and storage. However, few were interested to study vanadium oxide and bronze electrode materials for sodium-ion batteries. Hamani et al. reported the electrochemical properties vs. Na of the layered Naᵥ₂V₂O₇ phases having either octahedral or trigonal prismatic symmetries, which could reversibly insert 0.5 Na atoms per unit formula sustaining a reversible capacity of 120 mA h g⁻¹. NaᵥₓV₉O₁₅ nanorods also displayed stable sodium-ion insertion–deinsertion reversibility and delivered 142 mA h g⁻¹ sodium ions when they worked at a current density of 0.02 A g⁻¹. NaᵥₓV₉O₁₅ nanowires show a discharge capacity of 169.6 mA h g⁻¹ at a low current density. Vᵥ₂O₇ has showed high stability, good reversibility and high capacity as a cathode material for sodium-ion batteries, indicating cell feasibility and good cycling efficiency. Recently, a nanoscale ordered bilayered Vᵥ₂O₇ cathode material was operated at room temperature and it showed the theoretical capacity of 250 mA h g⁻¹ for a small diffusion length and a large surface area tested at 1.0 V. Double-layer single crystalline Vᵥ₂O₇ nanobelts also exhibited a high capacity of 231.4 mA h g⁻¹. It corresponds to the theoretical capacity to form NaᵥₓV₂O₇ on Na-ion insertion. Hollow VO₂H microspheres presented a capacity of 150 mA h g⁻¹. However, few people paid full attention to ammonium vanadium oxide cathode materials for lithium-ion and sodium-ion batteries.

Herein, we report for the first time the synthesis of new crystalline graphite nitrate-like ammonium vanadium bronze via a simple hydrothermal method requiring low cost manufacturing and ultra-low power consumption. Graphite nitrate-like ammonium vanadium bronze was prepared with a...
controlled phase structure and morphology. When they were used as cathode materials for sodium-ion batteries, graphene based graphite nitrate-like ammonium vanadium bronze composites showed better cycling stability and higher discharge capacity.

2. Experimental

Graphite nitrate-like ammonium vanadium bronze square platelets were prepared according to the following procedure. 0.16 g oxalic acid and 0.2 g ammonium metavanadate (NH₄VO₃) were dissolved in 30 ml deionized water under stirring at room temperature for 2 hours. After that, the mixture was transferred to a 50 ml Teflon-lined stainless autoclave, sealed, kept at 200 °C for 24 hours, cooled to room temperature, washed with deionized water and dried at 200 °C for 5 days (labeled as Sample v1-g0). Using the same procedure, graphite nitrate-like ammonium vanadium bronze platelets were prepared with 1.28 g oxalic acid, 0.59 g ammonium metavanadate (NH₄VO₃) and 0.4 g ammonium nitrate (labeled as Sample v2-g0). Their composites based on graphene were prepared with an addition of 3 mg graphene under identical conditions (the two samples are labeled as Sample v1-g3 and Sample v2-g3, respectively).

The morphological characteristics of the as-synthesized materials were observed using a Hitachi S-4800 field emission scanning electron microscope (SEM). Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G20 electron microscopy instrument. X-ray diffraction (XRD) patterns were recorded on a diffractometer (Co Kα, PANalytical, and X’Pert). XPS measurements were performed with a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source (hv = 1486.6 eV). A pass energy of 160 eV was used for recording the survey spectrum, while 40 eV pass energy was used for high-resolution measurements. A Vario EL elemental analyzer from German Elementar Analysen Systeme GmbH and Optima 8000 ICP-OES from American Perkin-Elmer were used for elemental analysis of nitrogen, carbon and vanadium, respectively. Thermal analysis measurements were performed with an American Perkin-Elmer TGA7 analyzer. Raman spectra were recorded at room temperature using a Micro-Raman spectrometer from English Renishaw. An Nd:YAG laser (532 nm) was used as the excitation source. A Land CT2001A battery tester was used to measure the electrode activities at room temperature.

The graphite nitrate-like ammonium vanadium bronzes and their composites based on graphene were tested as cathode materials for sodium-ion batteries. The composite of the positive electrode material consisted of the active material, a conductive material (super-pure carbon) and the binder polyvinylidene difluoride (PVDF) in a weight ratio of 7/2/1. The Na metal was used as the counter electrode. The electrolyte was 1 M NaClO₄ dissolved in the propylene carbonate (PC) solvent. Fluoroethylene carbonate (FEC) was also used as an electrolyte for sodium-ion batteries.

3. Results and discussion

Ammonium vanadium bronzes and their composites based on graphene were prepared by a two-step method, as described in the Experimental section. The reaction conditions of the products are summarized in Table 1. X-ray diffraction was performed to identify the crystalline structure of samples prepared without NH₄NO₃ at 200 °C for 5 days as shown in Fig. 1a (Sample v1-g0), which has the same crystalline structure as graphite nitrate (JCPDS 74-2328, rhombohedral, space group: R3m, space group number: 166). It has a strong diffraction peak at 7.90° with a d-spacing of 11.18 Å. The diffraction peaks of the graphene based composite prepared without NH₄NO₃ can also be ascribed to graphite nitrate (JCPDS 74-2328) as shown in Fig. 1b (Sample v1-g3). When NH₄NO₃ was added, the as-synthesized two samples (Sample v2-g0 and Sample v2-g3) can be ascribed to graphite nitrate (JCPDS 74-2328) as shown in Fig. 1c and d, respectively. Therefore, a series of graphite nitrate-like vanadium compounds and their composites based on graphene were prepared for the first time by a facile two-step method. It was also reported that hollow structures (the two samples are labeled as Sample v1-g3 and Sample v2-g3, respectively).

Table 1 The reaction conditions for ammonium vanadium bronze and their composites based on graphene

<table>
<thead>
<tr>
<th>Samples and reaction conditions</th>
<th>V1-g0</th>
<th>V1-g3</th>
<th>V2-g0</th>
<th>V2-g3</th>
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<tr>
<td>NH₄VO₃ (g)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.59</td>
<td>0.59</td>
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<tr>
<td>NH₄NO₃ (g)</td>
<td>—</td>
<td>—</td>
<td>0.4</td>
<td>0.4</td>
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<tr>
<td>Graphene (mg)</td>
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<td>—</td>
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<tr>
<td>Oxalic acid (g)</td>
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<td>0.16</td>
<td>1.28</td>
<td>1.28</td>
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<tr>
<td>Water (ml)</td>
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<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Reaction time (h)</td>
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<td>24</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>Heat treatments (day)</td>
<td>5</td>
<td>5</td>
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</table>

Fig. 1 Wide-angle powder XRD patterns of (a) ammonium vanadium bronze prepared without NH₄NO₃ (Sample V1-g0), (b) graphene based composites with (a), (c) ammonium vanadium bronze prepared with NH₄NO₃ and (d) graphene based composites with (c).
fullerene-like V$_2$O$_5$ nanoparticles could be prepared via crystallization of lower density amorphous nanoparticles under laser ablation conditions.\textsuperscript{26} It implies that it is possible to prepare other carbon-like vanadium oxides with proper vanadium precursors under certain conditions.

SEM observations show that the as-synthesized sample without an addition of ammonium nitrate is square platelets (Sample v1-g0) as shown in Fig. 2a. The magnified SEM image confirms that the length and width of a square platelet are both around 800 nm as shown in Fig. 2b. As some graphene was added, big blocks were obtained, as shown in Fig. 2c,d (Sample v1-g3). Short brick-like particles were prepared with NH$_4$NO$_3$ (sample v2-g0), as shown in Fig. 2e. The magnified SEM image shows that the brick-like particle is about 150 nm thick and 820 nm long (Fig. 2f). The magnified SEM image displays that these blocks were composed of thin platelets as shown in Fig. 2d. Microflower-like particles consisting of superimposed platelets prepared with NH$_4$NO$_3$ and graphene are observed and displayed in Fig. 2g (Sample v2-g3). The diameter of microflower-like particles could be up to 18 μm. The thickness of platelets is less than 50 nm as estimated from the magnified SEM image in Fig. 2h. NH$_4$NO$_3$ plays a great role in controlling the morphology and crystalline structure of vanadium precursors by affecting nucleation of vanadium precursors. In the absence of NH$_4$NO$_3$, an unknown block-like phase would be formed,\textsuperscript{27} while NH$_4$V$_4$O$_{10}$ will be formed with NH$_4$NO$_3$ under hydrothermal conditions.\textsuperscript{30}

X-ray photoelectron spectroscopy (XPS) was performed to identify the elemental composition of Sample v1-g0. The wide survey XPS spectrum shows that the surface of ammonium vanadium bronze is composed of N, V and O in Fig. 3a. The XPS spectrum of the V2p$_{3/2}$ peak is composed of two peaks at 517.7 and 516.6 eV, corresponding to V(V) and V(IV) in Fig. 3b, respectively.\textsuperscript{24} The average oxidation number of V is +4.9 calculated from X-ray photoelectron spectroscopy (XPS) data by their peak area ratios. Fig. 3c shows that the binding energy of N 1s is 401.4 eV, which is ascribed to NH$_4^+$.\textsuperscript{28} TG curves (Fig. 4) show that there is a weight loss of 4.8% from 200 to 440 °C, due to the release of NH$_3$. Elemental analysis (EA) and inductively coupled plasma spectroscopy (ICP) were performed...
to analyze the content of N and V, respectively. The results show that the weight content of N is 1.17%, while it is 44.5% for V. Based on the above analysis, the formula of graphite nitrate-like ammonium vanadium bronze (Sample v1-g0) can be expressed as \([\text{NH}_4]_{0.19}\text{V}_2\text{O}_5\cdot0.44\text{H}_2\text{O}\).

Raman spectra of graphene based graphite nitrate-like ammonium vanadium bronze composites (Samples v1-g3 and v2-g3) exhibit a series of bands at 142, 194, 281, 405, 520, 689, 990, 1351 and 1589 cm\(^{-1}\) same as those of \(\text{V}_2\text{O}_5\) in Fig. 5a and b, respectively. The peak at 990 cm\(^{-1}\) is characteristic of the \(V=\text{O}\) bond, implying that there is a \(\text{V}_2\text{O}_5\) unit in the formula of ammonium vanadium bronze. The band at 1351 cm\(^{-1}\) is called the D band,\(^{28}\) which is a disorder induced band.\(^{29}\) The band at 1589 cm\(^{-1}\) is ascribed to the G band due to the symmetry of the hexagonal lattice, which allows only one first order Raman band for graphene.\(^{29}\) Therefore, Raman spectra show that there are at least two kinds of carbon (disorder carbon and graphene) in the two graphene based composites (Samples v1-g3 and v2-g3). Elemental analysis (EA) was used to analyze the content of graphene. There is 2.006% graphene in Sample v1-g3, while 1.466% graphene in Sample v2-g3. Transmission electron microscopy (TEM) was further performed to study graphene based composites. Square platelet-like particles were observed and are displayed in Fig. 6a (Sample v1-g3). The magnified TEM image shows that there is a thin grey graphene platelet on the surface of graphite nitrate-like ammonium vanadium bronze platelets in Fig. 6b. For Sample v2-g3, the TEM image shows that there are many thin graphene platelets around the black graphite nitrate-like ammonium vanadium bronze particles in Fig. 6c. The magnified TEM image shows that much graphene was dispersed on the surface of graphite nitrate-like particles as shown in Fig. 6d. There is also some isolated graphene.

The electrochemical performance of graphite-like nitrate ammonium vanadium bronze platelets (Sample V1-g0) and their graphene composite (Sample V1-g3) was evaluated with an electrolyte of 1 M NaClO\(_4\) dissolved in the PC solvent. Fig. 7a and b show the first and second charge–discharge pro-

![Fig. 5](image1.png)

**Fig. 5** Raman spectra of graphite nitrate-like ammonium vanadium bronze based graphene composites (a) prepared without \(\text{NH}_4\text{NO}_3\) (Sample V1-g3) and (b) with \(\text{NH}_4\text{NO}_3\) (Sample V2-g3).

![Fig. 6](image2.png)

**Fig. 6** TEM images of ammonium vanadium bronze based graphene composites prepared without \(\text{NH}_4\text{NO}_3\) (a, b) (Sample V1-g3) and with \(\text{NH}_4\text{NO}_3\) (c, d) (Sample V2-g3).

![Fig. 7](image3.png)

**Fig. 7** The first and second charge–discharge profiles of (a) ammonium vanadium bronze (Sample V1-g0), (b) graphene based composite without an addition of FEC (Sample V1-g3) and (c) with an addition of FEC (Sample V1-g3), (d) ammonium vanadium bronze (Sample V2-g0), (e) graphene based composite without an addition of FEC (Sample V2-g3) and (f) with an addition of FEC (Sample V2-g3).
The graphene based ammonium vanadium bronze (Sample V2-g3) composite also has similar charge–discharge profiles with an addition of FEC as shown in Fig. 7f. But the discharge capacity of the graphene based graphite nitrate-like microflower composite (Sample V2-g3) is dramatically raised with or without an addition of FEC. It can be found that the graphene based graphite nitrate-like ammonium vanadium bronze microcomposite is a kind of cathode material with a high discharge capacity for Na-ion batteries.

Fig. 8 shows the cycling performance of ammonium vanadium bronzes and their composites based on graphene at a current density of 20 mA g\(^{-1}\) evacuated with two kinds of electrolytes. The graphite nitrate-like ammonium vanadium bronze microflower electrode without an addition of FEC shows an enhanced cycling performance compared to graphite nitrate-like ammonium vanadium bronze platelets, as shown in Fig. 8a and b, respectively. The microflower-like graphite nitrate electrode delivers an initial discharge capacity of 147.5 mA h g\(^{-1}\). A reversible capacity of 114.7 mA h g\(^{-1}\) remained after 14 cycles. The better cycling performance is most likely due to that microflower microstructures may reduce the solid state interface layer resistance, which favors a fast Li-ion transfer rate. For graphene based ammonium vanadium bronze composites (Samples V1-g3 and V2-g3), the cycling numbers are increased. Samples V1-g3 and V2-g3 show similar cycling performance in Fig. 8c and d, respectively. FEC was further added to the electrolyte of 1 M NaClO\(_4\) dissolved in the PC solvent for the cycling test for Sample V1-g3 and V2-g3 electrodes in Fig. 8e and f. The discharge capacity and cycling performance were improved dramatically. Sample V1-g3 and V2-g3 electrodes deliver a discharge capacity of 220.8 and 208.9 mA h g\(^{-1}\), respectively, for the second cycle. A reversible capacity of 116.6 and 141.5 mA h g\(^{-1}\) remained after 40 cycles. The order of electrochemical performance is as follows: Sample V2-g3 > Sample V1-g3 > Sample V2-g0 > Sample V1-g0. The effects of FEC additives may be attributed to the improvement of the Na-ion insertion and extraction rate.

The electrochemical impedance measurements were performed to elucidate the difference in electrochemical properties of ammonium vanadium bronze prepared with NH\(_4\)NO\(_3\) (□), and its composites based on graphene (○) as shown in Fig. 9. It can be found that the graphene based composite has smaller total impedance, which may be attributed to the improved electrochemical performance.

4. Conclusions

Graphite nitrate-like ammonium vanadium bronze (NH\(_4\))\(_{0.19}\)V\(_2\)O\(_5\)·0.44H\(_2\)O platelets, micro-flowers and their composites based on graphene were prepared with cheap reagents on a large scale via a facile template-free method. The enhancement of electrochemical performance for (NH\(_4\))\(_{0.19}\)V\(_2\)O\(_5\)·0.44H\(_2\)O platelets is offered by addition of graphene and FEC to the electrolyte and using graphite nitrate-like ammonium vanadium bronze microflowers as cathode materials, which may be attributed to the improvement of electrode's electrical conductivity, the reaction kinetics and the Na-ion transfer rate. This facile two-step method is significant to fabricate other novel crystalline ammonium vanadium bronzes.

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Notes and references


30 H. L. Fei, X. Liu, Y. S. Lin and M. D. Wei, *J. Colloid Interface Sci.*, 2014, 428, 73.