



# Graphene-bound $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ film electrode with excellent cycle and rate performance for Na-ion batteries

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## ABSTRACT

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is an attractive electrode material for Na-ion batteries due to high ionic conductivity and good stability, but suffers from low electronic conductivity. Here, a graphene-bound  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  film is fabricated by simple vacuum co-filtration and thermal treatment, which can be directly used as both cathode and anode for Na-ion batteries. In the film,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  nanoparticles are homogeneously bounded in a 3D continuous graphene network. As graphene acts as binder, conductive agent, and current collector simultaneously, the content of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  can easily reach up to about 93.3 wt%, promising a superior capacity calculated based on the total mass of the electrode. Furthermore, the 3D conductive graphene provides efficient electron pathways and buffers volume change during cycling. Therefore, the graphene-bound  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  electrode exhibits high capacity (114.6 mAh g<sup>-1</sup> at 1 C as cathode, 69.1 mAh g<sup>-1</sup> at 50 mA g<sup>-1</sup> as anode), ultra-long cycle stability (only about 0.005% of the capacity is decayed per cycle during 10 000 cycles) and excellent rate performance (89.7 mAh g<sup>-1</sup> at 30 C as cathode, 42.3 mAh g<sup>-1</sup> at 2 A g<sup>-1</sup> as anode). As a result, we believe the graphene-bound  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  film is a promising candidate for Na-ion batteries.

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## 1. Introduction

Compared with lithium, sodium belongs to the same group in the periodic table with the similar electrochemical properties, and has abundant resources as well as high economic efficiency. Therefore, sodium ion (Na-ion) batteries have received significant attention as a promising alternative to current lithium ion batteries [1,2]. The crucial challenge for the Na-ion batteries is finding suitable cathode/anode materials. In consideration of bigger and heavier  $\text{Na}^+$  (0.98 Å) than  $\text{Li}^+$  (0.69 Å), the intercalation and de-intercalation of  $\text{Na}^+$  in the cathode/anode materials is more difficult, and may cause more serious structure deterioration. In order to achieve long cycle stability and good rate performance of Na-ion batteries, tremendous efforts have been made to develop advanced electrode materials, such as layered transition metal oxides [3–5], polyanionic compounds [6–9], carbon materials [10–14] and

titanium-based materials [15,16]. Among these electrode materials, polyanionic compounds, with appropriate operating potential, have long cycle life and good safety [17]. Especially,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) has arisen intensive researches as a prospective electrode material because of its NASICON structure, which is good for fast  $\text{Na}^+$  transportation, and good thermal stability. The electrochemical behavior of the NVP electrode shows two potential plateaus at around 3.4 V and 1.6 V (vs.  $\text{Na}^+/\text{Na}$ ) corresponding to the  $\text{V}^{4+}/\text{V}^{3+}$  and  $\text{V}^{3+}/\text{V}^{2+}$  redox couple, respectively. The much different redox potential renders NVP a versatile material which can be used as both cathode and anode in Na-ion batteries [18,19]. However, NVP suffers from the low intrinsic electronic conductivity, which limits its electrochemical performance, particularly high-rate capacities.

There are mainly two strategies to enhance the electron transport kinetics in NVP electrodes. The first is to reduce the NVP particle sizes in order to shorten  $\text{Na}^+$  diffusion path [20–22]; the second is to coat NVP particles with a highly conductive layer [23–27]. To obtain NVP nanoparticles is not easy due to the inevitable growth of crystal particles in the high temperature calcination [28]. Many papers have demonstrated that the introduction of

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conductive carbons, such as carbon nanotubes [29–31], conductive carbon black [32], porous carbons [33–35] et al., is an efficient approach to improve the electronic conductivity of NVP materials. Among various carbon materials, graphene is a familiar two-dimensional (2D) carbon with remarkably high conductivity, thermal stability and mechanical properties, which has been widely used to improve the electronic conductivity for composite materials in the fields of energy storage/conversion materials [36–39]. Therefore, graphene has been added to NVP for preparing highly conductive composite materials. Zhang et al. [40] prepared NVP@rGO composites by spray drying which showed good rate performance (63 mAh g<sup>-1</sup> at 30 C). Rui et al. [41] synthesized NVP@C@rGO composites, which exhibited superior rate performance with a capacity of 86 mAh g<sup>-1</sup> at an ultra-high rate of 100 C and a capacity retention of 64% after 10 000 cycles at 100 C.

On the other hand, from the view of practical application, the electrochemical performance of a battery also depends strongly on the microstructure of the electrode, besides of active materials. Conventionally, the battery electrode is fabricated by coating the slurry of the active material, conductive agent (such as carbon black, graphite, carbon nanotubes) and polymer binder (such as PVDF, CMC) onto Al/Cu foil current collector. As the conductive agent and binder usually occupy 10–25% weight of the electrode with little capacity, the energy density of the battery decreases. Furthermore, the polymer binders are electrical insulators, leading to the increasing resistance and decreasing rate performance. Therefore, an ideal electrode should have high active material content and conductivity. In our recent report, it is found reduced graphene oxide (rGO) can be employed as a multi-functional conductive binder for fabrication of porous carbon electrodes for supercapacitors [42]. It is believed that a small amount of graphene can bound massive active materials, providing an integrity film with highly conductive framework, which can be directly used as electrode without the addition of conventional conductive agent and binder. In this regard, a graphene-bound NVP film electrode is expected to achieve both high NVP loading and high conductivity, resulting in high capacity, and good cycle and rate performance.

In this work, we fabricated a graphene-bound Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> film electrode by simple vacuum-assisted filtration of the mixture of NVP and graphene oxide (GO), and the subsequent thermal reduction treatment. As graphene can bound the active materials through the self-assembling of graphene nanosheets [42], the 3D network formed by graphene nanosheets enable the electrode to possess good integrity. Since graphene can act as conductive agent, binder, and current collector in the resulting architectures simultaneously, the NVP nanoparticles, with high electrochemical activity and short Na<sup>+</sup> diffusion path, can account for an extremely high mass ratio of about 93.3% in the film electrode. Furthermore, the 3D interconnected conductive graphene can facilitate fast charge transfer and accommodate volume change during cycling processes, thus generating remarkable electrochemical performance. As expected, the graphene-bound NVP electrode with 93.3% NVP shows good rate performance and cycling stability as both cathode and anode, providing a promising candidate for high-energy density Na-ion batteries.

## 2. Experimental

### 2.1. Materials preparation

NVP nanoparticles were synthesized by a typical sol-gel method. Stoichiometric amounts of oxalic acid (99.5%, Beijing Chemical Works), NH<sub>4</sub>VO<sub>3</sub> (99.0%, Tianjin Guangfu Fine Chemical Res. Inst.), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (99.0%, Tianjin Guangfu Fine Chemical Res. Inst.) and CH<sub>3</sub>COONa (99.0%, Xilong Chemical Co. Ltd) were

dissolved into DI water under stirring at 80 °C. The resultant solution was remained stirring for over 2 h until it became a sol. The sol was kept in an oven at 80 °C for completely drying. Then, after grinding, the powder was calcined at 800 °C for 8 h in N<sub>2</sub> atmosphere with a heating rate of 5 °C min<sup>-1</sup> to obtain pure NVP nanoparticles. NVP nanoparticles suspension was achieved by dissolving NVP nanoparticles into DI water with the help of 0.1 wt% CTAB. Then, 19 mL NVP nanoparticles suspension (0.5 mg mL<sup>-1</sup>) and 1 mL graphene oxide (GO, obtained from modified hummer's method) solution with a density of 1 mg mL<sup>-1</sup> were mixed under vigorous stirring for 0.5 h to achieve NVP/GO suspension. A film, which can be peeled off the membrane, was acquired by vacuum co-filtrating the NVP/GO suspension through a Celgard membrane. Finally, integral graphene-bound NVP electrode was obtained after annealing the intermediate NVP/GO film at 300 °C for 2 h in N<sub>2</sub> atmosphere with a heating rate of 5 °C min<sup>-1</sup>.

### 2.2. Materials characterization

X-ray diffraction (XRD) was used to measure the crystal structures of the NVP and graphene-bound NVP samples with a Cu K $\alpha$  radiation source in the 2 $\theta$  range of 10–60° at a scan rate of 5° min<sup>-1</sup>. Thermal gravimetric analysis (TGA, DTG-60 A) was carried out to determine the actual carbon content in graphene-bound NVP electrode from room temperature to 700 °C in air atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Scanning electron microscopy (SEM, Hitachi S4800) was performed to characterize the morphology of the NVP and graphene-bound NVP electrode samples.

### 2.3. Electrochemical measurement

The electrochemical measurements of the graphene-bound NVP electrode were carried out by using CR2025-type coin cells. As cathode or anode, the graphene-bound NVP electrode served as the working electrode and a metallic sodium plate served as the counter electrode, separated by a Whatman glass fiber. Ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 in volume) dissolving 1 M NaClO<sub>4</sub> made up the electrolyte. The coin cells were assembled in an argon atmosphere. As a reference, the conventional NVP electrode was prepared by slurring the active NVP material, super-P acetylene black, and PVDF binder in a weight ratio of 8:1:1 with N-methyl-2-pyrrolidone as a solvent and coating the slurry on current collector. The loading mass of the NVP active material in both the graphene-bound NVP electrode and the traditional PVDF-bound NVP electrode is kept at about 1 mg cm<sup>-2</sup>. Traditional PVDF-bound NVP electrode was also assembled using CR2025-type coin cells. Charge-discharge measurements of the coin cells were conducted by a land CT2001A battery test system at different current rates. The potential range is 2.0–4.0 V (vs. Na<sup>+</sup>/Na) for cathode and 1.0–3.0 V (vs. Na<sup>+</sup>/Na) for anode. To further know the electrochemical behavior of the graphene-bound NVP electrode as cathode and anode, cyclic voltammetry (CV) test was carried out on a CHI 600e electrochemical workstation at 0.1 mV s<sup>-1</sup> from 2.0 V to 4.0 V (vs. Na<sup>+</sup>/Na) as cathode and 1.0 V–3.0 V as anode.

## 3. Results and discussion

As illustrated in Fig. 1, the graphene-bound NVP electrode was synthesized by a simple vacuum co-filtration and the following thermal treatment. First, the NVP nanoparticles were gained by a sol-gel method using C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, NH<sub>4</sub>VO<sub>3</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and CH<sub>3</sub>COONa as raw materials. Then, NVP nanoparticles suspension was added to GO solution with a ratio of 95:10. The NVP nanoparticles and GO sheets were homogeneously mixed under vigorous stirring, and the resultant mixture was vacuum co-filtrated to form a NVP/GO film.

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