

Mg²⁺-doped Na₃V₂(PO₄)₃/C decorated with graphene sheets: An ultrafast Na-storage cathode for advanced energy storage

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ABSTRACT

NASICON-type Na₃V₂(PO₄)₃ is one of the most promising cathode materials for sodium-ion batteries, delivering about two Na⁺-ions extraction/insertion from/into the unit structure. However, the low electronic conductivity which leads to bad rate capability and poor cycle performance, limits its practical application for sodium-ion batteries. To overcome the kinetic problem, we attempt to prepare the carbon-coated Na₃V₂(PO₄)₃ nanocrystals further decorated by graphene sheets and doped with Mg²⁺ ion via the two steps of sol-gel process and solid-state treatment for the first time. Such architecture synergistically combines the advantages of two-dimensional graphene sheets and 0-dimensional Mg²⁺-doped Na₃V₂(PO₄)₃/C nanoparticles. It greatly increases the electron/Na⁺-ion transport kinetics and assures the electrode structure integrity, leading to attractive electrochemical performance. When used as sodium-ion batteries cathode, the hybrid composite delivers an initial discharge capacity of 115.2 mAh g⁻¹ at 0.2 C rate, and retains stable discharge capacities of 113.1, 109.0, 102.4, 94.0 and 85.2 mAh g⁻¹ at high current rates of 1, 2, 5, 10 and 20 C rate, respectively. Thus, this nanostructure design provides a promising pathway for developing high-performance Na₃V₂(PO₄)₃ material for sodium-ion batteries.

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1. Introduction

Nowadays, as one type of promising device for large-scale energy storage, the rechargeable sodium-ion battery is considered as the optimal alternative for the traditional lithium-ion battery due to its lower cost, more uniform distribution, and higher abundance of sodium resources in the earth's crust [1–4]. Among the compositions of sodium-ion battery, cathode material plays a key role in determining the electrochemical property of the battery. Hence, in order to develop superior sodium-ion batteries, one of the main challenges should be to enhance the electronic and ionic conductivities of the cathode materials to improve the Na-storage performances [5].

In recent years, many cathode materials, such as Na_xCoO₂ [6], NaLi_{0.2}Ni_{0.2}Mn_{0.6}O₂ [7], NaMnO₂ [8], Na_{0.95}V₃O₈ [9], Na₂FePO₄F/C [10], NaFePO₄ [11], Na₃V₂(PO₄)₃ [12–14], Na_{0.7}Fe_{0.7}Mn_{0.3}O₂ [15] and Na₃V₂(PO₄)₂F₃ [16], have been extensively studied for sodium-ion batteries and all of them have exhibited certain reversible capacity and cycling stability. Among the various materials, the NASICON-type Na₃V₂(PO₄)₃ has attracted much attention because

of its high theoretical energy density (400 Wh kg⁻¹), good thermal stability and open three-dimensional framework with large interstitial channels [17–19]. Nevertheless, the poor intrinsic electronic conductivity of the pure Na₃V₂(PO₄)₃, which results from the separation of the VO₆ octahedra from the PO₄ tetrahedra in the rhombohedral structure, limits its practical use [17]. In principle, there are two approaches of increasing the transport kinetics: the first is to vary the composition of the electrode material by doping a slight amount of other alien ions [20–22] in order to make it sufficiently mixed conducting; the second, which appears most promising in this case, is to modify the surface of Na₃V₂(PO₄)₃ with carbon [17,23–27] or graphene [28,29], and to provide an effective conducting network. For instance, Masquelier's group reported that substitution of aluminum for vanadium in Na₃Al_{0.5}V_{1.5}(PO₄)₃ significantly increases the theoretical energy density of the electrode (425 Wh kg⁻¹) [30]. Zhu et al. prepared a carbon-coated Na₃V₂(PO₄)₃ which could deliver a capacity of 44 mAh g⁻¹ at 200 C, which outshined of commonly used lithium-ion batteries cathode including LiCoO₂ and LiFePO₄ [24]. Meanwhile, Kim et al. suggested that graphene supported Na₃V₂(PO₄)₃ could provide a superior cyclability and 93% capacity retention can be obtained at a rate of 1 C after 100 cycles [31]. Although the rate performance and cycling stability have been largely enhanced recently, the achieved electrochemical property of NASICON-type

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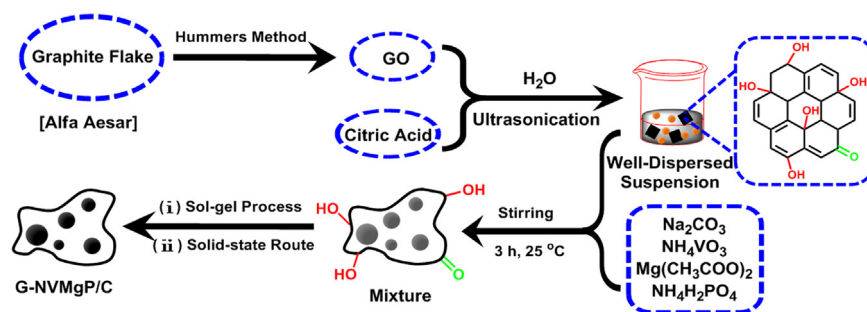


Fig. 1. Schematically illustrates the experimental procedures for the preparation of G-NVMgP/C composite.

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$, especially at high rate performance, is by no means comparable with high performance lithium-ion batteries cathode materials. Obviously, most of the previously reported papers are merely focused on one of the above approaches, and thus lead to a limited improvement in the battery performance.

Herein, we firstly attempt to synthesize and characterize the carbon-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanocrystals further decorated by graphene sheets and doped with Mg^{2+} ion using a sol-gel route and followed by the solid-state treatment. For comparison, the sample modified only with graphene as well as the pure $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ were also prepared by the same process. The charge/discharge capacities and cycling performances of the as-prepared electrode materials when used in sodium-ion batteries are investigated. As expected, this hybrid composite exhibits better battery performance than other electrodes. The possible reasons are studied and discussed in this paper in detail.

2. Experimental

2.1. Preparation of materials

Fabrication of graphene oxide (denoted as GO): The GO was produced from natural graphite flakes (Alfa Aesar) through a modified Hummers method [32]. The detailed experimental procedure was not described in this study.

Preparation of Mg^{2+} -doped $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ decorated with graphene nanosheets (denoted as G-NVMgP/C): Schematic synthesis, including the two steps of sol-gel process and solid-state treatment, is illustrated in Fig. 1. In a typical synthesis, GO and citric acid were firstly dissolved in deionized water under ultrasonication for 2 h to get a brown suspension. The citric acid was used as the chelating reagent and carbon source. Secondly, an appropriate amount of Na_2CO_3 , NH_4VO_3 , $\text{Mg}(\text{CH}_3\text{COO})_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ with a Na: V: Mg: P molar ratio of 3: 1.95: 0.05: 3 was added to the above solution with continuous stirring for 3 h at room temperature to form a sol solution. Then, the solution was heated at 80 °C under stirring to evaporate the residual water. The formed gel was dried at 100 °C under vacuum for 12 h and milled at 3000 rpm for 5 h. Finally, the obtained precursor was preheated at 350 °C in a nitrogen atmosphere for 4 h, followed by sintering at 800 °C for 10 h under flowing nitrogen to yield the final product. Moreover, the $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (denoted as NVP/C) and graphene-decorated $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (denoted as G-NVP/C) were also prepared using the same procedure as for G-NVMgP/C sample except that $\text{GO}@\text{Mg}(\text{CH}_3\text{COO})_2$ or $\text{Mg}(\text{CH}_3\text{COO})_2$ were not added.

2.2. Characterization

The phases and crystal structures of the obtained samples were tested using a powder X-ray diffraction (XRD, D/MAX 2500V, Rigaku, Japan) analysis system equipped with a Cu K α radiation

source. The lattice parameters of the obtained samples are calculated by Rietveld analysis using the General Structure Analysis System. The morphologies and nanostructures of the powders were characterized by a scanning electron microscopy (SEM, Hitachi, SU8000) and a transmission electron microscopy (TEM, JEOL, 2100F). The carbon contents were detected by a Vario EL III elemental analyzer (Elementar Analysen System GmbH, Germany). An X-ray Photoelectron Spectrometer (XPS) with Al K α radiation was used to investigate the chemical state of G-NVMgP/C sample.

2.3. Electrochemical measurements

The CR2032 coin-type cells were used to evaluate the electrochemical performance of the as-prepared NVP/C, G-NVP/C and G-NVMgP/C cathode materials. The working electrodes were prepared by blending 80 wt% active materials, 10 wt% carbon black and 10 wt% poly-vinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The obtained slurry was pasted onto an aluminum foil current collector and dried at 100 °C overnight in a vacuum oven. The typical loading mass of active material was around 2.6 mg cm^{-2} . The CR2032 coin cells were assembled in a glove box filled with high-purity argon using sodium metal foil as the counter electrode, Celgard 2400 as the separator and 1 M NaClO_4 in ethylene carbonate (EC)/propylene carbonate (PC) (1:1, v/v) as the electrolyte solution. The charge/discharge measurements were carried out on a NEWWARE battery test system (Shenzhen, China) in a voltage range of 2.5–4.0 V (vs. Na^+/Na). Note that all the capacity values were calculated based on the mass of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. Cyclic voltammetry (CV) measurement was carried out by using an electrochemical workstation (CHI660D, Shanghai, China) at a scan rate of 0.1 mV s^{-1} between 2.5 and 4.0 V. Electrochemical impedance spectroscopy (EIS) was performed using an electrochemical workstation (Zahner IM6ex) with an amplitude of 5 mV in the frequency range of 100 kHz to 0.01 Hz. It should be mentioned that all the electrochemical measurements were tested at room temperature.

3. Results and discussion

The XRD patterns of the as-prepared NVP/C, G-NVP/C and G-NVMgP/C samples are shown in Fig. 2. The characteristic peaks of all the samples can be readily indexed to a well-defined NASICON structure in a $R\bar{3}c$ space group, which are consistent well with the previous reports [21,25–28]. No diffraction peaks related to crystalline or amorphous carbon and graphene can be detected for the three samples in the XRD patterns. Furthermore, it is noting that doping a low amount of Mg^{2+} does not affect the structure of G-NVMgP/C sample. The lattice parameters of the samples calculated by XRD analysis are illustrated in Table 1. As can be seen, the Mg^{2+} doping decreases the total volume of the lattice, which is in good agreement with that of Mg^{2+} -doped NVP/

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