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Graphene modified sodium vanadium fluorophosphate as a high voltage cathode material for sodium ion batteries

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ABSTRACT

Substantial interests have been paid to Na-based electrode materials due to the abundance and low cost of sodium resources on earth. In this study, we improved the electrochemical performance of $NaVPO_4F$ cathode by coating graphene sheets. The structure, composition and morphology of $NaVPO_4F$/graphene composite were investigated by XRD, FT-IR, FE-SEM and TEM. FE-SEM and TEM analysis indicate that the graphene sheets were successfully coated on the surface of $NaVPO_4F$. The $NaVPO_4F$/graphene composite could be operated at a high working potential (3.95 V for average voltage), and displayed the highest capacity of 120.9 mAh g^{-1}. After 50 charge/discharge cycles at 0.05 C, the capacity retention of the cathode could reach up to 97.7%. Although the discharge capacity of $NaVPO_4F$/graphene decreased to 70.1 mAh g^{-1} under a high rate of 0.5 C, it returned back to 113.2 mAh g^{-1} once the rate was reduced to 0.05 C. EIS measurement further reveals that the $NaVPO_4F$/graphene electrode exhibited a faster sodium-ion diffusivity and less resistance compared with the pure $NaVPO_4F$. Our results demonstrate that $NaVPO_4F$/graphene is a promising cathode material for sodium ion batteries.

1. Introduction

Wide-scale implementation of renewable energy such as solar and wind power requires the large scale production of inexpensive and efficient energy storage systems (ESSs). At present, lithium-ion battery technology is quite mature and has been applied in ESSs. However, as the use of large format lithium-ion batteries (LIBs) becomes widespread in electric vehicles, increasing demands for Li commodity chemicals combined with geographically-constrained Li mineral reserves will drive up prices and limit their applications in ESSs [1]. Therefore, the development of cheaper and more sustainable energy storage technology as alternatives to LIBs is important [2–4]. Sodium-ion batteries (SIBs) have been considered as an attractive alternative to LIBs due to the abundant resources, low material cost and easy accessibility of sodium reserves. In addition, the well-established understanding of the lithium based electrochemical systems is beneficial to the development of Na counterpart. Therefore, SIBs can compete with LIBs in the markets where weight and size are not important such as stationary land-based power applications and electrical grid stabilization [5].

The battery performances such as specific capacity and operation voltage are mainly determined by the electrochemical properties of electrode materials [1]. Searching for new intercalation host materials with high energy density batteries is essential to push forward the implementation of new SIB technologies [1,6,7]. Recently, more attention has been paid to sodium vanadium phosphates $Na_3V_2(PO_4)_3$ [8–10] and sodium vanadium fluorophosphates materials, such as $NaVPO_4F$ [11,12], $Na_3V_2(PO_4)_2F_3$ [13,14], $Na_3(VO)_2(PO_4)_2F$ [15] and $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ [16], because of their good electrochemical performances. Among these cathode materials, sodium vanadium fluorophosphate ($NaVPO_4F$) shows good electrochemical properties, especially the high energy density. The inductive effects of both PO_4^{3-} and F^- anions lead to a high working potential of this material (plateaux at 3.7 and 4.2 V vs. Na/Na^+) [17]. Meanwhile, a high specific capacity and a good cycling ability can also be expected due to the structural rigidity of the fluorophosphate material [11]. Barker et al. [11] combined $NaVPO_4F$ and hard carbon to form sodium-ion batteries, and found that the reversible specific capacities for cathode and anode were 82 and 202 mAh g^{-1}, respectively. However, the discharge capacity of this battery decayed significantly after the cell cycled more than 30 times. In order to improve the electrochemical performance of $NaVPO_4F$, Zhuo and co-workers [18] doped Cr^{3+} into $NaVPO_4F$. Although the reversible specific capacities were improved

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insignificantly, the Cr-doped material showed a better capacity retention than the un-doped material, and the reversible capacity retention of the Cr-doped material could maintain 91.4% after 20 cycles.

Carbon coating is an effective way to improve the electrode performance [19–21]. Recently, Lu et al. [19] improved the electronic conductivity and electrochemical performance of the $NaVPO_4F$ via carbon coating, and found that the highest capacity of this material could reach 97.8 mAh g^{-1} and the capacity retention was 89% after 20 cycles. Graphene (G), the basic building unit of all carbon materials (fullerenes, carbon nanotubes, graphite, etc.) has a remarkably high electric conductivity and has been widely investigated in LIBs [22]. To the best of our knowledge, few studies have been reported on the electrochemical performances of sodium-vanadium fluorophosphates materials modified with graphene ($NaVPO_4F$/G). In this study, we reported the synthesis and electrode performance of $NaVPO_4F$/G in a sodium cell. Our results showed that graphene was an effective carbon source to obtain the micrometer-sized $NaVPO_4F$ by a simple solid state method, and the electrode performance was drastically improved. The highest capacity achieved for $NaVPO_4F$/G was 120.9 mAh g^{-1} and the capacity retention was 97.7% after 50 cycles at 0.05 C. When it was tested at 0.5 C, the initial discharge capacity was 70.1 mAh g^{-1} and it could be maintained after 10 cycles. From these results, we demonstrated the possibility of graphene coated $NaVPO_4F$ as the positive electrode for SIBs.

2. Experimental

2.1. Sample preparation

$NaVPO_4F$/graphene ($NaVPO_4F$/G) composite was synthesized via two step solid-state reaction. In the first step, VPO_4 powders were synthesized via a carbothermal reduction (CTR) method. Stoichiometric proportions of $NH_4H_2PO_4$, V_2O_5 and 5 wt% excessive glucose powder which could ensure the complete reduction of vanadium were put in the agate jar and ball-milled at 500 rpm for 12 h. The mixture was then pressed into a pellet and heated at 750 °C for 5 h in N_2 atmosphere. The reaction was shown in Eq. (1).

$$3V_2O_5 + 6NH_4H_2PO_4 + C_6H_{12}O_6 \rightarrow 6VPO_4 + 6NH_3 + 15H_2O + 6CO \quad (1)$$

In the second step, stoichiometric proportions of NaF, VPO_4 and a 10% mass of graphene were ball-milled for 6 h at 500 rpm. After that, they were transferred to a temperature-controlled tube furnace and heated to 750 °C in N_2 atmosphere for a dwell period of 1 h. The reaction was shown in Eq. (2).

$$NaF + VPO_4 + \text{Graphene} \rightarrow NaVPO_4F/G \quad (2)$$

Graphene could be obtained by chemical reduction of graphene oxide (GO) by hydrazine hydrate. GO was prepared using a modified Hummers method [23]. GO was then washed and exfoliated before centrifugation. After that, the centrifuged GO was dried under vacuum conditions for 24 h. $NaVPO_4F$ in the absence of graphene was also synthesized and used as the control.

2.2. Material characterization

In order to understand the crystalline structure of the material, X-ray diffraction (XRD) analysis was conducted using X-ray diffractometer (D8 DISCOVER) with Cu Kα radiation in the 2θ range of 10 ~ 60° with a scan rate of 5° min^{-1}. The morphology of the material was observed using field emission-scanning electron microscopy (FE-SEM, Hitachi, S4800) and transmission electron microscopy (TEM, JEOL, 2100F). The infrared (IR) spectrum was obtained using a FT-IR spectrometer (FTIR, Thermo scientific, Nicolet 6700) under a transmission mode in the range of 500–2000 cm^{-1}.

2.3. Electrochemical properties

The cathode mixture was composed of 80 wt% the active material ($NaVPO_4F$/G or $NaVPO_4F$), 10 wt% conductive carbon (acetylene black) and 10 wt% polyvinylidenefluoride (PVDF) binder, which was then dissolved in 1-methyl-2-pyrrolidone (NMP). The mixed slurry was plastered onto the aluminum foil as the current collector, which was then dried at 80 °C under vacuum for 24 h. The circular electrodes in a diameter of 10 mm were cut from the foil, dried at 120 °C under vacuum overnight and finally transferred in an argon filled glove box (MBRAUN, LABstar). The mass loading of the active material in the electrode was approximately 3.0 mg. 2032 coin-type testing cells were assembled with the as-prepared cathode, an anode (metallic sodium) and a glass microfiber separator (Whatman, GF/A). The electrolyte was 1 M $NaClO_4$ dissolved in propylene carbonate (PC). Galvanostatic charge/discharge reactions were carried out in the voltage of 1.5–4.3 V using the CT2001A LAND battery tester. The charging rates in the measurements were based on the following relationship: 1C = 143 mA g^{-1}. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured using an electrochemical workstation (ChenHua CHI660e), respectively. The CV characterization was performed at a scan rate from 0.1 to 1 mV s^{-1}, and the EIS was characterized with the amplitude of 5 mV in the frequency range of 0.1–100 mHz. All electrochemical tests were carried out at room temperature.

3. Results and discussion

3.1. Material Characterization

The XRD patterns of the as-synthesized $NaVPO_4F$ and $NaVPO_4F$/G powders are shown in Fig. 1. The position and intensity of the diffraction peaks agree well with those reported by Barker et al. [11]. The peak positions, intensity ratios and peak sharpness of these two samples are similar, indicating the good crystallinity of $NaVPO_4F$ and $NaVPO_4F$/G (Fig. 1). Structural refinement of the data using the *hkl* indices for a tetragonal symmetry structure with space group I4/mmm generated the following crystallographic parameters: $a = b = 0.641$ nm, $c = 1.068$ nm, which are in good accordance with the structure analysis of $NaVPO_4F$ phase

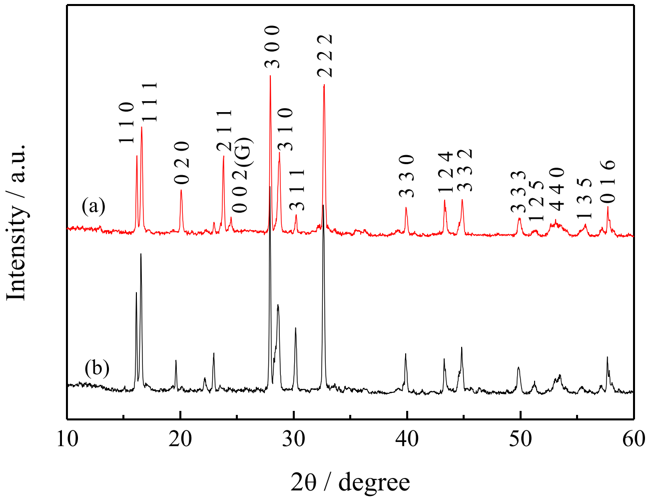

Fig. 1. The XRD patterns of $NaVPO_4F$/G composite (a) and pure $NaVPO_4F$ (b).