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Synthesis and electrochemical properties of $xLiFePO_4 \cdot (1-x) Na_3V_2(PO_4)_2F_3$/C composite for lithium-ion batteries

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ABSTRACT

To improve the operating voltage and the rate performance of $LiFePO_4$, the different ratios of the $xLiFePO_4 \cdot (1-x)Na_3V_2(PO_4)_2F_3$/C (LFP-NVPF/C) are synthesised via a carbothermal reduction method. The structure and morphology of the composite are analysed by X-ray diffraction (XRD) and electron microscopy. The as-prepared material is composed of a mixture of two phases: V-doped LFP and Fe-doped NVPF. Electrochemical tests show that the molar ratio of 9:1 is the optimum composition and the LFP-NVPF/C ($x = 0.9$) composite exhibits excellent performance with an initial discharge capacity of 151.2, 146.5, 120.6 and 100.2 mAh g^{-1} at 1.0, 2.0, 5.0 and 10 C, respectively, which is higher than that of single phase LFP/C, especially at high rates. According to the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), the introduction of NVPF improves charge transfer and Li^+ diffusion of LFP/C and provides excellent cycle stability at high rates.

1. Introduction

Lithium iron phosphate ($LiFePO_4$) is one of the most promising cathode materials for lithium-ion batteries, especially for electric vehicle (EV) applications, due to its low cost, better environmental compatibility and flat voltage profile in comparison to other materials [1–5]. However, the development of $LiFePO_4$ faces obstacles because of its low working voltage, poor ionic diffusivity and electronic conductivity, as well as bad cycle performance at high rates. In recent years, leading research has focussed on coating with conductive carbon [6,7], doping with metal ions [8] and reducing the particle size [9], which all have finite effects on improving the performance of the material.

The sodium vanadium fluorophosphates, including $NaVPO_4F$ [10], $Na_{1.5}VOPO_4F_{0.5}$ [11] and $Na_3V_2(PO_4)_2F_3$ [12] received more attention because of their high working voltages and safe applications. Among these materials, sodium vanadium three-fluorophosphates with a tetragonal crystal structure, firstly prepared by Meins [13], are viewed as one of the most appropriate materials as a candidate for electrodes in hybrid-ion batteries [14]. Barker et al. [15] introduced a graphite/Li^+ electrolyte/$Na_3V_2(PO_4)_2F_3$ hybrid-ion cell, which could undergo mixed Li/Na migration when joined with $Na_3V_2(PO_4)_2F_3$ as cathode material. Furthermore, sodium-ions are irreversibly extracted from the cathode material in the first charge/discharge cycle, which will not negatively influence the long-term work of the cell. However, $Na_3V_2(PO_4)_2F_3$/C composite has great ionic conductivity and demonstrates excellent charge and discharge performance at high rates as a cathode material in lithium-ion batteries [16]. According to the reported literatures, the lithium-ion diffusion coefficient of a NASICON-type $Na_3V_2(PO_4)_2F_3$ (10^{-10} cm^2 s^{-1}) [17,18] hybrid-ion battery is much higher than that in $LiFePO_4$ (10^{-16} to 10^{-14} cm^2 s^{-1}), as measured by Prosini et al. [19]. So far, there are few reports on the study of the two-component $xLiFePO_4 \cdot (1-x) Na_3V_2(PO_4)_2F_3$/C (LFP-NVPF/C)composite, which is expected to exhibit higher energy density and better cycle performance at high rates compared to the individual $LiFePO_4$/C composite. In this study, a certain amount of $Na_3V_2(PO_4)_2F_3$ is introduced into a $LiFePO_4$/C phase and different ratios of the $xLiFePO_4 \cdot (1-x)Na_3V_2(PO_4)_2F_3$/C hybrid composite are synthesised by the carbothermal reduction method; subsequently, the electrochemical performances at different rates and material characterisation are investigated.

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2. Experimental setup

2.1. Synthesis of $LiFePO_4$/C

The precursor $FePO_4 \cdot 2H_2O$ and Li_2CO_3 (molar ratio of 2:1) and a proper amount of glucose and alcohol were ground for 4 h in a planetary ball mill and then dried at 80 °C for 24 h. The mixture was then calcinated at 450 °C for 4 h and then heated to 650 °C in a tube furnace for 6 h in flowing argon atmosphere. The $LiFePO_4$/C composite was then removed from the furnace after cooling to room temperature.

2.2. Synthesis of $xLiFePO_4 \cdot (1-x)Na_3V_2(PO_4)_2F_3$/C

The different ratios of the $xLiFePO_4 \cdot (1-x)Na_3V_2(PO_4)_2F_3$/C was prepared by carbothermal reduction method. The EDTA-2Na, V_2O_5, $NH_4H_2PO_4$ and NH_4F (molar ratio of 3:2:4:6) and alcohol were ground for 1 h in a planetary ball mill; subsequently, different amounts of $LiFePO_4$/C were added to the mixture and ground for 3 h before being dried at 80 °C for 24 h. Finally, the mixture was calcinated at 450 °C for 4 h and then heated to 650 °C in a tube furnace for 6 h in a flowing argon atmosphere. The $xLiFePO_4 \cdot (1-x) Na_3V_2(PO_4)_2F_3$/C was taken from the furnace after cooling to room temperature.

2.3. Material characterisation

The crystalline phase of the synthesised materials was determined by X-ray diffraction (XRD) in the 2θ value range from 10° to 80° (D/max-r A type Cu Ka1, 40 kV, 300 mA, Japan). The lattice parameters were calculated from the XRD data by a least-squares method. The element states of vanadium and iron in the materials was determined by X-ray photoelectron spectroscopy (XPS). The structure of the samples was characterised by field-emission scanning electron microscope (SEM, JEOLJSM-6360LV, Japan) and transmission electron microscopy (TEM, Tecnai G2 F20).

2.4. Electrochemical characterisation

The electrochemical characterisations were evaluated using CR2025 coin cells [20]. Electrochemical tests were carried out using a LAND CT2001A Test system with galvanostatic charge and discharge in the voltage range of 2.5–4.3 V versus a Li/Li^+ electrode at room temperature. The rate test varied from 0.1 C to 10 C in the same potential range. Electrochemical impedance spectroscopy (EIS) measurements were performed on cells in the fully discharged state. Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (Model 2273A, PerkinElmer Co., USA) in a voltage range of 2.5–4.3 V.

3. Results and discussion

3.1. Phys-chemical performance

Fig. 1 shows the XRD patterns of LFP-NVPF/C composites. It is obvious that all the diffraction peaks correspond well to orthorhombic $LiFePO_4$ (space group Pnmb (62), JCPDS 40-1499) and the sharp peaks indicate that the composite materials are well crystallised. Patterns in Fig. 1(c) exhibit a pure phase of $LiFePO_4$, while patterns in Fig. 1(d–f) are diffraction peaks of two-component composites with different mole ratios of x:(1−x). There are no clear impurity phases matching the trace of Fe_2P, Li_3PO_4 or other phases in Fig. 1(c–e). It should be noted that with the increase of the mole fraction of $Na_3V_2(PO_4)_2F_3$, the XRD peaks of the $LiFePO_4$ phase become slightly weaker and reflection intensity of the

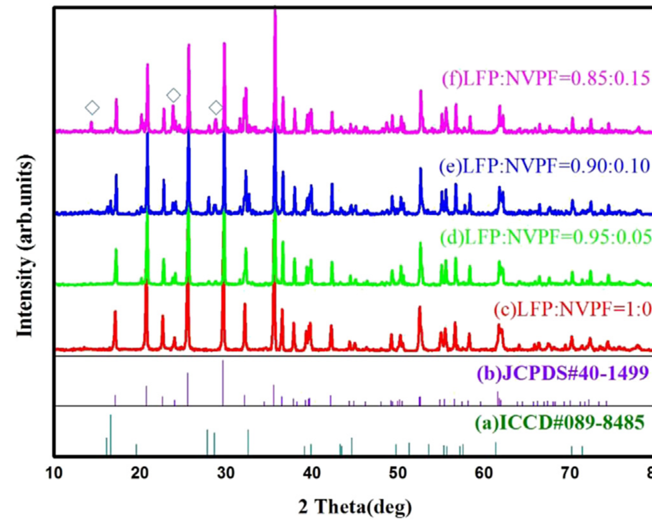

Fig. 1. XRD patterns of $xLiFePO_4 \cdot (1-x)Na_3V_2(PO_4)_2F_3$/C composites with different mole ratios of x:(1−x): (c) 1:0; (d) 0.95:0.05; (e) 0.90:0.10; (f) 0.85:0.15.

$Na_3V_2(PO_4)_2F_3$ phase gradually becomes evident. However, there is an impurity phase in Fig. 1(f), which corresponds well to $Na_3Fe_2(PO_4)_3$ (JCPDS 45-0319). The result also proves that too much NVPF can weaken the electrochemical performance of the materials. In addition, there is no evidence of diffraction peaks of carbon in any of the samples, which indicates that the coated carbon is amorphous or too small to be detected.

The XPS spectrum of V 2p taken from the LFP-NVPF/C (x = 0.9) composites is shown in Fig. 2 (a). It shows that the binding energy values of V 2p are 517.2 and 524.2 eV, which match well with energy level of V $2p_{3/2}$ and V $2p_{1/2}$, respectively. The binding energy value of V $2p_{3/2}$ of the composites conforms well to values observed in $LiVPO_4F$ (517.2 eV) [21,22] and V_2O_3 (517.3 eV) [23], which indicates that the oxidation state of V in the calcinated composites is +3. Fig. 2 (b) shows the Fe 2p XPS spectra of the LFP-NVPF/C (x = 0.9) composite. The two obvious peaks observed at 711.6 and 724.7 eV are related to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, which is in good agreement with reported literature values [24,25] and indicates that the oxidation state of Fe is +2.

Rietveld analysis of XRD diagrams related to the LFP-NVPF/C (x = 0.9) was conducted in order to get more accurate information. The corresponding refinement result, including observed, calculated and differential curves, are reported in Fig. 3. The refined lattice parameters are listed in Table 1. The figures of merit were Rw = 9.07% and the refinement result is acceptable. It should be noted that the cell volume of LFP in the LFP-NVPF/C (x = 0.9) composite is slightly smaller than in the pristine LFP (JCPDS 40-1499). Such a variation of the lattice parameters is an indication that V^{3+} is occurring in the LFP structure, as the ionic radius of V^{3+} (0.074 nm) is smaller than that of Fe^{2+} (0.078 nm). However, the cell volume of NVPF in the LFP-NVPF/C (x = 0.9) composite increases relative to the pristine NVPF (ICCD 089-8485), which also indicates that Fe atoms are introduced into the NVPF structure. Results, such as those mentioned above, suggest that there are two phases, vanadium-substitution LFP and iron-substitution NVPF, which gradually form in the process of the reaction and co-exist in the two-component LFP-NVPF/C (x = 0.9) composites. As we know, $LiFePO_4$ doped with V^{3+} displays improved electronic conductivity and electrochemical performance and the co-substitution can enhance their electrochemical performance for the two-component LFP-NVPF/C (x = 0.9) powders [26].

SEM images of LFP-NVPF/C composites with different mole