



Short communication

Improving the electrochemical performance of lithium vanadium fluorophosphate cathode material: Focus on interfacial stability



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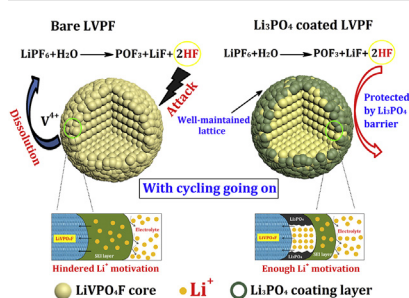
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HIGHLIGHTS

- Li_3PO_4 coating builds stable LiVPO_4F /electrolyte interface for the first time.
- LiVPO_4F coated with Li_3PO_4 shows enhanced cycle performance at 55 °C.
- Li_3PO_4 is proposed to act as a physical barrier as well as a Li^+ transfer media.

GRAPHICAL ABSTRACT



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ABSTRACT

To improve the stability of LiVPO_4F electrode/electrolyte interface, Li_3PO_4 is used to modify LiVPO_4F composite (P-LVPF) for the first time. Morphological characterization shows that LiVPO_4F particles are wrapped by amorphous carbon and lithium ionic conductor Li_3PO_4 as the interlayer and outer layer, respectively. Compared to the pristine sample, the resultant P-LVPF exhibits greatly improved rate capability and elevated-temperature cycle performance when applied as the cathode material for lithium ion batteries. Specifically, the Li_3PO_4 modified sample specific capacity maintains 77.6% at 1 C after 100 cycles under 55 °C. Such improvement is attributed to the fact that the Li_3PO_4 coating layer not only acts as a good ionic conductor for LiVPO_4F , but also serves as a physical barrier between electrode and electrolyte which can build a stable interface.

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1. Introduction

Lithium-ion batteries (LIBs) are regarded as one of the most

promising power sources for transport applications [1–5]. Materials based on the phosphate polyanions have been extensively investigated as safe and durable cathodes for LIBs [6]. Among these, favorite LiVPO_4F has been proposed as one of favorable alternatives for conventional oxide-based materials primarily because of its relatively high operating voltage (4.2 V) and excellent thermal stability [7–13]. However, LiVPO_4F suffers from poor cycling performance caused by its relatively low conductivity and unstable

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electrode/electrolyte interface [14–16]. Up to now, great efforts have been devoted to addressing this issue including the doping with metallic elements (Na [17], Mn [15], Al [18,19], Ti [20], etc.) and coating with the conductive materials (graphene [21], carbon nanotube [22], polyaniline [23], and Ag [24], etc.). Nevertheless, to the best of our knowledge, few attentions are directly paid to the chemistry and stability of LiVPO_4F /electrolyte interface [16,25,26], which is closely related to the cycling performance of high-voltage materials especially at elevated temperature. Therefore, it is of great importance to improve the interface stability of LiVPO_4F so that its high-temperature cycling performance can be enhanced.

Lithium phosphate (Li_3PO_4), especially in disordered phase, is an excellent and stable lithium ionic conductor [27,28]. Since Li_3PO_4 is chemically inert to the electrolyte in a wide voltage and temperature range, this material has been proven to be an effective coating agent to improve electrochemical performance of LiFePO_4 [29,30], $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ [31,32] and Li-rich layered oxides [33–35], etc. In this work, we report for the first time the use of amorphous Li_3PO_4 to modify $\text{LiVPO}_4\text{F}/\text{C}$ composite. With a skillful and mild aqueous solution method, Li_3PO_4 can be effectively coated on the surface of the LiVPO_4F nanoparticles. Considering Li_3PO_4 is a super ionic conductor, it would help to enhance the lithium ion diffusion of LiVPO_4F on the surface. More importantly, given the excellent chemical stability of Li_3PO_4 at high-voltage and elevated-temperature, the interface stability of Li_3PO_4 -coated LiVPO_4F is also expected to be improved.

2. Experimental sections

LiVPO_4F particles (LVPF) with an carbon content of 1.56 wt% were prepared as reported in previous works [13]. The Li_3PO_4 -coated LiVPO_4F (P-LVPF, 2.0 wt% Li_3PO_4) was synthesized via a solution method followed by low-temperature calcination, as illustrated in Figure S1. Firstly, 0.0528 g $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (AR, 99.0%) and 0.0198 g $\text{NH}_4\text{H}_2\text{PO}_4$ (AR, 99.0%) were dissolved in 100 mL deionized water with assistance of ultrasonic wave. After that, the prepared LVPF (1.0 g) was added into the resultant solution with magnetic stirring at 85 °C until the water was evaporated. Finally, the obtained slurry was dried in the oven at 120 °C for 12 h, grinded in an

agate mortar, and sintered at 450 °C for 5 h in a tube furnace under Ar atmosphere. For comparison, the other sample was obtained by treating LVPF through the same coating progress without addition of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ or $\text{NH}_4\text{H}_2\text{PO}_4$.

The X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu K α radiation was employed to characterize the crystal structure of the samples. Field-emission transmission electron microscope (TEM, Titan G12 with image corrector) were employed to characterize the morphologies of the prepared samples. The mass contents of elemental V dissolved in the electrolyte were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS intrepid XSP, Thermo Electron Corporation).

To fabricate the positive electrodes, the prepared active materials were mixed with conductive agent (carbon black; trade name: super P) and binder (polyvinylidene fluoride) in an 8:1:1 weight ratio in the *N*-methyl pyrrolidinone (NMP) solvent. Then, the blended slurry was cast onto an aluminum current collector, followed by drying at 120 °C for 6 h in oven. CR2025 cells composed of as-fabricated cathode (Φ 12 mm, the active material mass loading is ~1.5 mg), lithium plate anode, a porous polypropylene separator and 1 mol L⁻¹ LiPF_6 in EC/EMC/DMC (1:1:1 in volume), were assembled in a dry Ar-filled glove box for charge-discharge and electrochemical impedance spectroscopy (EIS) measurements. The impedance spectra were recorded by applying an AC voltage of 5 mV amplitude in the frequency range of 0.01 Hz–100 kHz.

3. Results and discussion

As shown in Fig. 1(a), after Li_3PO_4 coating, the P-LVPF sample presents the characteristic diffraction peaks of crystalline LiVPO_4F without any decrease in intensities of peaks, and no peak corresponding to crystallized Li_3PO_4 is observed, probably due to the limited thickness of Li_3PO_4 layer or its amorphous property. Interestingly, the P-LVPF displays perfect patterns without any peak of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ compared to pristine one, indicating the aqueous solution coating process may facilitate the formation of highly purified LiVPO_4F [36]. Note that, due to the loss of volatile fluorochemicals at high temperature, it is still a challenge to prepare high-purified LiVPO_4F without $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [13,37]. After

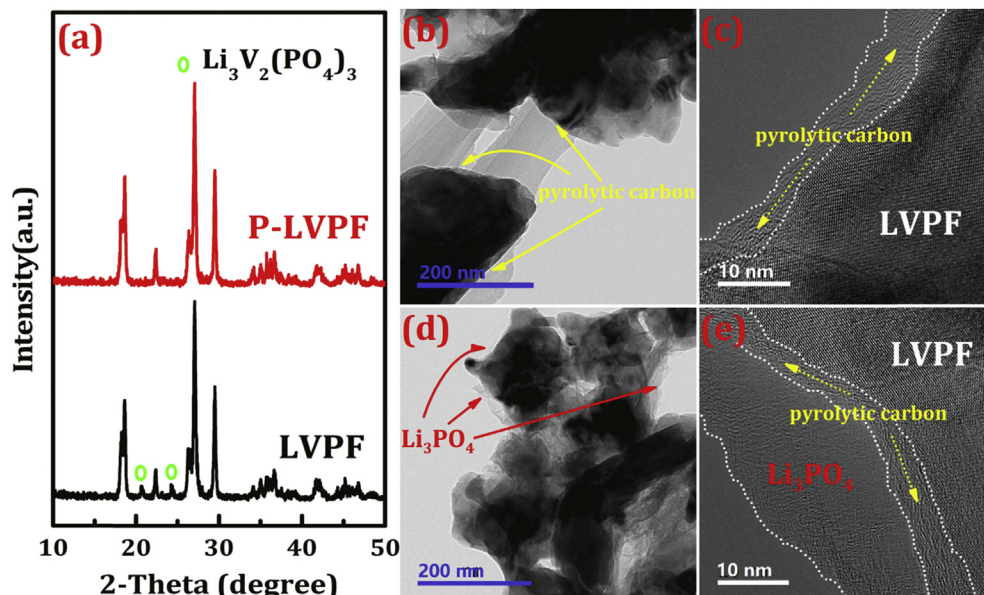


Fig. 1. (a) XRD patterns of LiVPO_4F materials before and after Li_3PO_4 coating; TEM and HRTEM images of (b, c) LVPF and (d, e) P-LVPF.

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