COMMUNICATION

Uniform 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes for high-performance Li-ion batteries

Shuquan Lianga, Xinxin Caoa, Yaping Wanga, Yang Hua, Anqiang Pana,⁎, Guozhong Caoa

School of Material Science and Engineering, Central South University, Changsha 410083, Hunan, PR China
Department of Materials Science & Engineering, University of Washington, Seattle, WA 98195, USA

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Abstract
The synthesis of novel nanostructures at high temperatures is a big challenge because of the particle growth and aggregations. In particular, the fabrication of two active components with uniform structures is rarely reported. Herein, uniform 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes have been synthesized by a one-pot, solid-state reaction in molten hydrocarbon, where the oleic acid functions as a surfactant. The composite components of LiFePO₄ and Li₃V₂(PO₄)₃ are distributed homogenously within the nanoflakes. Moreover, the nanoflakes are coated by in-situ generated carbon from oleic acid during the sintering process in H₂/Ar. The as-prepared 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes are approximately 20 50 nm in thickness and are stacked together to construct a porous structure, which have a surface area of 30.21 m² g⁻¹. The lithium ion diffusion coefficient can be greatly improved by making 8LiFePO₄·Li₃V₂(PO₄)₃/C composite. As cathode material for lithium ion batteries, the as-prepared material exhibits excellent electrochemical performances, including high reversible capacity, good cyclic stability and rate capability. The composite electrode delivers a high capacity of 161.5 mAh g⁻¹ at 0.1C, which is very close to the theoretical capacity. Even at 10C, the electrode can deliver a specific discharge capacity of 118.6 mA h g⁻¹. After the long-term 1000 cycles, the electrodes can still retain 93.21% and 88.7% of its maximum specific discharge capacities at the rates of 2C and 5C, respectively. The results demonstrate the 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes are promising cathode materials for high-performance lithium ion batteries.

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⁎Corresponding author at: School of Materials Science and Engineering, Central South University, Changsha, 410083, Hunan, PR China. Tel.: 86 0731 88836069; fax: 86 0731 88876692.
E-mail addresses: pananqiang@csu.edu.cn (A. Pan), gzcao@u.washington.edu (G. Cao).

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Introduction

Lithium-ion batteries have been the dominant power supplier for high-tech portable electronic devices for decades. However, other future broad applications, such as plug-in hybrid electric vehicles (PHEV) and plug-in electric vehicle (PEV), require further improvements in many perspectives, such as energy density, safety, durability and cost [1-4]. Recently, lithium transition metal phosphates (such as LiFePO4, LiMnPO4, and LiV2(PO4)3) have been extensively studied for lithium-ion batteries due to their high energy density, long lifespan, and good safety [5-11]. Among these phosphates, olivine structured LiFePO4, firstly proposed as a cathode material for lithium ion battery by Goodenough et al. in 1997 [12], has been commercialized successfully due to its relatively high capacity, thermal stability, environmental benignity and low cost. Nevertheless, some intrinsic drawbacks should be addressed before its applications in transportation and grid energy storage, such as poor electronic conductivity, and low Li-ion diffusion coefficients in transportation and grid energy storage, such as poor intrinsic drawbacks should be addressed before its applications. Due to its relatively high capacity, thermal stability, environmental benignity and low cost, some intrinsic drawbacks should be addressed before its applications. Although nanostructured phosphates have been prepared for sole LiMnPO4 or Li3V2(PO4)3, no work is reported on the preparation of the uniform nanocomposites of two active components, such as LiFePO4 and LiV2(PO4)3. The difficulty may be attributed to their structural growth priority for different materials.

Herein, uniform 8LiFePO4·Li3V2(PO4)3/C nanoflakes have been successfully prepared in a molten media using oleic acid as a surfactant. The LiFePO4 and LiV2(PO4)3 are homogeneously distributed through the nanoflakes. Moreover, the composite nanoflakes are coated by a carbon layer, which is in situ generated in the calcination process at high temperatures. As a cathode material for lithium-ion batteries, the 8LiFePO4·Li3V2(PO4)3/C nanoflakes exhibit superior electrochemical performance.

Experimental section

Preparation of FeC2O4·2H2O and VOC2O4·nH2O

The ferrous oxalate dihydrate (FeC2O4·2H2O) was prepared by precipitation reactions according to a previous report [37]. Briefly, FeSO4·7H2O and H2C2O4·2H2O in a stoichiometric ratio of 1:1 were added into a beaker with 200 ml deionized water under vigorous magnetic stirring at room temperature. Then 5 ml 10% Sulfuric acid was added to the beaker, followed by continuously stirring for another 4 h to form a bright yellow solution. The mixed solution was kept at 40 °C for 2 days before collecting the yellow precipitate by filtering and washed with distilled water for three times. The yellow precipitate was dried in an oven at 80°C overnight to obtain the bright yellow microcrystalline powder.

Vanadyl oxalate hydrate (VOC2O4·nH2O) as vanadium sources was prepared through a soft chemical route, which was similar to our previous reports [38-40]. In a typical procedure, V2O5 and H2C2O4·2H2O were completely dissolved in deionized water at a stoichiometric ratio of 1:3 and continuously stirred at room temperature until the color of the solution changed from yellow to dark-blue, which indicated the change of the valence of vanadium ions in the solution from +5 to +4. Oxalic acid here was used as both a chelating reagent and as a reducing agent. After the solution was dried in an oven at 80 °C for 12 h, VOC2O4·nH2O was obtained. The reaction may occur as follows:

\[
V_2O_5 + 3H_2C_2O_4 \rightarrow 2VOC_2O_4 \rightarrow 2CO_2 + 3H_2O \tag{1}
\]

Preparation of 8LiFePO4·Li3V2(PO4)3/C Nanoflake Composite, pristine LiFePO4/C and Li3V2(PO4)3/C

The nanoflake-stacked 8LiFePO4·Li3V2(PO4)3/C was synthesized via a one-step solid-state reaction in molten surfactant-paraffin media. Specifically, NH4H2PO4 was milled initially with oleic acid for 1 h using a QM-3B high-energy milling machine, followed by adding paraffin wax under milling for 30 min. Then, FeC2O4·2H2O and VOC2O4·nH2O were added, and milled for 10 min. Finally, CH3COOLi·2H2O was added and milled for another 10 min. The overall molar ratio of Li: Fe: V: P: oleic acid in the milling process was not only determined by the surfactant, but also the target materials themselves. Although nanostructured phosphates have been prepared for sole LiMnPO4 or Li3V2(PO4)3, no work is reported on the preparation of the uniform nanocomposites of two active components, such as LiFePO4 and LiV2(PO4)3. The difficulty may be attributed to their structural growth priority for different materials.
mixture is 11: 8: 2: 11: 11. The paraffin wax is twice weight of oleic acid. The viscous precursor slurry was dried in oven at 105 °C for 30 min. The obtained mixture was heated in a tube furnace at 750 °C for 8 h under the flowing of the mixture atmosphere of 5%H2/95%Ar to yield 8LiFePO4·Li3V2(PO4)3/C nanoflakes. The heating rate was set of 5 °C/min. The evaporated paraffin was collected at the cooler part of the tube furnace during the heat treatment process. For comparison, the pristine LiFePO4/C and Li3V2(PO4)3/C were synthesized using the molar ratios of Li: Fe: P: oleic acid=1: 1: 1 and Li: V: P: oleic acid=3: 2: 3: 3 in the milling mixture, respectively, while the other synthesis conditions were kept unchanged.

Material characterization

The crystallographic information was recorded by X-ray diffraction (XRD) measurements using a Rigaku D/max2500 X-ray diffractometer with non-monochromated Cu-Kα (λ=1.54178 Å) X-ray source. The samples were scanned in the range between 10° and 80° (2θ) with a step size of 0.02°. The morphology of the composites were characterized by a field-emission scanning electron microscope (FESEM, FEI Nova NanoSEM 230) with an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) images and high-resolution transmission electron microscope (HRTEM) images were gathered on transmission electron microscope (TEM, JEOL JEM-2100 F) operating at a 200 kV accelerating voltage. Elemental carbon content in the samples were determined by C–S analysis equipment (CS–2000, Eltar, Germany). The property of carbon layer was analyzed by Raman spectrometer (LabRAM HR8000c). Specific surface areas were estimated by Brunauer-Emmet-Teller ( BET) method using Nitrogen adsorption-desorption (NOVA 4200e, Quantachrome Instruments).

Electrode fabrication and electrochemical measurements

The electrochemical measurements were carried out by assembly of CR2032 coin cells in a glove box (MBraun, Germany) filled with ultra-high pure argon gas, which use lithium foil as the anode, polypropylene membrane as the separator, and 1.0 M solution of LiPF6 in ethylene carbon (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:1:1, by volume) as electrolyte. The cathode slurry was prepared by dispersing active materials, acetylene black, and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidione (NMP) solution with a weight ratio of 75: 15: 10. The mixed slurry was spread on aluminum foil, and was dried in a vacuum oven at 100 °C overnight prior cells assembly. The cells were first aged for 12 h before charge/discharge to ensure full absorption of the electrolyte into the electrodes. The electrode area was 1.131 cm² and the mass loading of the active material was 1−1.5 mg cm⁻². Cyclic voltammetry (CV) was tested on an electrochemical workstation (CHI604E, China) in the voltage range of 2.5−4.5 V (vs. Li/Li⁺) and electrochemical impedance spectroscopy (EIS) measurements were performed on a ZAHNER-IM6ex electrochemical workstation (ZAHNER Co., Germany) in the frequency range of 100 kHz to 10mHz on a cell in as-assembled condition. The galvanostatic charge/discharge performances of the electrodes were studied at ambient temperature in a potential range of 2.5−4.3 V vs Li/Li⁺ with a multichannel battery testing system (LAND CT2001A, China). The cells were charged under constant current and constant voltage (CCCV) mode, which was then discharged under constant current (CC) mode. The constant current charging is followed by a potentiostatic hold at 4.3 V until the current drops to one tenth of charge current. The cells were then discharge to 2.5 V. Here, 1 C refers to 170 mA g⁻¹ for the 8LiFePO4·Li3V2(PO4)3/C composite and pristine LiFePO4/C electrodes, but for pristine Li3V2(PO4)3/C electrodes, 1 C refers to 133 mA g⁻¹. The capacities were calculated based on the weight of active materials only.

Results and discussion

Figure 1 shows the powder X-ray diffraction (XRD) pattern of the prepared 8LiFePO4·Li3V2(PO4)3/C composite. The Rietveld refinement method (Jade 9.0 software, MDI, USA) was used to refine the X-ray diffraction patterns to analyze the crystal structures and phases of the material. The atomic positions of LiFePO4 and Li3V2(PO4)3/C composite and pristine LiFePO4/C composite are listed in Table S1. The crosses denote the observed data and the continuous red line covered above represents the fitted pattern. The difference pattern is also shown. The bottom vertical bars indicate the Bragg position of LiFePO4 and Li3V2(PO4)3/C.

![Figure 1 X-ray diffraction pattern with Rietveld refinement of 8LiFePO4·Li3V2(PO4)3/C composite. The crosses denote the observed data and the continuous red line covered above represents the fitted pattern. The difference pattern is also shown. The bottom vertical bars indicate the Bragg position of LiFePO4 and Li3V2(PO4)3/C.](image)
content of LiFePO4 and Li3V2(PO4)3 determined by multi-phase refinement is 75.7 ± 1.2 wt% and 24.3 ± 1.2 wt%, respectively. The unit cell volume of LiFePO4 in the 8LiFePO4·Li3V2(PO4)3/C composite decreases obviously, compared with that of pure phase LiFePO4, which may be attributed to the V doping into the LiFePO4 host lattice because the ionic radius of V4+ (0.74 Å) is smaller than that of Fe2+ (0.78 Å). However, the cell volume of Li3V2(PO4)3 in the 8LiFePO4·Li3V2(PO4)3/C composite increases compared with the pristine Li3V2(PO4)3, suggesting that Fe also entered into the Li3V2(PO4)3 host lattice. The above results indicate that most of the iron and vanadium in the raw materials tend to form the LiFePO4 and Li3V2(PO4)3 phases, and a small amount of Fe and V as the dopants enter into the lattice of Li3V2(PO4)3 and LiFePO4 (mutual doping), respectively. Furthermore, the calculated weight percent of LiFePO4 and Li3V2(PO4)3 phases for the sample deviates a little from the theoretical value, which is attributed to the mutual doping between the two materials. In earlier literatures [13,21,42,43], the LiFePO4 doping with V4+ as well as the Li3V2(PO4)3 doping with Fe2+ are beneficial to improve their electron conductivity and electrochemical performance. XRD patterns of the prepared pristine LiFePO4/C and Li3V2(PO4)3/C samples are illustrated in Figure S1. All diffraction reexxes can be well indexed to orthorhombic LiFePO4 (space group Pnma, in accordance with ICSD no. 162064) and monoclinic Li3V2(PO4)3 (space group P21/n, in accordance with ICSD no. 98362), respectively, and no evidence of secondary phases or crystalline carbon diffraction reexxes is present.

The morphological and microstructure features of the prepared materials were investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), as shown in Figure 2. The low-magnification FESEM image (Figure 2a) reveals the composite is composed of loose and interconnected nanoflakes. The nanoflake particles are homogeneously dispersed, and the shape of the nanoflakes is quite uniform. Figure 2b shows the SEM images of pristine LiFePO4/C and Li3V2(PO4)3/C prepared by the similar strategy. The LiFePO4 is composed of irregular nanoparticles and Li3V2(PO4)3 is constructed by loosely interconnected nanoflakes, which are in good accordance with the previous reports [10,16]. The result indicates the existence of Li3V2(PO4)3 in the 8LiFePO4·Li3V2(PO4)3/C composite is helpful to obtain uniform structures, although the addition amount of Li3V2(PO4)3 is only 1/9 in molar ratio. According to the elemental mapping result, the distribution of C, V, and Fe is very uniform within the aggregates, which suggest the high homogeneity of the composite (Figure S3). Figure 2c gives a much clear picture of the composite. The 8LiFePO4·Li3V2(PO4)3/C nanoflakes are approximately 20-50 nm in thickness and have an in-plane extension of about 1-2 μm. The high magnification TEM image (Figure 2c) reveals that the single 8LiFePO4·Li3V2(PO4)3/C nanoflake is composed of many infinitesimal interconnected nanoparticles with diameter of 30–100 nm and a multiplicity of mesoporous channels with a uniform pore size of 10-50 nm. Figure 2d shows the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of nanoflakes, which confirms homogeneous distribution of V and Fe in the prepared sample. The result indicates the high efficiency of making LiFePO4 and Li3V2(PO4)3 composite, rather than a simple macroscopical mixing. Furthermore, the coated carbon distributes evenly on the particle surface (Figure S3). According to the C-S analysis, the mass content of carbon is about 4.86%. The HRTEM images of the prepared sample are provided as shown in Figure 2e and f. The carbon layer with a thickness of about 5 nm can also be observed (inset of Figure 2e). The Fourier transform (FFT) images of regions (inset of Figure 2f) show the diffraction spots of LiFePO4, and Li3V2(PO4)3, respectively. By comparing interplanar distances measured from HRTEM with the theoretical value, the existence of LiFePO4 and Li3V2(PO4)3 is confirmed, consistent with the results from XRD crystal analysis.

In this work, oleic acid acts as a surfactant that directs the growth orientation of 8LiFePO4·Li3V2(PO4)3/C nanoflakes. Oleic acid (CH3(CH2)7CH=CH(CH2)7COOH), a mono-unsaturated omega-9 fatty acid found in various animal and vegetable sources, has been well known as a surfactant with carbonyl group, long alkyl chain and unsaturated bond. The carbonyl group in oleic acid could attach on the surface of nanoparticles. On the other hand, the presence of the long alkyl chain and unsaturated bond in oleic acid provides significant hydrophobicity to the nanoparticles and is beneficial for a good interfacial bonding between the nanoparticles and the matrix [35,36,44]. Such an oleic acid surfactant can extend its tail in molten paraffin media in a manner similar to self-assembly approach [44]. As a result, the nanoparticles modified by oleic acid can grow preferentially along specific directions to form the 8LiFePO4·Li3V2(PO4)3/C nanoflakes. Moreover, the 8LiFePO4·Li3V2(PO4)3 composite is carbon coated due to the in-situ decomposition of oleic acid on the active material, which may beneficial for the electron transportation for lithium ion batteries [20,34].

The existence of carbon in the composite has been confirmed by Raman scattering spectrum result (Figure 3a). The two broad bands at 1330 cm−1 and 1610 cm−1 can be assigned to the D-band (disorder-induced phonon mode) and G-band

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters</th>
<th>Phase content (wt%)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (nm)</td>
<td>b (nm)</td>
<td>c (nm)</td>
</tr>
<tr>
<td>LFP in 8LFP·LVP</td>
<td>1.03144</td>
<td>0.60021</td>
<td>0.46940</td>
</tr>
<tr>
<td>LFP</td>
<td>1.03182</td>
<td>0.60037</td>
<td>0.46937</td>
</tr>
<tr>
<td>LVP in 8LFP·LVP</td>
<td>0.85940</td>
<td>0.86027</td>
<td>1.20468</td>
</tr>
<tr>
<td>LVP</td>
<td>0.86056</td>
<td>0.85917</td>
<td>1.20380</td>
</tr>
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</table>
(graphite band), respectively, indicating the existence of the carbon layer in the material and the partial graphitization of the deposited carbon [17,45]. The peak intensity ratio between the D- and G-bands (ID/IG) generally provides a useful index about the degree of crystallinity of various carbon materials. In general, the high ordering degree of the carbon materials have high ID/IG values [46]. The intensity ratio of ID/IG in the as-synthesized 8LiFePO4-Li3V2(PO4)3/C nanoflakes is around 0.97, indicating a relatively high degree of graphitization, which will be beneficial for achieving better electronic conductivity for the composite material [47-49].

The nitrogen adsorption-desorption analysis was carried out to investigate the porosity of the 8LiFePO4-Li3V2(PO4)3/C nanoflakes and the results are shown in Figure 3b. The isotherm can be described as type II with a H3 hysteresis loop, which indicates the slit-shaped pores in the composite. According to the Brunauer-Emmet-Teller (BET) method, the surface area of the 8LiFePO4-Li3V2(PO4)3/C nanoflakes is...
the extraction of lithium ions from Li₃V₂(PO₄)₃ (Figure S4b), and around 3.60 V, 3.69 V and 4.10 V can be identified as the intercalation process. The charge plateaus located around 3.60 V, 3.69 V and 4.10 V indicate the multiple steps of lithium ions intercalation/deintercalation. The multiple plateaus in the charge/discharge curve of the first three cycles for the composite electrode, which exhibit the highest charge capacity of 153.1 mAh g⁻¹ and can retain 93.86% of its capacity after 500 cycles. The average capacity fading rate is 0.1% per cycle. The coulombic efficiency is above 98% during the whole cycling process, confirming the good reversibility of the electrode materials [33, 52].

Electrochemical impedance spectroscopy (EIS) measurements of 8LiFePO₄·Li₃V₂(PO₄)₃/C composite electrode after different cycles at 1 C rate were carried out in the frequency ranging from 100 kHz to 0.01 Hz (Figure 4d). All the Nyquist plots are composed of a small intercept in the highest frequency range, a depressed semicircle in the high-frequency region, and a slanted line in the low-frequency region. The high frequency intercept at the Zreal axis corresponds to the Ohmic resistance of the cell, including the resistance of electrolyte, separator, current collector and so on [53]. The semicircle is mainly ascribed to the charge transfer reaction at the electrode/electrolyte interface, and the slanted line is ascribed to the slow diffusion process of lithium ions in the bulk of the electrode material [54, 55]. Inset in Figure 4d shows the equivalent circuit model proposed for the interpretation of the impedance spectra. Rᵣ is the combination of electrolyte resistance and Ohmic resistances of cell components. Rₓ and CPE represent the charge transfer resistance and double-layer capacitance, respectively. Zₗ represents the diffusion-
controlled Warburg impedance and $C_{\text{int}}$ indicates the capacitance caused by the accumulation or loss of Li$^+$ in the crystal of electrode material. The simulated charge transfer resistances ($R_{\text{ct}}$) of the 8LiFePO$_4$·Li$_3$V$_2$(PO$_4$)$_3$/C samples are 158.2 $\Omega$ for the fresh electrode. After 10 and 100 cycles, their corresponding charge transfer resistances are 175.4 $\Omega$, and 327.1 $\Omega$, respectively (Table S2). The charge transfer resistance in the 10th and 100th cycle increase slightly. The charge transfer resistance increase is also reported in other composite electrode materials [47,48,56]. However, the little charge transfer resistance increase can be attributed to the carbon coated 8LiFePO$_4$·Li$_3$V$_2$(PO$_4$)$_3$ nanoflake structures, which can facilitate the generated electron transportation. Besides, the Nyquist plots (Figure S4d and S5d) show that the charge transfer resistance ($R_{\text{ct}}$) of both pristine LiFePO$_4$/C and Li$_3$V$_2$(PO$_4$)$_3$/C electrodes are much bigger than the 8LiFePO$_4$·Li$_3$V$_2$(PO$_4$)$_3$/C composite electrode (Table S2 and S3). This indicates that making the

Figure 4 Electrochemical characterizations of the 8LiFePO$_4$·Li$_3$V$_2$(PO$_4$)$_3$/C nanoflakes: (a) the first three successive cyclic voltammograms curves at a scan rate of 0.1 mV s$^{-1}$ in a voltage range of 2.5-4.3 V; (b) the first three charge-discharge profiles at a current density of 0.1 C (1 C = 170 mA g$^{-1}$); (c) cycling performance at the current density of 1 C between the voltage range of 2.5-4.3 V; (d) Nyquist plots of the sample after different cycles; (e) long-term cycling performance of the samples at 2 C and 5 C.

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**Figure 4** Electrochemical characterizations of the 8LiFePO$_4$·Li$_3$V$_2$(PO$_4$)$_3$/C nanoflakes: (a) the first three successive cyclic voltammograms curves at a scan rate of 0.1 mV s$^{-1}$ in a voltage range of 2.5-4.3 V; (b) the first three charge-discharge profiles at a current density of 0.1 C (1 C = 170 mA g$^{-1}$); (c) cycling performance at the current density of 1 C between the voltage range of 2.5-4.3 V; (d) Nyquist plots of the sample after different cycles; (e) long-term cycling performance of the samples at 2 C and 5 C.
composites with novel nanostructures indeed improves the charge transfer kinetics.

The long-term cycling performance at high rate is a critical requirement for high-power LIB applications such as plug-in hybrid electric vehicles (PHEV) and plug-in electric vehicle (PEV). Figure 4e shows the cycling performance of 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes electrode for 1000 cycles. The capacity increase in the initial cycles can be attributed to the activation process due to the gradual wetting of the electrode materials by electrolyte, which is commonly observed in various nanocomposite electrodes [48,54,57]. The composite electrodes can deliver the maximum specific discharge capacities of 144.3 and 132.8 mAh g⁻¹ at 2 C and 5 C, respectively. After 1000 cycles, it still can retain 134.5 mAh g⁻¹ at 2 C, 94% of its original capacity. And the composite electrode delivers 117.8 mAh g⁻¹ after 1000 cycles at 5 C, with an average capacity fading rate of 0.0113% per cycle. The results demonstrate the excellent long-term cyclic stability of the 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes compared with the pristine LiFePO₄/C (Figure 5a) and Li₃V₂(PO₄)₃/C (Figure 5c). The superior cycling performance can be attributed to the carbon coated 8LiFePO₄·Li₃V₂(PO₄)₃/C porous composite, in which the carbon can improve the conductivity of the electron and improve the stability of the electrode materials. Moreover, the porous structures can provide buffer space for the volume changes, keeping the structural integrity.

Figure 5 shows the rate capability of 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflake composite and their corresponding discharge/charge curves in the potential range of 2.5–4.3 V. As shown in Figure 5a, the 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflakes electrode exhibit superior rate capability. It can release the discharge capacities of 161.5, 157.3, 152.9, 145.9, and 132.8 mAh g⁻¹ at 0.1 C, 0.5 C, 1 C, 2 C, and 5 C, respectively. Even at 10 C, it still delivers a capacity of 118.6 mAh g⁻¹. When the current was reset to 1 C, a specific capacity of 151.1 mAh g⁻¹ could be restored. It is worth noting that the composite electrode exhibits good cyclic stability at all the rates. Figure 5b shows the corresponding charge-discharge curves at various rates. Even at 10 C, the discharge/charge plateaus can be clearly detected. The rate performance of the 8LiFePO₄·Li₃V₂(PO₄)₃/C nanoflake electrode is much better than the pristine LiFePO₄/C and Li₃V₂(PO₄)₃/C electrodes (Figure S4d and S5d). The nanoscaled thickness of the nanoflakes can greatly reduced the lithium ion diffusion distance, and the porous structures can provide the reaction sites and easy electrolyte penetration path ways. Furthermore, the carbon coating can improve the electron conductivity of the electrode materials.

In order to evaluate the structural stability of the 8LiFePO₄·Li₃V₂(PO₄)₃/C composite nanoflakes, the electrode materials after 1000 cycles were collected and studied by XRD and SEM techniques. As can be seen in Figure 6a, the XRD pattern of the electrode materials after 1000 cycles has no significant difference and both exhibit the main characteristic peaks of original 8LiFePO₄·Li₃V₂(PO₄)₃. Moreover, the nanoflakes can be well retained after 1000 cycles at 5 C (Figure 5f), which demonstrate their good structural stability upon cycling.

In order to further investigate the effect of fast ionic conducting Li₃V₂(PO₄)₃ additive on the electrochemical properties of LiFePO₄, the apparent diffusion coefficient of lithium ions is determined by cyclic voltammetry technique. Figure 6a shows the CV curves of the prepared sample at scan rates of 0.05, 0.1, 0.25, 0.5, 0.75, 1.0 mV s⁻¹ in the voltage range of 3.0–4.3 V. As shown in Figure 6a, with the increase of the scan rates, the anodic peaks shift right and the corresponding cathodic peaks move left, which indicates larger polarization at high scan rates. And the intensities of redox peaks increase with increasing scan rate. From Figure 6b, the peak current (Iₚ) has a linear relationship with the square root of scan rate (v₁/₂), indicating diffusion-controlled process [53,58]. For the semi-infinite and finite diffusion, the peak current is proportional to the square root of the scan rate and can be expressed by the classical Randles Sevchik method (Eq. (2)) [58].

\[ I_p = 2.69 \times 10^{9} n^{1/2} A^{1/2} v^{1/2} C_0 \]  

(2)

Where \( I_p \) is the peak current (A), \( n \) is the number of electrons per species reaction (for Li⁺, \( n=1 \)), \( A \) is the active
surface area of the electrode (here 1.131 cm² is used for simplicity), \( D \) is the diffusion coefficient of lithium ion (cm² s⁻¹), \( v \) is the scan rate (V s⁻¹), and \( C_0 \) is the is the concentration of lithium ions corresponding to the different specific electrochemical reaction steps (mol cm⁻³). Because the situation in this study is complex as the diffusion might be affected by the tortuous pass in the composite electrodes. We recommend the effective diffusion coefficients \( (D_{se}) \) herein just for the solid-state cathode electrode, and we used \( n_e \) and \( C_{se}^e \) as effective one respectively, and the values are listed (Table S4). Based on Eq. (2) and the slope of \( I_p \) versus \( v^{1/2} \) plots in Figure 6b, the diffusion coefficients of lithium ion in solid state composite are calculated and listed in Table 2. It can be seen that the values of \( D_{se} \) for the solid state composite are in the magnitude of \( 10^{-10} \) to \( 10^{-12} \) cm² s⁻¹ and close to each other. The Li-ion diffusion coefficients of 8LiFePO₄·LiₓV₂(PO₄)₃/C composite electrode after different cycles, listed in Table S5, are also calculated based on the Equation S1 and linear relationship between \( Z_0 \) vs. \( \omega^{-1/2} \) at low-frequency region (Figure S8). The values are at least 3 orders of magnitude larger than that of LiFePO₄ (10⁻¹³ to 10⁻¹⁵ cm² s⁻¹) [6], LiMnPO₄ (1.5 × 10⁻¹³ cm² s⁻¹) [24], and LiFe₇Mn₃PO₁₄ (10⁻¹⁵ to 10⁻¹⁷ cm² s⁻¹) [14], and are comparable with that of LiₓV₂(PO₄)₃ [33,53], xLiFePO₄·LiVPO₄F composite [59], and xLiₓV₂(PO₄)₃·LiVPO₄F composite [58]. The result demonstrate that the lithium ion diffusion coefficient has been greatly improved by making LiₓV₂(PO₄)₃/LiFePO₄ composite, although the amount of LiₓV₂(PO₄)₃ is quite small.

According to the above results, the excellent electrochemical performance of 8LiFePO₄·LiₓV₂(PO₄)₃/C nanoflakes, including high capacity, good cyclic stability and rate capability can be ascribed to the novel carbon coated 8LiFePO₄·LiₓV₂(PO₄)₃/C nanoflake composite: (1) the nanoscaled thickness of the nanoflakes reduce the lithium-ion diffusion distance and the porous structure further enlarges the contact area between electrode and electrolyte; (2) the ample space between nanoflakes provides the easy path for electrolyte penetration and better accommodates the volume change during charge/discharge process; (3) The mutual cross-doping between LiFePO₄ and LiₓV₂(PO₄)₃ is benificial to improve their conductivity and lithium ion diffusion coefficient; (4) the carbon coating on the composite nanoflakes would improve the electron transportation and better keep the structural integrity.

**Conclusions**

Uniform 8LiFePO₄·LiₓV₂(PO₄)₃/C nanoflake composite has been synthesized by a one-pot, solid-state method in a molten hydrocarbon, which is cost-effective, and environmental benign for large scale production. The LiFePO₄ and LiₓV₂(PO₄)₃ are homogenously distributed within the

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**Table 2** The diffusion coefficients of lithium-ion in composite electrode calculated from CV based on the classical Randles Sevchik equation.

<table>
<thead>
<tr>
<th>State</th>
<th>Anodic oxidation process</th>
<th>Cathodic reduction process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak</td>
<td>( D_{se} ) (cm² s⁻¹)</td>
</tr>
<tr>
<td>8FePO₄·LiₓV₂(PO₄)₃</td>
<td>A1</td>
<td>( 4.6 \times 10^{-10} )</td>
</tr>
<tr>
<td>8FePO₄·Li₂V₂(PO₄)₃</td>
<td>B1</td>
<td>–</td>
</tr>
<tr>
<td>8FePO₄·LiV₂(PO₄)₃</td>
<td>B2</td>
<td>–</td>
</tr>
<tr>
<td>8FePO₄·LiV₂(PO₄)₃</td>
<td>B3</td>
<td>( 1.6 \times 10^{-9} )</td>
</tr>
</tbody>
</table>
nanoflakes and are carbon coated. Moreover, the lithium ion diffusion coefficient is greatly improved in the composite as compared to LiFePO₄ due to the mutual doping effect. As cathode materials for lithium ion batteries, the resulting 8LiFePO₄·Li₂V₂(PO₄)₃/C nanoflakes exhibit excellent electrochemical performances, including high reversible capacity, excellent cyclic stability and good rate capability. The synthesis strategy may also be used to explore other nanocomposites, especially for high temperature synthesis.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.02.002.

References


Prof Shuquan Liang received his Ph.D. degree from Central South University (P.R. China) in 2000. He has been the Dean of School of Materials Science and Engineering in Central South University (CSU) since 2010. He is the winner of Monash University Engineering Sir John Medal. He hosted 5 state research projects including national 973 sub-project and national 863 project. He has published more than 60 papers in frontier journals. Currently, his main research interests include micro/nanostructured functional materials, nanocomposites and their energy storage and conversion devices.

Xinxin Cao received his Bachelor's degree in Materials science and Engineering from Central South University (CSU) in 2014. He is now a Ph.D. candidate in School of Materials science and Engineering, Central South University supervised by Prof. Shuquan Liang. His research focuses on the synthesis and application of nanomaterials and composites for clean energy storage, such as high-power/high-energy lithium ion batteries, and sodium ion batteries.

Yaping Wang received her B.E. degree in Mineral Process Engineering from Central South University in 2013 and she is currently a postgraduate student at the School of Materials Science and Engineering, Central South University (PR China). Her current research focuses on hollow-structured materials for electrochemical energy storage applications.

Yang Hu received his B.E. in Materials Science and Engineering from Central south university (PR China) in 2013. Currently, under the guidance of Prof. Liang, he is studying for his Ph.D. Degree in Materials Physics and Chemistry in Central South University. His current research interest is nanostructured cathode materials for lithium ion batteries.

Anqiang Pan received his B. E. (2005) and D. Phil. (2011) degrees in Materials Physics and Chemistry from Central South University. He worked in Prof. Guozhong Cao's group at University of Washington as an exchange student (2008-2009). Then, he worked in PNNL as a visiting scholar in Dr. Ji-Guang Zhang and Dr. Jun Liu's group (2009-2011). He joined Prof. Xiongwen (David) Lou's group at Nanyang Technological University as a research fellow (2011-2012). He joined Central South University as a Sheng-Hua Professor in 2013. His current interests are on lithium ion batteries, and supercapacitors.

Guozhong Cao is Boeing-Steiner Professor of Materials Science and Engineering, Professor of Chemical Engineering, and Adjunct Professor of Mechanical Engineering at University of Washington, and also a Professor at Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences and Dalian University of Technology. His current research is focused on chemical processing of nanomaterials for energy related applications including solar cells, rechargeable batteries, supercapacitors, and hydrogen storage.