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Surfactant-assisted solid-state synthesis of $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocomposite for lithium-ion batteries

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Herein, nanosized LiMnPO_4/C , $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$, and $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode materials were synthesized by a facile surfactant-assisted solid-state method. Lauric acid was used as a surfactant and carbon source to fabricate the carbon-coated nanoparticles. The phase compositions and elemental distribution of $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ were analyzed via X-ray diffraction and energy dispersive spectroscopy. Due to the unique heterogeneous nanostructure, $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ exhibits superior electrochemical performance as compared to the individual $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ and LiMnPO_4/C . The composite cathode delivers large discharge capacities of 162 and 167 mA h g^{-1} at 0.1C in the voltage range of 2.0–4.5 V and 2.0–4.8 V, respectively, along with good rate capability and long cycle life.

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1. Introduction

During the recent decade, the rapidly developing electric vehicles and hybrid electric vehicles urgently need safe lithium-ion batteries as a driving power source. Compared to commercial metal-oxide cathode materials, polyanionic LiMPO_4 ($\text{M} = \text{Fe}$, Mn , and Co) cathodes exhibit superior structural and thermal stability due to the existence of strong covalent P–O bonds.^{1,2} LiMnPO_4 shows great potential for application in power batteries owing to the virtues of large theoretical capacity (171 mA h g^{-1}), high discharge voltage (4.1 V vs. Li/Li^+), and an abundant manganese source.³ However, the low electronic conductivity of LiMnPO_4 ($<10^{-10} \text{ S cm}^{-1}$) restricts its reversible capacity at high currents.⁴

Recent reports have proven that the electrochemical kinetics of LiMnPO_4 can be remarkably improved by partially replacing Mn with Fe.^{5–26} Various $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ ($0 < y < 1$) solid solutions, such as $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$,^{11,12} $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$,^{13–16} $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$,^{17–19} $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$,²⁰ $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$,^{21–23} etc., exhibit much better electrochemical performance than the pristine LiMnPO_4 . Yang *et al.*²⁴ synthesized a $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ composite using a co-precipitation method, which provided a specific capacity of 160.6 mA h g^{-1} at 0.05C. Xiang *et al.*²⁵ reported the template-engaged synthesis of $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4/\text{C}$ porous spheres, and the spheres exhibited capacity retention of 90.7% over 100 cycles at 1C. In general, the reversible capacity of $\text{LiFe}_y\text{Mn}_{1-y}\text{PO}_4$ increases with an increase in the Fe content. However, high Fe content reduces the energy density of

$\text{LiFe}_y\text{Mn}_{1-y}\text{PO}_4$ due to the relatively low redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (3.5 V vs. Li/Li^+). More recently, the reported multiphase composites of $x\text{LiFePO}_4 \cdot y\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $x\text{LiMnPO}_4 \cdot y\text{Li}_3\text{V}_2(\text{PO}_4)_3$ presented superior rate capability than individual LiFePO_4 and LiMnPO_4 , respectively.^{26–30} The electrochemical activity of LiFePO_4 and LiMnPO_4 can be obviously enhanced by blending with the fast ion conductor $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.^{31–33} For example, Qin *et al.*³⁴ prepared $(1-x)\text{LiMnPO}_4 \cdot x\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites through a solid-state method, and $0.6\text{LiMnPO}_4 \cdot 0.4\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ showed much larger capacity of 130 mA h g^{-1} at 0.1C than 76 mA h g^{-1} of pristine LiMnPO_4/C . According to the abovementioned studies, a novel strategy of combining the advantages of a solid solution and multiphase composite was proposed to prepare high-performance LiMnPO_4 -based composite cathode materials.³⁵ Wu *et al.*³⁶ reported the synthesis of $5\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$, which showed satisfactory performance with the specific capacity of 158 mA h g^{-1} at 0.05C as compared to 70 mA h g^{-1} of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4/\text{C}$. Although $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is a fast rate cathode for rechargeable lithium batteries, the theoretical capacity of 133 mA h g^{-1} while charging to 4.3 V is relatively lower. Furthermore, the cost of V is much higher than that of Mn or Fe; thus, the high cost of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ restricts its large-scale application in power batteries. Based on the cost and performance of the cathode material, $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ incorporated with a small quantity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ may be a feasible choice.

The simple solid-state reaction method has been widely employed in industry to prepare various cathode materials for lithium batteries. However, the nanoparticles tend to aggregate and grow further during the high-temperature calcination. The big particle size usually causes slow lithium ion diffusion in the polyanionic cathode materials. To synthesize high dispersing nanoparticles using a solid-state reaction, several surfactants,

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such as oleic acid,^{37,38} poly(acrylic acid),³⁹ Tween,⁴⁰ Span,⁴¹ *etc.*, have been introduced to suppress the particle growth and aggregation. In this study, we described a facile solid-state synthesis of $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocomposites using lauric acid as a surfactant and carbon source. Moreover, physical characterization and electrochemical properties of $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ were studied in detail.

2. Experimental

Stoichiometric amounts of Li_2CO_3 , $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, FeC_2O_4 , NH_4VO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, and lauric acid were mixed with ethanol media and ball-milled in a zirconia container at 400 rpm for 5 h. The molar ratio of Li/lauric acid was 1 : 2.5. The obtained precursor mixture was pre-decomposed at 350 °C for 4 h and subsequently heated at 700 °C under an Ar/ H_2 atmosphere (7% H_2) for 10 h to yield the $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite. For comparison, the LiMnPO_4/C and $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ composites were synthesized in a similar manner. LiMnPO_4/C , $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$, and $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ have been abbreviated as LMP/C, LMFP/C, and 6LMFP·LVP/C, respectively.

The phase structure was determined using a powder X-ray diffractometer (XRD, Rigaku D/max-2550VL/PC, Cu K α radiation), operating at 40 kV and 200 mA. The morphology, carbon layer, and elemental distribution of the as-synthesized composites were characterized by scanning electron microscopy (SEM, Hitachi-SU8020) and high-resolution transmission electron microscopy (HRTEM, JEOL-2100F) equipped with an energy dispersive X-ray spectroscopy (EDS). The carbon amounts of all the composites were evaluated by an elemental analyzer (Vario EL Cube). The chemical composition of the cathode material was analyzed *via* inductively coupled plasma atomic emission spectroscopy (ICP, iCAP 7600).

The electrochemical properties of the LMP/C, LMFP/C, and 6LMFP·LVP/C composites were studied using coin cells with lithium-foil as the anode and Entek ET20-26 membrane as the separator. The cathode consisted of 80 wt% active composite, 10 wt% Super P conducting carbon, and 10 wt% poly(vinylidene fluoride). A 1 M solution of LiPF_6 in the mixed solvents of ethylene carbonate and dimethyl carbonate (1 : 1, v/v) acted as the electrolyte. The charge–discharge measurements were performed using a battery testing system (LANHE CT2001) in the voltage range of 2.0–4.5 V and 2.0–4.8 V, respectively. The elevated temperature performance of 6LMFP·LVP/C was also determined at 50 °C. The cyclic voltammogram (CV) and electrochemical impedance spectra (EIS) were obtained using an electrochemical analyzer (CHI 650D).

3. Results and discussion

Fig. 1 presents the XRD patterns of the as-synthesized composites and Rietveld refinement of 6LMFP·LVP/C. The sharp diffraction peaks of LMP/C can be fully assigned to the olivine-type crystal structure with the *Pnmb* space group (JCPDS no. 74-0375). Moreover, the diffraction peaks of LMFP/C are similar to those of LMP/C without any indefinite peak,

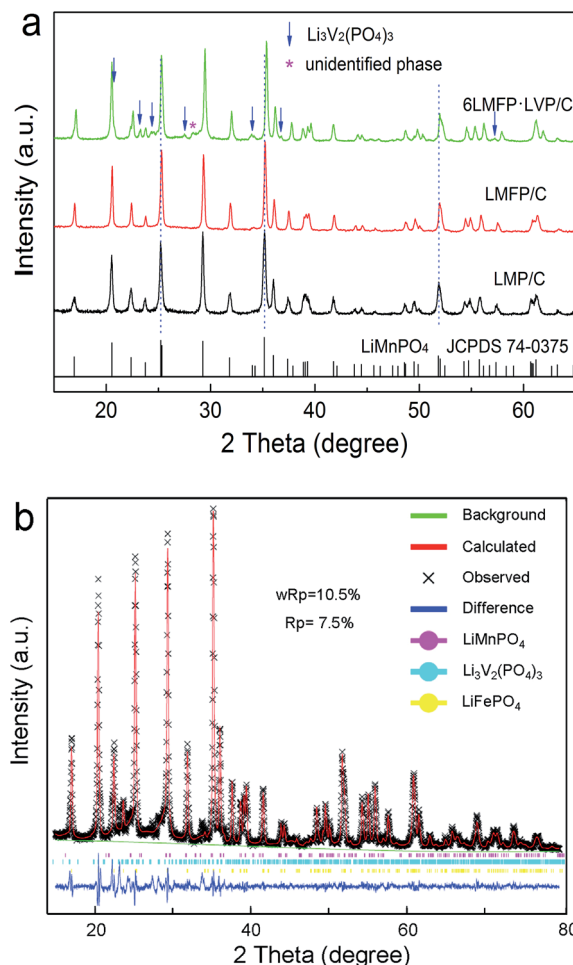


Fig. 1 XRD patterns of the as-synthesized composites (a) and Rietveld refinement of 6LMFP·LVP/C (b).

indicating the pure solid solution phase of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$. Both the $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phases were observed in the 6LMFP·LVP/C composite with a small unidentified phase at 28.3°. The diffraction peaks of LMFP/C and 6LMFP·LVP/C slightly shifted to higher 2θ angles relative to those of LMP/C, which may be attributed to the smaller ionic radius of Fe^{2+} (0.78 Å) and V^{3+} (0.74 Å) than that of Mn^{2+} (0.80 Å). The lattice parameters of the olivine phase in LMP/C, LMFP/C, and 6LMFP·LVP/C composites, analyzed *via* Rietveld refinement, are compared in Table 1. The cell volume of LiMnPO_4 decreases when Fe is introduced, and it further decreases when $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is incorporated, which indicates that some Fe and V diffuse into the LiMnPO_4 host lattice. Previous studies have revealed that doping LiMnPO_4 with Fe^{2+} and V^{3+} could improve the electronic and electrochemical kinetics.^{5,31,32}

Table 1 Lattice parameters of the olivine phase in the composites

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
LMP	6.0942	10.4358	4.7487	302.01
LMFP	6.0671	10.4262	4.7358	299.57
6LMFP·LVP	6.0558	10.4168	4.7273	298.21



Fig. 2a–c show the SEM images of the LMP/C, LMFP/C, and 6LMFP·LVP/C powders. All the samples illustrate similar nanoparticles morphology with the size of *ca.* 100–150 nm and narrow distribution. The TEM images (Fig. 2d and e) exhibit that the well-dispersed 6LMFP·LVP/C granules are

interconnected by the amorphous carbon layer rather than agglomerated into larger blocks. A homogenous carbon layer formed from the pyrolysis of lauric acid is tightly coated on the surface of the 6LMFP·LVP nanoparticles in a thickness of *ca.* 3 nm. The carbon contents evaluated by elemental analysis are

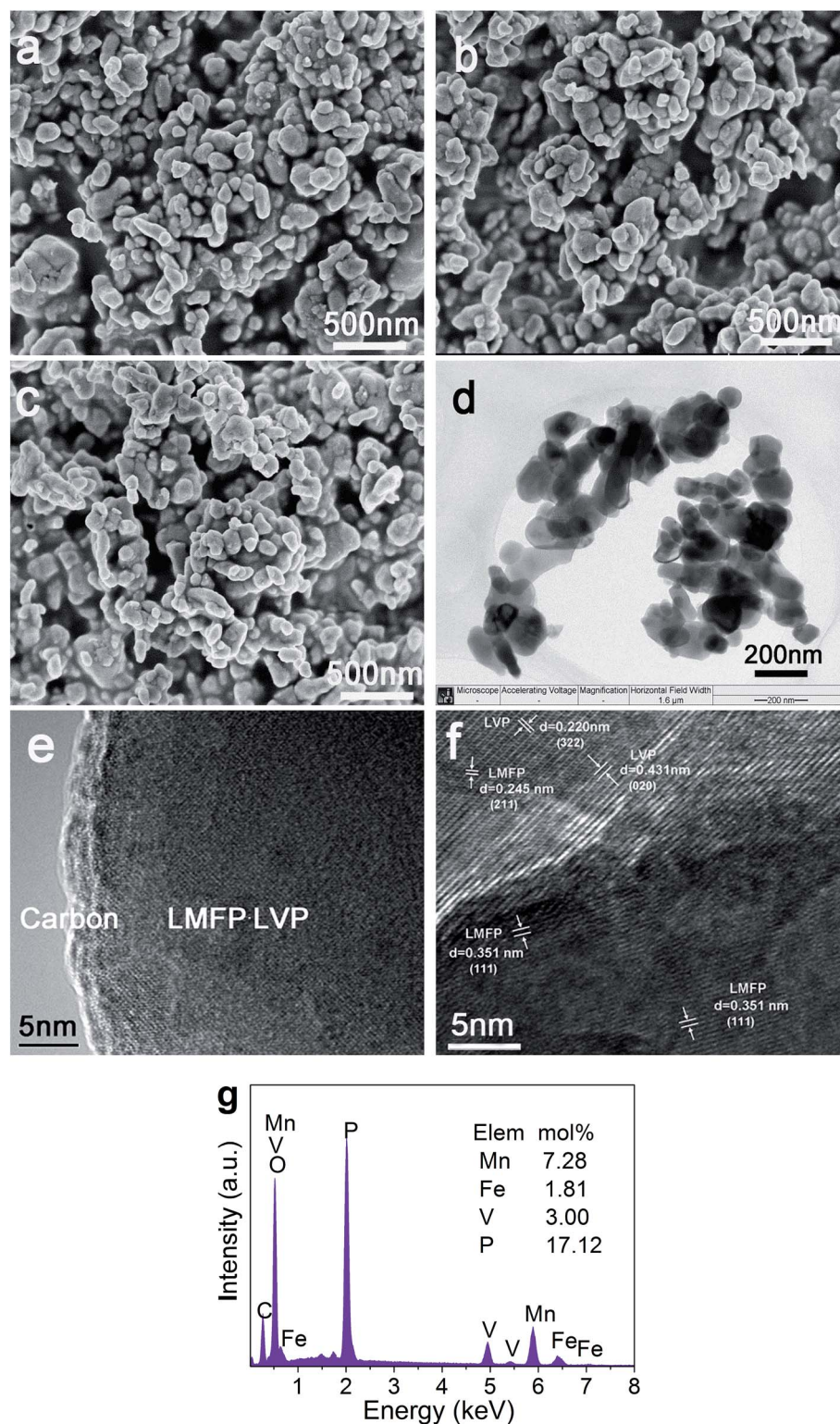


Fig. 2 SEM images of LMP/C (a), LMFP/C (b), and 6LMFP·LVP/C (c); TEM images (d and e), HRTEM image (f), and EDS pattern (g) of 6LMFP·LVP/C.



6.27 wt%, 6.32 wt%, and 6.43 wt% for the LMP/C, LMFP/C, and 6LMFP·LVP/C powders, respectively. The phase compositions of 6LMFP·LVP/C are indicated in the HRTEM image (Fig. 2f). The interplanar spacing of 0.351 and 0.245 nm correspond to the (111) and (211) planes of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$, whereas the interplanar spacing of 0.431 nm and 0.220 are attributed to the (020) and (322) planes of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The results imply that both $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phases coexist in the 6LMFP·LVP/C composite particles. The EDS spectrum of 6LMFP·LVP/C (Fig. 2g) displays the characteristic peaks of Mn, Fe, V, P, O, and C. The molar ratio of Mn : Fe : V is 7.28 : 1.81 : 3.00, which is basically in accordance with the theoretical ratio of 2.4 : 0.6 : 1. The chemical composition of 6LMFP·LVP/C was further measured by ICP and is listed in Table 2.

Fig. 3 illustrates the formation procedure of 6LMFP·LVP/C. Lauric acid ($\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$) is a saturated fatty acid with a relatively low melting point of 44 °C. During the heating process, lauric acid can form a molten media in which the carboxylic groups of lauric acid conjugate the inorganic cations and the long carbon chains separate the precursors. Thus, the 6LMFP·LVP crystallites can grow in a confined environment. Moreover, the crystallites are enveloped in an *in situ* conductive carbon layer generated from the decomposition of lauric acid. This effectively restrains the aggregation of the nanoparticles and further growth. Lauric acid, acted as a surfactant and carbon source, is favorable for fabricating granular nanocomposites with good dispersion. The distribution of the elements in 6LMFP·LVP/C was characterized by EDS. As shown in Fig. 4, the elements Mn, Fe, V, and P are homogeneously dispersed in every 6LMFP·LVP/C nanoparticle, such as a particle marked as A. The EDS mappings, together with HRTEM image (Fig. 2f), indicate that the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase uniformly diffuses into the $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ matrix, forming a multiphase dispersoid rather than existing as individual $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles.

Fig. 5a shows the initial charge–discharge curves of the LMP/C, LMFP/C, and 6LMFP·LVP/C composites. The cells were charged to 4.5 V at 0.1C rate (17 mA g^{−1}), kept at 4.5 V until the current decreased to 0.02C, and then discharged to 2.0 V at 0.1C rate. As observed for LMP/C, a pair of sloping voltage plateaus (4.22/3.93 V) corresponds to the phase transition of $\text{LiMnPO}_4 \leftrightarrow \text{MnPO}_4$.^{1,2} Compared with LMP/C, LMFP/C presents another pair of voltage plateaus (3.62/3.58 V), associating with the phase transition of $\text{LiFePO}_4 \leftrightarrow \text{FePO}_4$.^{9,10} For the 6LMFP·LVP/C sample, three pairs of voltage plateaus (3.59/3.58, 3.68/3.66,

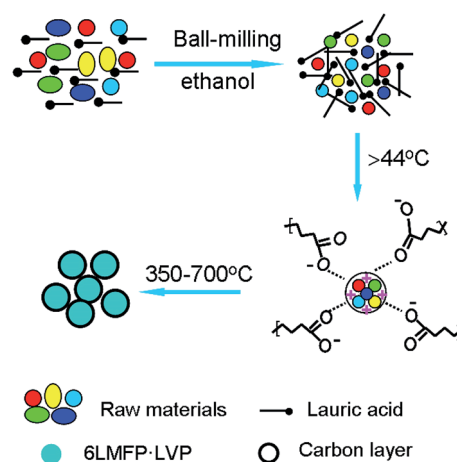


Fig. 3 Schematic of the synthesis of carbon-coated 6LMFP·LVP.

4.08/4.02 V) are assigned to the sequential phase transitions of $\text{Li}_3\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{LiV}_2(\text{PO}_4)_3$,^{32,36,42} respectively. However, the charge plateau of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is invisible because of overlapping with the plateau of $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ (x from 3 to 2.5). Note that the voltage difference between the charge and discharge plateaus corresponding to $\text{LiMnPO}_4 \leftrightarrow \text{MnPO}_4$ decreases when Fe is introduced and further decreases when $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is introduced, demonstrating smaller polarization and higher electrochemical kinetics. Moreover, the initial discharge capacity reaches 162 mA h g^{−1} for the 6LMFP·LVP/C sample at 0.1C rate, whereas it reaches 144 mA h g^{−1} for LMFP/C and 124 mA h g^{−1} for LMP/C under the same conditions.

Fig. 5b exhibits the rate capabilities of the LMP/C, LMFP/C, and 6LMFP·LVP/C composites. Obviously, the rate capability of 6LMFP·LVP/C is superior to those of LMFP/C and LMP/C. The discharge capacities of 6LMFP·LVP/C at 0.5, 1, and 2C rates are 150, 146, and 139 mA h g^{−1}, compared to 133, 125, and 111 mA h g^{−1} for LMFP/C and 111, 102, and 92 mA h g^{−1} for LMP/C. Even at 5C, a higher discharge capacity of 128 mA h g^{−1} for 6LMFP·LVP/C was achieved. The rate performance of the as-prepared 6LMFP·LVP/C nanocomposite exceeded those of the reported $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$,¹³ $0.5\text{LiMnPO}_4 \cdot 0.5\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$,³⁰ $5\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (ref. 36), and $0.95\text{LiMn}_{0.95}\text{Fe}_{0.05}\text{PO}_4 \cdot 0.05\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (ref. 35) composites. The cycling stabilities of LMP/C, LMFP/C, and 6LMFP·LVP/C were characterized at 0.5C after the rate capability test. It can be observed that the discharge capacities of these composites decrease with the increasing C-rate. More importantly, when the discharge rate returns to 0.5C after testing at 5C, the capacities of three composites resumed the former state and faded less than 5% after subsequent 100 cycles, implying high electrochemical reversibility and structural stability for all the samples. The superior high-rate performance of 6LMFP·LVP/C could be attributed to its unique heterogeneous nanostructures. First, the collaborative effect of Fe and V co-doping and the complete conductive carbon coating effectively promote the electrical conductivity in the bulk phase and at the surface, respectively.³ Second, the dispersion of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ crystallites in the

Table 2 Molar ratio of the prepared 6LMFP·LVP/C measured by ICP

Element	Molar ratio	
	Theoretical	6LMFP·LVP/C
Li	4.5	4.63
Mn	2.4	2.43
Fe	0.6	0.58
V	1	1
P	4.5	4.42



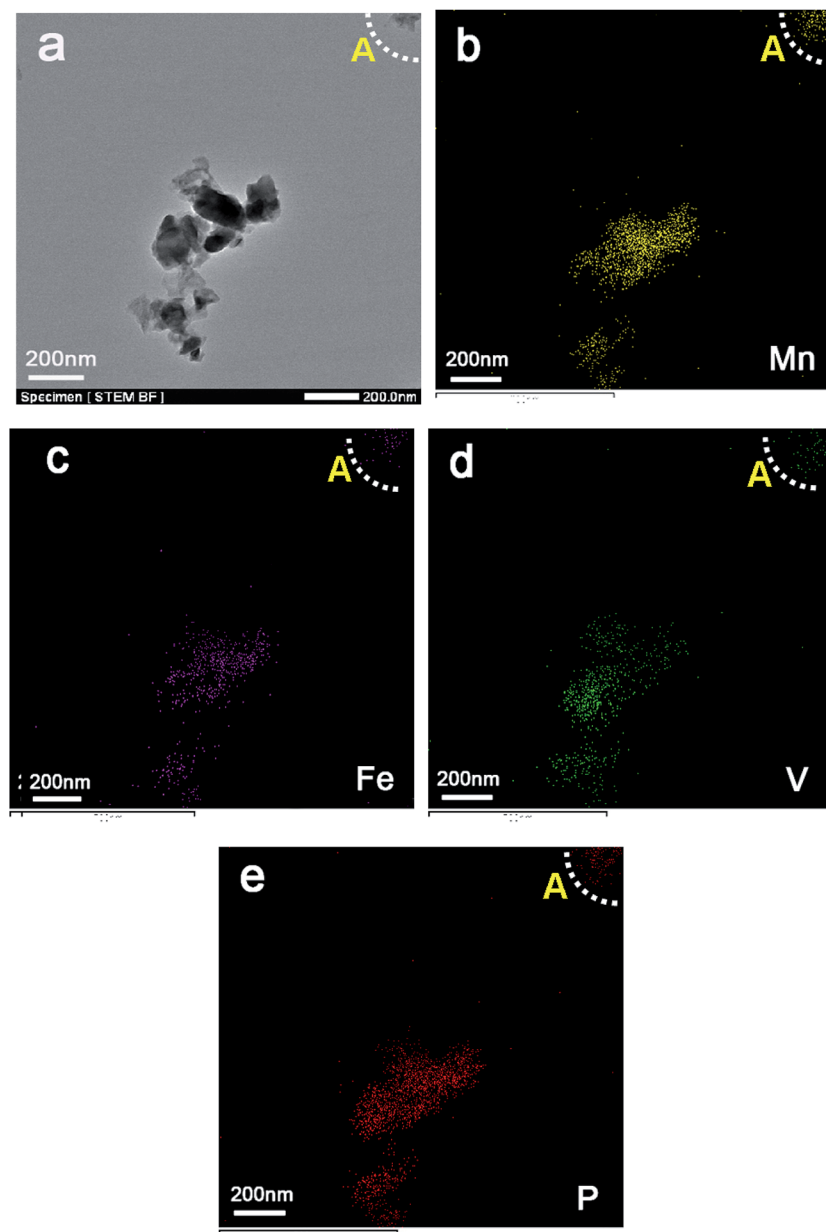


Fig. 4 EDS mappings of 6LMFP·LVP/C for Mn, Fe, V, and P.

$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ matrix reduces the Li^+ diffusion pathway in bulk LiMnPO_4 , which facilitates faster Li-ion intercalation kinetics.

The electrochemical performance of the 6LMFP·LVP/C composite cycled in a wide voltage range of 2.0–4.8 V was also been investigated. Fig. 6a displays the typical charge–discharge curves of 6LMFP·LVP/C at 0.1C and 0.5C. When the end-of-charge voltage extended to 4.8 V, another plateau at 4.52 V in the charge curve was observed, which belonged to the extraction of the third Li^+ from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The charge and discharge capacities of 6LMFP·LVP/C at the second cycle are 178 and 167 mA h g^{-1} at 0.1C rate, respectively, with the corresponding coulombic efficiency of 93.8%. At a 0.5C rate, a discharge capacity of 143 mA h g^{-1} was still

achieved, and the capacity retention was as high as 91% at the end of 250 cycles. The slight capacity loss may be induced by the deterioration of the electrode/electrolyte interface, resulting from the electrolyte decomposition at high potential.

Fig. 7 describes the charge–discharge curve and cycle life (inset) of 6LMFP·LVP/C at 50 °C. In comparison with the charge–discharge curve obtained at room temperature, as shown in Fig. 5a, 6LMFP·LVP/C presents smaller hysteresis between charge and discharge and flatter charge plateau of $\text{Mn}^{3+}/\text{Mn}^{2+}$ at elevated temperature. Furthermore, the charge plateaus of $\text{Fe}^{3+}/\text{Fe}^{2+}$ (3.55 V) and $\text{V}^{5+}/\text{V}^{4+}$ (4.47 V) can be distinctly observed, demonstrating its improved electrode kinetics at high temperature. The 6LMFP·LVP/C delivers



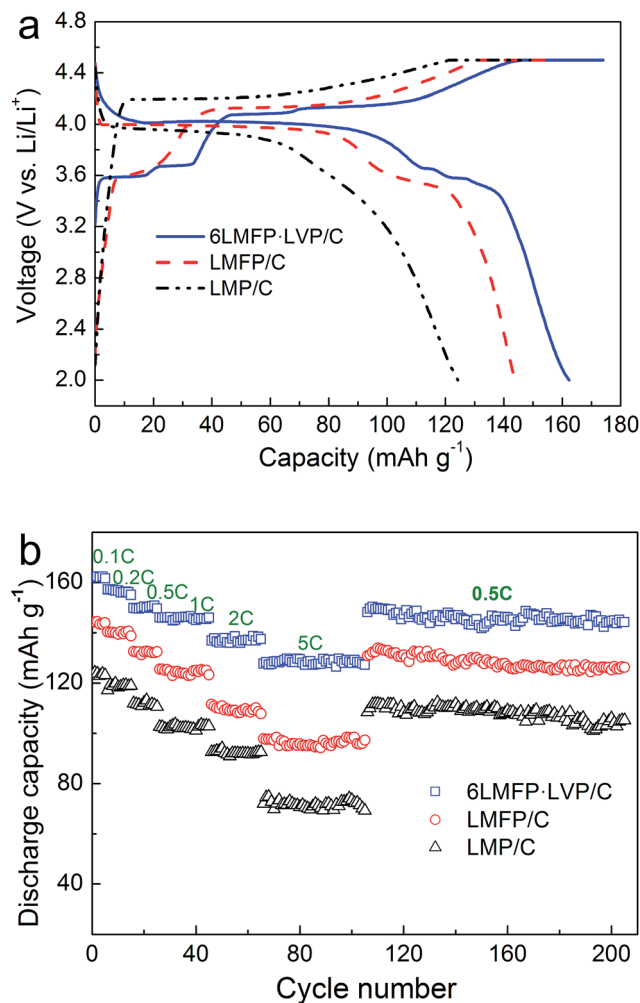


Fig. 5 Charge–discharge curves at 0.1C rate (a) and rate capabilities (b) of LMP/C, LMFP/C and 6LMFP·LVP/C.

a large reversible capacity of 154 mA h g⁻¹ at 1C rate and provides a capacity retention of about 90% over 100 cycles, illustrating a good high-temperature stability of the electrode.

To further clarify the synergistic effects of the solid solution and multiphase composition, cyclic voltammetry was employed to analyze the lithiation/delithiation behavior. Fig. 8 compares the CV curves of LMP/C, LMFP/C, and 6LMFP·LVP/C electrodes at a scan speed of 0.1 mV s⁻¹. One couple peak located at 3.68/3.51 V for LMFP/C and three couple peaks located at 3.62/3.57, 3.70/3.65, and 4.11/4.04 V for 6LMFP·LVP/C are ascribed to the redox of Fe³⁺/Fe²⁺ and V⁴⁺/V³⁺, respectively. The peak couples at 4.33/3.92 for LMP/C, 4.23/3.92 for LMFP/C, and 4.20/3.95 V for 6LMFP·LVP/C are associated with the redox of Mn³⁺/Mn²⁺. More significantly, the separation potentials between the Mn³⁺/Mn²⁺ redox peaks decrease from 0.41 V of LMP/C to 0.31 V of LMFP/C and 0.25 V of 6LMFP·LVP/C. The abovementioned results are in accordance with the charge–discharge curves, which suggest that the electrochemical activity of LiMnPO₄ is remarkably enhanced by the appropriate Fe substitution and combination of Li₃V₂(PO₄)₃.

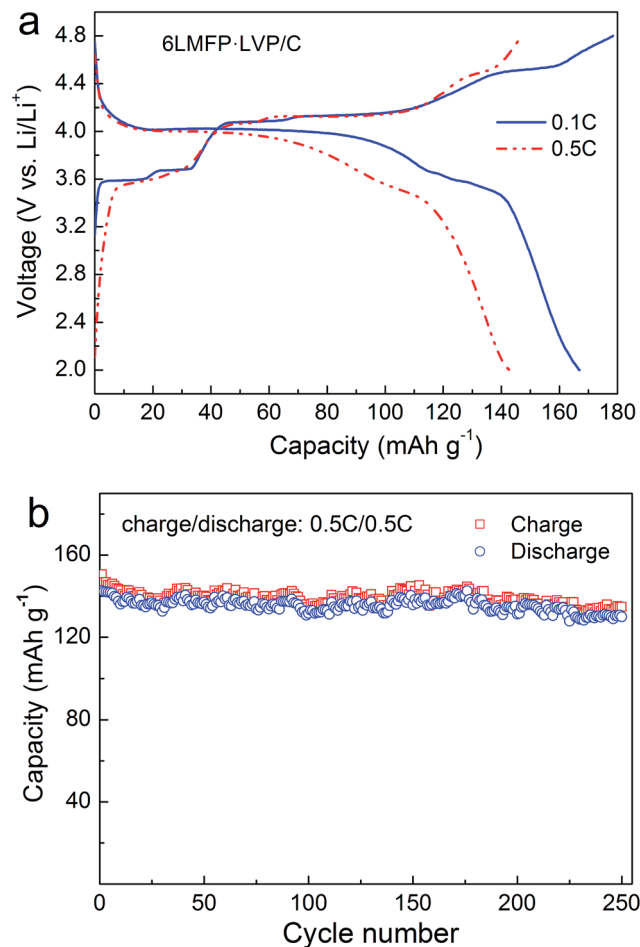


Fig. 6 Charge–discharge curves (a) and cycling performance (b) of 6LMFP·LVP/C between 2.0 and 4.8 V.

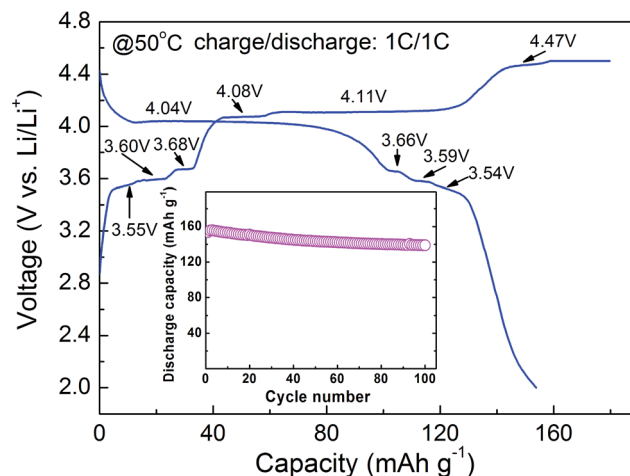


Fig. 7 Charge–discharge curve and cycle life (inset) of 6LMFP·LVP/C at 50 °C.

Fig. 9 shows the AC impedance spectra of LMP/C, LMFP/C, and 6LMFP·LVP/C electrodes at the fully discharged state after 100 cycles. All the spectra present a depressed semicircle in



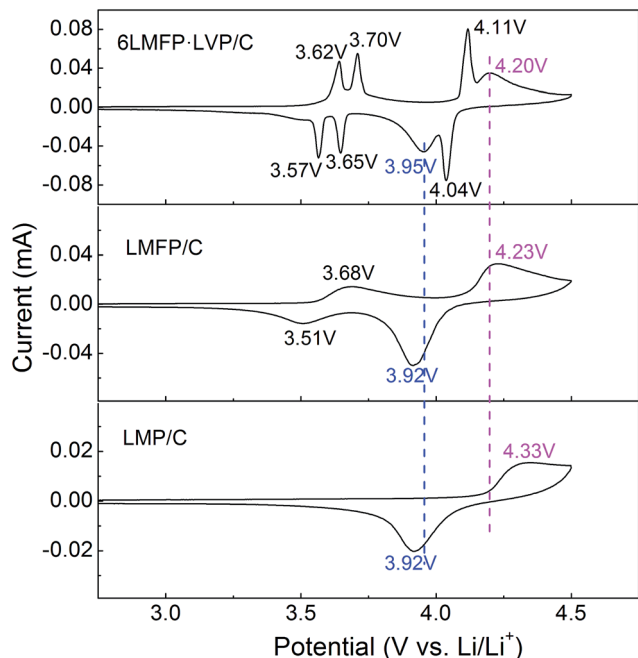


Fig. 8 CV curves of the LMP/C, LMFP/C, and 6LMFP·LVP/C electrodes.

the high-medium frequency region, corresponding to the charge-transfer impedance at the electrode/electrolyte interface, and a straight line in the low frequency region, relating to the Li^+ diffusion in the electrode material. The slope of the straight line is proportional to the Li^+ diffusion coefficient.^{13,42} By comparing the diameter of the semicircles and the slope of the straight lines, it was found that 6LMFP·LVP/C exhibits smaller interface impedance and much faster Li^+ diffusion than LMFP/C and LMP/C. This demonstrates that the electronic and ionic conductivity of 6LMFP·LVP/C are better than those of LMFP/C and LMP/C and also clarifies the fast rate capability of 6LMFP·LVP/C.

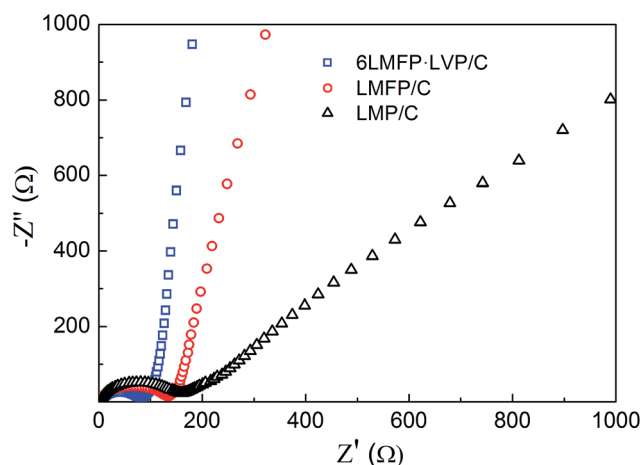


Fig. 9 EIS spectra of the LMP/C, LMFP/C, and 6LMFP·LVP/C electrodes after 100 cycles.

4. Conclusions

The $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite with the size of ca. 100–150 nm was successfully synthesized *via* a surfactant-assisted solid-state method employing lauric acid as a surfactant and carbon source. The use of lauric acid is beneficial for the fabrication of uniform nanoparticles with high dispersion. XRD and EDS mapping illustrate that the composite consists of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phases, and the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase uniformly diffuses into the $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ matrix. The $6\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite exhibits much higher specific capacity and better rate capability than the individual $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ and LiMnPO_4/C . The enhanced electrochemical performance of the multiphase composite demonstrates its use as a promising cathode material for high-power lithium ion batteries.

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References

- 1 S. M. Oh, S. W. Oh, C. S. Yoon, B. Scrosati, K. Amine and Y. K. Sun, *Adv. Funct. Mater.*, 2010, **20**, 3260–3265.
- 2 T. Drezen, N.-H. Kwon, P. Bowen, I. Teerlinck, M. Isono and I. Exnar, *J. Power Sources*, 2007, **174**, 949–953.
- 3 C. Hu, H. Yi, H. Fang, B. Yang, Y. Yao, W. Ma and Y. Dai, *Electrochem. Commun.*, 2010, **12**, 1784–1787.
- 4 J. Xiong, Y. Wang, Y. Wang and J. Zhang, *Ceram. Int.*, 2016, **42**, 9018–9024.
- 5 S. Novikova, S. Yaroslavlsev, V. Rusakov, A. Chekannikov, T. Kulova, A. Skundin and A. Yaroslavlsev, *J. Power Sources*, 2015, **300**, 444–452.
- 6 Y. Hong, Z. Tang, Z. Hong and Z. Zhang, *J. Power Sources*, 2014, **248**, 655–659.
- 7 S. Li, Z. Su, A. Muslim, X. Jiang and X. Wang, *Ceram. Int.*, 2015, **41**, 11132–11135.
- 8 R. V. Hagen, H. Lorrman, K.-C. Möller and S. Mathur, *Adv. Energy Mater.*, 2012, **2**, 553–559.
- 9 L. Chen, Y.-Q. Yuan, X. Feng and M.-W. Li, *J. Power Sources*, 2012, **214**, 344–350.
- 10 S.-Y. Yan, C.-Y. Wang, R.-M. Gu, S. Sun and M.-W. Li, *J. Alloys Compd.*, 2015, **628**, 471–479.
- 11 F. Ye, L. Wang, X. He, M. Fang, Z. Dai, J. Wang, C. Huang, F. Lian, J. Wang, G. Tian and M. Ouyang, *J. Power Sources*, 2014, **253**, 143–149.



- 12 P. Zuo, G. Cheng, L. Wang, Y. Ma, C. Du, X. Cheng, Z. Wang and G. Yin, *J. Power Sources*, 2013, **243**, 872–879.
- 13 B. Z. Li, Y. Wang, L. Xue, X. P. Li and W. S. Li, *J. Power Sources*, 2013, **232**, 12–16.
- 14 L. Yang, Y. Xia, L. Qin, G. Yuan, B. Qiu, J. Shi and Z. Liu, *J. Power Sources*, 2016, **304**, 293–300.
- 15 L. Yang, Y. Xia, X. Fan, L. Qin, B. Qiu and Z. Liu, *Electrochim. Acta*, 2016, **191**, 200–206.
- 16 Q.-Q. Zou, G.-N. Zhu and Y.-Y. Xia, *J. Power Sources*, 2012, **206**, 222–229.
- 17 J. Liu, W. Liao and A. Yu, *J. Alloys Compd.*, 2014, **587**, 133–137.
- 18 Y. P. Huang, T. Tao, Z. Chen, W. Han, Y. Wu, C. Kuang, S. Zhou and Y. Chen, *J. Mater. Chem. A*, 2014, **2**, 18831–18837.
- 19 C. Xu, L. Li, F. Qiu, C. An, Y. Xu, Y. Wang, Y. Wang, L. Jiao and H. Yuan, *J. Energy Chem.*, 2014, **23**, 397–402.
- 20 Z.-X. Chi, W. Zhang, X.-S. Wang, F.-Q. Cheng, J.-T. Chen, A.-M. Cao and L.-J. Wan, *J. Mater. Chem. A*, 2014, **2**, 17359–17365.
- 21 Y. Mi, P. Gao, W. Liu, W. Zhang and H. Zhou, *J. Power Sources*, 2014, **267**, 459–468.
- 22 W. Liu, P. Gao, Y. Mi, J. Chen, H. Zhou and X. Zhang, *J. Mater. Chem. A*, 2013, **1**, 2411–2417.
- 23 X. Yang, Y. Mi, W. Zhang, B. Wu and H. Zhou, *J. Power Sources*, 2015, **275**, 823–830.
- 24 W. Yang, Y. Bi, Y. Qin, Y. Liu, X. Zhang, B. Yang, Q. Wu, D. Wang and S. Shi, *J. Power Sources*, 2015, **275**, 785–791.
- 25 W. Xiang, E.-H. Wang, M.-Z. Chen, H.-H. Shen, S.-L. Chou, H. Chen, X.-D. Guo, B.-H. Zhong and X. Wang, *Electrochim. Acta*, 2015, **178**, 353–360.
- 26 C. Gao, H. Liu, G. Liu, J. Zhang and W. Wang, *Mater. Sci. Eng., B*, 2013, **178**, 272–276.
- 27 Y. Guo, Y. Huang, D. Jia, X. Wang, N. Sharma, Z. Guo and X. Tang, *J. Power Sources*, 2014, **246**, 912–917.
- 28 J.-f. Zhang, C. Shen, B. Zhang, J.-c. Zheng, C.-l. Peng, X.-w. Wang, X.-b. Yuan, H. Li and G.-m. Chen, *J. Power Sources*, 2014, **267**, 227–234.
- 29 B. Zhang, X.-w. Wang and J.-f. Zhang, *RSC Adv.*, 2014, **4**, 49123–49127.
- 30 S. Li, Z. Su and X. Wang, *RSC Adv.*, 2015, **5**, 80170–80175.
- 31 F. Wang, J. Yang, Y. NuLi and J. Wang, *Electrochim. Acta*, 2013, **103**, 96–102.
- 32 C. Wang, Y. Bi, Y. Liu, Y. Qin, Y. Fang and D. Wang, *J. Power Sources*, 2014, **263**, 332–337.
- 33 S. Zhong, L. Wu, J. Zheng and J. Liu, *Powder Technol.*, 2012, **219**, 45–48.
- 34 L. Qin, Y. Xia, B. Qiu, H. Cao, Y. Liu and Z. Liu, *J. Power Sources*, 2013, **239**, 144–150.
- 35 L. Chen, B. Yan, H. Wang, X. Jiang and G. Yang, *J. Power Sources*, 2015, **287**, 316–322.
- 36 L. Wu, J. Lu, G. Wei, P. Wang, H. Ding, J. Zheng, X. Li and S. Zhong, *Electrochim. Acta*, 2014, **146**, 288–294.
- 37 X. Zhou, Y. Xie, Y. Deng, X. Qin and G. Chen, *J. Mater. Chem. A*, 2015, **3**, 996–1004.
- 38 L. Zhang, Q. Qu, L. Zhang, J. Li and H. Zheng, *J. Mater. Chem. A*, 2014, **2**, 711–719.
- 39 M. Secchiaroli, F. Nobili, R. Tossici, G. Giuli and R. Marassi, *J. Power Sources*, 2015, **275**, 792–798.
- 40 Q. Li, F. Zheng, Y. Huang, X. Zhang, Q. Wu, D. Fu, J. Zhang, J. Yin and H. Wang, *J. Mater. Chem. A*, 2015, **3**, 2025–2035.
- 41 F. Zheng, C. Yang, X. Ji, D. Hu, Y. Chen and M. Liu, *J. Power Sources*, 2015, **288**, 337–344.
- 42 L. Mai, S. Li, Y. Dong, Y. Zhao, Y. Luo and H. Xu, *Nanoscale*, 2013, **5**, 4864–4869.

