

Research Article

An Alternative Synthesis Route of LiFePO_4 -Carbon Composites for Li-Ion Cathodes

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LiFePO_4 -Carbon (LFP/C) composites with high purity and good crystallinity were prepared by an improved environmentally benign and low-cost solvothermal method. Capping agent polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG-400) showed no significant dispersive effect during the synthesis. These capping agents were converted into networking carbons after annealing, which consequently improved the charge and discharge performance. It was able to deliver a high initial discharge specific capacity of 154.1 mAh g^{-1} for sample prepared with PVP and 145.6 mAh g^{-1} for sample prepared with PEG-400 while having great capacity retention. The rate capability and cycling performance of LFP/C samples prepared with PVP or PEG-400 at high current rates were significantly improved compared to the LFP/C sample prepared without a capping agent.

1. Introduction

Lithium-ion batteries with high potential, high energy density, and high reversible capacity are now considered as the most promising next generation power sources for future electric vehicles (EVs), hybrid EVs, and plug-in hybrid EVs [1, 2]. An ideal cathode material for lithium-ion batteries should have various advantages, such as high theoretical capacity, prominent long-term cycling performance, outstanding high-rate capability, environmental benignity, high safety, and low-cost abundant material [3]. LiFePO_4 (LFP) with the olivine structure has been developed to become one of the most successful cathode materials for large scale applications due to its relatively low cost, good electrochemical performance, and no negative impact on the environment [4]. However, some drawbacks, namely, poor electronic conductivity, low density, and low ionic diffusivity, limited the application of LFP [5]. To surmount these drawbacks, numerous techniques and strategies including carbon coating [6], mixing with conducting materials [7], reducing the particle size [8], anion doping [9], and supervalent cation doping [4, 10] have been developed, but the effect is still

controversial. Among other modifications than the above mentioned, nanostructured LFP has recently been gaining more and more concerns [11]. These nanosized LFP particles exhibited good cycling performance and excellent high-rate discharge property because of large reaction areas and faster transfer of electrons and lithium ions [12]. A great deal of work has been devoted to developing new synthetic methods for preparation of different forms of nanostructured LFP particles to search for favorable morphologies of this material [8, 12], such as hydrothermal/solvothermal synthesis [13–15], sol-gel approach [16, 17], precipitation method [18], spray pyrolysis [19], and hard-template synthesis [20]. Here, we report an alternative route to prepare LFP/C composite materials with high purity and good crystallinity by developing a mild solvothermal method, using low cost and abundant precursors. Two different low cost capping agents, PVP and PEG, were added during the preparation to improve the electrochemical performance of LFP/C composite. The galvanostatic charge/discharge characteristics and electrochemical impedance spectroscopy (EIS) results demonstrated that these modifications of LFP/Li battery exhibited significant improvement in their electrochemical performances.

2. Materials and Methods

For a typical preparation of LFP/C sample, the starting materials were $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_3PO_4 , $\text{LiOH} \cdot \text{H}_2\text{O}$ and citric acid with mole ratio 1 : 1 : 3 : 1/3. The $\text{LiOH} \cdot \text{H}_2\text{O}$ and H_3PO_4 were first dissolved in water and ethylene glycol mixing solvent (mole ratio 1:1) under ultrasonication. Then, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and citric acid were slowly added with stirring. All the starting materials were thoroughly dissolved into solution under ultrasonication prior to solvothermal reaction. The reaction mixture solution was transferred into a Teflon-lined autoclave of 50 mL capacity. After having been sealed, the autoclave was kept at 180°C for 6 hrs and then cooled down to room temperature. The solid grey-green precipitates were filtered, washed several times with absolute alcohol and distilled water, respectively, and then dried at 40°C for 8 hrs. PVP and PEG-400 were added, respectively, along with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to produce LFP samples with capping agents, while all other procedures were same as above. Sucrose was mixed with the prepared LFP samples (LFP : sucrose = 1 : 0.25, w/w) and then heated at 600°C for 6 hrs under N_2 gas flow to produce LFP/C samples.

X-ray diffraction (XRD) characterization was carried out with a Philips X'Pert Pro MPD X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM; Hitachi S-3400N II and JEOL JEM-2010F). FT-IR spectra were recorded with pressed KBr pellets using a Bruker Tensor 27 Fourier transform spectrophotometer. The carbon content of the LFP/C composite was evaluated by thermogravimetry (TG; NETZSCH STA 449F3) at a heating rate of 5°C min^{-1} from ambient temperature to 800°C in oxygen atmosphere. EIS was carried out with a CHI660D (Chenghua, Shanghai) electrochemistry workstation. The applied frequency range was 100 kHz to 0.01 Hz, and the oscillation voltage was 5 mV.

For cathode fabrication, LFP/C, ethylene black, and polyvinylidene fluoride (PVDF) were mixed at weight ratio 80 : 12 : 8. N-Methylpyrrolidone (NMP) was added and blended with a pestle and mortar. The mixture slurry was applied onto a round aluminum disk (1 cm diam.). The disk was dried at 100°C for 24 hrs to remove NMP and then pressed using hydrostatic press under 20 MPa. Pure lithium metal was used as an anode. Celgard2300 PPE micro film was used as a separator, and 1.0 mol/L $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1 : 1) was used as an electrolyte. CR2032 type button cell was assembled under nitrogen protection in Vigor VG1200/750TS vacuum glove box. Cells were tested using an automatic charge-discharge instrument (Model CT2001A, Land Co., China) in the cutoff voltage of 2.0–4.2 V.

3. Results and Discussion

IR spectrum of PO_4^{3-} usually shows four fundamental modes (ν_1 – ν_4) as follows: the symmetric stretching ν_1 at $\sim 965\text{ cm}^{-1}$, the doublet ν_2 at 466 – 503 cm^{-1} , the triplet ν_3 , and ν_4 at 1051 – 1093 cm^{-1} and 578 – 645 cm^{-1} , respectively [21, 22]. In an olivine LFP, FeO_6 octahedra are linked with PO_4^{3-} tetrahedron; therefore, the four fundamental modes

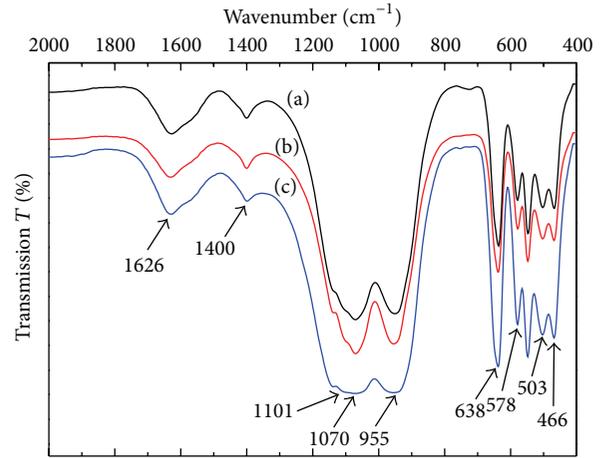


FIGURE 1: IR spectra of LFP samples: (a) no capping agent; (b) with PVP; (c) with PEG-400.

(ν_1 – ν_4) of PO_4^{3-} will split into many components due to the correlation effect induced by Fe-O units. All three samples clearly exhibited these fundamental modes of PO_4^{3-} at $955(\nu_1)$, $503/466(\nu_2)$, $1070/1101(\nu_3)$, and $638/578\text{ cm}^{-1}$ (ν_4), indicating that the LFP was well crystallized after solvothermal synthesis, which was consistent with the XRD analysis results (Figure 1). The peaks at 1626 cm^{-1} and 1400 cm^{-1} were due to the asymmetric stretch and symmetric stretch of carboxylate from the reducing agent of citric acid.

Figure 2 shows the SEM images of three different LFP/C composite samples. The particle sizes were in the range of 100 to 300 nm for all three samples. The particles shape and size were similar for all three samples, indicating that there was no significant dispersive effect for PVP and PEG-400. Instead, agglomeration could be seen in sample (c), which would be a major cause of the deterioration of the electrochemical performance of this material. The capping agent turned into networking carbons in the final composite particles after sintering, as seen in SEM, which would improve the conductivity of the cathode materials.

The XRD patterns of LFP/C samples were shown in a Figure 2 insert. The diffraction peaks of all three samples were indexed to an orthorhombic system with the space group $Pnma$. The Rietveld refinement on the XRD pattern was performed to obtain the lattice parameters (sample (a): $a = 1.040\text{ nm}$, $b = 0.609\text{ nm}$, and $c = 0.445\text{ nm}$; sample (b): $a = 1.012\text{ nm}$, $b = 0.614\text{ nm}$, and $c = 0.435\text{ nm}$; and sample (c): $a = 1.028\text{ nm}$, $b = 0.630\text{ nm}$, and $c = 0.470\text{ nm}$). The calculated data were consistent with standard pattern (JCPDS card 81-1173, $a = 1.0330\text{ nm}$, $b = 0.6010\text{ nm}$, and $c = 0.4692\text{ nm}$). The peaks of samples (b) and (c) were very sharp, intense, and symmetric which indicated that both of these samples are crystallized. But in sample (a), the mixed valence iron oxyphosphate Fe_2PO_5 (JCPDS card 75-2367) impurity could be defined as the derivative of $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$ due to its thermal decomposition and partial oxidation. With the addition of capping agents, the purity of LFP was substantially improved. No diffraction peaks were found for crystalline

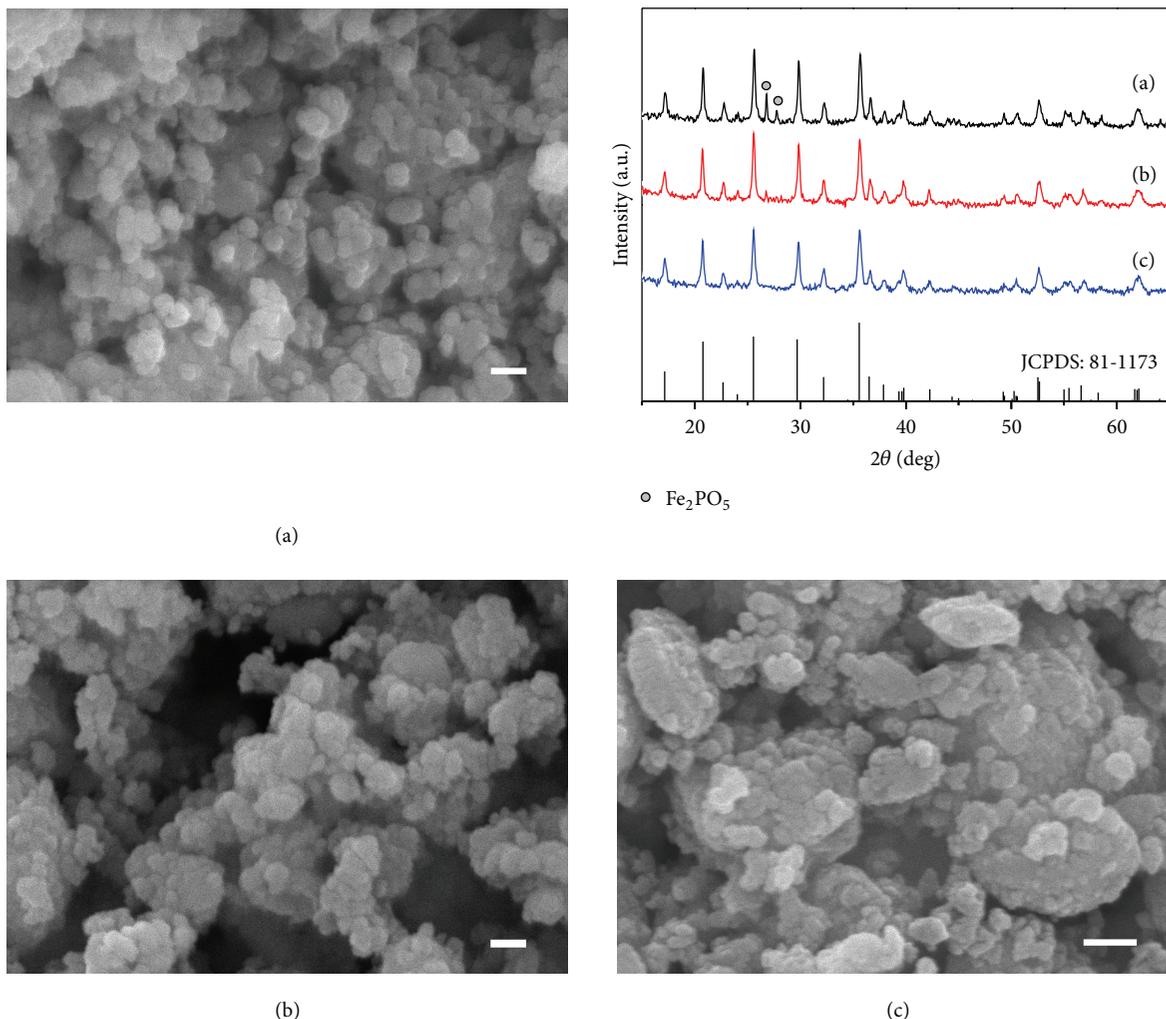


FIGURE 2: SEM images (scale bar 400 nm) and XRD spectra (insert) of LFP/C samples: (a) no capping agent; (b) with PVP; (c) with PEG-400.

carbon, so the carbon in the composite was amorphous with a small amount which was further confirmed by the thermogravimetric analysis.

The amount of carbon was determined by heating the coated LFP in oxygen (TG data in Figure 3). The mass drop seen for all samples below 230°C was due to the evaporation of absorbed water. The LFP could be completely oxidized from Fe(II) to Fe(III) in the temperature range of 300–400°C in oxygen atmosphere, which gave a theoretical 5.1% weight increase [23, 24]. The carbon content in LFP/C remained intact below 450°C. The amount of carbon coated on the olivine could be estimated by $\% \text{carbon} = (\text{total weight gain of LFP} - \text{total weight gain of LFP/C})$ [23]. The weight gain for sample (a) is 3.0% which was determined by the weight difference from the highest point to the plateau divided by the mass at the plateau. The carbon coating level for sample (a) was estimated as $5.1\% - 3.0\% = 2.1\%$. In a similar way, the carbon coating levels for sample (b) and sample (c) were estimated as 3.2% and 2.3%, respectively.

Figure 4 showed the electrochemical performance of LFP/C composite cathodes for three different samples.

The first cycle of charge and discharge profiles of LFP/C composite cathodes at 0.1 C between 2.0 and 4.2 V was presented in Figure 4(a). The flat voltage plateau at 3.4 V indicated the two-phase nature of lithium-ion extraction and insertion reaction between LiFePO_4 and FePO_4 which was very close to the theoretical value of 3.45 V [25]. Sample (b) displayed a longer discharge plateau than samples (a) and (c), which should be attributed to relatively better electric conducting characteristics of PVP-induced networking carbon and lower degree of polarization loss during the electrochemical reaction.

The rate capability and cycling performance were measured and plotted in Figure 4(b). LFP/C sample prepared with capping agent PVP had an initial discharge capacity of 154.1 mAh g^{-1} at 0.1 C. It exhibited a good rate capability with a high discharge capacity of 108.0 mAh g^{-1} and retained about 70% capacity at 0.5 C with an excellent cycling performance with no noticeable fade. It also delivered a specific capacity of 100.0 mAh g^{-1} at 1 C with a good power capability. LFP/C samples prepared with capping agent PEG-400 had an initial discharge capacity of 145.6 mAh g^{-1} at 0.1 C. It also exhibited

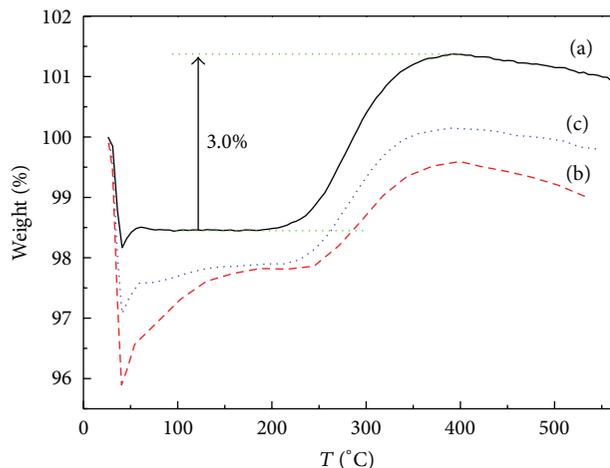
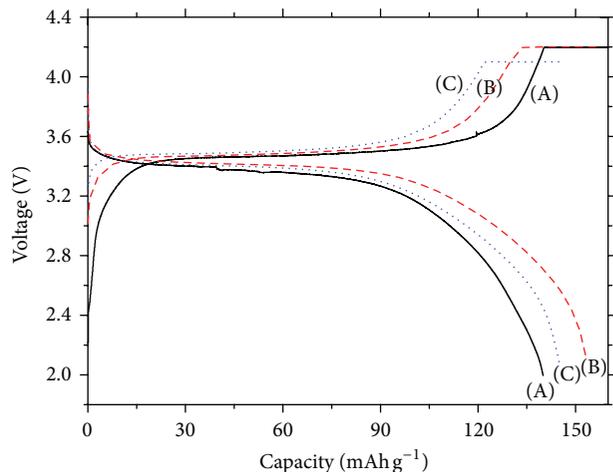


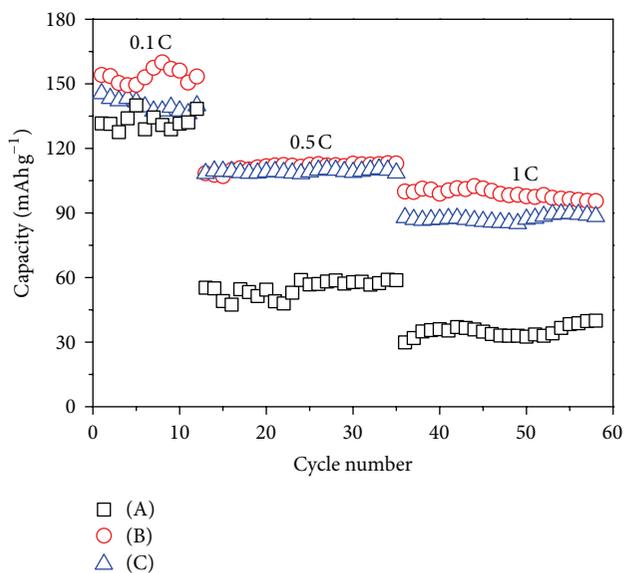
FIGURE 3: TG curves of LFP/C samples: (a) no capping agent; (b) with PVP; (c) with PEG-400.

a good rate capability with a high discharge capacity of 108.4 mAh g^{-1} at 0.5 C with an excellent cycling performance with no noticeable fade. It only delivered a specific capacity of 87.9 mAh g^{-1} at 1 C. The electrochemical performance of LFP/C sample prepared with PVP was superior to LFP/C sample prepared with PEG-400 which could be due to the higher carbon coating level that decreased the charge transfer resistance. Comparing to LFP/C prepared without capping agent, the electrochemical performance was greatly improved for capping agent assisted LFP/C samples due to the relatively higher carbon coating level and networking carbon of these samples.

Figure 5 showed the EIS of the LFP/C samples which were collected with a two-electrode coin cell after first charge-discharge cycle. The Nyquist plots of the LFP/C samples showed a semicircle, followed by a sloping line at low frequencies. The impedance spectra could be explained on the basis of an equivalent circuit with uncompensated resistance (R_u), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}), and the Warburg impedance (Z_w) [17, 26], as indicated in a Figure 5 insert. The high-frequency intercept of the semicircle gave the uncompensated resistance (R_u), which included the electrolyte resistance, particle-particle contact resistance, and the resistance between the electrode and the current collector. On the other hand, the diameter of the semicircle corresponded to the charge transfer resistance (R_{ct}), which was related to the electrochemical reaction at the electrode-electrolyte interface and particle-particle contact. The sloping line in the very low-frequency region was attributed to the Warburg impedance (Z_w), which was associated with the lithium-ion diffusion in the bulk of the active material. It was found that the R_{ct} showed a trend of LFP/C, with PVP < LFP/C, with PEG-400 < LFP/C. As the impedance was inversely proportional to electric conductivity, this suggested charge transfer rate with a trend of LFP/C with PVP > LFP/C with PEG-400 > LFP/C, which consisted well with their electrochemical performance. The slope of the impedance of LFP/C with PVP and LFP/C with



(a)



(b)

FIGURE 4: (a) Initial charge and discharge curves at 0.1 C, (b) cycling performance (discharge capacities versus cycle number) at different charge rates of LFP/C samples: (A) no capping agent; (B) with PVP; (C) with PEG-400.

PEG-400 samples in the low-frequency region was bigger than that of LFP/C without a capping agent, indicating that the capping agent indeed enhanced the electrochemical activity of LFP/C effectively.

4. Conclusions

In summary, LFP/C composites with high purity, good crystallinity, and great electrochemical performance were successfully prepared with a solvothermal method at relatively low temperature with cheap starting materials: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_3PO_4 , $\text{LiOH} \cdot \text{H}_2\text{O}$, and citric acid. The synthesized LFP/C composite materials exhibited very promising electrochemical performances. The initial discharge capacity reached

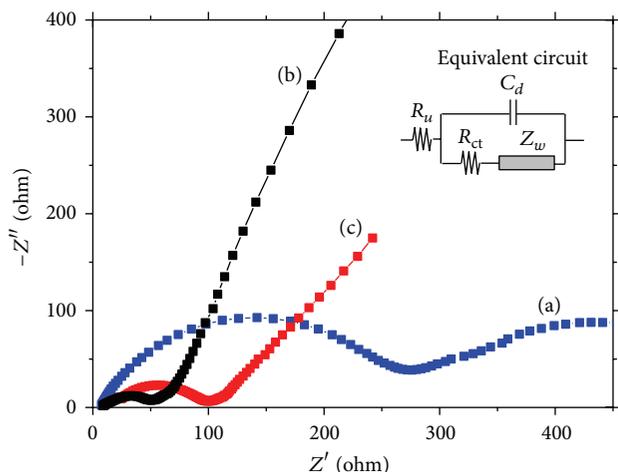


FIGURE 5: Impedance spectra of LFP/C samples: (a) no capping agent; (b) with PVP; (c) with PEG-400.

154.1 mAh g^{-1} and 145.6 mAh g^{-1} at 0.1C for samples prepared with PVP and PEG-400, respectively. The rate capability and cycling performance of LFP/C samples prepared with PVP or PEG-400 at high current rates were significantly improved compared to the sample prepared without a capping agent, which could be attributed to the higher networking carbon coating layer to decrease the charge transfer resistance.

Conflict of Interests

The authors declare that they have no direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of the authors.

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