

Synthesis and effect of forming Fe₂P phase on the physics and electrochemical properties of LiFePO₄/C materials

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Abstract

Series LiFePO₄/C materials have been prepared by a so-called reformative solid-coordination method, which uses citric acid as the coordination agent and carbon source. A monodenate coordination band of –COO–M was proved to form gradually and that would help to disperse Li⁺ or Fe²⁺ among the homogeneous gel during the grinding process. Impure phase Fe₂P was detected out among the LiFePO₄/C composites with increasing annealed temperature. The remnant coating carbon was considered to be the reductive under the pure nitrogen gas. The amounts of carbon, particle size and morphology were investigated in detail and all the results showed to be related to the formation of Fe₂P. The electro-conductive Fe₂P phase among LiFePO₄/C composites acts as important role in increasing electronic conductivity and evidently improves the electrochemical performance of LiFePO₄/C including the less polarization phenomenon, comparatively high reversible capability, stable cycling performance and slight trend of less loss of rate capability.

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Keywords: LiFePO₄/C; Carbon coating; Cathode; Fe₂P; Reformative solid-coordination

1. Introduction

Lithium ion batteries, the advanced power sources, have been widely used in modern portable electronics, such as cellular phones and notebook computers. In the lithium-ion batteries, it is the cathode host providing lithium ion source for battery work. Among the several cathode materials, LiFePO₄ is one of the most interesting materials due to its low cost, non-toxicity, high specific capability and good cycle performance [1]. For LiFePO₄, its theoretical capacity is 170 mAh g⁻¹ and the charge/discharge voltage is about 3.4 V versus Li/Li⁺. However, the low ion and electronic conductivity ($\sim 10^{-9}$ S cm⁻¹) greatly limited the electrochemical properties of this material [1–3]. Therefore, many efforts have been devoted to improve and optimize the properties of LiFePO₄ materials [2–17].

Two main methods have been proved to be effective in enhancement the conductivities of LiFePO₄: (i) coating with high conductivity materials like carbon [2,4–8] or metals [9–10]; (ii) doping with supervalent metal ion (Mg²⁺, Al³⁺, Zr⁴⁺, Nb⁵⁺

or W⁶⁺) [11]. All their results are very promising; especially the approach of doping with supervalent metal increases the electronic conductivity of LiFePO₄ by a factor of about 10⁸. In recent research by Nazar et al. [12], it was suggest that the impure and amorphous phase iron phosphocarbide or Fe₂P maybe act as more important role in increasing electronic conductivity of Zr-doped LiFePO₄ materials even than the doping ions. High temperatures and reductive environment (such as carbon or H₂) result in the formation of Fe₂P during the synthesis of carbon-coating or doped LiFePO₄ [11–13]. However, after the importance of Fe₂P (or its amorphous phase) was first recognized by Nazar's group, less researches have paid attention to discussing the effect of Fe₂P on improving the physics and electrochemical properties of LiFePO₄ materials.

A practical and effective method is necessary in synthesis of LiFePO₄/C materials with fine properties [14–17]. In this investigation, we prepared series LiFePO₄/C composites by firing the homogenous precursors, which was obtained with a so-called reformative solid-coordination method with citric acid. Among those LiFePO₄/C composites, impure phase Fe₂P was detected out as increasing annealed temperature. Further research showed that the formation of Fe₂P greatly optimized the properties of

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LiFePO₄/C composites, especially the conductivity and electrochemical performance.

2. Experimental

2.1. Synthesis procedure

Calculated ratio of citric acid was dissolved in ethanol, used as the coordination agent and the carbon source. Then stoichiometries of LiOH·H₂O, FeC₂O₄·2H₂O and (NH₄)₂HPO₄ were added respectively and ground to form a homogeneous gel in air. This ethanol-gel was easily dried to incompact precursor powders under infrared light. In pure nitrogen flow, the precursor powders were first calcined at 400 °C for 12 h to decompose the framework of citrate, then reground and annealed at different temperatures (625, 675, and 725 °C) for 30 h. At last, LiFePO₄/C products were obtained after cooling to ambient temperature at that protected atmosphere. The residue coating carbon content among the LiFePO₄/C composites was determined on the element analysis apparatus of Vario-EL (Germany). Standard LiFePO₄ was prepared all as above process but without citric acid, and annealed at 675 °C.

For directing that preparation process, the combined thermal analysis (TG/DTA) on the precursor mixture was examined in pure N₂ on a WCT-2A thermal analyzer (Beijing, China) at a sweep rate of 10 °C min⁻¹. α-Al₂O₃ was used as the reference materials and the same crucible as the vessel for sample.

2.2. Structural and morphological characterization

IR spectra (Nicolet Nexus 670 FT-IR, KBr) were used for detecting the formation of coordination bond. X-ray diffraction (Rigaku D/max-2400, Cu Kα radiation) was used to examine the phase homogeneity and measured the particle size with Scherrer expressions. And SEM (HITACHI S-4300) was used to observe the particle morphology.

2.3. Electronic conductivity measurement

Each 150 mg LiFePO₄/C sample was pressed to disc-shaped pellets under 20 MPa. The pellets were then sintered at 700 °C for 8 h under pure nitrogen flow. Conductivities of these samples were then measured by four-point dc methods using a SZ-82 Digital Meter (China).

2.4. Electrochemical testing

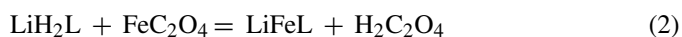
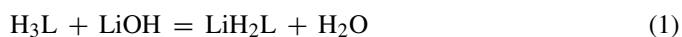
Dispersing active LiFePO₄/total carbon (including residue coating carbon and carbon black)/PVDF with weight ratio 75/20/5 were used to make the cathodes. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate and dimethyl carbonate (EC:DMC = 1:1, v/v). Celgard 2400 was used as the separator. Counter and reference electrodes were lithium metal foil. Assemblage of the cells was performed in an argon box. The testing cells was controlled with a Land automatic batteries tester (China) and performed between 2.5 and 4.0 V versus

Li/Li⁺ at room temperature. And cyclic voltammograms (CV) results were collected with CHI-600B.

3. Results and discussion

3.1. Synthesis of series LiFePO₄/C composites

The solid-coordination reaction can be described as Eqs. (1) and (2) with adding LiOH



and FeC₂O₄, respectively (H₃L is the abbreviation of citric acid C₆H₈O₇). And IR Spectra (Fig. 1) had gradually detected the process of these reactions. For Eq. (1), the typical IR spectrogram of LiH₂L was collected and the characteristic peak of ν(-COOH) = 1721 cm⁻¹ has obviously decreased with the neutralization between citric acid and LiOH. For Eq. (2), a serials pursuing IR spectral results with grinding time for 10, 20, 40, 60 and 120 min were collected, respectively and showed that the characteristic peak of ν(-COOH) = 1721 cm⁻¹ was decreasing gradually with prolonging the grinding time and the corresponding ν_{as}(CO₂⁻) = 1629 cm⁻¹ and ν_s(CO₂⁻) = 1400 cm⁻¹ peaks were increasing gradually at the same time. The value of Δ[ν_{as}(CO₂⁻) - ν_s(CO₂⁻)] was 229 cm⁻¹ that exceeded the 200 cm⁻¹ for the normal value of Δ[ν_{as}(CO₂⁻) - ν_s(CO₂⁻)] in citric acid trisodium salt, which indicated the formation of a monodenate coordination band like -COO-M [18]. With the coordination function, Li⁺ or Fe²⁺ is easily dispersed around the PO₄³⁻ at molecule level with the homogeneous citrate gel during mixed (NH₄)₂HPO₄ into the system. Then several ratios (mol mol⁻¹) of 0, 1/3, 1/2 and 2/3 for citric acid/LiFePO₄ in precursor powders were used to respectively prepare standard LiFePO₄ and series LiFePO₄/C composites with increasing coating carbon.

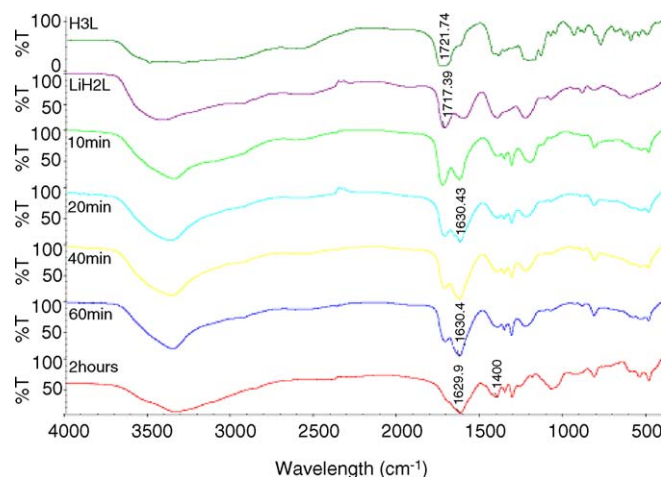


Fig. 1. The series pursuing IR spectral results of Eqs. (1) and (2) with grinding time for 10, 20, 40, 60 and 120 min, respectively.

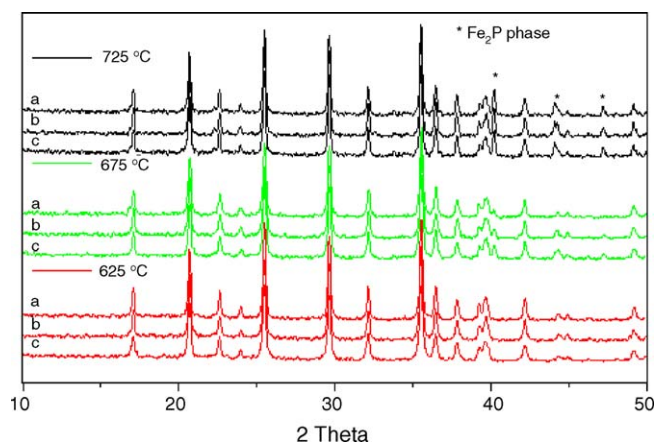


Fig. 2. The XRD results of series LiFePO₄/C materials annealed at 625, 675 and 725 °C. (a–c) The citric acid ratio of 1/3, 1/2 and 2/3, respectively.

3.2. Formation of impure Fe₂P phase

Fig. 2 shows the XRD results of series LiFePO₄/C composites annealed at 625, 675 and 725 °C, respectively. The citric acid ratio has no obvious influence on the structure of LiFePO₄ materials. Homogeneous materials can be obtained at 625 °C without impurity peaks. At 675 °C, the illegible Fe₂P peaks ($2\theta = 40.28^\circ$; 44.20° ; 47.29°) in XRD patterns indicate that it begins to form the iron phosphide phase (barringerite Fe₂P) during the annealed process. At 725 °C, the growth of impurity Fe₂P peaks is obvious in the XRD patterns. Arnold et al. [13] ascribed the generation of barringerite to reduction of phosphate and iron in the precursor by the presence of any reductive under the pure nitrogen atmosphere. We also have collected the XRD results of standard LiFePO₄ and have not found the illegible Fe₂P peaks, it means that the residue coating carbon originated from the citrate framework has acted as the reductive under pure N₂ atmosphere during the annealed process in our synthesis system.

We have performed the combined thermal analysis TG–DTA (Fig. 3) on the precursor in the temperature range from room

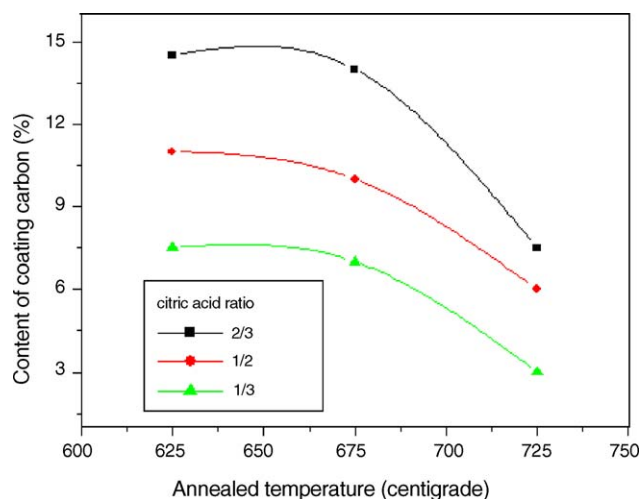


Fig. 4. The contents of remnant coating carbon among the LiFePO₄ materials as a function of annealed temperatures.

temperature to 750 °C under pure N₂ atmosphere. As for DTA and TG results, three endothermic peaks occurred at ca. 172, 209 and 404 °C, which accompanied with weight-loss regions of H₂O, NH₃ and CO₂/CO. After 400 °C, there is no obviously endothermic reaction and less weight-loss appear. Base on that results, we have supposed the generation of Fe₂P during the annealed process as following: Amorphous LiFePO₄ and carbon were firstly formed after 400 °C at pure N₂ atmosphere; During the annealed process, most amorphous LiFePO₄ phase gradually crystallizes and aggregates, but a little nearby element Fe²⁺ and P⁵⁺ would have chance to be deoxidized to Fe₂P by coating carbon at the surface of LiFePO₄ particle and forms minor Li₃PO₄ phase (weak peaks $2\theta = 22.32^\circ$; 23.16° in Fig. 2 725 °C) at the same time. The acute decrease of remnant coating carbon in the series LiFePO₄/C composites from 675 to 725 °C, which is shown in Fig. 4, indicates that more remnant coating carbon was oxidized to CO or CO₂ gas during that process. Comparing with the less weight-loss after 400 °C in thermal analysis results

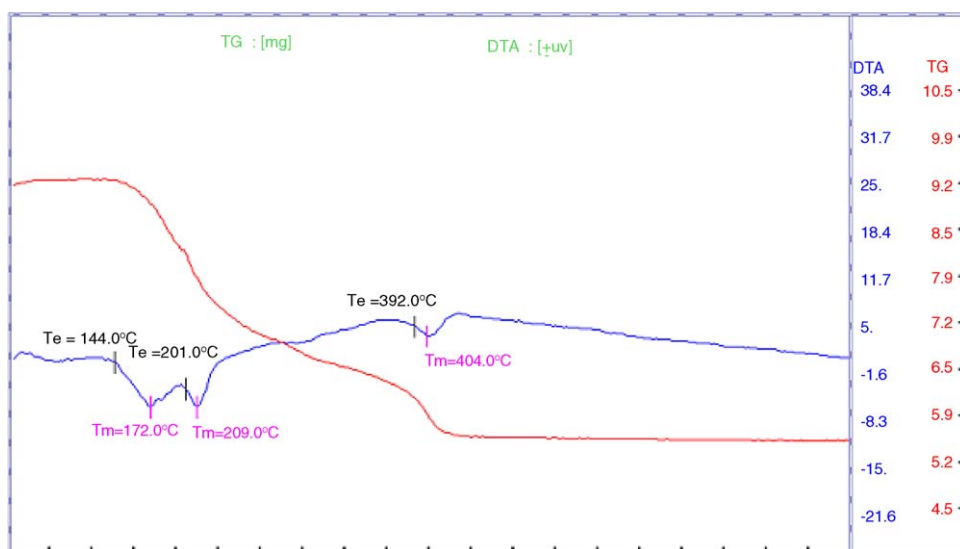


Fig. 3. The combined thermal analysis TG–DTA results of the precursor in the temperature range from room temperature to 750 °C under pure N₂ atmosphere.

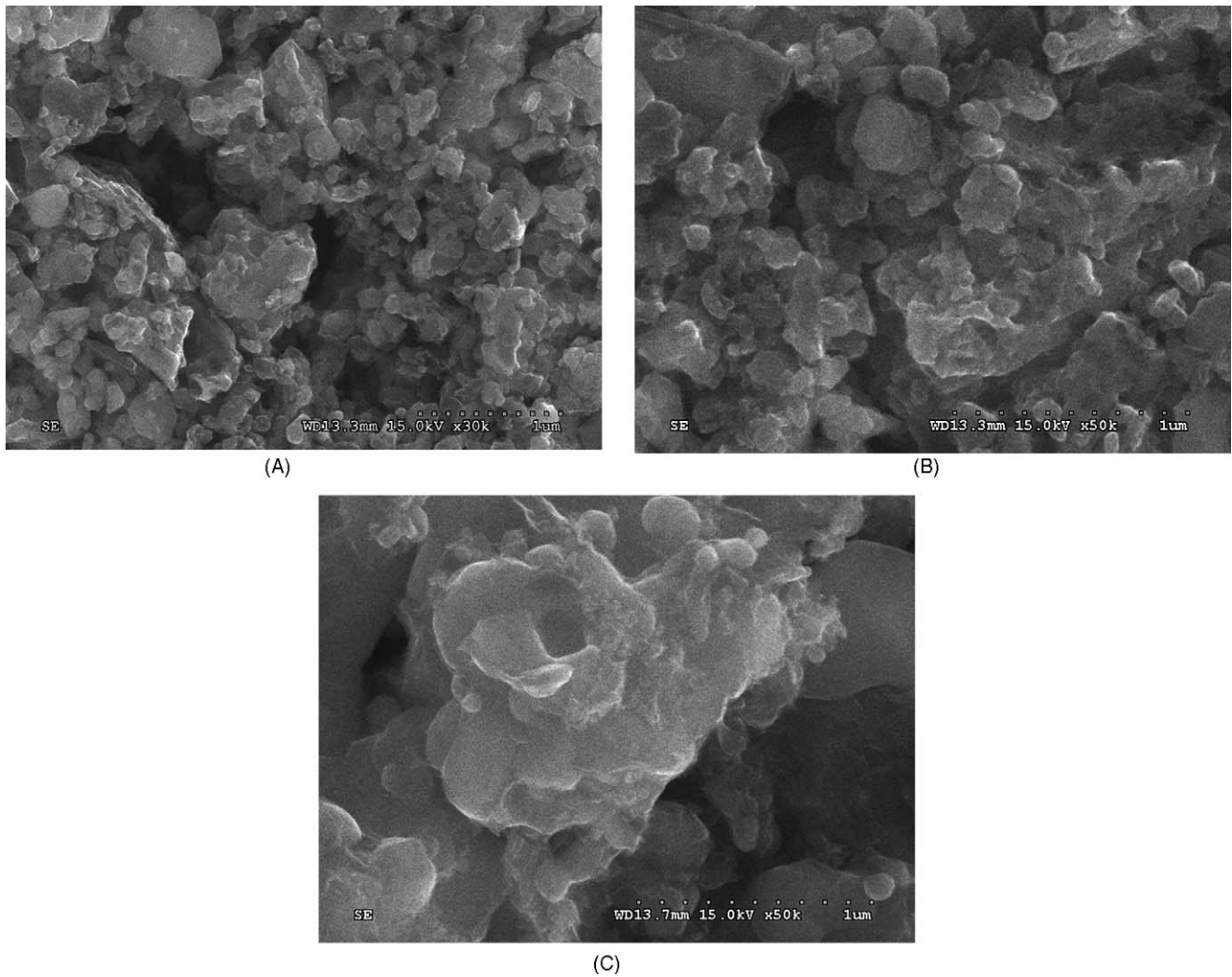


Fig. 5. The SEM of series LiFePO_4/C particles annealed at: (A) 625°C ; (B) 675°C ; (C) 725°C . The citric acid ratio of 1/2 was used.

(~ 0.5 h), maybe the longer annealed time (30 h) in synthesis process helps to form Fe_2P during the carbothermal reduction.

3.3. Effect of forming Fe_2P on the physics and electrochemical properties of LiFePO_4/C composites

The presence of coating carbon closely affects the morphology of LiFePO_4/C particles. As shown in Fig. 5(A) and (B), at temperature of 625°C or 675°C , the remnant coating carbon from citrate framework makes for preparing LiFePO_4/C powder with smaller primary particle size (100–200 nm), and has hold in the undesirable particle growth of LiFePO_4/C crystal. In Fig. 5(C), the SEM observation reveals an abrupt particle growth above 675°C , which is clearly linked with the acute decrease of coating carbon and is consistent with the formation of Fe_2P . In Table 1, same trends can be found and corroborated among the grain size results, which are calculated with Scherrer expressions and have summarized five crystal lattice indexes of (0 1 1), (0 2 1), (1 2 1), (1 3 1) and (2 2 2). The average particle size at 725°C grows twice than their sizes at 625 or 675°C in Table 1. With the acute decrease of coating carbon, it is possible that

divided small LiFePO_4 particles grow into big one and then the increasing Fe_2P surface film replaced that incompact coating carbon, and connects the primary particles to become denser.

The existence of Fe_2P phase, one of the surprising transition metal pnictide materials [19–21], would also endow the LiFePO_4/C composites with some significant interest properties. The physics and electrochemical results of series LiFePO_4/C (A–C for samples obtained from the same precursor with citric acid ratio of 1/2 and annealed at 625 , 675 , 725°C , respectively) are shown and compared as follows.

Fig. 6 shows the conductivity plots of samples A–C and Fe_2P . At room temperature, the conductive Fe_2P composite has

Table 1
The grain size of series LiFePO_4/C particles calculated with Scherrer expressions

Ratio (mol mol ⁻¹) of citric acid/ LiFePO_4	625°C	675°C	725°C
1/3	75–80 nm	58–88 nm	118–176 nm
1/2	63–89 nm	58–86 nm	118–166 nm
2/3	52–68 nm	65–76 nm	87–170 nm

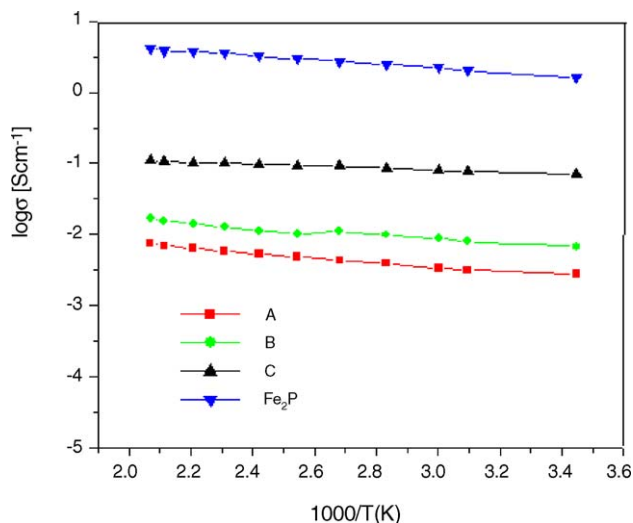
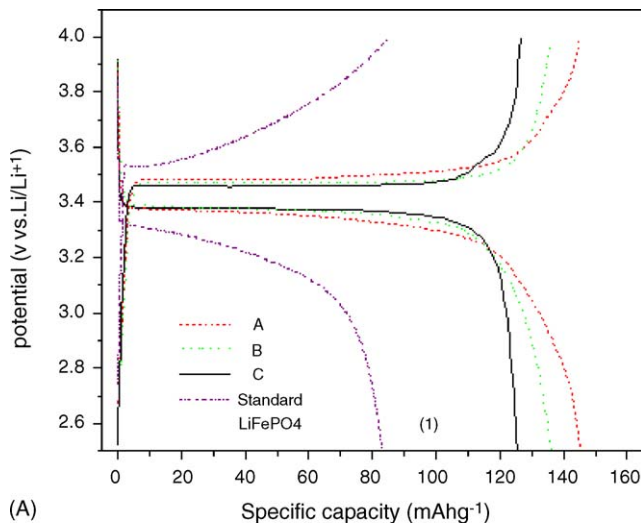


Fig. 6. The electro-conductivity plots of samples A–C and Fe_2P as a function of temperatures.

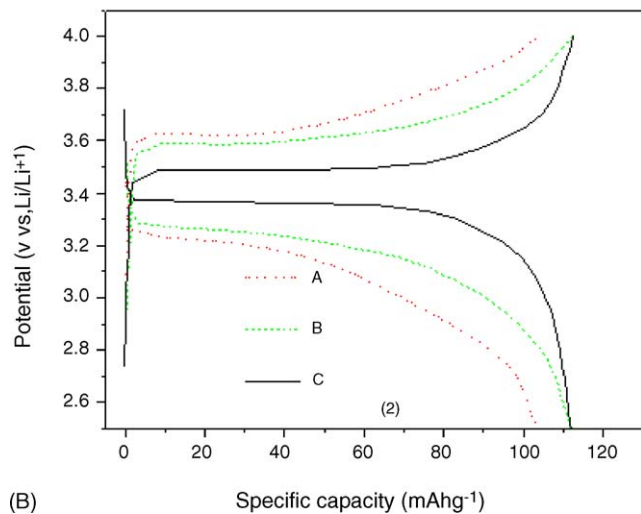
an electronic conductivity of 1.5 S cm^{-1} . The sample-A (only containing coating carbon) has improved the electronic conductivity of LiFePO_4 from a magnitude of 10^{-9} to $10^{-3} \text{ S cm}^{-1}$. Several groups [22–24] also have obtained similar results of 10^{-5} to $10^{-3} \text{ S cm}^{-1}$ for LiFePO_4/C composites. It indicates that LiFePO_4/C composites cannot reach conductivity of a magnitude $10^{-1} \text{ S cm}^{-1}$. However, with the increasing Fe_2P phase, electronic conductivity can be improved from 10^{-3} to $10^{-1} \text{ S cm}^{-1}$ (sample-C). It is concluded and supports Nazar's viewpoint [12] that the existence of Fe_2P phase is the important factor on improving the electronic conductivity.

Fig. 7 shows the voltage profiles of standard LiFePO_4 and the series LiFePO_4/C composites for A–C, respectively. Comparing with results of standard LiFePO_4 , samples of A–C obviously shows excellent reversible charge or discharge capability with a fine voltage flat around 3.45 V at charge/discharge rate of $C/8$ (Fig. 7(1)) and above 80% Li^+ can be inserted or extracted successfully from the LiFePO_4/C particles. In the discharge curves, all the voltage profiles rapidly dropped off from the end charging voltage (4.0 V) to about 3.4 V, after about 5% of the charge had been passed. This voltage was kept almost constant during the following intercalation step and more than 85% of the charging occurred at a flat average voltage of 3.38 V. During the remaining part of the charge, the voltage quickly dropped off to reach the end charging voltage (2.5 V). However, difference of polarization phenomenon can be found among the voltage curves, especially when increasing the discharge rate to $C5/8$ (Fig. 7(2)). The less polarization result was observed at sample-C (725°C), in which sample the negative factors of relatively larger particle size and less of coating carbon were occurred except for the formation of Fe_2P phase. So presence of minor Fe_2P phase is deemed to have restrained the polarization phenomenon.

The stability of the LiFePO_4/C materials has been studied at room temperature by cyclic voltammetry with scan rate of 0.1 mV s^{-1} . Fig. 8 compares the behaviour of testing cells loading with different LiFePO_4/C composites annealed at 625, 675



(A)



(B)

Fig. 7. The voltage profiles of standard LiFePO_4 and LiFePO_4/C cathode for annealed temperatures of 625°C (A), 675°C (B) and 725°C (C) with decreasing coating carbon of 11.07%, 10% and 6%, respectively. The test was performed galvanostatically at charge/discharge rate or current density: (1) $C/8$ (0.1 mA cm^{-2}); (2) $C5/8$ (0.5 mA cm^{-2}).

and 725°C . Peaks are broadened at low temperature (625°C , sample-A) due to its slower kinetics; contrary, some decrease of separations at high temperature (725°C , sample-C) between the cathodic and anodic peaks is representative of its excellent kinetics, that can be explained with the improving of electro-conductive by the conductive Fe_2P phase. In this case, though all the LiFePO_4/C materials being stable as cathode, the phenomenon is also closely relative to the forming Fe_2P .

Fig. 9 shows the room temperature cycling performance of the series of LiFePO_4/C composites. At C -rate of $C/8$, sample-A offers comparatively good capability. Once the C -rate is increased to $C/4$ and $C5/8$, there is a distinct trend that the cell performance is not ameliorated with decreasing the particle size or increasing the coating carbon but with the increasing formation of Fe_2P and the sample-C (annealed at 725°C) shows comparatively high reversible capability, stable cycling performance and slight trend of less loss of rate capability.

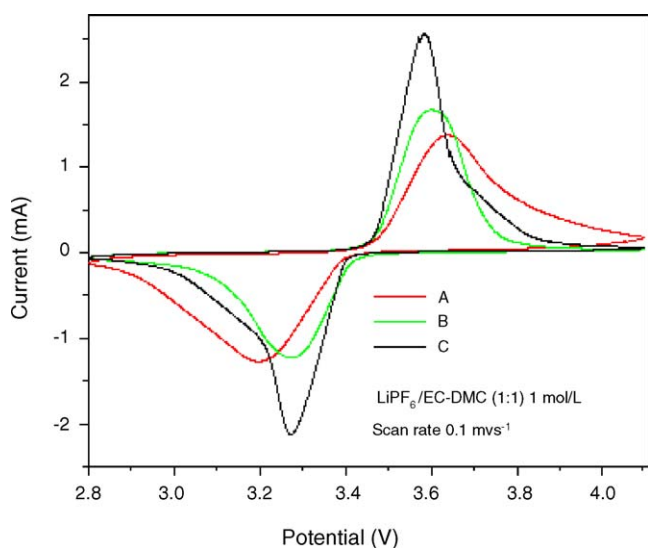


Fig. 8. The CV results of the LiFePO₄/C cathode for annealed temperatures of 625 °C (A), 675 °C (B) and 725 °C (C) with decreasing coating carbon of 11.07%, 10% and 6%, respectively.

The other two series of LiFePO₄/C composites (prepared with citric acid ratios of 1/3 and 2/3) also shows same physics and electrochemical trends and is closely relative to the forming Fe₂P. Nevertheless, how does the impure Fe₂P phase work for the high conductivity of the series LiFePO₄/C composites and then improve their electrochemical properties? We have prepared the Fe₂P materials and then have directly added 15 wt.% Fe₂P into the standard LiFePO₄ with solid-state method. Its electro-conductivity shows no obvious improvement than the standard LiFePO₄, with a magnitude of less than 10⁻⁷ S cm⁻¹. It demonstrates that simple mixing Fe₂P is not effective in enhancing the electro-conductivity of LiFePO₄; the beneficial role of forming Fe₂P among LiFePO₄/C composites in enhanc-

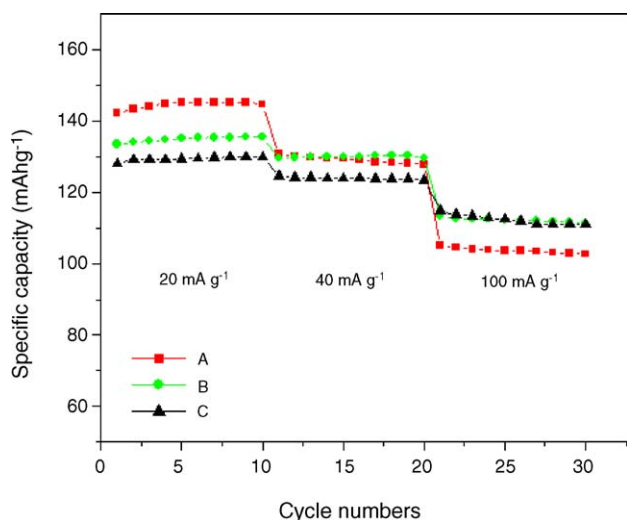


Fig. 9. The room temperature cycling performance of the series of LiFePO₄/C cathode for annealed temperatures of 625 °C (A), 675 °C (B) and 725 °C (C) with decreasing coating carbon of 11.07%, 10% and 6%, respectively. And the test was performed at three discharge rate: C/8 (20 mA g⁻¹), C/4 (40 mA g⁻¹) and C5/8 (100 mA g⁻¹).

ing electro-conductivity property may be tentatively explained by assuming that new forming Fe₂P replaces and connects with those incompact coating carbon together to build a denser conductive framework around the LiFePO₄ particle, this more helping in free transfer of conductive electron among the LiFePO₄/C composites than only coating with carbon. So the Fe₂P phase, which is similar and even better than the functions of conductive carbon, can be a promising candidate for optimizing the bulk conductivity and electrochemical properties of LiFePO₄.

4. Conclusion

In this investigation, the reformative solid-coordination method was suggested to synthesize LiFePO₄ cathode materials with coating carbon. A monodentate coordination band of -COO-M was proved to form gradually and that is beneficial to disperse Li⁺ or Fe²⁺ among the homogeneous gel during the grinding process. Fe₂P phase occurs as an impure phase among the LiFePO₄/C materials when they are prepared at relatively high-annealed temperature. The fine dispersed coating carbon was considered have acted as the reductive additive under the pure nitrogen gas. The amounts of carbon, morphology and particle size were investigated in detail and all the results showed to be directly related to the formation of Fe₂P. Further electrochemical research concluded that the electro-conductive Fe₂P phase acts as important role in improving their electronic-conductivity and electrochemical performance of including the less polarization phenomenon, comparatively high reversible capability, stable cycling performance and slight trend of less loss of rate capability. The Fe₂P phase is hoped to be a promising conductive additive for improving the properties of LiFePO₄ materials; therefore LiFePO₄ can develop to be an applied cathode material.

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