Synthesis and electrochemical properties of olivine-type LiFePO$_4$/C composite cathode material prepared from a poly(vinyl alcohol)-containing precursor

Nan Ji Yun, Hyung-Wook Ha, Kyung Hee Jeong, Heon-Yong Park, Keon Kim[*]

Division of Chemistry and Molecular Engineering, Department of Chemistry, Korea University, Seoul 136-701, South Korea

Abstract

Olivine structure LiFePO$_4$/C composite powders are synthesized as cathode materials for Li-ion batteries via a conventional solid-state reaction. Improvement in electrochemical performance has been achieved by using poly(vinyl alcohol) as the carbon sources for the as-prepared materials. The influence of the heat treatment on the physical and the electrochemical properties of LiFePO$_4$/C materials is investigated. To examine the effect of added carbon content on the properties of materials, a one-step heat treatment has been employed with control of the PVA content in the precursor. Six samples were prepared with 0, 1, 3, 5, 10 and 30 wt.% PVA added to the raw materials. The particle size of LiFePO$_4$ decreases as the carbon content increases. Materials with medium carbon contents have a small charge-transfer resistance and thus exhibit superior electrochemical performance. Interestingly, for a LiFePO$_4$/C composite with a low PVA content, an unusual plateau at 4.3 V is observed. It is considered that this is due to the Fe^{3+}/Fe^{4+} redox reaction of Fe^{3+} compounds that are present as an impurity. For samples with a high PVA amount, a thicker carbon coating provides an obstacle to improve the electrochemical properties.

Keywords: Li-ion batteries; Cathode material; Olivine; LiFePO$_4$; Poly(vinyl alcohol); Carbon coating

1. Introduction

Interest in LiFePO$_4$ as a cathode material for Li-ion batteries has increased dramatically since it was first proposed by Padhi et al. [1]. Phospho-olivine-type LiFePO$_4$ has the P$_{tet}$–O–Fe$_{oct}$ linkage in the structure that generates a suitable Fe^{3+}/Fe^{2+} redox energy of 3.4 V versus Li/Li$^+$, which is called the 'inductive effect'. Also, this material exhibits not only an excellent reversibility on cycling but also an acceptable safety characteristic when the battery is fully charged. This former feature is due to the fact that LiFePO$_4$ and FePO$_4$ are isostructural (space group *Pnma*) with only a slight difference in the cell parameter. Further, LiFePO$_4$ has a three-dimensional structure that contains pathways for lithium ions, but has a reversible capacity loss at high current density. Its poor high rate capability has been attributed to low electronic conductivity and slow Li$^+$ diffusion across the two-phase interface [1–4]. As Li$^+$ diffusion crosses the LiFePO$_4$/FePO$_4$ interface, the interface area diminishes. The concentration of Li$^+$ that moves through the decreased interface is not sufficient to sustain the current and thus leads to a loss in reversible capacity.

Two approaches have recently been attempted to overcome the above problems. One approach is to enhance the electronic conductivity by introducing conductive additives, i.e., coating carbon through the synthesis of a LiFePO$_4$/C composite [5–9], or selective doping with supervalent cations [2,10]. The second approach is, to control the particle size by optimizing the synthesis conditions [4]. It has been reported [7,9] that addition of carbon to as-prepared materials is the most effective solution. Addition of carbon before the formation of the crystalline phase suppresses particle growth during the sintering process and enhances electronic conductivity through improved contacts between particles. Various carbon sources have been reported for the LiFePO$_4$/C composite, e.g., naphthalenetetracarboxylic dianhydride [5], hydroxyethyl-cellulose [6], resorcinol-formaldehyde gel [7], white table

---

[*] Corresponding author. Tel.: +82 2 953 1172; fax: +82 2 953 1172.
E-mail address: kkim@korea.ac.kr (K. Kim).

sugar [8], carbon black [9], polypropylene [11], and sucrose [12].

Recently, it has been reported [5,13] that the structure of the residual carbon on $LiFePO_4$ particles is an important determinant of electrochemical performance [5,13]. It was confirmed that coated carbon with an increased sp^2 character relative to the sp^3 character for particles gave rise to improved electronic conductivity, which resulted in enhanced electrochemical performance. Poly(vinyl alcohol) (PVA) is a known aliphatic polymer with a measurable char yield of about 4% and for which a pyrolysis pathway was proposed by Gilman et al. [14]. According to their report, PVA is ultimately converted into substituted aromatics and substituted olefins at temperatures up to 400 °C. In the char resulting from pyrolysis of PVA at a high temperature of 700–800 °C, only these types of structures survive. In addition, the release of hydrogen makes the immediate environment of $LiFePO_4$ a reductive atmosphere. This micro-environment is helpful in preventing the formation of Fe^{3+} compounds.

In this study, PVA is used as a carbon source and three heat treatments are applied in preparing $LiFePO_4/C$ composite materials. Thus, an investigation is made of the influence of heat treatment of a PVA-containing precursor on the physical and electrochemical properties. In addition, the effect of the amount of PVA on the properties of the materials is evaluated.

2. Experimental

$LiFePO_4/C$ composite powder was prepared by a conventional solid-state reaction using Li_2CO_3 (Junsei, >99.0%), $FeC_2O_4 \cdot 2H_2O$ (Kanto, 98.5%), and $NH_4H_2PO_4$ (Aldrich, >98%) as starting materials. An appropriate amount of PVA (degree of polymerization 1500, Junsei) as the carbon source was added to the raw materials. A mixture of the raw materials and PVA was dispersed in acetone and mixed by ball-milling for 24 h. After evaporating the acetone, a PVA-containing precursor was obtained for preparing the olivine structure $LiFePO_4/C$ composite. In this study, the precursor was heat-treated according to three different methods as follows:

(i) the pelletized precursor was sintered at 800 °C for 9 h or
(ii) the precursor was heated at 300 °C for 6 h to expel the gases and yield a decomposed powder that was reground with a mortar and pestle, pressed into pellets and sintered at 800 °C for 9 h;
(iii) instead of pre-sintering at 300 °C, the precursor was heated at 500 °C for 6 h and the other processes were performed as for synthesizing the $LiFePO_4/C$ material in method (ii).

An inert atmosphere of argon gas was used during all heat treatments to prevent the formation of undesirable Fe^{3+} compounds. The thermal behaviour of the PVA-containing precursor and PVA were examined by thermogravimetric (TG) analysis using a Mettler Toledo TA50 instrument at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. After heat treatment, the powders were allowed to cool to ambient temperature and washed with distilled water. As a final step, the products were dried overnight at 120 °C.

The crystal structures of the prepared samples were investigated by powder X-ray diffraction (XRD) using a Rigaku DMAX-IIIA diffractometer. Scan data were collected over the 2θ range of 15–90° and the step size was 0.020° with a counting time of 1.0 s. The morphology of the $LiFePO_4/C$ powder was examined by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300, Japan). The residual carbon content of the powders was determined by means of an automatic elemental analyzer (EA, Flash EA1112, CE Instruments, Italy).

The electrochemical properties of the powders were characterized using a laboratory-made, two-electrode, electrochemical cell. The cathode consisted of 10 mg of active material and 6 mg of conductive binder (i.e., 4 mg of teflonized acetylene black and 2 mg of graphite). The fabricated cathode was pressed and then vacuum-dried overnight at 120 °C. Lithium metal and polypropylene film were used as an anode and a separator, respectively. The electrolyte was 1 M $LiPF_6$ in a 1:1 (wt.%) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (TECHNO Semichem Co.). The entire cell was assembled in an argon-filled glove box. The electrochemical performance of the various compounds was evaluated by cycling at the 0.1 and 1 C rates over the potential range 2.5–4.5 V versus Li/Li$^+$ using a WBCS 3000 instrument (WonA Tech., Korea). Cyclic voltammetry (CV) was performed with an IM6 electrochemical instrument (ZAHNER elektrik, Germany) at scan rate of 0.1 mV s^{-1} between 2.5 and 4.5 V.

3. Results and discussion

3.1. Effect of heat treatment on PVA-containing precursor

Thermogravimetric (TG) analysis was used to determine the appropriate temperature for heat treatment. The TG curve of the PVA-containing precursor (Fig. 1) is typical of a powder mixture consisting of Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$, and $NH_4H_2PO_4$ for preparing $LiFePO_4$ in good accordance with that reported by Wang et al. [15]. In addition, it has been previously reported [14] that pyrolysis of PVA in a nitrogen gas flow occurs at 300–425 °C and that only a small amount of residue survives at temperatures up to 450 °C. For the PVA-containing precursor,
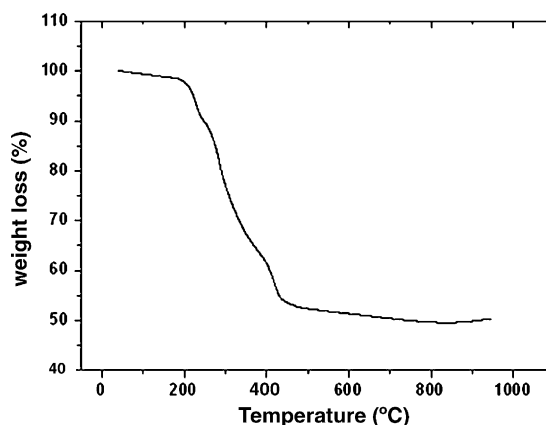

Fig. 1. TG curve of PVA-containing precursor at heating rate of 10 °C min^{-1} in nitrogen at a flow rate of 15 mL min^{-1}.

there is an initial loss of lattice water from $FeC_2O_4 \cdot 2H_2O$ and the $NH_4H_2PO_4$ decomposes at <250 °C. In the temperature range of 250–420 °C, there is a weight loss due to decomposition of FeC_2O_4 and a reaction with the decomposed product of $NH_4H_2PO_4$ while the PVA rapidly decomposes. After the formation of $LiFePO_4$ at 470 °C, the product weight decreases slightly. A gradual weight loss is observed above the temperature of $LiFePO_4$ formation in PVA-containing precursor because the pyrolysis of the remaining PVA continues until 600 °C. The TG pattern also indicates that the formation of $LiFePO_4$ and the pyrolysis of PVA occur within the same temperature range. This suggests that it is possible to coat carbon simultaneously with the formation of $LiFePO_4$ grains.

From the results of TG analysis, we were able to determine the temperatures of the heat treatments. First, we attempted a simple one-step heat treatment at 800 °C. Second, two pre-sintering temperatures, namely, 300 and 500 °C, were applied to a two-step heat treatment which consisted of the pre-sintering steps and a subsequent final heating at 800 °C for the formation and crystallization of $LiFePO_4$. The condition of the one-step heat treatment at 800 °C is sufficient to make a well-ordered olivine $LiFePO_4$ crystalline compound. Nevertheless, it is expected that the morphology of the particles and/or the electrochemical properties should be related to the nature of heat treatment. With pre-sintering at 300 °C, it is anticipated that the starting materials decompose and merely gases are released without the formation of $LiFePO_4$ and also the pyrolysis of PVA. After pre-sintering at 500 °C; however, it is expected that a $LiFePO_4$ crystalline compound will be formed with little remaining PVA.

With 5 wt.% PVA in the starting material, 2.06 wt.% of elemental carbon is found in the resultant $LiFePO_4/C$ composite formed by one-step heat treatment at 800 °C. This content
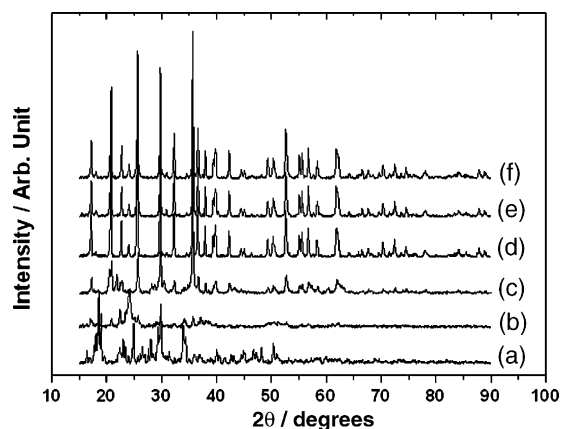

Fig. 2. XRD patterns of: (a) PVA-containing precursor before heat treatment; (b) powder formed after pre-sintering at 300 °C; (c) powder formed after pre-sintering at 500 °C. XRD pattern of resultant products from: (d) one-step heat treatment; (e) final heat treatment after pre-sintering at 300 °C; (f) final heat treatment after pre-sintering at 500 °C.

exceeds the residual carbon of both final samples when using the two-step treatment. The $LiFePO_4/C$ prepared by the two-step heat treatment, including pre-sintering at 500 °C, has the least carbon content at 1.56 wt.%. This result is ascribed to the pre-sintering temperature, and suggests that a large portion of PVA disappears after heating at 500 °C and, furthermore, a part of the residual carbon is lost during the second heat treatment.

To confirm selection of the heat treatments according to the results of TG analysis, XRD analysis was conducted on the powders after pre-sintering at 300 and 500 °C, as well as on the PVA-containing precursor, as shown in Fig. 2(a–c). When comparing the XRD patterns of the three samples, almost all the
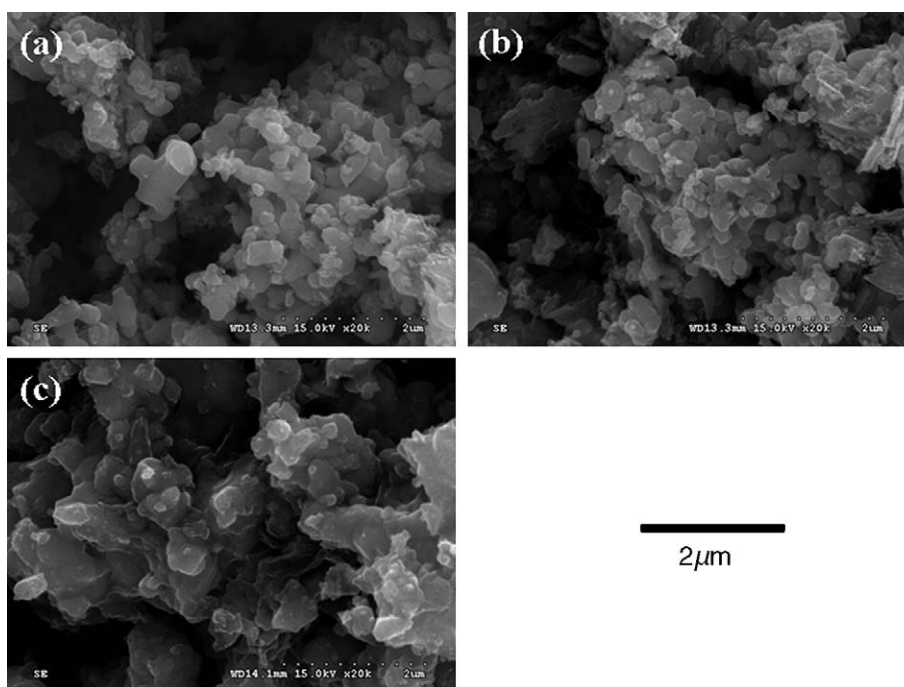

Fig. 3. Scanning electron micrographs of $LiFePO_4/C$ composites prepared by: (a) one-step heat treatment; (b) final heat treatment after pre-sintering at 300 °C; (c) final heat treatment after pre-sintering at 500 °C.

diffraction peaks in the precursor before heat treatment disappear in the powders obtained after heating at 300 and 500 °C. Even the powder heat-treated at 500 °C shows the peaks of olivine structured LiFePO$_4$ due to a heating temperature above 470 °C which corresponds to the temperature of structure formation. It is concluded that after heating at 300 °C, the only starting materials are decomposed, and the olivine structured LiFePO$_4$ is not formed. Fig. 2(d–f) presents the XRD patterns of the resultant products after final heating at 800 °C. All the final products have an ordered olivine structured LiFePO$_4$ with orthorhombic *Pnma* independent of the type of heat treatments. There are no additional diffraction peaks associated with crystal modification by carbon. It appears that PVA as a carbon source remains as elemental carbon in an amorphous phase.

The morphologies of the LiFePO$_4$ powders following the various heat treatments are illustrated in Fig. 3. From the SEM observation, the individual particles are estimated to be between 200 and 300 nm, although those of the powder prepared by final heat treatment after pre-sintering at 500 °C appear to be somewhat larger. The particles are relatively small because the residual carbon from the PVA-containing precursor plays an important role in reducing particle size to hinder the growth of LiFePO$_4$/C particles during heating. As shown in Fig. 3(a), the sample using the one-step heat treatment is completely crystallized and not substantially agglomerated. This sample contains some residual carbon as an impurity phase that is not coated on the LiFePO$_4$ particles, whereas the samples from two-step heat treatments have little carbon as an impurity phase. The agglomeration of particles increased with the two-step heat treatments. In particular, the powder pre-sintered at 500 °C exhibits a serious coalescence of the particles that is so extensive as to prohibit a distinction between the shapes of individual particles, as shown in Fig. 3(c). Based on these observations, it is clear that the final heating temperature of 800 °C after crystallization of the particles leads only to growth and agglomeration of particles, but does not further improve the crystallinity of the LiFePO$_4$/C composite. In summary, carbon-coated LiFePO$_4$/C with an appropriate crystallinity and morphology can be prepared satisfactorily by one-step heat treatment of the PVA-containing precursor without the need for pre-sintering, and by two-step heat treatment with pre-sintering at 300 °C.

The discharge capacity of LiFePO$_4$ cells at the 0.1 C rate in the voltage range of 2.5–4.5 V is given as a function of cycle number in Fig. 4. The materials prepared by one-step heat treatment and by two-step heat treatment with pre-sintering at 300 °C deliver a high first discharge capacity of 153 and 149 mAh g^{-1}, respectively. Both materials show a higher reversible capacity than material pre-sintered at 500 °C due to the latter's larger size as a result of particle coalescence. In addition, the formed two samples demonstrate remarkably good capacity retention at a low current density with >90% of the initial capacity remaining after 30 cycles. It has been reported [4,9,12] that controlling particle size and morphology is important for the LiFePO$_4$/C composite to achieve satisfactory electrochemical performance. It was confirmed that the presence of uncoated residual carbon as an impurity and only slight agglomeration of particles have an opposite effect on electrochemical properties.
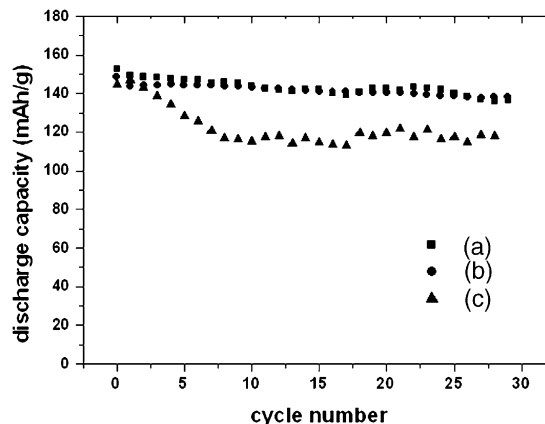

Fig. 4. Cycling performance of LiFePO$_4$/C composite at current density of 0.1 C rate in voltage range of 2.5–4.5 V: (a) one-step heat treatment; (b) two-step heat treatment with pre-sintering at 300 °C; (c) two-step heat treatment with of pre-sintering at 500 °C.

The material synthesized by the two-step heat treatment with pre-sintering at 300 °C is equivalent to that material prepared using the one-step heat treatment in terms of electrochemical properties, viz., specific capacity and capacity retention. The latter synthetic route is, however, considerably more complicated. Therefore, it is concluded that the one-step heat treatment is worth studying further for the effect of residual carbon content on the properties of LiFePO$_4$/C composites.

3.2. Effect of carbon content on LiFePO$_4$/C composite materials

By altering the heat treatment, it has been found that the residual carbon from the precursor hinders the growth of particles. To extend the investigation of the effect of carbon content on the properties of materials, the one-step heat treatment has been employed with control of the PVA content in the precursor.

Six samples were prepared with 0, 1, 3, 5, 10 and 30 wt.% PVA added to the raw materials. The amount of remaining carbon in the products is listed in Table 1. Carbon is not detectable in the LiFePO$_4$/C powder obtained using precursors with 0 and 1 wt.% PVA. On adding more PVA, however, residual carbon is found by elemental analysis to be proportional to the amount of added PVA. As the residual carbon content increases, the colour of the powders changes progressively from medium to dark grey, even to deep black for the sample with 8.31 wt.% carbon.

Table 1
Carbon content in various LiFePO$_4$/C composite powders prepared by one-step heat treatment

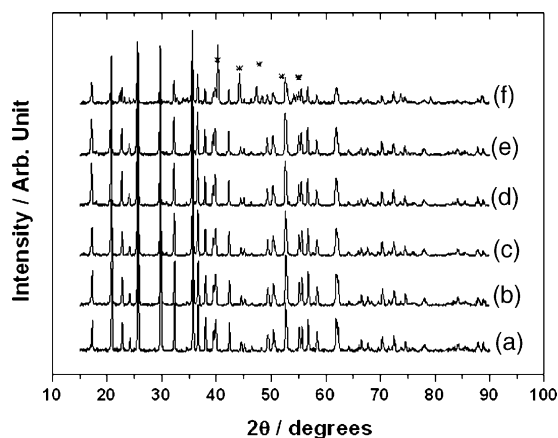| Added PVA content (wt.%)	Residual carbon amount (wt.%)
0	0
1	∼0
3	1.00
5	2.06
10	3.20
30	8.31

Fig. 5. XRD patterns of LiFePO$_4$/C composite prepared with: (a) 0 wt.%; (b) 1 wt.%; (c) 3 wt.%; (d) 5 wt.%; (e) 10 wt.%; (f) 30 wt.% PVA. Asterisk (*) represents impurity phase of Fe$_2$P.

The XRD patterns of LiFePO$_4$/C composites with various amounts of residual carbon are shown in Fig. 5, where all samples are LiFePO$_4$ with an ordered olivine structure indexed by orthorhombic *Pnma*. The formation of Fe^{3+} compounds is prevented by relying on the reducing properties of specific carbons such as PVA and polypropylene [11] without using a reductive gas mixture of inert gas and H$_2$ [16,17]. As the XRD results in the previous section indicated, there is no evidence of the formation of crystalline or amorphous carbon in the XRD curves. The XRD pattern of LiFePO$_4$ powder from a precursor containing excessive PVA (i.e., 30 wt.%) takes on a different aspect. As shown in Fig. 5(f), a small amount of the impurity phase remains. This result is due to the high carbon content combined with an elevated temperature of 800 °C which leads to the undesirable result of reduction of Fe in LiFePO$_4$ and the formation of impurities such as Fe$_2$P [16]. Moreover, the diffraction peaks are broadened and the crystallinity of the LiFePO$_4$ powder is decreased due to suppression of the formation of crystalline LiFePO$_4$ by the excess carbon content.

Scanning electron micrographs of LiFePO$_4$/C composite materials are presented in Fig. 6. For all samples, well-crystallized shapes are observed, although samples with a PVA content >3 wt.% in the precursor have traces of elemental carbon as an impurity phase. It is clear that the particle size of LiFePO$_4$ decreases as the carbon content increases. Therefore, it is reasonable to suggest that the effect of added carbon is to suppress the growth of LiFePO$_4$/C particles during the sintering process. The elemental carbon exists as a carbon layer coated on the LiFePO$_4$ particles and this layer inhibits particle growth by restricting the diffusion of atoms.

The first three cyclic voltammograms (CVs) of selected Li/LiFePO$_4$ cells between 2.5 and 4.5 V are presented in Fig. 7. An anodic peak, which is indicative of lithium ion extraction from LiFePO$_4$, occurs at ~3.5 V versus Li/Li$^+$. A cathodic peak corresponding to the anodic peak occurs at ~3.3 V and signifies a Fe^{2+}/Fe^{3+} redox potential. The small potential difference of about 0.2 V between the anodic and cathodic peaks demonstrates good reversibility on charge–discharge cycling. In addition, the CV curves of the samples have well-defined peaks and subsequent curves after the first cycle show excellent reproducibility. These features denote the high reactivity and good reversibility of Li/LiFePO$_4$ cells. However, it is interesting to see an anodic peak at 4.3 V on the first cycle of samples, as shown in Fig. 7. The LiFePO$_4$ composite prepared by a precursor with a low PVA content has a relatively large peak at 4.3 V, whereas the intensity of this peak is negligible in samples with higher PVA contents. The origin of the 4.3 V peak is not fully understood, but is thought to represent oxidation of Fe^{3+} to Fe^{4+}. This peak disappears after the first cycle, which means that the phase is stabilized in subsequent cycles. Even if an impurity phase is not to be found in the XRD curve, small quantities of impurities exist as Fe^{3+} compounds in LiFePO$_4$/C materials with low residual carbon contents.

The initial charge–discharge voltage curves of prepared samples at the 0.1 C rate in the voltage range of 2.5–4.5 V are shown in Fig. 8. A flat profile over a wide range at ~3.4 V indi-
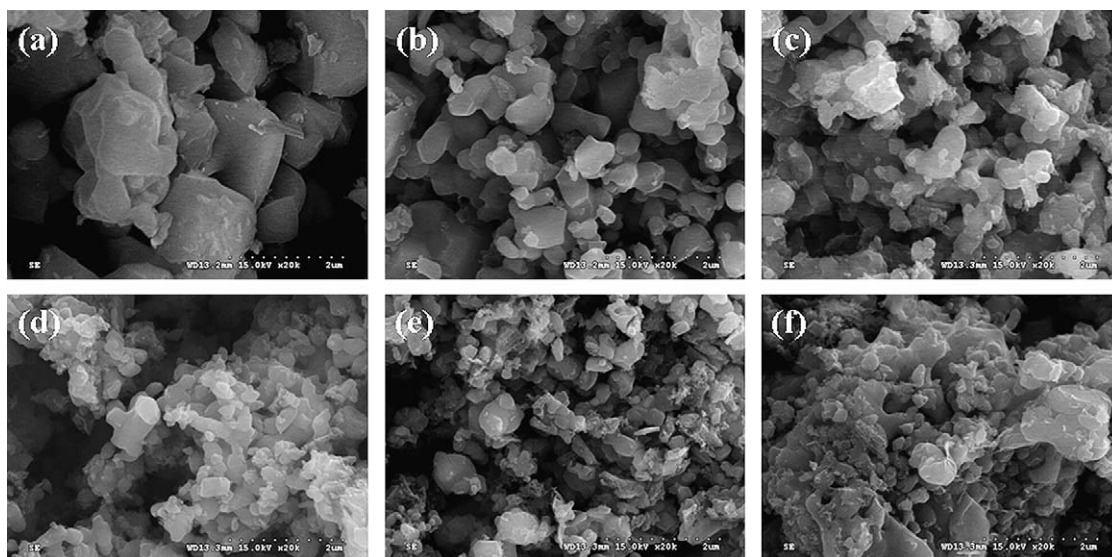

Fig. 6. Scanning electron micrographs of LiFePO$_4$/C composite prepared with: (a) 0 wt.%; (b) 1 wt.%; (c) 3 wt.%; (d) 5 wt.%; (e) 10 wt.%; (f) 30 wt.% PVA.
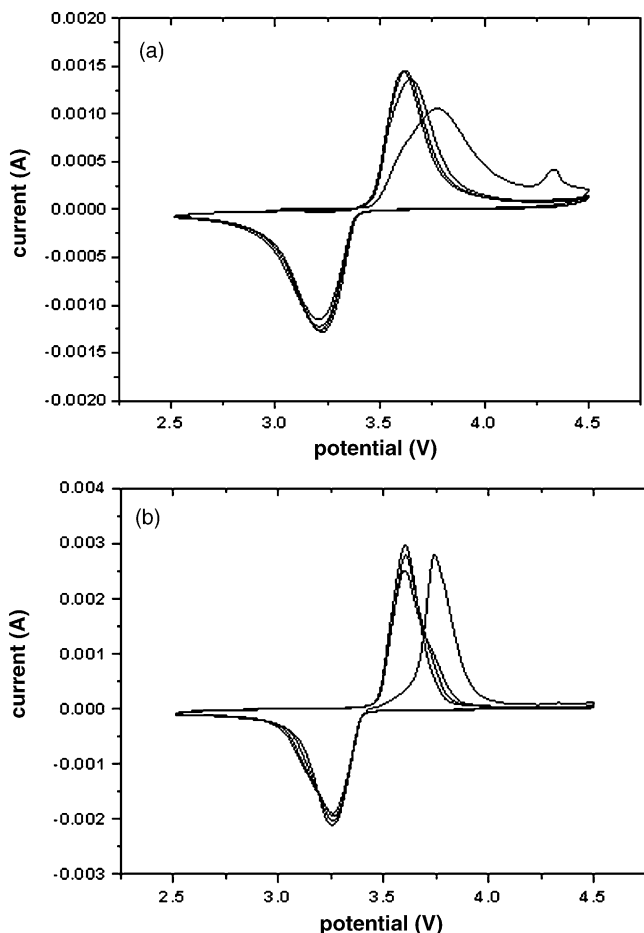
Fig. 7. Cyclic voltammograms curves of LiFePO$_4$/C composite prepared with: (a) 1 wt.% and (b) 5 wt.% PVA.

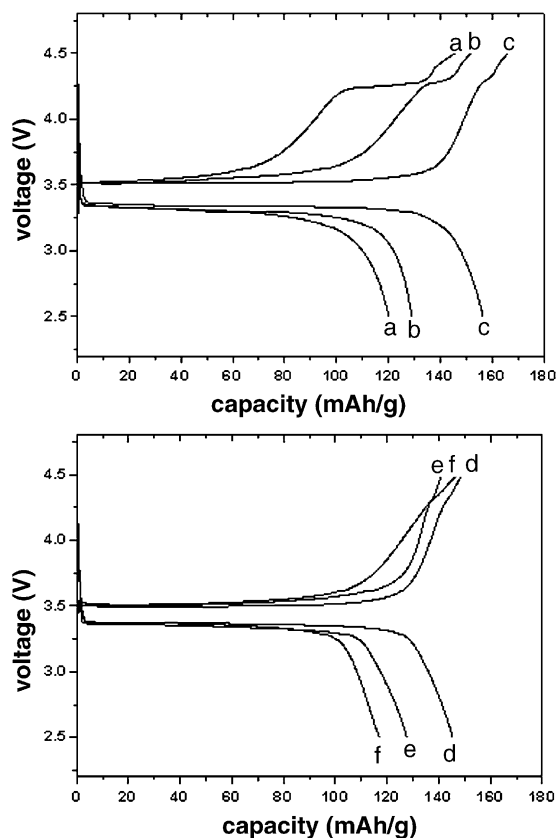Fig. 8. Voltage profiles on first cycle of LiFePO$_4$/C composite prepared with: (a) 0 wt.%; (b) 1 wt.%; (c) 3 wt.%; (d) 5 wt.%; (e) 10 wt.%; (f) 30 wt.% PVA.

cates that the extraction and the insertion reactions of lithium ions proceed by the motion of a two-phase interface between FePO$_4$ and LiFePO$_4$. For samples with a low PVA content, i.e., about 0, 1 and 3 wt.%, an unusual plateau is observed at 4.3 V in addition to the typical plateau of the Fe^{2+}/Fe^{3+} redox reaction in LiFePO$_4$ at 3.4 V. This is consistent with prior CV results.

Fig. 9 presents the discharge capacities of LiFePO$_4$/C composites at the 0.1 C rate with a charge cut-off voltage of 4.5 V. Although there is little difference in the XRD patterns of the LiFePO$_4$/C composites, the cell performance of the cathode materials depends on the added PVA amount in the precursor. Samples with 3, 5, and 10 wt.% PVA deliver high initial discharge capacities of similar value. The LiFePO$_4$/C material with 3 wt.% PVA gives the highest capacity, viz., 156 mAh g^{-1}, which corresponds to over 90% of the theoretical capacity of olivine LiFePO$_4$. On the other hand, the reversible capacity of this material fades as cycling proceeds. This indicates poor capacity retention. LiFePO$_4$/C materials with 5 wt.% PVA deliver a small discharge capacity of 153 mAh g^{-1} with reasonable capacity retention. The excellent reversibility of Li/LiFePO$_4$ cells during cycling is caused by the structural similarity of LiFePO$_4$ and FePO$_4$. Samples prepared from a precursor with a low PVA amount have diminished capacity retention,

especially when using a precursor without PVA. In the absence of PVA, an initial discharge capacity of 120 mAh g^{-1} decreases 54 mAh g^{-1} after 30 cycles with severe capacity fading. This decline is attributed to a stabilized structure after first cycle that impedes the extraction and insertion of lithium ions. As proposed by Wang et al. [17], the formation of cracks after cycling will lead to poor electrical contact between the active materials and the conductive materials and this explains the capacity
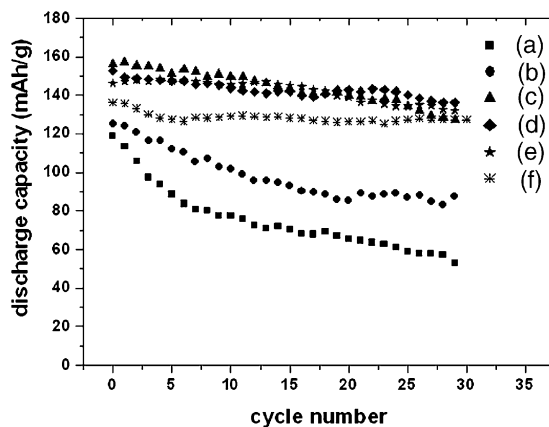

Fig. 9. Discharge capacities vs. cycle number at 0.1 C rate between 2.5 and 4.5 V for Li/LiFePO$_4$ cells. LiFePO$_4$/C composites as cathode materials are synthesized with: (a) 0 wt.%; (b) 1 wt.%; (c) 3 wt.%; (d) 5 wt.%; (e) 10 wt.%; (f) 30 wt.% PVA.

Fig. 10. Cycling performance at 1 C rate over voltage range 2.5–4.5 V for Li/LiFePO$_4$ cells. LiFePO$_4$/C composites as cathode materials are synthesized with: (a) 0 wt.%; (b) 1 wt.%; (c) 3 wt.%; (d) 5 wt.%; (e) 10 wt.%; (f) 30 wt.% PVA.
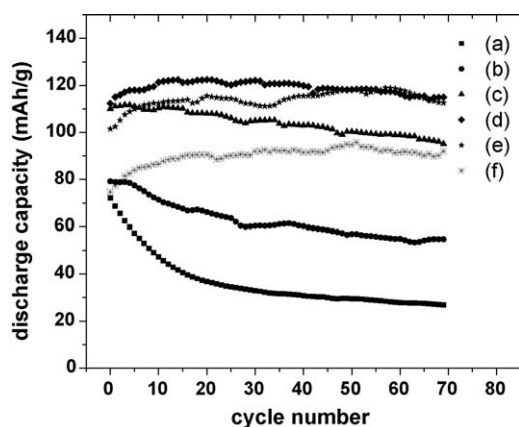
fading of pure LiFePO$_4$ when there is no carbon coating. Among the samples, the LiFePO$_4$/C composite with 30 wt.% PVA display excellent capacity retention, although a small reversible discharge capacity is observed. A slightly reduced discharge capacity originates with the thicker carbon coating, and is based on the following: (i) a decrease in theoretical capacity due to the presence of excess carbon as an inactive mass at about 8 wt.%; (ii) difficulty in lithium ion diffusion through the thick carbon coating layer; (iii) a lessening of the surface for Li$^+$ extraction and insertion with hindrance of electrolyte penetration into electrode.

To investigate electrochemical performance such as capacity and cycle life at high current density, a charge–discharge test was performed for up to 70 cycles at the 1 C rate over the same voltage range with the cell test at the 0.1 C rate. The results at 1 C rate are similar to those of the cell tested at the 0.1 C rate (see Fig. 10). Although applying a high current density, the half-cell using a LiFePO$_4$/C composite with 5 wt.% PVA maintained a reversible capacity of about 115 mAh g^{-1} during cycling. Clearly a 2.06 wt.% carbon-coated LiFePO$_4$/C with 5 wt.% PVA in raw materials provided the best electrochemical properties. The reversible capacity loss at high current density in samples with a low carbon content is due to a large particle size besides the same reason mentioned above. In case of LiFePO$_4$ with 30 wt.% PVA, the thicker carbon coating impedes charge-transfer through the cathode, which is responsible for low reversible capacity. It is because the residual carbon exists mostly as an amorphous phase and an electronic insulator. Detailed investigation of this phenomenon is required and further study should examine charge-transfer resistance by means of electrochemical impedance spectroscopy (EIS).

In summary, carbon coating of particles by co-synthesizing the compounds with carbon can control particle growth, provide improved electrical contact between particles, and enhance the surface electronic conductivity—all of which contribute to an improvement in electrochemical performance, especially in rate capability.

4. Conclusion

In this study, a solid-state reaction using PVA as a carbon source with one-step heat treatment at 800 °C is sufficient to prepare an olivine structured LiFePO$_4$/C composite. This process is adequate for preparing carbon-coated LiFePO$_4$/C materials without a pre-sintering treatment step.

The effect of the amount of carbon on both the structural and electrochemical properties of LiFePO$_4$/C powders has been evaluated. All samples with various contents of PVA were LiFePO$_4$ with an ordered olivine structure. For materials with a low PVA content, although an impurity phase is not found in the XRD pattern, an unusual plateau is observed at 4.3 V in addition to the typical plateau of the Fe^{2+}/Fe^{3+} redox reaction in LiFePO$_4$ at 3.4 V. It is proposed that the 4.3 V plateau is related to a Fe^{3+}/Fe^{4+} redox couple of undetectable Fe^{3+} compounds that are present as an impurity. For materials with high PVA contents, the Li/LiFePO$_4$ cells deliver a small discharge capacity due to a thicker carbon coating by a large amount of residual carbon. In addition, an impurity phase of Fe$_2$P exists in the sample prepared from a precursor with 30 wt.% PVA content due to the highly reductive atmosphere from the pyrolysis of PVA during the sintering process. It is found that a 2.06 wt.% carbon-coated LiFePO$_4$/C composite material prepared from a by 5 wt.% PVA-containing precursor displays the best electrochemical properties, e.g., discharge capacity, capacity retention, and rate capability.

The addition of PVA into as-prepared materials plays an important role in reducing particle size to hinder the growth of LiFePO$_4$/C particles during heating. This provides better electrical contact between particles, and thereby enhances the surface electronic conductivity. A further advantage of PVA is to produce a reductive atmosphere during pyrolysis to aid the synthesis of LiFePO$_4$/C powders.

References

[1] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[2] S.-Y. Chung, J.T. Bloking, Y.-M. Chiang, Nat. Mater. 1 (2002) 123.
[3] A.S. Andersson, B. Kalska, L. Häggström, J.O. Thomas, Solid State Ionics 130 (2000) 41.
[4] A. Yamada, S.C. Chung, K. Hinikuma, J. Electrochem. Soc. 148 (2001) A224.
[5] M.M. Doeff, Y. Hu, F. McLarnon, R. Kostecki, Electrochem. Solid-State Lett. 6 (2003) A207.
[6] R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnik, J. Jamnik, J. Electrochem. Soc. 152 (2005) A607.
[7] H. Huang, S.-C. Yin, L.F. Nazar, Electrochem. Solid-State Lett. 4 (2001) A170.
[8] Z. Chen, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1184.

[9] G. Li, H. Azuma, M. Tohda, J. Electrochem. Soc. 149 (2002) A743.

[10] G.X. Wang, S. Bewlay, J. Yao, J.H. Ahn, S.X. Dou, H.K. Liu, Electrochem. Solid-State Lett. 7 (2004) A503.

[11] C.H. Mi, X.B. Zhao, G.S. Cao, J.P. Tu, J. Electrochem. Soc. 152 (2005) A483.

[12] X.-Z. Liao, Z.-F. Ma, Y.-S. He, X.-M. Zhang, L. Wang, Y. Jiang, J. Electrochem. Soc. 152 (2005) A1969.

[13] Y. Hu, M.M. Doeff, R. Kostecki, R. Finones, J. Electrochem. Soc. 151 (2004) A1279.

[14] J.W. Gilman, D.L. VanderHart, T. Kashiwagi, Fire and polymers II: materials and test for hazard prevention, in: ACS Symposium Series 599, American Chemical Society, Washington, DC, August 21–26, 1994, p. 161 (Chapter 11).

[15] D. Wang, H. Li, Z. Wang, X. Wu, Y. Sun, X. Huang, L. Chen, J. Solid State Chem. 177 (2004) 4582.

[16] A. Audemer, C. Wurm, M. Morcrette, S. Gwizdala, C. Masquelier, World Patent WO 2004/001881 A2.

[17] D. Wang, X. Wu, Z. Wang, L. Chen, J. Power Sources 140 (2005) 125.