Journal of Power Sources 189 (2009) 423–428

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Effect of synthesis temperature on the properties of $LiFePO_4$/C composites prepared by carbothermal reduction

L. Wang*, G.C. Liang, X.Q. Ou, X.K. Zhi, J.P. Zhang, J.Y. Cui

Institute of Power Source & Ecomaterials Science, Box 1055, Hebei University of Technology, 300130 Tianjin, China

ARTICLE INFO

Article history:
Received 19 June 2008
Accepted 8 July 2008
Available online 25 July 2008

Keywords:
$LiFePO_4$/C
Carbothermal reduction
$FePO_4$
Synthesis temperature

ABSTRACT

$LiFePO_4$/C composite cathode materials were synthesized by carbothermal reduction method using inexpensive $FePO_4$ as raw materials and glucose as conductive additive and reducing agent. The precursor of $LiFePO_4$/C was characterized by differential thermal analysis and thermogravimetry. The microstructure and morphology of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and particle size analysis. Cyclic voltammetry (CV) and charge/discharge cycling performance were used to characterize their electrochemical properties. The results showed that the $LiFePO_4$/C composite synthesized at 650 °C for 9 h exhibited the most homogeneous particle size distribution. Residual carbon during processing was coated on $LiFePO_4$, resulting in the enhancement of the material's electronic properties. Electrochemical measurements showed that the discharge capacity first increased and then decreased with the increase of synthesis temperature. The optimal sample synthesized at 650 °C for 9 h exhibited a highest initial discharge capacity of 151.2 mA h g^{-1} at 0.2 C rate and 144.1 mA h g^{-1} at 1 C rate with satisfactory capacity retention rate.

1. Introduction

Secondary lithium batteries are attractive power sources for portable electronic devices as well as electrical vehicle. Lithium batteries have high energy and power density and good cycle life compared with those of Ni/MH and Ni/Cd batteries [1]. Recently, olivine-structured $LiFePO_4$ proposed by Padhi et al. [2] is gaining particular interest as a candidate cathode material for rechargeable lithium batteries due to its high energy density, low cost, environmental friendliness and safety.

However, $LiFePO_4$ has very poor electronic conductivity ($\sim 10^{-9}$ S cm^{-1}) and Li-ion diffusion coefficient ($\sim 1.8 \times 10^{-14}$ cm^2 s^{-1}) at room temperature, leading to its poor rate capability. Two approaches have been attempted to overcome this problem. One is to enhance its electronic conductivity by coating an electron-conducting layer around the particles or by selective doping with supervalent cations [3–5]. The other is to minimize the particle size by modifying synthesis conditions [6–8]. Furthermore, synthesis route would significantly affect the material's electrochemical performances. Several alternative processing routes have been reported to prepare $LiFePO_4$ with fine and homogeneous particle size, such as sintering at low-temperature, co-precipitation in aqueous medium [9], hydrothermal synthesis [10] and mechanochemical activation [11]. The electrochemical properties of $LiFePO_4$ powders prepared by the above approaches have achieved high specific capacity. However, expensive raw material of iron oxalate limits the practical application of $LiFePO_4$.

From the above reviews, in order to obtain a well-crystallized $LiFePO_4$ with relatively small particle size, cut down the cost, simplify the synthesis technology and enhance the specific capacity of the material, we introduced a novel carbothermal reduction method to synthesize $LiFePO_4$/C composite by using $FePO_4$ as raw materials, and glucose as conductive additive and reducing agent. Especially, the influence of synthesis temperature on the microstructure and electrochemical properties was systematically investigated.

2. Experimental

Stoichiometric amounts of $FePO_4$ (A.R.), Li_2CO_3 (A.R.) and glucose (24.8 g per mole $FePO_4$) were mixed and then ground uniformly in a mortar. The mixture was transferred to a temperature-controlled furnace and fired under the flowing nitrogen for 9 h at 550, 600, 650, 700 and 750 °C, respectively, to synthesize $LiFePO_4$ powders with in situ coated carbon. The resulting products were defined as L550, L600, L650, L700 and L750, respectively.

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* Corresponding author. Tel.: +86 22 4850; fax: +86 22 4850.
E-mail address: tigerwl29@yahoo.com.cn (L. Wang).

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doi:10.1016/j.jpowsour.2008.07.032

Thermogravimetric (TG) analysis was investigated on a SDT Q600 TG–differential thermal analysis (DTA) apparatus. The crystal structures of the prepared samples were analyzed by X-ray diffraction (XRD) on a Rigaku-D/MAX-2550PC diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) using a 2θ step of 0.02°. The morphology and microstructure were observed using field emission-scanning electron microscopy (FE-SEM) with a FEI SIRION microscope and high-resolution transmission electron microscope (HR-TEM) with Philips Tecnai F20. The particle size distribution of the sample was determined by Laser Particle Sizer (LS800). The electronic conductivity was measured on disk samples using the two-point probe method. A high impedance multimeter was used to measure the resistance at room temperature. Conductivity was calculated from the resistance and specimen dimensions.

The electrochemical characteristics were evaluated by using a 2430 coin type cell with a lithium metal anode and 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume) electrolyte. The separator used was a Celgard 2400 microporous membrane. The cathode electrode was made in the following way. We mixed the $LiFePO_4$/C powder with acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 80:10:10, then rolled the mixture into a 0.16 mm thick sheet and cut it into pellets. The cells were assembled in an argon-filled glove box. Cyclic voltammetry (CV) measurements were performed using Arbin instrument between 2.5 and 4.5 V at a scan rate of 0.1 mV s^{-1}. The galvanostatic charge/discharge test was performed between 2.3 and 4.2 V at room temperature with different current densities (0.2 and 1 C), and 1 C rate was 150 mA h g^{-1}. Current density and specific capacities were calculated based on the mass of $LiFePO_4$/C in the electrode.

3. Results and discussion

Fig. 1 shows the TG/DTA curves of the $FePO_4{\cdot}2H_2O$ powders with a heating rate of 10 °C min^{-1} from room temperature to 900 °C in air. On the DTA curve near 200 °C, there is a very strong endothermic peak, associating with the sharp weight loss on the TG curve, which is related to the quick dehydration of $FePO_4{\cdot}2H_2O$. During 200–600 °C, the TG curve indicates the slow elimination of residual H_2O in $FePO_4{\cdot}2H_2O$, whose weight loss can reach 19.8%, exactly corresponding to the loss of crystalline water of $FePO_4{\cdot}2H_2O$. And one exothermic peak is displayed at higher temperature of 663 °C, which is not accompanied by appreciable weight loss in the TG curve, indicating the transformation of the amorphous $FePO_4$ to hexagonal $FePO_4$ crystal. Based on the above analysis, we pre-heat-treated the $FePO_4{\cdot}2H_2O$ powders at 700 °C for certain time in air to obtain anhydrous hexagonal $FePO_4$ powders, which were used as the precursors to synthesize $LiFePO_4$/C composites.

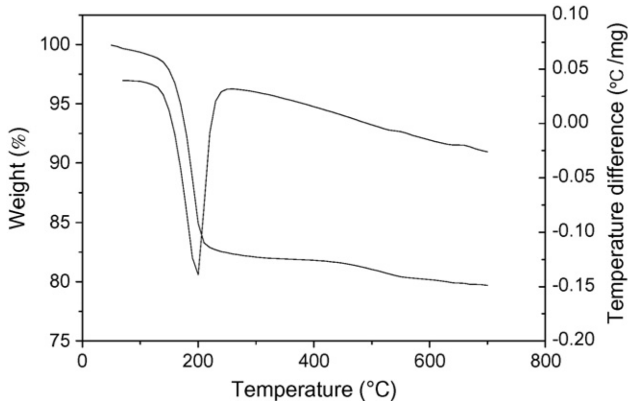

Fig. 1. TG/DTA curves of the $FePO_4{\cdot}2H_2O$.

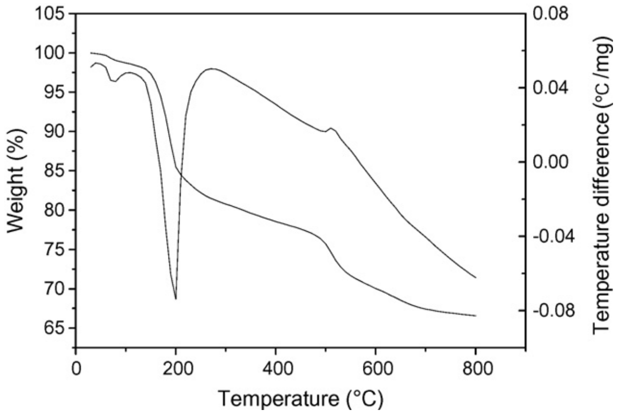

Fig. 2. TG/DTA curves of the mixture of $FePO_4{\cdot}2H_2O$, Li_2CO_3 and glucose from room temperature to 900 °C with a heating rate of 10 °C min^{-1} in a nitrogen flow.

The process for the formation of carbon-coated $LiFePO_4$ composites from $FePO_4$, Li_2CO_3 and glucose is assumed to be carried out according to the following steps:

$$C_6H_{12}O_6{\cdot}H_2O \rightarrow 6C + 7H_2O \tag{1}$$

$$2FePO_4 + Li_2CO_3 + 0.5C \rightarrow 2LiFePO_4 + 1.5CO_2 \tag{2}$$

or

$$2FePO_4 + Li_2CO_3 + 2C \rightarrow 2LiFePO_4 + 3CO \tag{3}$$

Fig. 2 shows the TG/DTA curves of the mixture of $FePO_4{\cdot}2H_2O$, Li_2CO_3 and glucose from room temperature to 900 °C with a heating rate of 10 °C min^{-1} in a nitrogen flow rate of 100 mL min^{-1}. From Fig. 2 we can see that the TG curve shows three obvious weight loss steps over the temperature range from ambient to 530 °C. The peak at around 90 °C in DTA curve can be assigned to the loss of absorption water of the mixture. The weight loss from 150 to 300 °C in TG curve is related to the loss of crystalline water of the precursor $FePO_4{\cdot}2H_2O$. And the exothermic peak at 530 °C in DTA curve, accompanied by a weight loss in the TG curve, may be ascribed to the carbothermal reduction and the formation of $LiFePO_4$, indicating that the synthesis temperature must be higher than 530 °C. Therefore, we choose the different synthesis temperatures as 550, 600, 650, 700 and 750 °C.

Fig. 3 shows the XRD patterns of the $LiFePO_4$/C composites synthesized at 550, 600, 650, 700 and 750 °C, respectively. The main phase of all the samples can be identified as $LiFePO_4$ with an ordered olivine structure indexed to orthorhombic *Pnmb* (JCPDS

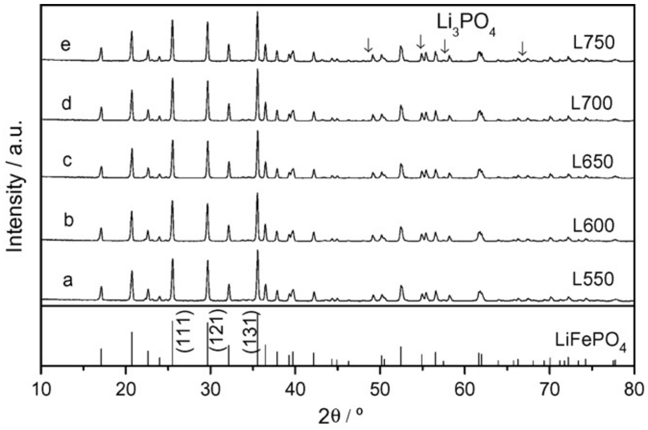

Fig. 3. XRD patterns of $LiFePO_4$/C composites synthesized at different temperatures.

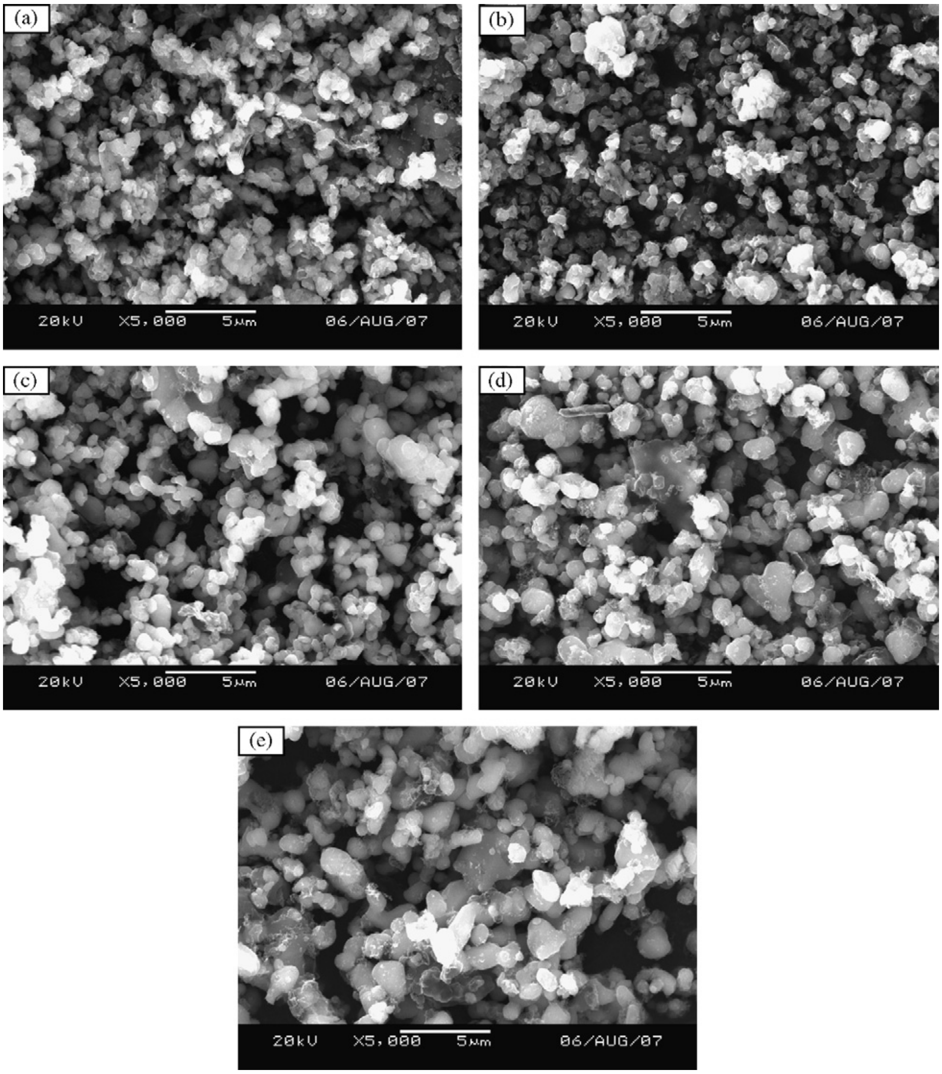

Fig. 4. SEM images of $LiFePO_4$/C composites synthesized at different temperatures (a) L550, (b) L600, (c) L650, (d) L700 and (e) L750.

card number: 40-1499) [12]. And Table 1 lists the lattice parameters of all the samples, which are very close to the standard data ($a = 0.6019$ nm, $b = 1.0347$ nm, $c = 0.4704$ nm, $V = 0.2930$ nm^3), but slightly increase with the synthesis temperature increasing. Besides the major phase, there are little amounts of impurity phase Li_3PO_4, which may be caused by the higher content of PO_4^{3-} in $FePO_4$, thus leading to its combination with Li^+. From Fig. 3 we can also see that the peak intensity of $LiFePO_4$ increases slightly with increasing the synthesis temperature from 550 to 650 °C, indicating an increase of crystallinity as may occur from growth of grain size, ordering of local structure, and release of lattice strain [13]. However, the further increase of synthesis temperature to 750 °C does not lead to an obvious increase of peak intensity, indicating that the full crystallization can be obtained at temperature higher than 650 °C. On the other hand, there is no evidence of diffraction peaks for carbon due to its amorphous structure and/or low content in the composites, and its presence does not influence the structure of $LiFePO_4$. Based on Scherrer formula $D = k\lambda/\beta\cos\theta$, where k is 0.9, λ is 0.15406 nm and β is the full-width-at-half-maximum (FWHM) of the diffraction peak on a 2θ scale, we can get the crystallite size (D) of the $LiFePO_4$/C composites synthesized at different temperatures according to D_{131}, D_{111} and D_{121} values, as tabulated in Table 1. From Table 1 we can see that the D values of $LiFePO_4$/C composites prepared at 550, 600, 650, 700 and 750 °C are 50.8, 51.5, 56.2, 58.2 and 61.9 nm, respectively. It is found that the crystallite size increases with synthesis temperature due to enhanced crystal growth caused by higher synthesis temperature, which is still smaller than that of the corresponding $LiFePO_4$ sample prepared by conventional solid-state reaction due to the inhibition of crystal growth by the presence of carbon generated from glucose.

Table 1
Structure parameters of $LiFePO_4$/C composites synthesized at different temperatures

	Standard	L550	L600	L650	L700	L750
a (nm)	0.6019	0.60085	0.60089	0.60121	0.60128	0.60129
b (nm)	1.0347	1.03320	1.03312	1.03363	1.03376	1.03376
c (nm)	0.4704	0.46942	0.46958	0.46968	0.46990	0.46996
V (nm^3)	0.2930	0.29141	0.29151	0.29187	0.29208	0.29212
D (nm)	–	50.8	51.5	56.2	58.2	61.9

Fig. 4 shows the SEM images of $LiFePO_4$/C composites synthesized at (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C and (e) 750 °C. All the powders synthesized at different temperatures show a spherical morphology. A fine powder with an average size of about <1 μm was obtained by calcinations at 550, 600 and 650 °C. The particles of samples L700 and L750 are also fine except for a few agglom-

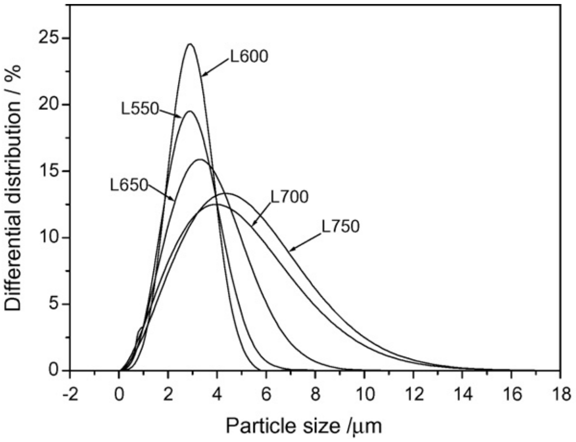

Fig. 5. The particle size distribution curves of $LiFePO_4/C$ composites synthesized at different temperatures.

Table 2
The D_{50} values and electronic conductivity (σ) of $LiFePO_4/C$ composites synthesized at different temperatures

	L550	L600	L650	L700	L750
D_{50} (μm)	2.25	2.35	2.49	2.84	3.18
σ ($S\,cm^{-1}$)	1.99×10^{-5}	3.51×10^{-4}	1.82×10^{-3}	1.18×10^{-2}	1.70×10^{-2}

erated abnormal particles (Fig. 4d and e). The fine particle size is what we expected due to the lower diffusion coefficient of Li-ion in $LiFePO_4$ cathode. Obviously, the higher synthesis temperature will result in undesirable particle growth, which is believed to be disadvantageous to the electrochemical performance. This observation is also supported by the particle size distribution curves shown in Fig. 5. The narrower distribution curves of the samples synthesized at lower temperatures (<650 °C) indicate the homogeneous particle size distribution of the powders. However, the samples synthesized at higher temperatures (>650 °C) show a broadened distribution curve due to the inhomogeneous particle size distribution caused by the agglomeration of some small particles into larger ones. Among which, the sample synthesized at 650 °C exhibits the narrowest particle size distribution curve, indicating its most uniform particle size distribution, which is believed to be advantageous to the improvement of electrochemical properties. It is generally accepted that the value at 50% cumulative population (D_{50}) represents the average particle size, which is listed in Table 2. From Table 2 we can see that with the temperature increasing from 550 to 650 °C, the D_{50} values increase slightly from 2.25 (L550) to 2.49 μm (L650), and when temperature increases further to 750 °C, the D_{50} values increase abruptly to 3.18 μm (L750), which is in good agreement with the SEM observations in Fig. 4.

Fig. 6 shows TEM images of $LiFePO_4/C$ composite synthesized at 650 °C (L650). From the TEM images, we can see that the primary particles are larger than the average size of the monocrystallite grains deduced from the application of the Scherrer formula on the XRD pattern. Therefore, the primary particles are polycrystallites of $LiFePO_4$ made of a few monocrystallites of $LiFePO_4$. The amorphous carbon layer is well observed in Fig. 6a and b. A network formation of carbon appears in the interstitial grain-boundary region, which can explain the electrical continuity between $LiFePO_4$ crystallites. In the micrographs, the $LiFePO_4$ crystallites appear as the darker regions while the carbon coating is surrounding the primary particle as the grayish region. And the presence of this amorphous carbon layer is believed to inhibit grain growth of the material as well as improve the electronic conductivity of the product phase, thus leading to the enhancement of electrochemical properties.

Compared with the $LiFePO_4$ compounds synthesized by conventional solid-state reaction [6,14–16], the fine particle sizes obtained here indicate that the *in-situ* coating of carbon from the pyrolysis of glucose on the surface of $LiFePO_4$ particles hinders the particle growth efficiently. According to the XRD patterns (Fig. 3) and SEM images (Fig. 4), we can also conclude that using a synthesis temperature higher than 650 °C leads only to particle growth but does not improve the crystallinity of $LiFePO_4$ further.

Table 2 also lists the electronic conductivity (σ) of all samples obtained from the two-point probe method. It can be seen that with the increase of synthesis temperature, the electronic conductivity increases from 1.99×10^{-5} (L550) to $1.70 \times 10^{-2}\,S\,cm^{-1}$ (L750). The lower electronic conductivity of the samples synthesized at lower temperatures (<650 °C) may be due to the thinner carbon layer on the surfaces caused by the smaller particle size and larger surface areas, because the amount of carbon from the pyrolysis of glucose is constant. Compared with pure $LiFePO_4$ ($\sim10^{-9}\,S\,cm^{-1}$), the *in-situ* carbon-coated $LiFePO_4$ composites synthesized at different temperatures exhibit a $\sim10^4$ to 10^7 increase in electronic conductivity, comparable to those in the lithium storage cathodes currently used, such as $LiCoO_2$ ($\sim10^{-3}\,S\,cm^{-1}$) [17] and $LiMn_2O_4$ (2×10^{-5} to $5 \times 10^{-5}\,S\,cm^{-1}$) [18]. The improvement of electronic conductivity is believed to be beneficial for the enhancement of electrochemical performance.

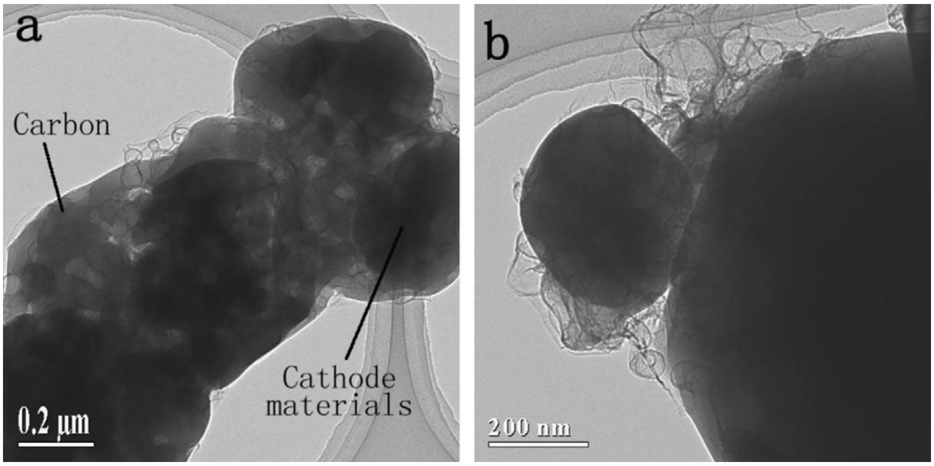

Fig. 6. TEM images of $LiFePO_4/C$ composite synthesized at 650 °C (L650).

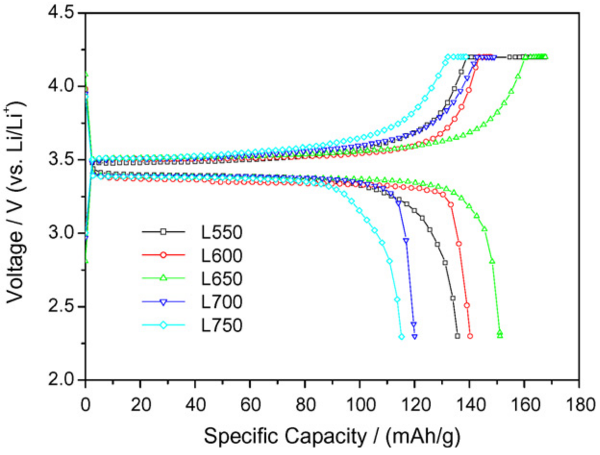

Fig. 7. Initial charge/discharge curves of $LiFePO_4/C$ composites synthesized at different temperatures.

The initial charge/discharge curves of $LiFePO_4/C$ samples synthesized at different temperatures at 0.2 C rate are illustrated in Fig. 7. All the samples exhibit a flat and long voltage plateau at ~3.4 V, which indicates the two-phase redox reaction proceeds via a first-order transition between $LiFePO_4$ and $FePO_4$ [2]. The initial discharge capacities for $LiFePO_4/C$ composites prepared at 550, 600, 650, 700 and 750 °C are 135.6, 140.2, 151.2, 120.1 and 115.2 mA h g^{-1}, respectively. The small voltage difference between the charge and discharge plateaus of about 0.15 V is representative of their good kinetics, especially on consideration of the low electrochemical diffusion rate of lithium ions in a solid phase.

Fig. 8 presents the initial discharge capacities of $LiFePO_4/C$ composites synthesized at different temperatures. It can be seen that the discharge capacity depends highly on the synthesis temperature, which first increases and then decreases with the temperature increasing from 550 to 750 °C. It is generally accepted that the electrochemical insertion/extraction performances in/from $LiFePO_4$ are dependent on several factors, including the powder morphology, particle sizes and homogeneity, crystallinity, and electronic conductivity of the material [15,19,20]. The lower discharge capacity of $LiFePO_4/C$ samples synthesized at temperature below 650 °C may be attributed to their lower crystallinity and electronic conductivity, although the sample particles synthesized at lower temperature are very fine (see Fig. 4). However, the abrupt increase of particle size leads to the lower discharge capacity of the samples synthesized at temperatures higher than 650 °C with higher crystallinity and electronic conductivity, thus prolonging the diffusion length of lithium ion from surface to center part, which is believed to be detrimental to the electrochemical performance. Thus we can conclude that crystallization degree and electronic conductivity determine the electrochemical capacities of the samples synthesized at lower temperatures (<650 °C), while for the samples synthesized at higher temperatures (>650 °C), particle size becomes a dominating factor. The present investigation shows that the composite synthesized at 650 °C is well crystallized and homogeneous fine sized at the same time, ensuring an electrochemical capacity higher than those of the other samples here.

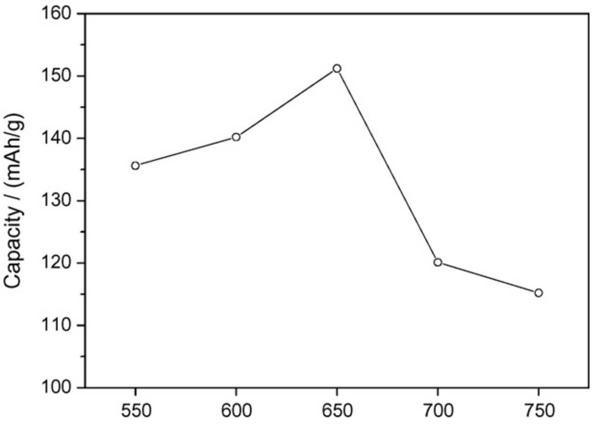

Fig. 8. Relationship between synthesis temperature and initial discharge capacities of $LiFePO_4/C$ composites.

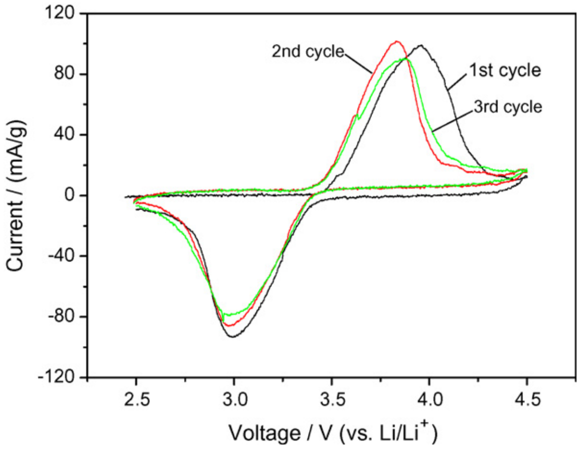

Fig. 9. Cyclic voltammogram curves of sample L650 in the first three cycles.

Fig. 9 shows the CV profiles of sample L650 in the first three cycles at a scanning rate of 0.1 mV s^{-1} from 2.5 to 4.5 V. We can see that the voltage charge/discharge profiles of all three cycles are almost reduplicate. There is only one peak pair, consisting of one anodic peak (charge) and one cathodic peak (discharge), which corresponds to the two-phase charge/discharge reaction of the Fe^{2+}/Fe^{3+} redox couple. During the initial three cycles, the cathodic peak of sample L650 has a shift to the higher voltage and the anodic peak has a shift to the lower voltage, suggesting the decrease in the redox potential separation, which implies that the electrode reactivity is improved in initial cycling. The reproducibility of the peaks in the CV plots confirms the good reversibility of lithium extraction/insertion reactions in the $LiFePO_4/C$ composites.

The cycling behaviors of $LiFePO_4/C$ composites synthesized at different temperatures at 0.2 and 1 C rates are described in Fig. 10.

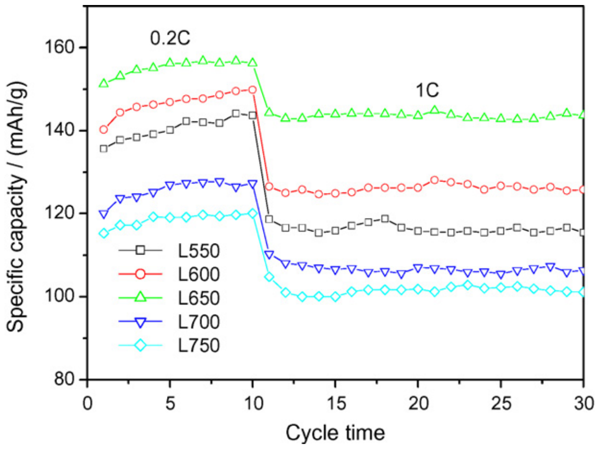

Fig. 10. Cycling behaviors of $LiFePO_4/C$ composites synthesized at different temperatures.

We can see that the capacities of all samples at 0.2 C rate gradually increase in the initial cycles. This is due to the incomplete dispersion of the electrolyte into the electrode materials at the beginning. On the other hand, all the samples show excellent cycling behaviors at 1 C rate, which can be attributed to the enhancement of the electronic conductivity by the carbon coating, and also to the excellent cycle ability of $LiFePO_4$ itself due to the high stability of the olivine structure and the minor lattice adjustment upon cycling [6]. The optimal sample synthesized at 650 °C exhibits a highest discharge capacity of 156.8 mA h g^{-1} at 0.2 C rate and 144.1 mA h g^{-1} at 1 C rate. The decrease of discharge capacity with the increase of discharge current is caused by the intrinsic low diffusion rate of lithium ions in the $LiFePO_4$ particles [2].

4. Conclusions

In order to cut down the cost and simplify the synthesis technology, the $LiFePO_4$/C composite cathode materials were synthesized by carbothermal reduction method using $FePO_4$ as raw materials and glucose as conductive additive and reducing agent. The pyrolysis of glucose during the synthesis process ensures the reduction of Fe^{3+} to Fe^{2+}, and the residual carbon controls the morphology and sizes of the powders, and enhances the surface electronic conductivity of $LiFePO_4$/C composites, which is believed to be advantageous to their electrochemical performances. The electrochemical results showed that the discharge capacity of the $LiFePO_4$/C composites first increased and then decreased with the increase of synthesis temperature. The material synthesized at 650 °C for 9 h had best electrochemical performance and its discharge capacity could reach 156.8 mA h g^{-1} at 0.2 C rate and 144.1 mA h g^{-1} at 1 C rate with satisfactory capacity retention rate. On a general point, we believe the carbothermal reduction is a promising method for mass production of $LiFePO_4$/C composite with improved electrochemical performances and low cost.

References

[1] M. Armand, Solid State Ionics 69 (1994) 309.
[2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
[3] N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 97/98 (2001) 503.
[4] F. Croce, A.D. Epifanio, J. Hassoun, A. Deptula, T. Olezac, B. Scrosati, Electrochem. Solid-State Lett. 5 (2002) A47.
[5] K. Konstantinov, S. Bewlay, G.X. Wang, M. Lindsay, J.Z. Wang, H.K. Liu, S.X. Dou, J.-H. Ahn, Electrochim. Acta 50 (2004) 421.
[6] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
[7] P.P. Prosini, M. Carewska, S. Scaccia, P. Wisniewski, M. Pasquali, Electrochim. Acta 48 (2003) 4205.
[8] H.S. Kim, B.W. Cho, W. Cho, J. Power Sources 132 (2004) 235.
[9] G. Amold, J. Garche, R. Hemmer, S. Strobele, C. Vogler, M. Wohlfahrt-Mehrens, J. Power Sources 119–121 (2003) 247.
[10] S.F. Yang, P.Y. Zavalij, M. Whittingham, Electrochem. Commun. 3 (2001) 505.
[11] N. Kosova, E. Devyatkina, Solid State Ionics 172 (2004) 181.
[12] M. Takahashi, S. Tobishima, K. Takei, Y. Sakurai, J. Power Sources 97/98 (2001) 508.
[13] S.S. Zhang, J.L. Allen, K. Xu, T.R. Jow, J. Power Sources 147 (2005) 234.
[14] H. Huang, S.C. Yin, L.F. Nazar, Electrochem. Solid-State Lett. 4 (2001) A170.
[15] A.S. Andersson, J.O. Thomas, J. Power Sources 97/98 (2001) 498.
[16] P.P. Prosini, M. Carewska, S. Scaccia, P. Wisniewski, S. Passweini, M. Pasquali, J. Electrochem. Soc. 149 (2002) A886.
[17] J. Molenda, A. Stoklosa, T. Bak, Solid State Ionics 36 (1989) 53.
[18] H. Kawaia, M. Nagatab, H. Kageyamac, H. Tukamoto, A.R. West, Electrochim. Acta 45 (1999) 315.
[19] S. Yang, Y. Song, P.Y. Zavalij, M.S. Whittingham, Electrochem. Commun. 4 (2002) 239.
[20] S. Franger, F.L. Cras, C. Bourbon, H. Rouault, Electrochem. Solid-State Lett. 5 (2002) A231.