

## Optimizing a new synthesis route for LiFePO<sub>4</sub>/C composites

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We synthesized LiFePO<sub>4</sub>/C composites from an aqueous solution that contained LiNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and sucrose. We utilized the sucrose as synthesizing agent and carbon source. The LiFePO<sub>4</sub>/C composites were synthesized under various conditions such as the calcination temperature and amount of sucrose to optimize our new synthesis route. In this paper, we discuss the electrochemical properties of the composites as a function of calcination temperature and amount of sucrose. The LiFePO<sub>4</sub>/C composite synthesized at 750 °C with 6.85 wt.% residual carbon showed a high discharge capacity 134 mAhg<sup>-1</sup> at a current density 100 mA g<sup>-1</sup>.

**Key words:** LiFePO<sub>4</sub>, Synthesis, Sucrose, Cathode, Lithium battery.

### Introduction

Recently, the iron-based materials such as LiFeO<sub>2</sub>, LiFePO<sub>4</sub>, Li<sub>3+x</sub>Fe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> become promising secondary battery materials because of their abundance and non-toxicity as Fe sources. Among them, LiFePO<sub>4</sub> can deliver 169 mAhg<sup>-1</sup> capacity by a redox process of Fe<sup>3+</sup>/Fe<sup>2+</sup> around 3.5 V vs. lithium. In 1997, Padhi *et al.* reported that LiFePO<sub>4</sub> could be used as a cathode material and ca. 0.6-0.7 mol of Li<sup>+</sup> ions (110 mAhg<sup>-1</sup>) could intercalate/de-intercalate by applying a very low current density of 2 mA g<sup>-1</sup> [1]. Yamada *et al.* also suggested that 95% of theoretical capacity could be utilized by the optimization of a synthetic route controlling the particle size and residual amount of Fe<sup>3+</sup> when cycled at a current density of 0.12 mAcm<sup>-2</sup> [2].

Generally, a cathode material in a lithium rechargeable battery should be a good mixed conductor because the electrical conductivity of the cathode especially affects the rate capability of the battery. Unfortunately, LiFePO<sub>4</sub> has a low electrical conductivity and a low lithium diffusivity at the interface between LiFePO<sub>4</sub> (triphylite) and FePO<sub>4</sub> (heterosite) [1, 3]. Thus, the electrochemical properties of LiFePO<sub>4</sub> are limited by its low electrical conductivity. Much effort, therefore, has been devoted to increase the electrical conductivity and optimize rate capability of LiFePO<sub>4</sub>. Up to now, although, they are not the way to change the intrinsic electrical conductivity of LiFePO<sub>4</sub>, two representative methods have been reported as follows: one is to minimize the particle size, and the other is to coat particles with carbon [2, 4]. In particular, carbon coating was found to be very effective in enhancing the rate capability [5-8].

In making a LiFePO<sub>4</sub>/C composite, several methods have been suggested [4-9]. One of them is to use sugar as a source of carbon. N. Ravet, J.B. Goodenough and S. Besner mixed a sugar solution with a synthesized LiFePO<sub>4</sub> powder and heated the mixture to make carbon coated LiFePO<sub>4</sub> [4]. Z. Chen and J.R. Dahn suggested a different method to produce a LiFePO<sub>4</sub>/C composite: sugar was added to the raw materials of LiFePO<sub>4</sub> before mixing, and subsequently mixed in the solid state and heat-treated [6]. Carbon would be more homogeneously mixed with the LiFePO<sub>4</sub> powders and the result was a better rate capability was obtained in with latter method. Thus, it is certain that the way making a LiFePO<sub>4</sub>/C composite is important to determine the properties of the LiFePO<sub>4</sub>/C composite.

Every LiFePO<sub>4</sub>/C composite reported up to now has been synthesized partly based on a solid-state reaction, which means that all or some of the raw materials are mixed in the solid-state and subsequently heat-treated. In a previous report, we suggested a simple and novel way of producing a LiFePO<sub>4</sub>/C composite using an aqueous solution of LiNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and sucrose. We also showed a different morphology of the carbon in the LiFePO<sub>4</sub>/C composite and good electrochemical properties [10]. In this paper, we report the optimized synthesis conditions to get the best electrochemical properties of LiFePO<sub>4</sub>/C composites in terms of calcination temperature and amount of sucrose.

### Experimental

The LiFePO<sub>4</sub>/C composites were synthesized an aqueous solution of the raw materials and sucrose. The precursor was prepared by heating an aqueous solution of LiNO<sub>3</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and a sucrose solution above 200 °C. We heated the precursor at 400 °C for 5 h in air and then ground the result into powder. This powder was calcined again between 550 °C and 850 °C for 10 h in the inert atmosphere to make the LiFePO<sub>4</sub>/C composites.

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X-ray diffraction experiments were carried out on the precursor and the  $\text{LiFePO}_4/\text{C}$  composites. The lattice parameters of the  $\text{LiFePO}_4/\text{C}$  composites were calculated by the least squares method. The morphologies of the precursor and the composites were observed by scanning electron microscopy (SEM). The amount of carbon in the composites was determined: A specific amount of the  $\text{LiFePO}_4/\text{C}$  composite was dissolved in hydrochloric acid. This solution was filtered and the residue, carbon, was washed with distilled water, dried and then weighed [11]. Fe K-edge X-ray absorption spectra were recorded at the 3C1 beam line of PLS (Pohang Light Source, Korea) with a Si (111) double crystal monochromator. The storage ring was operated with an electron energy of 2 GeV and a current from 100 to 120 mA. The data were collected in the transmittance mode. Energy calibration was carried out before all measurements using an Fe metal foil. The electrical resistance of the  $\text{LiFePO}_4/\text{C}$  composite was measured by a two-point DC method.

The cathode slurry was fabricated by mixing the  $\text{LiFePO}_4/\text{C}$  composite, graphite as conducting material and PVDF (polyvinylidene fluoride) as the binder in the weight ratio 85 : 10 : 5. The slurry was spread on a Ni ex-met and dried at 120 °C for 24 h in a vacuum oven. The screw type half-cells were assembled with the prepared cathode, lithium foil as anode and 1 M  $\text{LiPF}_6$  in EC/DEC (1 : 1 vol%) as electrolyte in an Ar filled glove box. The electrochemical properties of the cathode were characterized by a galvanostatic method between 2.5 V and 4.0 V vs. lithium by applying various current densities at 25 °C. The experimental procedure is represented in Fig. 1.

## Results and Discussion

### The role of sucrose

The  $\text{LiFePO}_4/\text{C}$  composites were synthesized from the

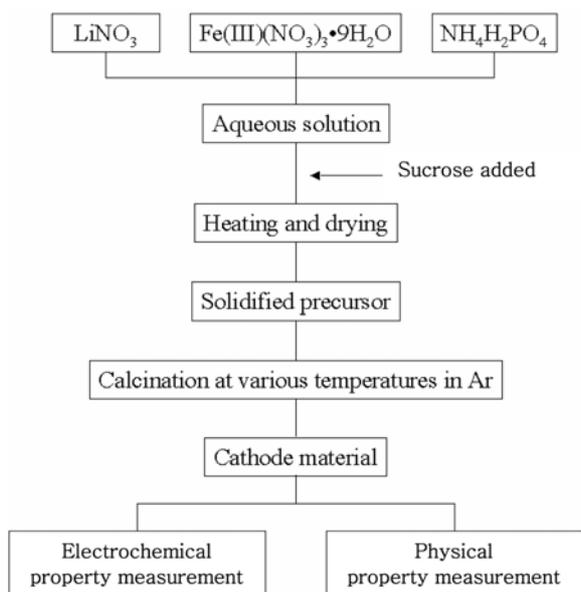


Fig. 1. The flow chart of experimental procedure.

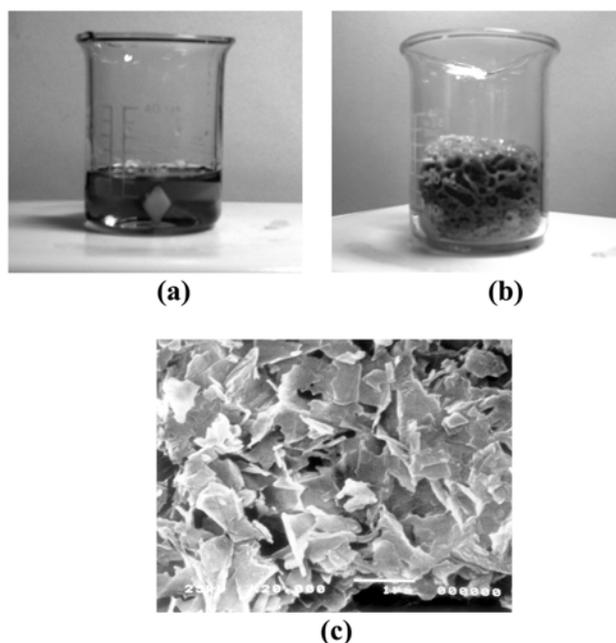
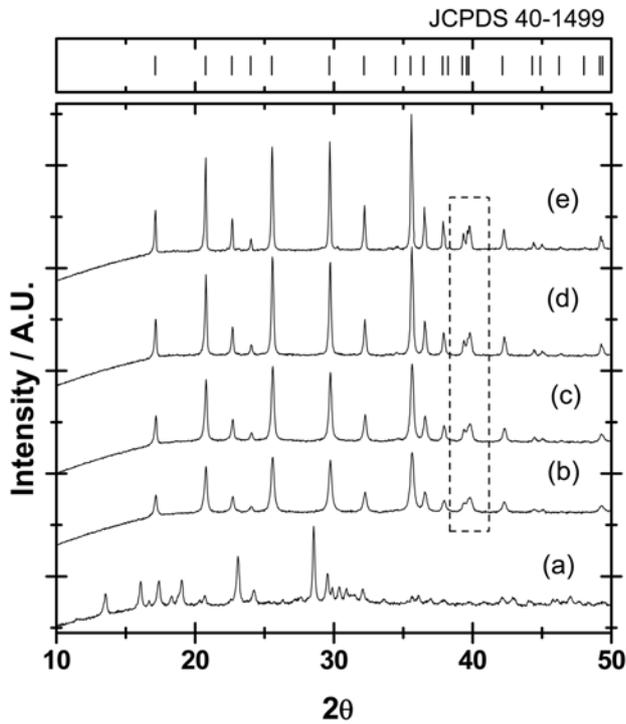


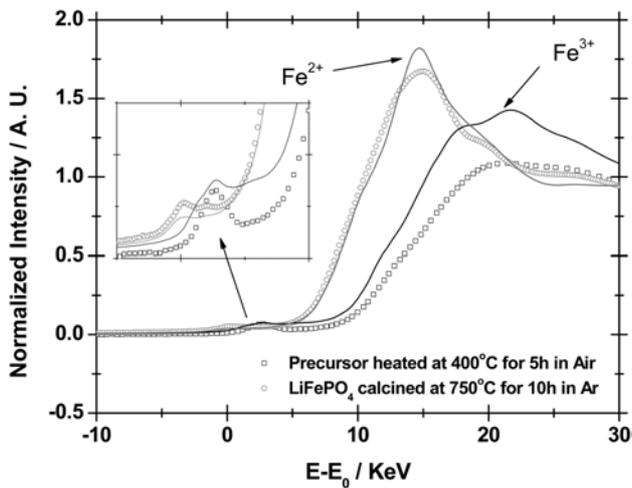
Fig. 2. Photograph of (a) the aqueous solution, (b) heated precursor and (c) SEM image of heated precursor above 200 °C.

aqueous solution of  $\text{LiNO}_3$ ,  $\text{F}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and sucrose with molar ratios 1 : 1 : 1 : 0.3. We utilized sucrose as the synthesizing agent and as a source of carbon. Generally, disaccharide sucrose dissolves in distilled water and then it decomposes into glucose and fructose by hydrolysis. When the sucrose solution is heated, water as the solvent in the solution evaporates and the solution becomes a viscous liquid with a brownish color, which is the maillard reaction. After that, the sucrose solution turns suddenly into a dark brown solid around 195 °C. We used these properties of sucrose to prevent the inhomogeneous precipitation and re-crystallization of the aqueous solution during making the precursor. When the solution was heated, it turned into a porous solid above 200 °C as in Fig. 2(a) and 2(b). This sudden solidification could form a homogeneous precursor without the inhomogeneous re-crystallization of the raw materials. The precursor had a flat shape with 1  $\mu\text{m}$  and homogeneous morphology as in the SEM image of Fig. 2(c). The precursor was heated at 400 °C for 5 h in air and then calcined between 550 °C and 850 °C for 10 hr in an inert atmosphere. Fig. 3 shows the XRD patterns of the precursor and the  $\text{LiFePO}_4/\text{C}$  composites with an increase in the calcination temperature. The XRD patterns of the composites agreed well with JCPDS 40-1499 that is the XRD pattern of  $\text{LiFePO}_4$  with an orthorhombic structure. These data indicate that the  $\text{LiFePO}_4/\text{C}$  composites were successfully synthesized over all the calcination temperature range.

Because we used  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as Fe source in which the Fe ions are trivalent, Fe should be reduced to make the  $\text{LiFePO}_4/\text{C}$  composites in which the Fe ions are divalent. Fig. 4 shows XANES spectra of the Fe K-edge for the precursor heated at 400 °C for 5 h in air and the  $\text{LiFePO}_4/\text{C}$  composite calcined at 750 °C for 10 h in Ar with  $\text{FeC}_2\text{O}_4$



**Fig. 3.** The collected XRD data of the precursor (a) and the  $\text{LiFePO}_4/\text{C}$  composites calcined at (b) 550 °C, (c) 650 °C, (d) 750 °C and (e) 850 °C in an inert atmosphere.



**Fig. 4.** XANES spectra of the Fe K-edge for the precursor heated at 400 °C for 5 h in air and the  $\text{LiFePO}_4/\text{C}$  composite calcined at 750 °C for 10 h in Ar.  $E_0 = 7112$  eV.

and  $\text{Fe}_2\text{O}_3$  as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  references, respectively. The pre-edge region gives us the valence state of the Fe ions. The pre-edge peak positions of the heated precursor and calcined  $\text{LiFePO}_4/\text{C}$  composite were similar to those of  $\text{Fe}_2\text{O}_3$  and  $\text{FeC}_2\text{O}_4$ , respectively. These data mean that the valence state of Fe in the calcined  $\text{LiFePO}_4/\text{C}$  is divalent and the Fe ions reduce during calcination. We believe that the carbon from the sucrose provides a reducing force under an inert atmosphere. Therefore, sucrose could play the roles as synthesizing and reducing agents in our experiments

**Table 1.** Full width at half maximum, lattice parameter and residual carbon content of the  $\text{LiFePO}_4/\text{C}$  composites synthesized at various temperature in Ar atmosphere

Sample	T55	T65	T75	T85
Calcination temp./°C	550	650	750	850
Carbon amount/wt%	5.28	6.15	6.85	3.35
hkl	FWHM (Full Width at Half Maximum)			
101	0.2152	0.1681	0.1314	0.1036
111	0.2257	0.1791	0.1338	0.1019
020	0.2365	0.1890	0.1368	0.1016
301	0.2437	0.1950	0.1390	0.1020
311	0.2542	0.2033	0.1425	0.1032
Lattice parameters				
a/Å	10.3206	10.3191	10.3211	10.3278
b/Å	6.0041	6.0023	6.0030	6.0060
c/Å	4.6942	4.6903	4.6896	4.6922
Cell volume / Å <sup>3</sup>	290.8821	290.5092	290.5533	291.0513

and we believe that the residual carbon after some being consumed as a reducer could improve the electronic conductivity of the composites.

### Electrochemical properties as a function of calcination temperature

The  $\text{LiFePO}_4/\text{C}$  composites were synthesized at various temperature and their electrochemical properties as a function of calcination temperature were measured. The full width at half maximum (FWHM) of several peaks, lattice parameters, the amount of residual carbon and sample names of the composites are listed in Table 1. The FWHMs of peaks became small and the peak split around a  $2\theta$  of 39° giving remarkable XRD patterns with an increase in calcination temperature. These results indicate that the crystallinity of  $\text{LiFePO}_4$  increase with increasing temperature. Fig. 5 shows SEM images of the composites. The average particle size was less than 1  $\mu\text{m}$  in T55, T65 and T75. However the size of T85 was 3–4  $\mu\text{m}$ . The residual carbon amount increased with increasing temperature but the amount of T85 was ca. 3.35wt%. These results indicate that the carbon loss and particle growth occur at 850 °C.

The electrochemical properties of the  $\text{LiFePO}_4/\text{C}$  composites were examined between 2.5 V and 4.0 V by applying a current density of 100  $\text{mA g}^{-1}$  at 25 °C. Fig. 6(a) shows the first cycle curves of the composites. When  $\text{LiFePO}_4$  serves as a cathode in a lithium secondary battery system, it shows a single plateau around 3.5 V vs. Li by the redox process of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  [12]. The single plateau around 3.5 V was observed in T65, T75 and T85 but T55 a having low crystallization exhibited no plateau with a low discharge capacity of 20  $\text{mAh g}^{-1}$ . The discharge capacity increased with an increase of the temperature up to 750 °C but fell sharply at 850 °C. This reduction of capacity at 850 °C might be due to the low amount of carbon and large grain size because the conductive agent and particle size are important factors in the electrochemical properties in a  $\text{LiFePO}_4$  system [2, 5]. Fig. 6(b) shows residual amount

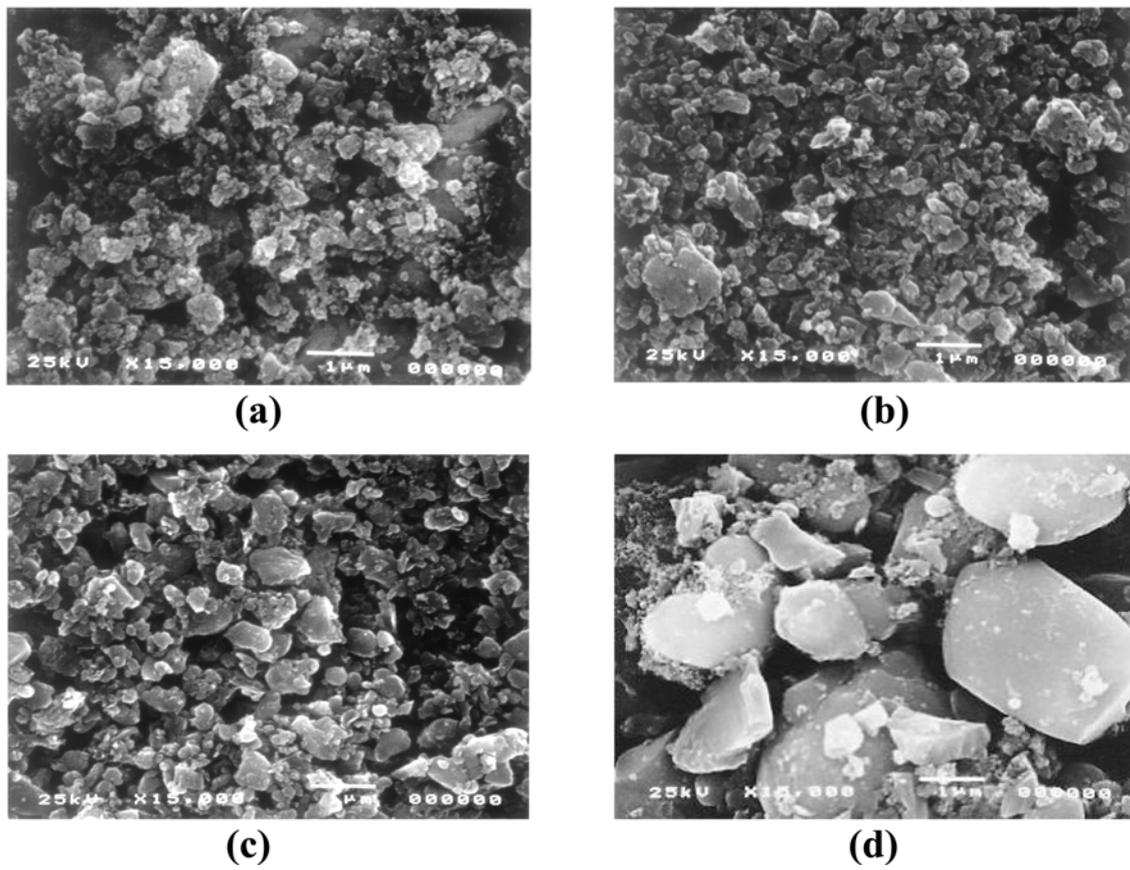


Fig. 5. SEM images of (a) T55, (b) T65, (c) T75 and (d) T85.

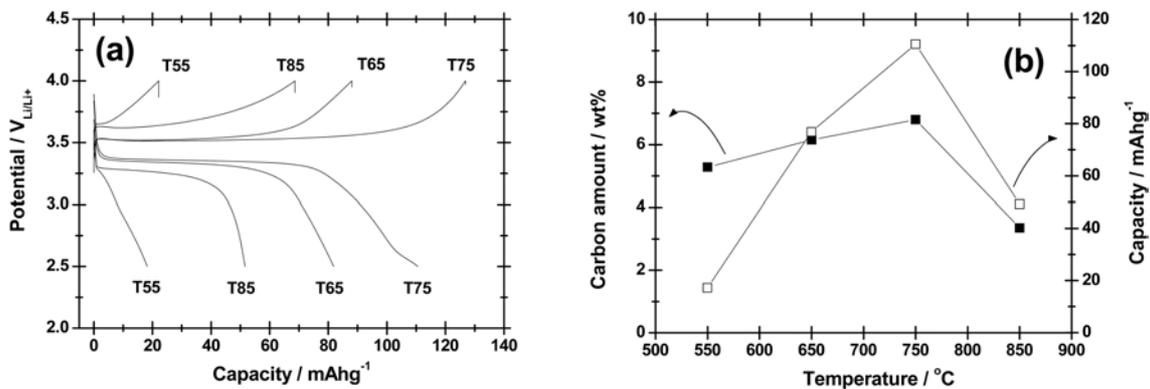
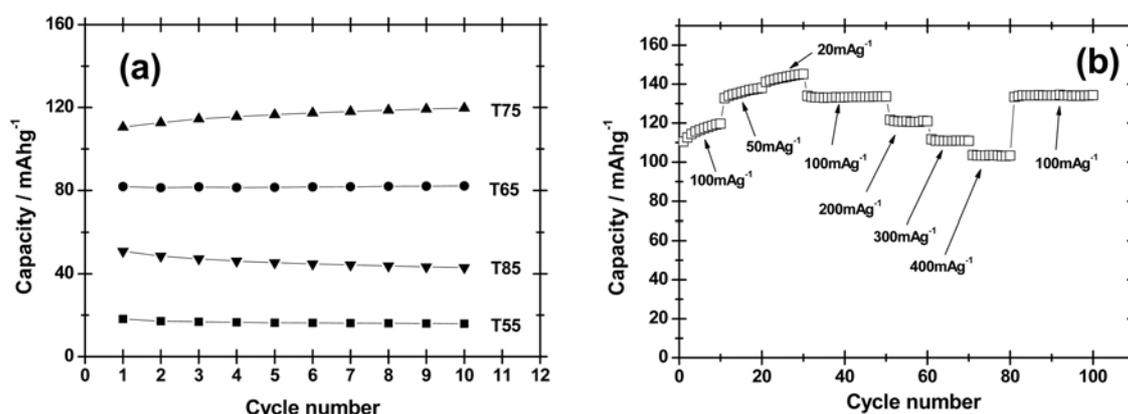


Fig. 6. The first cycle curves of the  $\text{LiFePO}_4/\text{C}$  composites cycled between 2.5 V and 4.0 V by applying a current density of  $100 \text{ mA g}^{-1}$  at  $25^\circ\text{C}$  (a) and the amount of carbon vs. capacity plot as a function of calcination temperature (b).

of carbon and discharge capacities of composites as a function of the calcination temperature. Although the particle size and the amount of carbon showed little difference among the composites except for T85, the capacity increased with an increase in the temperature. We believe that the low capacities of T55 and T65 are probably due to low crystallinity and the residual  $\text{Fe}^{3+}$  ions.

Fig. 7(a) shows the discharge capacities of the  $\text{LiFePO}_4/\text{C}$  composites up to the 10<sup>th</sup> cycle with an applied current density of  $100 \text{ mA g}^{-1}$  at  $25^\circ\text{C}$ . A capacity loss was observed with T55 and T85, whereas T65 and T75 showed a

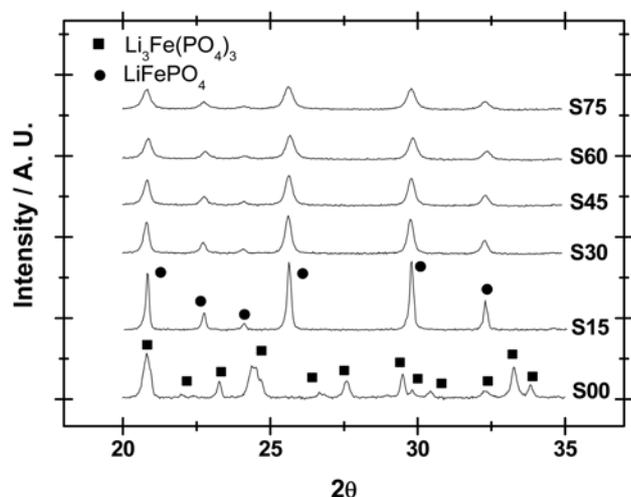
capacity gain of about 0.3% and 7.66%, respectively. Also T75 showed good capacity retention as well as a high discharge capacity, ca.  $120 \text{ mA h g}^{-1}$ . Fig. 7(b) shows the rate capability of T75 with various current densities at  $25^\circ\text{C}$ . The discharge capacity of T75 was sensitive to the applied current density. The discharge capacity reached  $145 \text{ mA h g}^{-1}$  at a current of  $20 \text{ mA g}^{-1}$  and the capacity dwindled to  $103 \text{ mA h g}^{-1}$  with an increase in the current density. When a current of  $100 \text{ mA g}^{-1}$  was applied again, T75 showed a discharge capacity of  $134 \text{ mA h g}^{-1}$  and good capacity retention in the 100<sup>th</sup> cycle without capacity



**Fig. 7.** The discharge capacities of the  $\text{LiFePO}_4/\text{C}$  composites up to the 10<sup>th</sup> cycle cycled between 2.5 V and 4.0 V at  $100 \text{ mA g}^{-1}$  at  $25^\circ\text{C}$  (a). The rate capability of T75 cycled at various current densities at  $25^\circ\text{C}$ . The residual carbon content is not considered in calculating the gravimetric capacity (b).

**Table 2.** Residual amount of carbon, electrical resistance and color of the  $\text{LiFePO}_4/\text{C}$  composites with the amount of sucrose

Sample name	S00	S15	S30	S45	S60	S75
Sucrose/mol	0	0.15	0.3	0.45	0.60	0.75
Carbon/wt%	0	< 1	6.85	14.55	20.58	25.45
Color	Orange	Gray	Black	Black	Black	Black
Electrical resistance	-	Over 100 M $\Omega$	6.3 K $\Omega$	6.1 K $\Omega$	5.1 K $\Omega$	6.7 K $\Omega$



**Fig. 8.** The collected XRD data for the  $\text{LiFePO}_4/\text{C}$  composites calcined at  $750^\circ\text{C}$  for 10 h in an inert atmosphere with various amounts of sucrose.

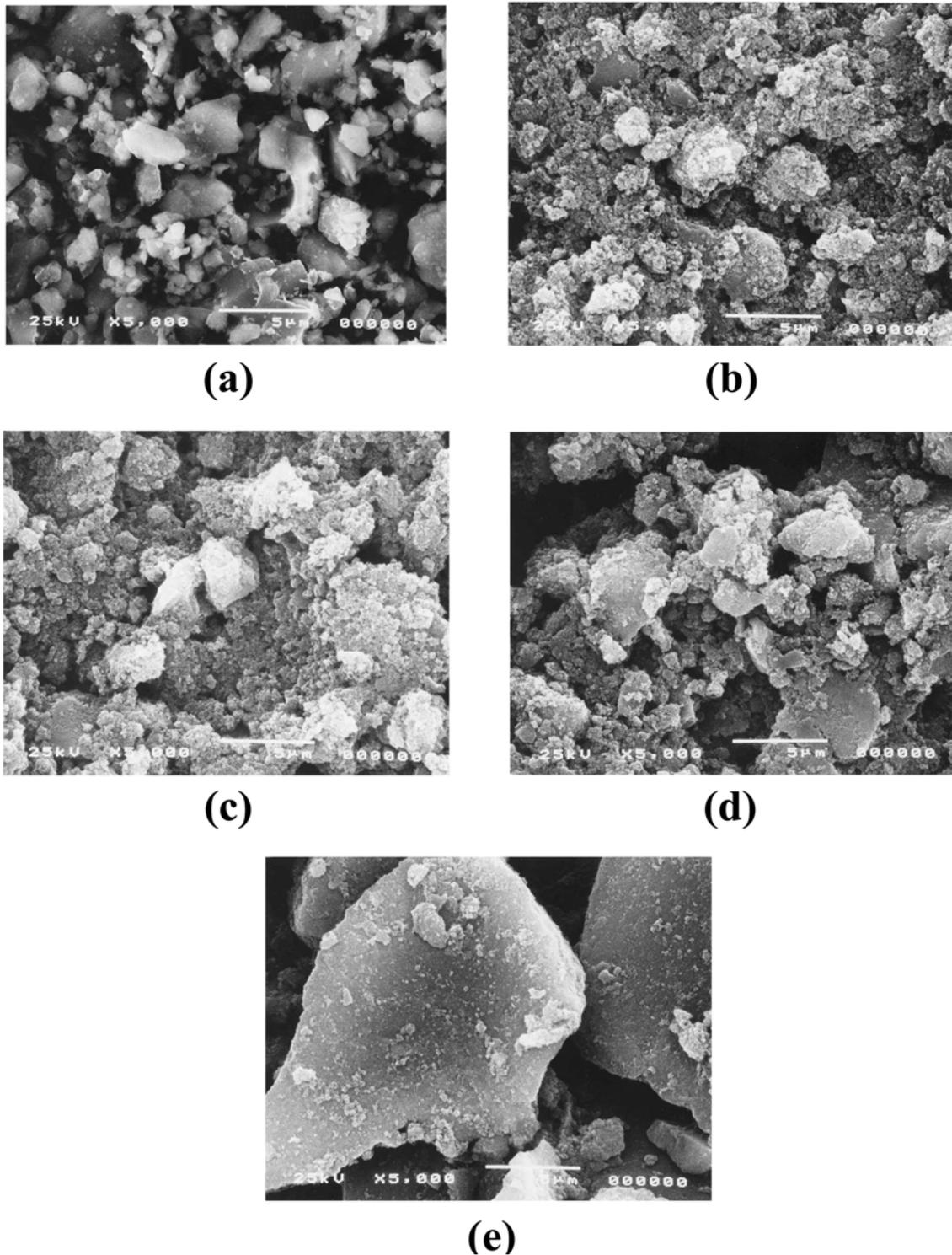
loss. Therefore, we conclude that the optimum calcination temperature is  $750^\circ\text{C}$  to make a  $\text{LiFePO}_4/\text{C}$  composite with good electrochemical properties by our method.

### Electrochemical properties as a function of the amount of carbon

The electrochemical properties of the  $\text{LiFePO}_4/\text{C}$  composites were characterized with a function of carbon. We changed the amount of sucrose from 0 mol to 0.75 mol against 1 mol  $\text{LiFePO}_4$ . Residual amounts of carbon, the electrical resistance, the colors and the sample names of the

$\text{LiFePO}_4/\text{C}$  composites with amount of sucrose are listed in Table 2. Fig. 8 shows the XRD patterns for the composites calcined at  $750^\circ\text{C}$  for 10 h in an inert atmosphere with various amounts of sucrose. A  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$  phase, which has  $\text{Fe}^{3+}$  ions, was observed in the S00 with an orange color. It is reasonable that S00, without sucrose, does not have a chance to reduce the  $\text{Fe}^{3+}$  ions in the  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  we used. However, the composites calcined with sucrose had a  $\text{LiFePO}_4$  phase even though the colors of the composites were different. S15 was gray but the others were black. S15 had little carbon, below 1 wt%, because carbon is consumed during calcination to reduce the  $\text{Fe}^{3+}$  ions. The amount of residual carbon in the composites increased with an increase in the amount of sucrose. Therefore, we confirmed that carbon coming from sucrose plays a role as a reducing agent during the calcination and the amount of sucrose should be higher than 0.15 mol to produce a  $\text{LiFePO}_4/\text{C}$  composite using our method.

The morphologies of the particles in the  $\text{LiFePO}_4/\text{C}$  composites were observed by SEM and shown in Fig. 9. The particle size of S15 was 2–3  $\mu\text{m}$  and the surface of the particles was smooth due to little residual carbon. However, the composites with residual carbon showed different particle morphologies, viz. the surfaces of these particles were rough. Also the particle size of S30 and S45 were less 1  $\mu\text{m}$  and the particles tend to aggregate. Also the degree of aggregation became larger with an increase in the amount of residual carbon, in particular the aggregation size of S75 was over 10  $\mu\text{m}$  with an aggregated particle densification. These results indicate that a suitable amount of carbon suppress particle growth but a surplus content of

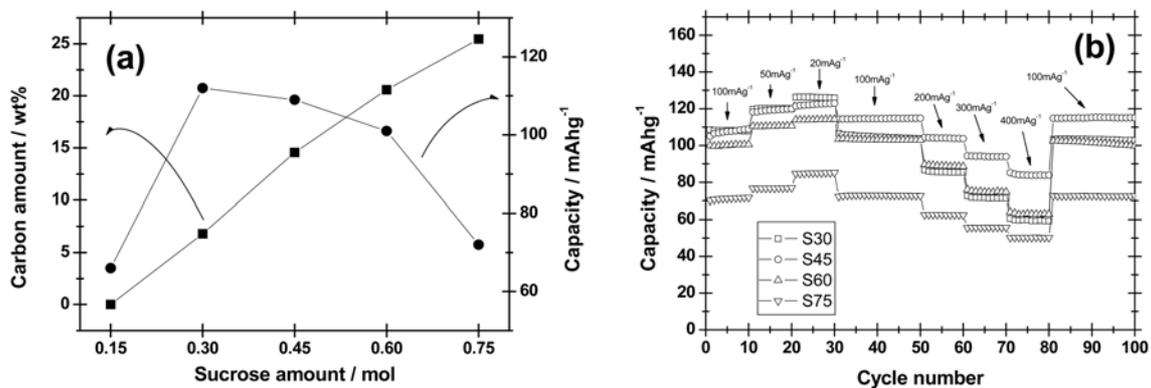


**Fig. 9.** SEM images of (a) S15, (b) S30, (c) S45, (d) S60, and (e) S75 calcined at 750 °C for 10 h in an inert atmosphere.

carbon can enhance the aggregation of particles. Moreover, the electrical resistance of S15 was over 100 M because of the small residual carbon content but the resistances of other composites were between 5 K and 7 K as listed in Table 2. These data indicate that the residual carbon in the composite can reduce the electrical resistance but a greater carbon content cannot give more electrical conductivity.

Consequently, an inordinate carbon quantities rather reduces the gravimetric and volumetric energy density.

To know the effect on the electrochemical properties of the  $\text{LiFePO}_4/\text{C}$  composites with the residual amount of carbon, we cycled the composites between 2.5 V and 4.0 V at various current densities at 25 °C. The residual carbon content was used to calculate the gravimetric capacity



**Fig. 10.** Amount of carbon vs. the first discharge capacity plot of the LiFePO<sub>4</sub>/C composites (a) and rate capability with the amount of sucrose (b) cycled between 2.5V and 4.0V at various current densities at 25 °C.

of the cathode. Fig. 10(a) shows the residual carbon content and the first discharge capacity of the LiFePO<sub>4</sub>/C composites as a function of the amount of sucrose. The carbon content increased linearly with an increase in the amount of sucrose, but the capacity showed a peak at S30 and then decreased. Low capacities were observed in S15 and S75 due probably to the small residual carbon content and large aggregated particle size, respectively. Fig. 10(b) shows the rate capability of the composites with the amount of sucrose at various current densities. Although the first discharge capacity of S30 showed the highest capacity among the composites, it dramatically decreased and did not recover the first capacity when we applied a current of 100 mAg<sup>-1</sup> again. The discharge capacities of the composites, which have higher residual carbon content than S30, were less sensitive to the current density than S30 but S60 and S75 showed lower gravimetric capacities due to the high residual carbon content in their cathodes. From these results, we think that 0.45 mol sucrose is an optimal amount of sucrose from the standpoint of the specific and gravimetric energy densities.

### Conclusions

The LiFePO<sub>4</sub>/C composites were synthesized from an aqueous solution of LiNO<sub>3</sub>, Fe(III)(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and sucrose. In the our synthesis process, sucrose played the roles as synthesizing and reducing agents and the residual carbon content after some consumption as a reducing agent improved the electronic conductivity of the composites.

The LiFePO<sub>4</sub>/C composites synthesized at 750 °C showed good electrochemical properties. This temperature can prevent the composite from a low crystallization, residual Fe<sup>3+</sup> ions and undesirable particle growth. A suitable amount of sucrose which suppressed particle growth and improved the electronic conductivity of the composite was 0.45 mol%. It is certain that the residual carbon in the composite can reduce the electrical resistance but a larger carbon content cannot give more electrical conductivity. The LiFePO<sub>4</sub>/C composite synthesized with optimum conditions, 750 °C and

0.45 mol% sucrose, showed the best electrochemical properties. Therefore, we suggest that the calcination temperature and amount of carbon should be controlled to produce a LiFePO<sub>4</sub>/C composite with better electrochemical properties.

### Acknowledgements

This work was supported by grant No R05-2004-00-11649-0 from the Korea Research Foundation. We thank for that support.

### References

1. A.K. Padhi, K.S. Nanjundaswamy and J.B. Goodenough, *J. Electrochem. Soc.*, 144 (1997) 1188-1194.
2. A. Yamada, S.C. Chung and K. Hinokuma, *J. Electrochem. Soc.*, 148 (2001) 224-229.
3. A.S. Andersson, J.O. Thomas and J. Power Sources, 97-98 (2001) 498-502.
4. N. Ravet, J.B. Goodenough, S.Besner, M. Simoneau, P. Hovington, M. Armand, *Electrochem. Soc. Abst. #127* (1999) 99-102.
5. H. Huang, S.C. Yin and L.F. Nazar, *Electrochem. Solid-State Lett.* 4 (2001) A170-172.
6. Z. Chen and J.R. Dahn, *J. Electrochem. Soc.* 149 (2002) A1184-A1189.
7. P.P. Prosini, D. Zane and M. Pasquali, *Electrochimica Acta* 46 (2001) 3517-3523.
8. R. Dominko, M. Gaberscek, J. Drogenik, M. Bele and S. Pejovnik, *Electrochem Solid-State Lett.* 4 (2001) A187-A19a0.
9. S. Yang, Y. Song, K. Ngala, P.Y. Zavalij and M.S. Whittingham, *J. Power Source* 119-121 (2003) 239-246.
10. H.-T. Chung, S.-K. Jang, H.-W. Ryu and K.-B. Shim, *Solid State Communications*, 131 (2004) 549-554.
11. P.P. Prosini, M. Lisi, D. Zane and M. Pasquali, *Solid State Ionics*, 148, (2002) 45-51.
12. A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada and J.B. Goodenough, *J. Electrochem. Soc.*, 144 (1997) 1609-1613.