



ELSEVIER

Journal of Power Sources 97–98 (2001) 508–511

JOURNAL OF  
POWER  
SOURCES

www.elsevier.com/locate/jpowersour

# Characterization of $\text{LiFePO}_4$ as the cathode material for rechargeable lithium batteries

Masaya Takahashi\*, Shinichi Tobishima, Koji Takei, Yoji Sakurai

*NTT Telecommunications Energy Laboratories, Tokai-mura, Naka-gun, Ibaraki-ken 319-1193, Japan*

Received 23 June 2000; accepted 29 January 2001

## Abstract

We investigated the electrochemical characteristics of  $\text{LiFePO}_4$  when used as the cathode material for rechargeable lithium batteries. We also studied the change in the crystal structure of the material during discharge. The material prepared at a relatively low temperature of  $675^\circ\text{C}$  showed a higher charge and discharge capacity than that prepared at higher temperatures. This was because material prepared at a low temperature has a relatively small particle size and a rough surface morphology. We also found that the crystal structure of electrochemically delithiated  $\text{LiFePO}_4$  was similar to a heterosite structure and the sample reverted to its original triphylite structure after electrochemical lithiation. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lithium ion batteries; Lithium iron phosphate; Cathode material; Preparation temperature; Crystal structure

## 1. Introduction

Recently, iron-based compounds containing polyanions such as  $(\text{SO}_4)^{2-}$ ,  $(\text{PO}_4)^{3-}$  or  $(\text{AsO}_4)^{3-}$  have been investigated intensively as potential cathode materials for rechargeable lithium ion batteries [1–6]. They are environmentally benign, cheap and abundant. Orthorhombic  $\text{LiFePO}_4$ , which has an ordered olivine structure, has attracted particular interest. This material has a relatively large theoretical capacity of  $170 \text{ mAh g}^{-1}$  compared with other iron-based compounds, good thermal stability in the fully charged state and little hygroscopicity, making it easy to handle [3,4]. However, it is reported that charging and discharging with a higher current density are difficult to achieve in an ordinary liquid electrolyte cell at room temperature [3]. Recently, this material has been reported to perform well in a lithium battery system [7]. The effect of the operating temperature on the cycling performance of the material has also been examined [8]. In this paper, we describe the influence of the preparation temperature on the morphology of  $\text{LiFePO}_4$  particles and the electrochemical characteristics of the material. We also investigated the change in the crystal structure during the electrochemical lithiation of electrochemically delithiated  $\text{Li}_{1-x}\text{FePO}_4$ .

## 2. Experimental

We prepared the  $\text{LiFePO}_4$  by firing a stoichiometric mixture of  $\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{LiOH} \cdot \text{H}_2\text{O}$  in an argon atmosphere. First, we heated a mixture of these materials at  $350^\circ\text{C}$  for 5 h to decompose them. After heating, the mixture was ground and pressed into pellets. The pellets were then fired at various temperatures from  $675$  to  $800^\circ\text{C}$  for 24 h and cooled to  $70^\circ\text{C}$  for 14 h. We evaluated their electrochemical characteristics by using a 2320 coin type cell with a lithium metal anode and 1 M  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (1:1 in volume) electrolyte. The separator we used was a Celgard 3501 microporous membrane. The cathode electrode was made in the following way. We mixed the  $\text{LiFePO}_4$  powder with acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 70:25:5. We then rolled the mixture into a 0.6 mm thick sheet and cut it into pellets. We assembled the cell in dry air. Unless otherwise noted, we cycled the cells galvanostatically between 3.0 and 4.0 V at  $0.5 \text{ mA cm}^{-2}$ .

We characterized the structure of the materials by X-ray diffraction (Rigaku RINT 2500HF) with  $\text{Cu K}\alpha$  radiation. The XRD samples were delithiated and lithiated in coin type cells. After charging the cells to 4.0 V at  $0.25 \text{ mA cm}^{-2}$  and  $60^\circ\text{C}$ , we discharged each cell for the required time at the same temperature and current. Then we took the cathode pellets from the cells, rinsed them with dimethyl carbonate

\* Corresponding author. Fax: +81-292877863.  
E-mail address: takahasi@iba.iecl.ntt.co.jp (M. Takahashi).

and dried them. We measured the XRD charts using these pellets. We undertook Rietveld analysis with the aid of the computer program RIQAS (Materials Data Inc.). We assumed a space group *Pnma* with orthorhombic symmetry [9].

### 3. Results and discussion

We expected the  $\text{LiFePO}_4$  preparation temperature to influence the charge/discharge capacity of the material because the temperature affects the degree of particle sintering. Fig. 1 shows the charge and discharge curves of the  $\text{Li}/\text{LiFePO}_4$  cells at the 10th cycle using various  $\text{LiFePO}_4$  samples prepared at 675, 725 and 800°C. The cells were measured at 20°C. The capacity of the material increased as the preparation temperature decreased and reached  $115 \text{ mAh g}^{-1}$  for the sample prepared at 675°C. This is about double the capacity for the sample prepared at 800°C. The shapes of all the curves, which have large voltage plateaus, suggest that the charge and discharge reaction proceeds as a two-phase reaction. The plateau voltages are almost the same regardless of the preparation temperature. This means that the preparation temperature did not affect the overvoltage of the  $\text{LiFePO}_4$  electrochemical reaction, at least in the surface region of the particles where the early charge/discharge reaction takes place. We assumed the differences in the capacity and the voltage plateau length to relate to the degree to which the electrode material was used in the reaction.

We confirmed the influence of the preparation temperature on the morphology of the  $\text{LiFePO}_4$  particles. Fig. 2 shows SEM images of  $\text{LiFePO}_4$  particles prepared at 675, 725 and 800°C. The SEM observations showed that high temperature preparation causes particle growth and provides a smooth surface. In contrast, the sample prepared at 675°C showed that there was insufficient sintering and small particles agglomerated. The specific surface areas of the materials prepared at 675, 725 and 800°C were 3.6, 1.2 and

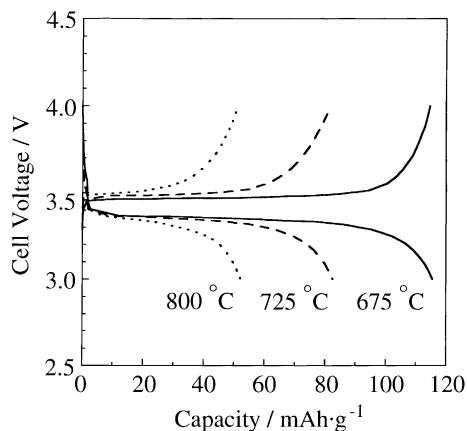


Fig. 1. Charge/discharge curves of  $\text{Li}/\text{LiFePO}_4$  cells at the 10th cycle with  $\text{LiFePO}_4$  prepared at 675, 725, and 800°C. The measurement temperature was 20°C and the current was  $0.5 \text{ mA cm}^{-2}$ .

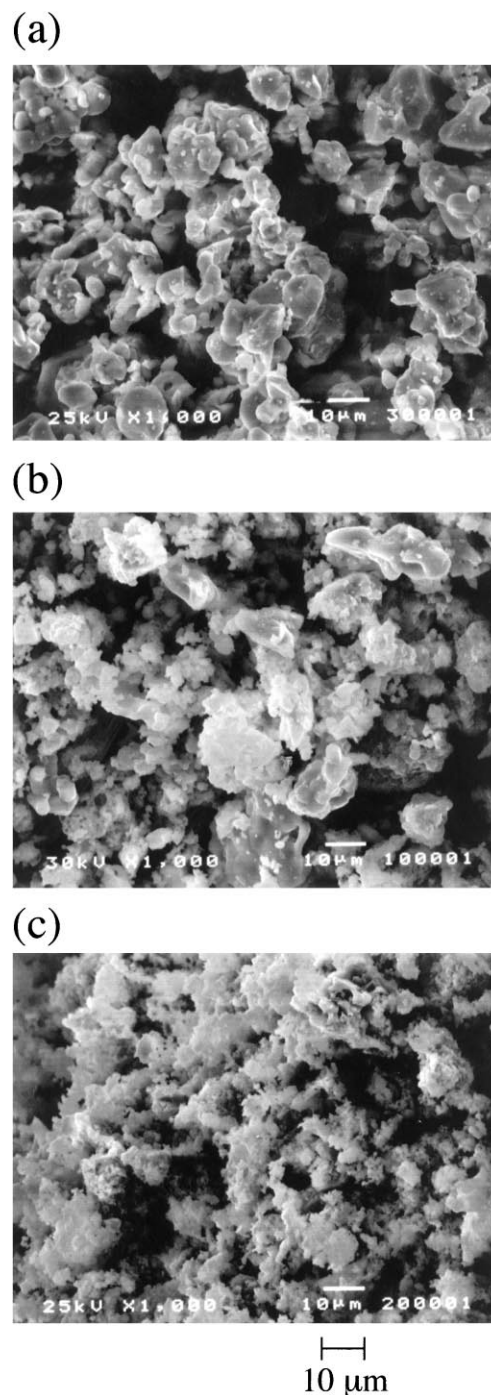


Fig. 2. SEM images of  $\text{LiFePO}_4$  powder prepared at (a) 800°C, (b) 725°C, and (c) 675°C.

$0.6 \text{ m}^2 \text{ g}^{-1}$ , respectively. Material with a high capacity had a large specific area. It has been reported that the capacity of the  $\text{LiFePO}_4$  electrode is limited by the diffusion rate of the lithium ions in the  $\text{LiFePO}_4$  particles [3]. In particles with a large diameter and a smooth surface, the lithium ions have to diffuse over greater distances between the surface and center during lithium insertion or extraction, and the  $\text{LiFePO}_4$  near the particle center contributes very little to the charge/discharge reaction. Hence, material prepared at a low

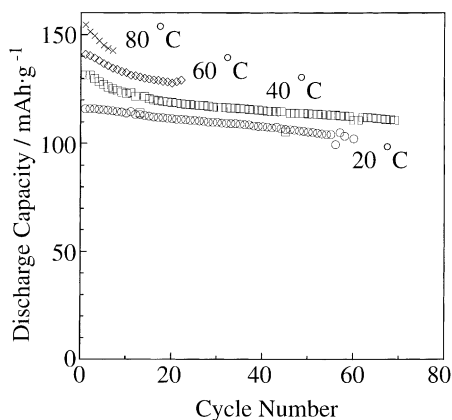


Fig. 3. Cycle performance of the Li/LiFePO<sub>4</sub> cells at 20, 40, 60, and 80°C. LiFePO<sub>4</sub> was prepared at 675°C and the charge/discharge current was 0.5 mA cm<sup>-2</sup>.

temperature has a high capacity because of the increase in the quantity of LiFePO<sub>4</sub> particles that can be utilized.

Since the low rate of lithium diffusion in the LiFePO<sub>4</sub> particles limits the cell capacity, the cell operating temperature may also affect the capacity. It has been reported that a larger capacity is obtained for cells cycled at an elevated temperature [8]. We examined the effect of the operating temperature on the electrochemical characteristics of LiFePO<sub>4</sub>. Fig. 3 shows the cycle performance of Li/LiFePO<sub>4</sub> cells operated at 20, 40, 60 and 80°C. The LiFePO<sub>4</sub> used here was prepared at 675°C. The discharge capacity of the cell increased as the operating temperature was raised. At 80°C, the initial discharge capacity reached 155 mAh g<sup>-1</sup>, approximately 1.4 times higher than that observed at 20°C. The voltage of the plateaus shown in the charge and discharge curves was almost the same regardless of the operating temperature. This capacity increase indicates that the lithium diffusion in LiFePO<sub>4</sub> particles is enhanced by elevated temperature and LiFePO<sub>4</sub> compounds nearer the center of the particle are utilized. All the cycling tests ended as the result of an internal short caused by the deposition of lithium dendrites on the anode.

High temperature charging made it possible to extract more Li ions from the LiFePO<sub>4</sub>. We investigated the crystal structure change during discharge. Fig. 4 shows the change in the XRD pattern for cathode electrode pellets with different degrees of discharging at 60°C. The material we used here was prepared at 675°C. Pattern (a) was measured with the sample charged to 4 V at a constant current of 0.25 mA cm<sup>-2</sup>. The electricity used for the charging was 156.2 mAh g<sup>-1</sup>, corresponding to that used for preparing the Li<sub>0.08</sub>FePO<sub>4</sub>. The XRD pattern agreed well with that of heterosite ((Fe, Mn)PO<sub>4</sub>) and was similar to that of the chemically delithiated product [3]. We observed no other obvious phases in this pattern. The refined parameters of the XRD pattern are shown in Table 1. We calculated the refined lattice parameters of the pristine LiFePO<sub>4</sub> (triphylite) prepared at 675°C to be  $a = 10.3215(1)$ ,  $b = 6.0045(1)$  and  $c = 4.6903(1)$ . These values agreed well with those shown

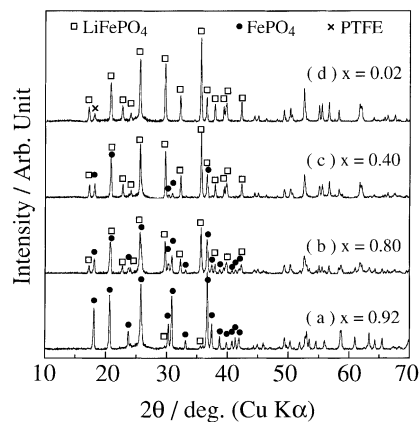


Fig. 4. XRD patterns of electrochemically delithiated Li<sub>1-x</sub>FePO<sub>4</sub> cathode pellets: (a)  $x = 0.92$ ; (b)  $x = 0.80$ ; (c)  $x = 0.40$ ; and (d)  $x = 0.02$ .

in [3]. The delithiated structure is basically similar to that of triphylite with no lithium atom occupancy in the 4a site, although their lattice parameters differ slightly. Pattern (b) was obtained from a sample that we delithiated under the same conditions as the pattern (a) sample, then electrochemically lithiated until Li<sub>0.2</sub>FePO<sub>4</sub> was prepared. We obtained pattern (c) from a sample that was lithiated until Li<sub>0.6</sub>FePO<sub>4</sub> was prepared. The two phases, LiFePO<sub>4</sub> and FePO<sub>4</sub>, exist together in these samples and the LiFePO<sub>4</sub> phase ratio increases as electrochemical lithiation proceeds. This coexistence of the two phases corresponds to the flat charge/discharge profiles shown in Fig. 1. Pattern (d) was discharged to 3.0 V after charging to 4.0 V. The electricity for discharging was 152.5 mAh g<sup>-1</sup>, corresponding to Li<sub>0.98</sub>FePO<sub>4</sub>. The heterosite like pattern disappeared and the sample reverted to single phase LiFePO<sub>4</sub>. These results indicate that the charge/discharge reaction is a continuous single reaction with little change in the crystal structure and that LiFePO<sub>4</sub> has good reversibility in terms of lithium extraction and insertion. The calculated Li–O, Fe–O, and P–O distances of the LiFePO<sub>4</sub> prepared at 675°C are 2.08–2.16, 2.08–2.26, and 1.52–1.58 Å, respectively. These values agree well with the sums of ionic radii, according to the reported values of 0.90 Å for Li<sup>+</sup> (coordination number CN = 6), 0.92 Å for Fe<sup>2+</sup> (high spin, CN = 6), 0.31 Å for P<sup>5+</sup> (CN = 4), and 1.26 Å for O<sup>2-</sup> [10]. These results indicate the highly ionic nature of LiFePO<sub>4</sub>.

Table 1  
Structural parameters of FePO<sub>4</sub><sup>a</sup>

| Atom | Site | $x$      | $y$      | $z$      |
|------|------|----------|----------|----------|
| Fe   | 4c   | 0.275(1) | 0.25     | 0.950(1) |
| P    | 4c   | 0.095(1) | 0.25     | 0.394(2) |
| O(1) | 4c   | 0.119(1) | 0.25     | 0.720(3) |
| O(2) | 4c   | 0.440(2) | 0.25     | 0.185(3) |
| O(3) | 8d   | 0.158(1) | 0.040(2) | 0.253(2) |

<sup>a</sup> Space group:  $Pnma$ ,  $Z = 4$ ,  $a = 9.8201(8)$ ,  $b = 5.7940(4)$ ,  $c = 4.7808(4)$ ,  $R_{wp} = 16.1$  ( $B(\text{Fe}) = B(\text{P}) = 0.3$ ,  $B(\text{O}) = 0.4$  were assumed).

#### 4. Conclusions

LiFePO<sub>4</sub> prepared at a relatively low temperature of 675°C has a high capacity as a cathode material for rechargeable lithium batteries. This is because it has small and rough surface particles meaning that more material near the center of the particles can be utilized. The cell capacity increases as the cell operating temperature is raised because the lithium ion diffusion in the LiFePO<sub>4</sub> particles is enhanced. From XRD observations of Li<sub>1-x</sub>FePO<sub>4</sub> with various states of discharge, we found that electrochemical lithiation/delithiation occurs as a two-phase reaction and the structure of the delithiated product is similar to heterosite, the same as that of chemically delithiated product. Good reversibility is expected from the small structural change between LiFePO<sub>4</sub> and FePO<sub>4</sub>, which coexist during lithium insertion and extraction.

#### Acknowledgements

The authors express their gratitude to Dr. I. Yamada for his encouragement during the course of this study. The authors also thank Dr. H. Arai for the Rietveld analysis of the X-ray

diffraction pattern and Ms Y. Nemoto for the SEM observation. The authors also thank Ms N. Kurusu for technical assistance.

#### References

- [1] A. Manthiram, J.B. Goodenough, *J. Power Sources* 403 (1989) 403.
- [2] K.S. Nanjundaswamy, A.K. Padhi, J.B. Goodenough, S. Okada, H. Ohtsuka, H. Arai, J. Yamaki, *Solid State Ionics* 92 (1996) 1.
- [3] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [4] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1609.
- [5] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 2581.
- [6] C. Masquelier, A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Solid State Chem.* 135 (1998) 228.
- [7] N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, in: *Proceedings of the 1999 Joint International Meeting, Hawaii, 17–22 October 1999* (Abstract no. 127).
- [8] A.S. Andersson, J.O. Thomas, L. Kalska, B. Häggström, *Electrochem. Solid-State Lett.* 3 (2000) 66.
- [9] R.W.G. Wyckoff, *Crystal Structures*, 2nd Edition, Vol. 3, Robert E. Krieger Publishing Company, 1981, pp. 91–93.
- [10] R.D. Shannon, *Acta Cryst. A* 32 (1976) 751.