

## Solid-state Synthesis of $\text{LiFePO}_4$ Cathode Materials for Lithium Ion Batteries Controlling Particles Size of Precursor

Dae-Kyoo Jun, hu Li, Kyung-Hee Park, Hal-Bon Gu and Bok-Kee Park\*

Dept. of Electrical Eng., Chonnam National Univ., Dept. of Electrical Eng., Howon National Univ.\*

**Abstract :** The  $\text{LiFePO}_4$  as cathode materials for lithium ion batteries was synthesized by the solid-state reaction using ballmiller and employed one step heat treatment at  $650\text{ }^\circ\text{C}$ . The influence of the heating time on the structure, particle size and cycle performance was investigated.  $\text{LiFePO}_4$  heated at  $650\text{ }^\circ\text{C}$  for 3 h exhibited higher discharge capacity of 140 mAh/g and excellent cycle performance.

**Key Words :** Olivine, Cathode, Solid-state reaction, Charge/Discharge

### 1. Introduction

Recently, There is an increasing demand for batteries which have high energy density due to continuous growth of hybrid electric vehicles(HEVs), power storage, portable electronic devices, etc.  $\text{LiCoO}_2$  has so far been used as cathode material for commercial lithium batteries. However, the replaceable materials have been investigated by reason of its high cost, environmental pollution and thermal instability. In many kinds of materials,  $\text{LiFePO}_4$  have particularly been expecting a candidate for cathode material of lithium batteries due to the good capabilities of providing long cycle life and high rate in spite of high temperatures. And, it shows a very flat voltage curve with a plateau around 3.4 V vs.  $\text{Li/Li}^+$  and excellent theoretical capacity of 170 mAh/g based on the  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . Nevertheless, it is difficult to the practical use of full theoretical capacity at high rate, because the separation of the chain of  $\text{FeO}_6$  edge-shared octahedral contributes extremely low electronic conductivity. Many researchers proposed to overcome this problem as follows: (i) coating with conductive layer around particles; (ii) ionic substitution to enhance its electrochemical properties (iii) the synthesis of particles with well-defined morphology.[1~4]

The Olivine  $\text{LiFePO}_4$  can be synthesized by a solid-state reaction method, sol-gel, mechanical activation(MA), microwave heating, etc. To be formed olivine phase of  $\text{LiFePO}_4$ , these methods are generally accepted by heating treatment at high temperature,  $>500\text{ }^\circ\text{C}$ . The solid-state reaction is widely adopted for synthesis of pure crystalline olivine phase  $\text{LiFePO}_4$ . However, these method was carried out through complex synthesis process as follows repeated grinding to gain homogenous particles and several heating steps at high temperature to protect impurity phase. These repeated firing treatment result in a large particle size.

In this study, we prepared  $\text{LiFePO}_4$  cathode materials for lithium ion batteries by solid-state reaction method using ballmiller and one-step firing condition. To optimize thermal processing conditions, heating time were investigated by HR-XRD, FE-SEM, and electrochemical performance of these active materials was evaluated.

### 2. Experimental

$\text{LiFePO}_4$  was prepared by the solid-state reaction of stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  (Aldrich Co.),  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (Aldrich Co.) and  $\text{NH}_4\text{H}_2\text{PO}_4$ (Aldrich Co.). The precursors were mixed by ball-milling(Planetary Mono Mill, FRITCH Co.) in the N-methyl-2-pyrrolidinone(NMP, Aldrich Co.) for 24 h. After the mixed powder was dried at  $90\text{ }^\circ\text{C}$  for 24h, precursors were pelletized and then heated at  $650\text{ }^\circ\text{C}$  for different time intervals in a nitrogen atmosphere, followed by furnace cooling down to room temperature. The resulting  $\text{LiFePO}_4$  composites were obtained after ball-milling for 6 h. The crystalline phase of the calcined powders were obtained using a high resolution X-ray diffractometer(HR-XRD, D/MAX Ultima III, Rigaku). The particle size was observed by field emission scanning electron microscope(FE-SEM, S-4700, HITACHI). For the electrochemical testing, the composite electrodes were fabricated using as-prepared cathode materials, SP-270 and polyvinylidene fluoride(PVDF) with a weight ratio of 70:20:10 in NMP. The obtained slurry was coated onto Al foil and dried at  $90\text{ }^\circ\text{C}$  for 1 h before roll-pressing, and then the electrodes were dried again at  $110\text{ }^\circ\text{C}$  for 24 h under vacuum prior to use. The cells were assembled with lithium ribbon as anode and 1M  $\text{LiPF}_6/\text{EC-DEC}(1:1)$  electrolyte in argon-filled glove box. The charge-discharge cycle performance was examined between 2.5 and 4.0 V at a constant current density of  $0.1\text{ mA}/\text{cm}^2$

at 25 °C.

### 3. Results and discussion

Fig. 1. showed the X-ray diffraction patterns of the sintered LiFePO<sub>4</sub> at 600 °C for different time intervals. All diffraction peaks of LiFePO<sub>4</sub> prepared at 600°C for 1h, 3h, 6h was indexed to an orthorhombic crystal structure. As for but LiFePO<sub>4</sub> heated for 12h, the impurity phase of Fe<sub>2</sub>P were detected about  $2\theta = 40^\circ$ .

The particle morphology observed by FE-SEM was shown Fig. 2. The particle size increased slightly with higher heating time. The heated LiFePO<sub>4</sub> at 600 °C showed the smallest particle size among them.

Fig. 3. displayed the cycle performance of sintered LiFePO<sub>4</sub> at various heating time. The heated LiFePO<sub>4</sub> for 3h exhibited higher 140 mAh/g of the discharge capacity. Other samples showed that discharge capacity increased after first cycle. This was due to appearance of impurity Fe<sub>2</sub>P and improvement of particle size.

### 4. Conclusions

LiFePO<sub>4</sub> as cathode materials for lithium ion batteries was synthesized by the solid-state reaction and employed one step heat treatment at 650 °C. LiFePO<sub>4</sub> heated for 3h exhibited higher discharge capacity of 140 mAh/g and excellent cycle performance due to small particle size and no impurity phases.

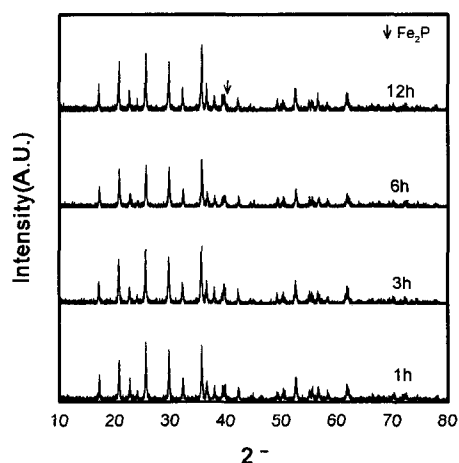


Fig. 1. XRD patterns of LiFePO<sub>4</sub> heated at 600 °C for different time intervals.

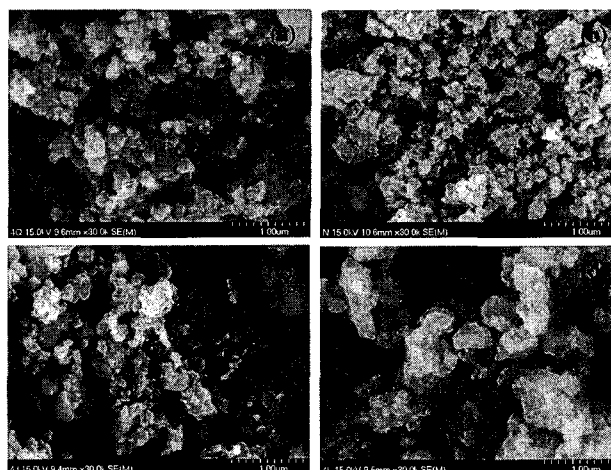


Fig. 2. FE-SEM photographs of LiFePO<sub>4</sub> under different heating time at 600°C: (a) 1 h, (b) 3 h, (c) 6 h and (d) 12 h.

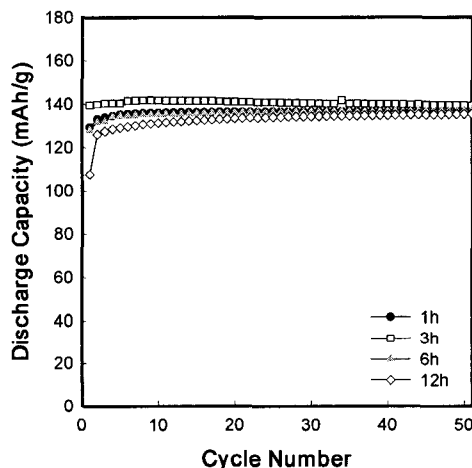


Fig. 3. Cycle performance of lithium cells with heated LiFePO<sub>4</sub> under different heating time.

### Acknowledgements

The participants in this research received supporting funds from the second-stage BK 21.

### References

- [1] K. Phadhi, K.S. Nanjundaswamy J.B. Goodenough, J. Electrochem. Soc., Vol. 144, p. 1188, 1997.
- [2] A. Yamada, S.C. Chung and K. Hinokuma: J. Electrochem. Soc., Vol. 148, p. A224, 2001.
- [3] H. Huang, S.C. Yin and L.F. Nazar: Electrochem. Solid State Lett., Vol. 4, p. A170, 2001.
- [4] S.Y. Chung, J.T. Bloking and Y.M. Chiang: Nat. Mater. Vol. 1, p. 123, 2002.