

Short communication

## Cycling performance of $\text{LiFePO}_4$ cathode material for lithium secondary batteries

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### Abstract

Lithium iron phosphate ( $\text{LiFePO}_4$ ) cathode material has been synthesized by a solid-state reaction which uses  $\text{Li}_3\text{PO}_4$  and  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  as starting materials. These materials were mixed with alumina balls and treated thermally at various temperatures in an argon and hydrogen atmosphere. The crystalline intensity of  $\text{LiFePO}_4$  powder prepared at  $700^\circ\text{C}$  is higher than that of powders prepared at  $600$  and  $800^\circ\text{C}$ . The particle size increases as the heat-treatment temperature increases. The material prepared at  $700^\circ\text{C}$  gives a higher discharge capacity than the other materials, namely,  $100 \text{ mAh g}^{-1}$  at the  $C/5$  rate, which corresponds to  $0.25 \text{ mA cm}^{-2}$  and at room temperature. Although the capacity increases as the operating temperature is raised, the degree of capacity fade also increases.

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*Keywords:* Lithium iron phosphate; Cathode material; Rechargeable lithium battery; Cycle performance; Discharge capacity

### 1. Introduction

Lithium iron phosphate ( $\text{LiFePO}_4$ ) is a promising cathode material for lithium rechargeable batteries. This material has many advantages compared with conventional cathode materials such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$ , namely, it is environmentally benign, inexpensive, and thermally stable in the fully-charged state [1–4]. In addition,  $\text{LiFePO}_4$  has a large theoretical capacity of  $170 \text{ mAh g}^{-1}$ , good cycle stability, and a flat discharge potential of  $3.4 \text{ V}$  versus  $\text{Li/Li}^+$ .

Many efforts have been made to prepare the material since it was discovered [5] that  $\text{LiFePO}_4$  could be used as a cathode material in lithium secondary batteries. In general,  $\text{LiFePO}_4$  powder has been synthesized by a solid-state reaction under an inert atmosphere. Because it is easy to oxidize  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  during the heat-treatment reaction,  $\text{LiFePO}_4$  has a very low electronic conductivity. Therefore, the rate capability of the material must be lowered.

Ravet et al. [6] improved significantly the electrochemical performance of  $\text{LiFePO}_4$  by applying carbon coating. Takahashi et al. [7] investigated the effect of operating temperature on cycle performance. It was found that the capacity increases as the cell operating temperature is raised. Prosrini et al. [8] suggested that the capacity of  $\text{LiFePO}_4$  can be

greatly improved by the addition of fine particles of carbon black during its synthesis. Improvements in the rate capability have also been achieved by synthesizing small particles [9] and by the addition of silver or copper [10]. It has been reported that a specific capacity of  $120 \text{ mAh g}^{-1}$  can be obtained at a high rate [11].

This study describes the influence of preparation temperature on the electrochemical performance and the physical properties, such as morphology and crystalline structure, of  $\text{LiFePO}_4$  material.

### 2. Experimental

The starting materials were  $\text{Li}_3\text{PO}_4$  (99%, Aldrich) and  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (99%, Aldrich). These materials are environmentally benign compared with other materials because they do not exhaust pollutant gases such as ammonia, acetates, and oxalates. These were weighed in stoichiometric ratios and homogenized in a alumina ball mixer.  $\text{LiFePO}_4$  powder was prepared by a direct solid-state reaction of two starting materials. To decompose the phosphate compound, the mixture was placed in a tubular furnace and heated at  $300^\circ\text{C}$  in a  $\text{Ar} + 5\% \text{ H}_2$  atmosphere for 20 h. The resultant powder was cooled to room temperature and mixed with 10 wt.% of acetylene black. After grinding and homogenization again, the mixture was transferred to the furnace calcined at various temperatures ( $600$ ,  $700$ , and  $800^\circ\text{C}$ ) in an

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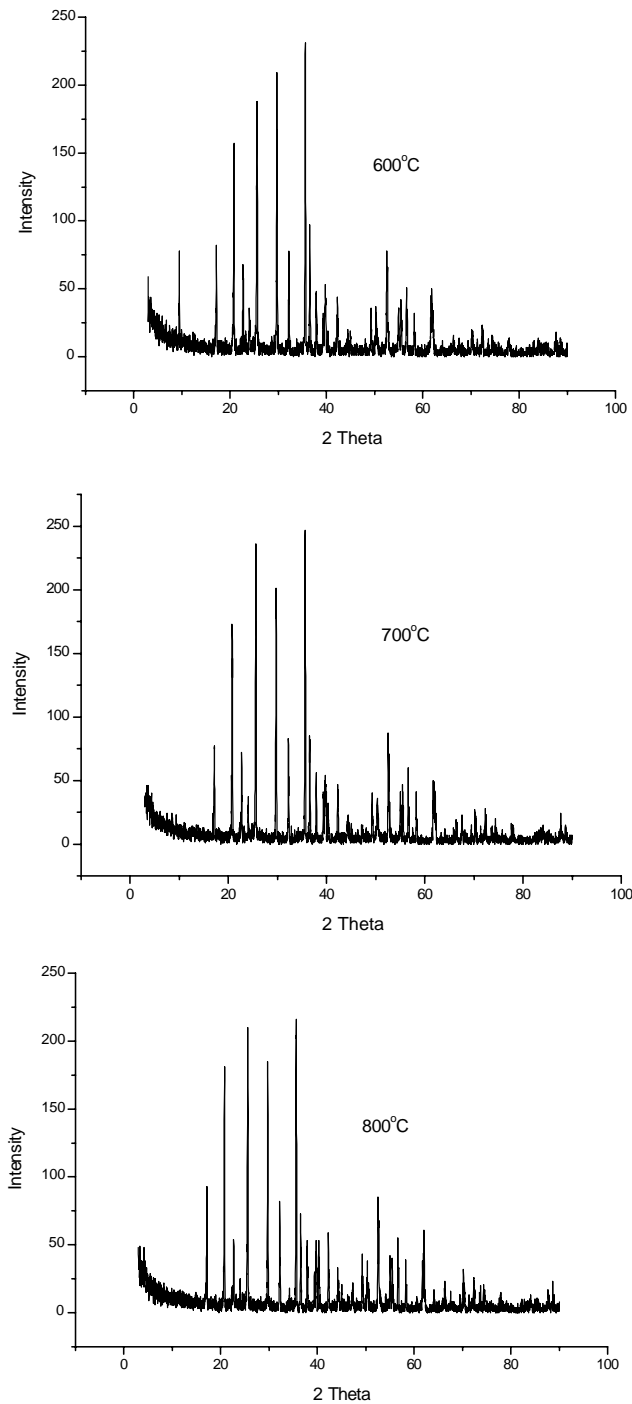


Fig. 1. XRD patterns of  $\text{LiFePO}_4$  powders prepared at different temperatures.

Table 1  
Chemical composition of  $\text{LiFePO}_4$  powders prepared at different temperatures

| Temperature ( $^{\circ}\text{C}$ ) | Chemical composition (wt.%) |      |      |
|------------------------------------|-----------------------------|------|------|
|                                    | Li                          | Fe   | P    |
| 600                                | 3.57                        | 32.5 | 17.2 |
| 700                                | 3.59                        | 32.7 | 17.9 |
| 800                                | 3.64                        | 33.1 | 18.1 |

Ar + 5%  $\text{H}_2$  atmosphere for 16 h. After this time, the black powder was cooled naturally to room temperature.

The crystallographic structure of the powder was analyzed by X-ray diffraction (XRD) (Rint/Dmax-2500, Rigaku) with Cu  $\text{K}\alpha$  radiation. Examination of the morphology of the powder was conducted by scanning electron microscopy (Hi-

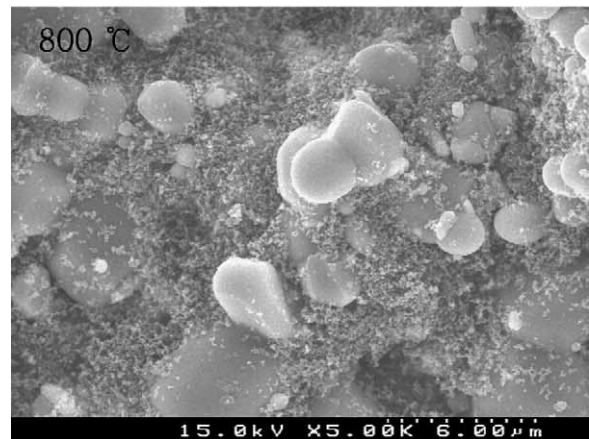
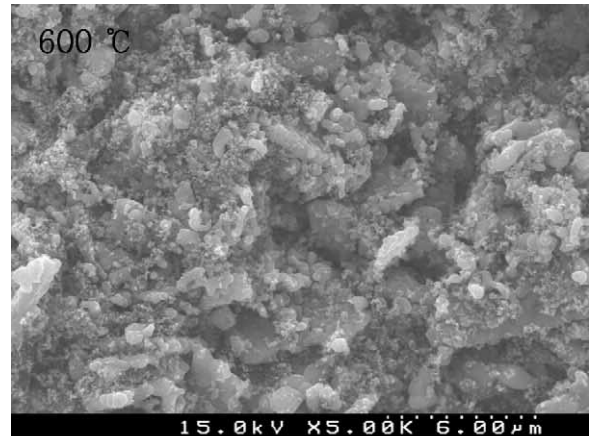


Fig. 2. Scanning electron micrographs of  $\text{LiFePO}_4$  powders prepared at different temperatures.

tachi S-4200). The chemical composition of the samples (Li, Fe, and P) was determined by atomic absorption spectrometry (spectra AA 800 series, Varian) and inductively coupled plasma (ICP, Thermal Jarrell ASH). To examine the electrochemical characteristics,  $\text{LiFePO}_4$  powder, poly(vinylidene fluoride) binder (5 wt.%) and *N*-methyl pyrrolidinone organic solvent were blended together in a high-speed mixer.

The viscous slurry was then cast on to an aluminum current-collector by the doctor blade technique and dried at  $80^\circ\text{C}$  under vacuum for 24 h. The resulting electrode was used as a cathode in a cell with a lithium metal anode and 1 M  $\text{LiPF}_6$  in ethylene carbonate:dimethyl carbonate:ethyl methyl carbonate (1:1:1 in vol.%) electrolyte. The separator was a Celgard 2400 microporous membrane. All cells were enveloped in aluminum plastic pouches and sealed under vacuum in a dry room (dew point;  $-50^\circ\text{C}$ ). The assembled cells were cycled galvanostatically between 2.8 and 4.0 V using Maccor battery cycler.

### 3. Results and discussion

The X-ray diffraction patterns of  $\text{LiFePO}_4$  powder prepared at different temperatures are shown in Fig. 1. The samples have the same XRD patterns because the carbon coating of the powder prevents the conversion of ferric ions to ferrous ions. The crystalline intensity of samples prepared at 600 and  $800^\circ\text{C}$  is less developed than that of the sample prepared at  $700^\circ\text{C}$ . The compositions of the samples are listed in Table 1. The molar ratio for Li:Fe:P is almost 1:1:1 for the three compounds, irrespective of the heat-treatment temperature. These results suggest that prepa-

ration temperature does not affect the presence of other impurities.

Electron micrographs of  $\text{LiFePO}_4$  powders prepared at 600, 700, and  $800^\circ\text{C}$  are presented in Fig. 2. The particle size increases with increase in heat-treatment temperature. In addition, the powder prepared at  $600^\circ\text{C}$  contains agglomerates of small particles agglomerated due to the insufficient sintering. This result is similar to the finding by Takahashi et al. [7]. These workers also reported that the specific area of powders increased as the preparation temperature increased. Therefore, the sample prepared at low temperature has about double the capacity compared with the sample prepared at high temperature.

The discharge cycling performance of  $\text{Li|LiFePO}_4$  cells was investigated as a function of temperature at various current rates. The cycles were performed at current densities between the  $C/5$  and  $1C$  rates. The discharge capacity of  $\text{LiFePO}_4$  prepared at  $600^\circ\text{C}$  is shown in Fig. 3. At room temperature, the discharge capacity during the initial cycle at the  $C/5$  rate is 70% of that at  $50^\circ\text{C}$ . This result supports the idea that the large capacity of  $\text{LiFePO}_4$  observed at high temperature is caused by the fast lithium diffusion rate in  $\text{LiFePO}_4$ . The discharge capacity of  $\text{LiFePO}_4$  prepared at  $700^\circ\text{C}$  is also influenced by the operating temperature (see Fig. 4). At  $50^\circ\text{C}$ , the discharge specific capacity is close to the theoretical value of  $170\text{ mAh g}^{-1}$  at the  $C/5$  rate, but decreases abruptly when the discharge current is increased. At room temperature, the material gives about  $100\text{ mAh g}^{-1}$  at the  $C/5$  rate and good cycle stability at even higher rates.

This effect can be attributed to the well-developed crystalline structure compared with powder prepared at

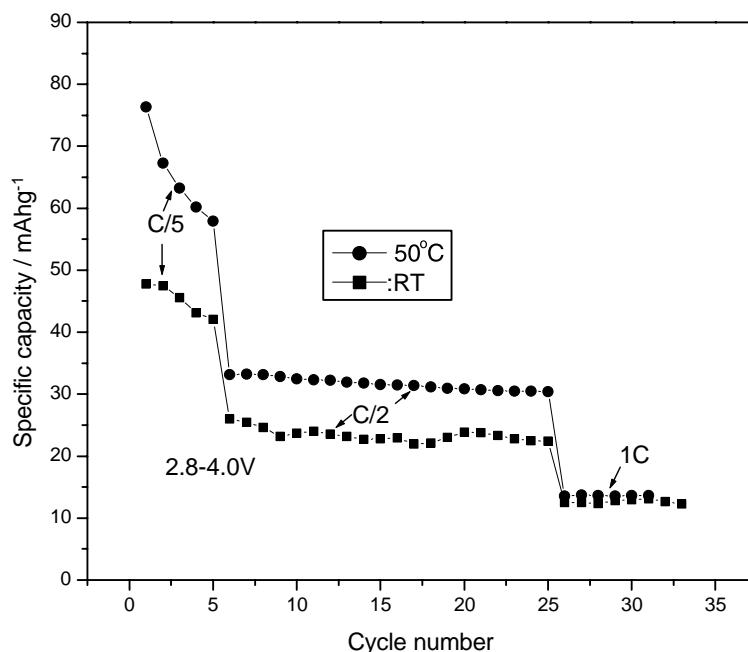


Fig. 3. Cycling performance of  $\text{Li|LiFePO}_4$  cell at different temperatures ( $\text{LiFePO}_4$  powder prepared at  $600^\circ\text{C}$ , 1 M  $\text{LiPF}_6/\text{EC}:\text{DMC}:\text{EMC}$ ).

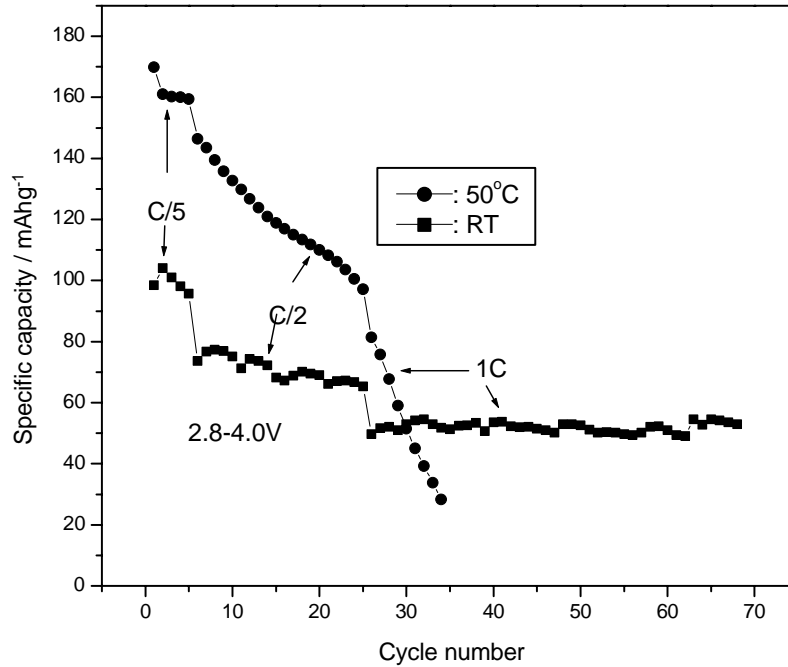


Fig. 4. Cycling performance of LiLiFePO<sub>4</sub> cell at different temperatures (LiFePO<sub>4</sub> powder prepared at 700 °C, 1 M LiPF<sub>6</sub>/EC:DMC:EMC).

600 °C. Also, the charge–discharge efficiency is almost 96% at the current densities investigated. This confirms the reversibility of LiFePO<sub>4</sub> powder during the lithium ion intercalation–de-intercalation process.

The cycling performance of LiFePO<sub>4</sub> powder prepared at 800 °C is shown in Fig. 5. The discharge capacity is lower than that of the materials prepared at other temperatures. As mentioned above, the higher the heat-treatment tempera-

ture, the larger are the particles of LiFePO<sub>4</sub> powder (Fig. 2). Therefore, the slow diffusion of lithium ions into this material prevents the utilization of the larger particles. As pointed out by Franger et al. [9], the specific capacity is very dependant on the particle size. The reduction in grain size can be related to the fact that the carbon particles, uniformly distributed between the starting materials, can interfere with the coalescence of the grains.

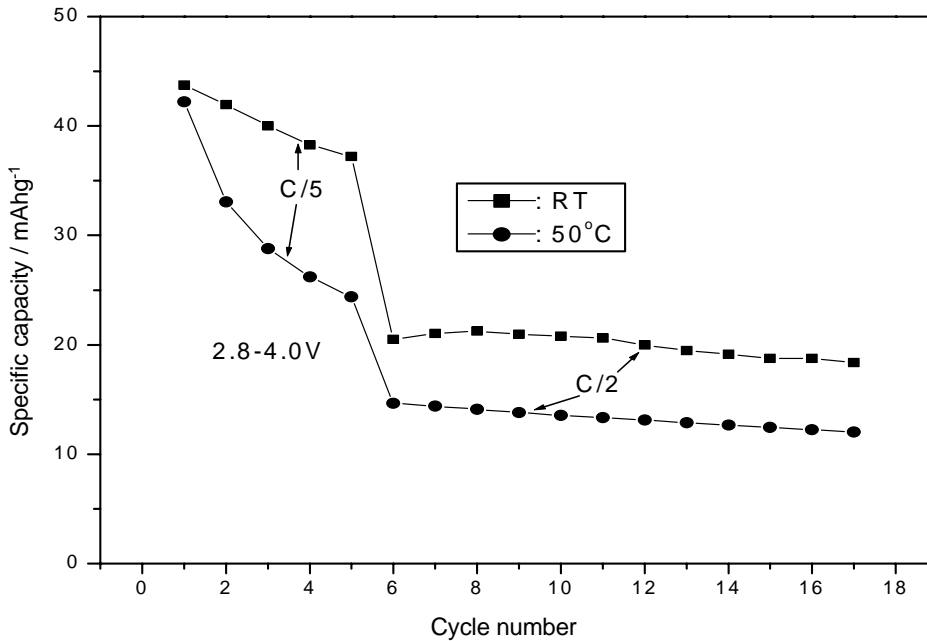


Fig. 5. Cycling performance of LiLiFePO<sub>4</sub> cell at different temperatures (LiFePO<sub>4</sub> powder prepared at 800 °C, 1 M LiPF<sub>6</sub>/EC:DMC:EMC).

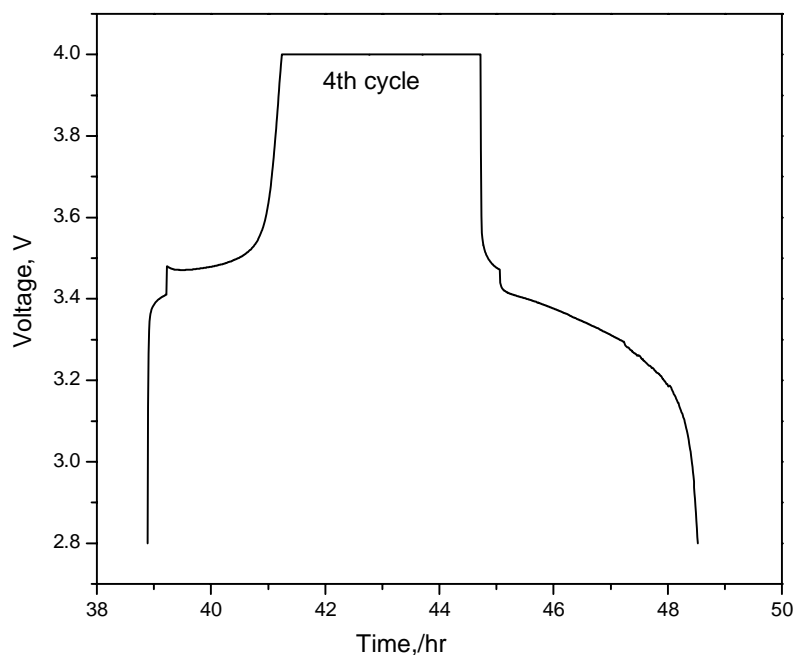


Fig. 6. Voltage profile of Li|LiFePO<sub>4</sub> cell at room temperature (LiFePO<sub>4</sub> powder prepared at 700 °C, C/5 rate).

Charge–discharge voltage curves (C/5 rate) of a Li|LiFePO<sub>4</sub> cell using LiFePO<sub>4</sub> powder prepared at 700 °C are shown in Fig. 6. The voltage plateaux in the discharge curves are not exactly flat due to the high resistance of the LiFePO<sub>4</sub> powder. Although the addition of fine particles of carbon black during synthesis of the LiFePO<sub>4</sub> powders cause some reduction in electrical resistance, there is no major improvement in electrochemical performance. Therefore, it is necessary to choose a proper conductive material to obtain a satisfactory discharge capacity even at low temperatures.

#### 4. Conclusions

LiFePO<sub>4</sub> powder prepared at 700 °C has a higher capacity compared with powders prepared at 600 and 800 °C. This is because it has a well-developed crystalline structure and optimum particle size. At high operating temperatures, the capacity of a Li|LiFePO<sub>4</sub> cell is increased, but the capacity fade per cycle is much more severe. The discharge curves do not exhibit flat potential plateaux due to the high electrical resistance of the powder. It is expected, however, that this problem can be solved by increasing the conductivity of the powders by using a more suitable conductive additive.

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