Electrochemical Reactivity of $LiFePO_4$ Prepared by Hydrothermal Method

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$LiFePO_4$ was prepared by hydrothermal method starting from CH_3COOLi, $FeSO_4$, and $(NH_4)_2HPO_4$ at 170 °C. The particle size of the obtained $LiFePO_4$ was about 3 μm. The performance of the $LiFePO_4$ as a positive electrode material for rechargeable lithium battery was evaluated in an organic electrolyte. The $LiFePO_4$ exhibited a discharge capacity of 145 $mA\,h\,g^{-1}$ at the electrode potential of 3.5 V vs Li/Li^+.

Phosphates $LiMPO_4$ ($M = $ Mn, Fe, Co, or Ni) have been investigated intensively as promising positive electrode materials for lithium batteries.[1–11] Among these materials, $LiFePO_4$ is of the lowest cost and highly compatible to the environment. $LiFePO_4$ has a highly stable three-dimensional framework due to strong P–O covalent bonds in $(PO_4)^{3-}$ polyanion, which prohibits the liberation of oxygen. These characteristics provide an excellent safety under abuse conditions of the batteries.[1–4] $LiFePO_4$ can be synthesized using conventional solid-state reactions.[1] However, it is difficult to attain its full capacity because of its low electronic conductivity and slow diffusion of Li^+ ion in the olivine structure.[1] In order to overcome these weak points, several alternative synthetic methods have been applied to the preparation of $LiFePO_4$. So far, it has been reported that the control of particle size is useful in increasing the charge and discharge capacities of $LiFePO_4$.[4,5] In addition, highly dispersed conductive substances such as carbonaceous materials and some metals in the positive electrode have been reported as being efficient additives.[5–9]

The hydrothermal synthesis is a useful method for preparing fine particles. It also has other advantages such as simple synthesis process and energy efficient. $LiFePO_4$ can be prepared by hydrothermal reaction.[12–17] We have prepared $LiFePO_4$ from weak basic precursor solutions consisting of LiOH, $FeSO_4$, and $(NH_4)_3PO_4$ by hydrothermal method and reported that an amorphous component existing on the $LiFePO_4$ particle gives a significant influence on its electrochemical reactivity.[14–16] The post-annealing at high temperatures (≈400 °C) was effective in improving the crystallinity and enhancing the electrochemical reactivity of the hydrothermally synthesized $LiFePO_4$.[14–16] In the present study, $LiFePO_4$ was prepared by hydrothermal method using weak acidic precursor solutions at 170 °C, and the electrochemical reactivity of thus prepared $LiFePO_4$ without post-annealing was evaluated.

The starting materials were CH_3COOLi, $FeSO_4\cdot 7H_2O$, and $(NH_4)_2HPO_4$, which were purchased from Wako Pure Chemical Industries. CH_3COOLi and $(NH_4)_2HPO_4$ were dissolved into deionized water, and then aqueous $FeSO_4$ solution was added subsequently. In order to prohibit the conversion of Fe^{2+} to Fe^{3+}, the water was degassed by N_2 gas bubbling for 30 min prior to preparing the solution, and the mixing process was carried out under nitrogen atmosphere. The molar ratio of Li:Fe:P in the precursor solution was 3:1:1. The concentration of Fe^{2+} (C_{Fe}) in the solution was in the range of 0.2–1.0 $mol\,dm^{-3}$. Forty milliliters of the precursor solution was put into a Teflon vessel (inner volume: 120 mL) sealed in a stainless steel autoclave, and the reactor was heated at 170 °C in an oven for 12 h. During this hydrothermal process, precipitation took place inside the reactor. After the hydrothermal reaction, the reactor was cooled down to room temperature. The precipitated powder was washed with deionized water and acetone. Then, the obtained powder was dried at 110 °C for 1 h under vacuum. The crystalline phases were identified with X-ray diffraction (XRD, RINT-2000, Rigaku) with Cu Kα radiation. The morphology of the particle was observed by a scanning electron microscope (SEM, JSM-5310, JEOL).

The performance of the $LiFePO_4$ as positive electrode was evaluated using a coin-type cell (size 2016) with a lithium metal negative electrode. A composite electrode was prepared by mixing the $LiFePO_4$, Ketjen black, and polytetrafluoroethylene in the weight ratio of 80:15:5. This composite was rolled into a thin sheet with uniform thickness (ca. 150 μm), and it was cut into a circle shape (13-mm diameter). The mass of $LiFePO_4$ contained in the composite positive electrode was 24.6 mg. The electrolyte was a mixed solvent of ethylene carbonate and diethyl carbonate (1:1 by volume) containing 1.0 $mol\,dm^{-3}$ $LiClO_4$. Galvanostatic charge and discharge tests were performed using an automatic charge–discharge equipment (HJR-110mSM6, Hokuto Denko) in the voltage range of 2.0–4.2 V at 17 $mA\,g^{-1}$ (0.3 $mA\,cm^{-2}$). All electrochemical measurements were carried out at 25 °C.

XRD pattern of $LiFePO_4$ prepared from the solution of $C_{Fe} = 1\,mol\,dm^{-3}$ is shown in Figure 1. All the XRD patterns of the prepared materials agreed with that of phospho-olivine $LiFePO_4$,[18] and no impurity phase was detected. Although all solid products could not be collected, the yields were about 95% for each case. This suggested that Fe^{2+} species in the pre-

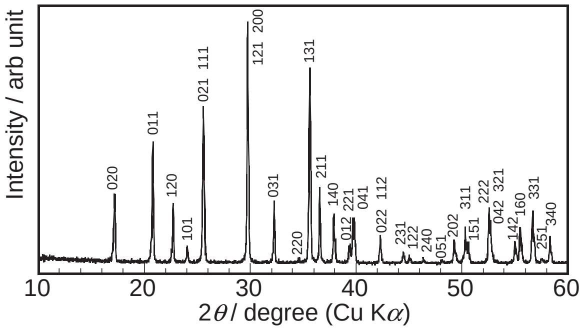

Figure 1. XRD pattern of $LiFePO_4$ prepared by hydrothermal method from the solution of $C_{Fe} = 1.0\,mol\,dm^{-3}$.

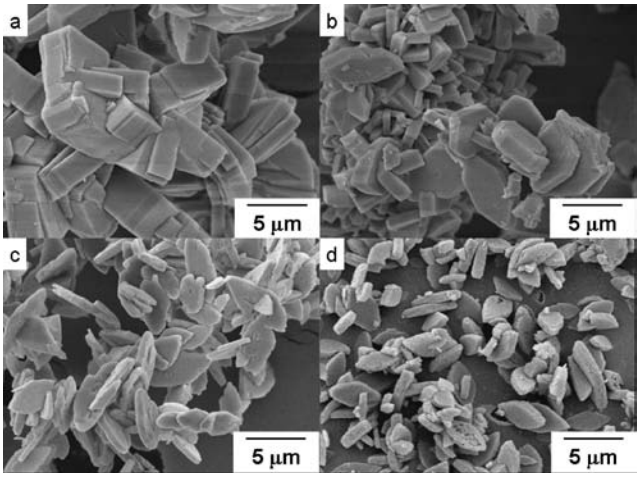

Figure 2. SEM images of $LiFePO_4$ prepared by hydrothermal method from the solutions of $C_{Fe} = 0.2$ (a), 0.5 (b), 0.8 (c), and 1.0 mol dm^{-3} (d).

cursor solutions were mostly converted to $LiFePO_4$. The pH value of the precursor solution was ranging from 5.5 to 5.1, and it decreased as increasing the concentration. According to the report by Lee et al., strong basic condition should be avoided to prepare $LiFePO_4$ without impurity phase.[17] Actually, in our previous work, $Fe_2(PO_4)OH$ and Li_3PO_4 were obtained as impurities in the basic condition (pH ≈ 9.5).[15] It is suggested that weak acidic or neutral or weak basic precursor solutions are preferable to obtain single phase of $LiFePO_4$ by hydrothermal reaction. Figure 2 displays SEM images of the prepared $LiFePO_4$ powders. The powders were composed of beautiful tabular particles. In fact, the peak intensity ratio in the XRD pattern (Figure 1) is different from that in the literature[11] probably owing to the asymmetric particle texture. The sharp XRD peaks and the beautiful particle shape indicated the high crystallinity of the prepared $LiFePO_4$. The particle size of the $LiFePO_4$ decreased as increasing the concentration of precursor. The particle size of the $LiFePO_4$ prepared from the solution of $C_{Fe} = 1$ mol dm^{-3} was about 3 μm, and the thickness of the particle was ca. 1 μm. The powders prepared from the solutions of $C_{Fe} = 0.2$ and 0.5 mol dm^{-3} were composed of agglomerated particles. On the other hand, highly dispersed particles were obtained from the highest concentrated solution. However, the nucleation and agglomeration mechanisms are not clear at present.

The electronic conductivity of $LiFePO_4$ is very low, and diffusion of Li^+ ion in the olivine structure is slow.[1] The small particle size, which is helpful for accessibility of the redox centers, is preferable to achieve large discharge capacity.[4,5] Therefore, galvanostatic charge/discharge test was carried out for the smallest $LiFePO_4$ particles prepared from the solution of $C_{Fe} =$ 1.0 mol dm^{-3}. The charge and discharge curves of hydrothermally synthesized $LiFePO_4$ are shown in Figure 3. The plateaus were observed in both charge and discharge curves at the potential of 3.5 V vs Li/Li^+. This electrochemical behavior corresponded to the solid-state redox of $Fe^{2+/3+}$ in the $LiFePO_4$ accompanying with Li^+ ion extraction and insertion.[1] The discharge capacity was 145 mA h g^{-1}, which was as high as 85% of the theoretical capacity (170 mA h g^{-1}).

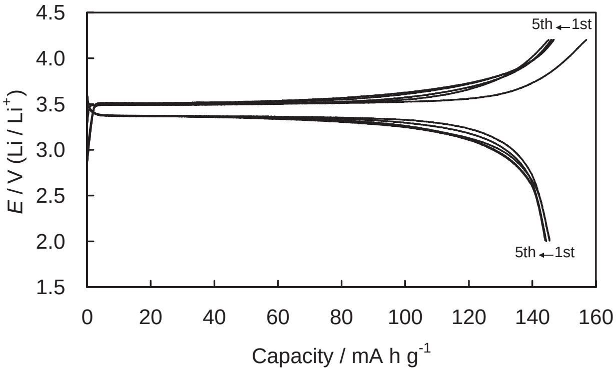

Figure 3. Charge and discharge curves of $LiFePO_4$ measured at a constant current of 17 mA g^{-1}. $LiFePO_4$ was prepared by hydrothermal method from the solution of $C_{Fe} = 1.0$ mol dm^{-3}.

In conclusion, $LiFePO_4$ with high electrochemical reactivity was prepared by simple hydrothermal method at low temperature as 170 °C. It was considered that the high electrochemical reactivity was due to the small particle size and high crystallinity.

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