

## Hydrothermal synthesis of $\text{LiFePO}_4$ as a cathode material for lithium batteries

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**Abstract**  $\text{LiFePO}_4$  (space group: *Pnma*) was prepared by hydrothermal method at 170 °C.  $\text{LiFePO}_4$  was prepared from precursor solutions consisting of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and three kinds of Li sources.  $\text{LiCl}$ ,  $\text{Li}(\text{CH}_3\text{COO})$ , and  $\text{LiOH} \cdot \text{H}_2\text{O}$  were used as Li sources. The pH of the precursor solution varied depending on Li source. The particle size, particle shape, and crystal texture of the obtained  $\text{LiFePO}_4$  changed depending on pH. The electrochemical properties of the prepared  $\text{LiFePO}_4$  were characterized as a cathode material for lithium batteries in an organic electrolyte at room temperature. The  $\text{LiFePO}_4$  particle prepared from the precursor solution with  $\text{Li}(\text{CH}_3\text{COO})$  was flake-like crystal (particle size: 1–2  $\mu\text{m}$ ) and had a preferred crystal orientation with a (020) texture. This  $\text{LiFePO}_4$  exhibited a discharge capacity of 147  $\text{mA h g}^{-1}$ , which was 85% of the theoretical capacity 170  $\text{mA h g}^{-1}$ .

### Introduction

$\text{LiFePO}_4$  has been prepared by various methods, in order to improve its electrochemical performance as a cathode material of rechargeable lithium batteries [1–6]. Usually, transition metal oxides such as  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  have

been utilized as cathode materials for rechargeable lithium batteries. However, present cathodes have been suffered from a safety problem, which is due to oxygen release from the transition metal oxides under abuse conditions [7]. The oxygen release causes a rapid temperature increase in the battery, which sometimes leads to an explosion of battery. In order to realize real safety of rechargeable lithium batteries, new type cathode materials have to be developed. Recently, phosphate compounds have been paid much attention in a sense of safety and cost of cathode materials. Especially,  $\text{LiFePO}_4$  has been intensively studied by many research groups [1–6]. The  $\text{Li}^+$  ion can be extracted/inserted from/into  $\text{LiFePO}_4$  at the electrode potential of 3.5 V versus  $\text{Li}/\text{Li}^+$ , and the theoretical discharge capacity of  $\text{LiFePO}_4$  is 170  $\text{mA h g}^{-1}$ . In addition, iron compounds are usually very cheap compared with other transition metal compounds. A main problem of  $\text{LiFePO}_4$  is its low electronic conductivity. Several researchers reported that carbon-coating on  $\text{LiFePO}_4$  particle was effective in improving its electrochemical performance [8–14]. On the other hand, high crystalline small particles of  $\text{LiFePO}_4$  have been prepared by using various methods, such as hydrothermal process, sol–gel process, and so on [15–19]. In the case of hydrothermal process, the composition of precursor solution strongly influences on particle nature of  $\text{LiFePO}_4$ . Moreover, the oxidation state of iron ion during hydrothermal treatment is very important to obtain  $\text{LiFePO}_4$  without any impurities [20]. In order to increase the utilization of  $\text{LiFePO}_4$  for charge and discharge, smaller particle should be prepared under suitable conditions because the shorter electronic conduction path is helpful in reducing ohmic resistance within the particle.

The crystal texture of  $\text{LiFePO}_4$  particle is also an important aspect, which is strongly related to electrode kinetics [21–24]. The  $\text{Li}^+$  ion diffusion takes place along

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*b*-axis in the crystal of orthorhombic  $\text{LiFePO}_4$  (space group: *Pnma*) during charge and discharge, and the charge transfer ( $\text{Li}^+$  ion transfer) takes place mainly on the (020) plane [24]. Therefore, if a crystal with a (020) texture is obtained, faster electrochemical reaction can be achieved.

In this study,  $\text{LiFePO}_4$  was prepared by hydrothermal method from  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and three kinds of Li sources.  $\text{LiCl}$ ,  $\text{Li}(\text{CH}_3\text{COO})$ , and  $\text{LiOH} \cdot \text{H}_2\text{O}$  were used as Li sources. The pH of the precursor solution varied depending on Li source. The particle size, particle shape, and crystal texture of the obtained  $\text{LiFePO}_4$  changed depending on the pH. The crystal characteristics and electrochemical properties of the prepared  $\text{LiFePO}_4$  were investigated. Especially, the effects of crystal texture of  $\text{LiFePO}_4$  on its electrochemical properties were discussed.

## Experimental

$\text{LiFePO}_4$  was prepared by the hydrothermal method with three kinds of Li sources  $\text{LiCl}$ ,  $\text{LiCH}_3\text{COO}$ , and  $\text{LiOH} \cdot \text{H}_2\text{O}$ . The  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  were used as Fe and P sources, respectively. These starting materials were dissolved into ultra pure water. This mixed solution (40 mL) was put into Teflon-lined Parr reactor (inner volume: 120 mL). Table 1 shows the molar ratio of each compound and concentration of  $\text{FeSO}_4$  for the hydrothermal process. Using these three different solutions, the hydrothermal process was performed at 170 °C for 12 h using a stainless steel autoclave. These processes were performed under  $\text{N}_2$  atmosphere in order to prevent the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  [25]. After filtration, the prepared sample was dried under vacuum at 100 °C for 1 h. The prepared samples were characterized with X-ray diffraction (XRD). The charge and discharge measurements of prepared samples were conducted using 2016 coin-type cells. The cathode was prepared from a mixture of prepared sample, Ketjen black, and PTFE with weight ratio of 80:15:5. The anode was lithium metal and a mixed solvent of ethylene carbonate and diethylcarbonate with volume ratio of 1:1 containing 1.0 mol  $\text{dm}^{-3}$   $\text{LiClO}_4$  was used as the electrolyte. The charge and discharge tests were performed at 0.1 C rate (17 mA  $\text{g}^{-1}$ - $\text{LiFePO}_4$ ). The electrochemical test was conducted in an argon-filled glove box at room temperature.

## Results and discussion

The pH of precursor solution depended on lithium salt used as a starting material. In the case of  $\text{LiOH}$ , the precursor solution was most basic condition, and the pH was 8.99. The precursor solution prepared using  $\text{LiCl}$  as Li source

was most acidic and the pH was 3.44. When  $\text{Li}(\text{CH}_3\text{COO})$  was used as Li source, pH of the precursor solution was 5.11. The differences in Li source and pH of precursor solutions influenced on the particle shape of resulting  $\text{LiFePO}_4$ . Figure 1 shows the scanning electron micrographs of hydrothermally synthesized samples. Using  $\text{LiOH}$  as a Li source, the smallest particles were prepared. The particles were agglomerated, and the particle size was less than 1  $\mu\text{m}$ . Among the three samples, the largest particle was obtained using  $\text{LiCl}$  as Li source. The particle was very thin and flake-like crystal, which was different from that prepared in the solution containing  $\text{LiOH}$ . On the other hand, the precursor solution with  $\text{Li}(\text{CH}_3\text{COO})$  provided thick flake-like crystals. The particles were well dispersed, and the particle size was estimated to be 1–2  $\mu\text{m}$ . In this way, the particle nature of  $\text{LiFePO}_4$  strongly depended on Li source and/or pH of the precursor solution.

Figure 2 shows XRD patterns of  $\text{LiFePO}_4$  samples prepared from three precursor solutions. All of the peaks in three x-ray diffraction patterns can be assigned to those of orthorhombic  $\text{LiFePO}_4$  (space group: *Pnma*) reported in the literature [16–18]. Therefore, it can be said that three samples are the single phase of  $\text{LiFePO}_4$ . However, the yield of  $\text{LiFePO}_4$  (conversion ratio of  $\text{Fe}^{2+}$  in the precursor to  $\text{LiFePO}_4$ ) depended on the acidic condition of the solution as shown in Table 1. When the pH of the precursor was higher than 5, the yield was more than 90%. However, the yield was as small as 55% in the case of precursor with  $\text{LiCl}$  because of the strong acid condition. Probably, the solubility of  $\text{LiFePO}_4$  would be higher under acidic condition pH <4 at high temperatures ( $\sim 170$  °C).

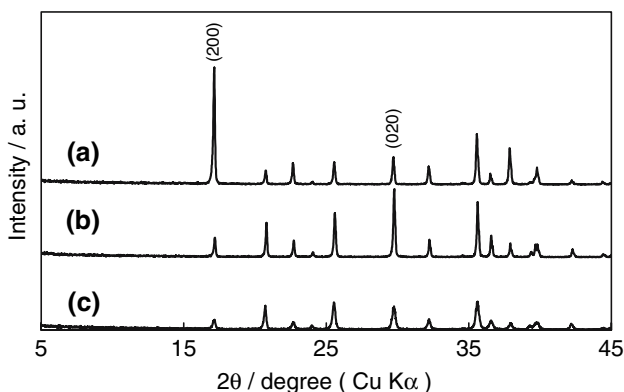
Although the all XRD patterns in Fig. 2 were assigned to the  $\text{LiFePO}_4$  with olivine structure, the relative intensities of the peaks were completely different between three samples. The peak intensity ratio of the  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{LiOH}$  was very similar to that reported in the literature [11–14], and the particle had a random crystal orientation. Indeed, the obtained particles were agglomerated polycrystalline particles as shown in Fig. 1c. However, the peak intensity of (200) of the  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{LiCl}$  was strongest, which suggested that the  $\text{LiFePO}_4$  flake particle had a preferred crystal orientation with a (200) texture. On the other hand, the (020) peak of the  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{Li}(\text{CH}_3\text{COO})$  was strongest, which suggested that the  $\text{LiFePO}_4$  flake crystal had a preferred crystal orientation with a (020) texture. In this way, the crystal texture of  $\text{LiFePO}_4$  was strongly influenced by Li source and/or pH of the precursor solution. These results suggested that the preferred crystal growth orientation changed depending on the pH of solution. The crystal texture of particles gives significant

**Table 1** Molar ratio of each starting materials and concentration of  $\text{FeSO}_4$ , pH of the precursor solution, and yield of  $\text{LiFePO}_4$

Molar ratio of starting materials			Concentration of $\text{FeSO}_4/\text{M}$	pH	Yield/%
$\text{FeSO}_4$	$(\text{NH}_4)_2\text{HPO}_4$	$\text{LiOH} \cdot \text{H}_2\text{O}$	0.5 M	8.99	98.2
1	1	2			
$\text{FeSO}_4$	$(\text{NH}_4)_2\text{HPO}_4$	$\text{Li}(\text{CH}_3\text{COO})$	1.0 M	5.15	94.5
1	1	3			
$\text{FeSO}_4$	$(\text{NH}_4)_2\text{HPO}_4$	$\text{LiCl}$	1.0 M	3.44	54.9
1	1	3			

The yield was defined as conversion ratio of  $\text{Fe}^{2+}$  in the precursor to  $\text{LiFePO}_4$

**Fig. 1** Scanning electron micrographs of  $\text{LiFePO}_4$  prepared from precursor solutions with  $\text{LiCl}$  (a),  $\text{Li}(\text{CH}_3\text{COO})$  (b), and  $\text{LiOH} \cdot \text{H}_2\text{O}$  (c)

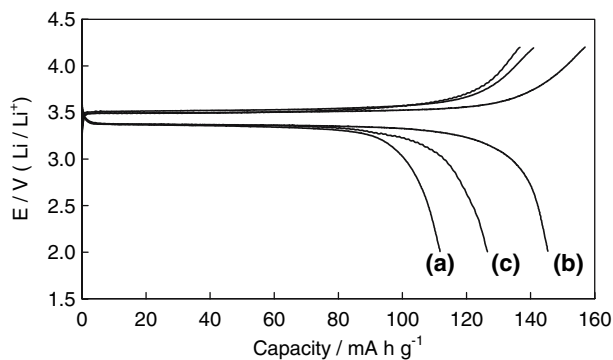


**Fig. 2** X-ray diffraction patterns of  $\text{LiFePO}_4$  prepared from precursor solutions with  $\text{LiCl}$  (a),  $\text{Li}(\text{CH}_3\text{COO})$  (b), and  $\text{LiOH} \cdot \text{H}_2\text{O}$  (c)

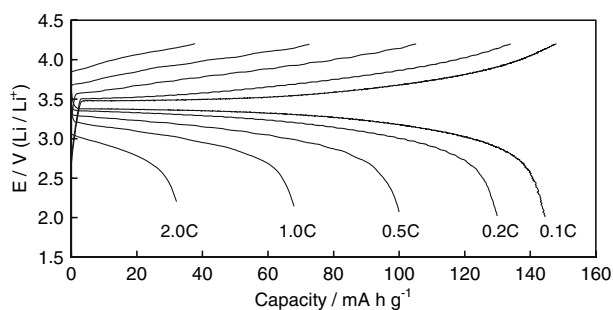
effects on the electrochemical properties of  $\text{LiFePO}_4$ . The following electrochemical measurements were conducted for these  $\text{LiFePO}_4$  samples.

Figure 3 shows the charge and discharge curves of  $\text{LiFePO}_4$  prepared from three different precursor solutions. The largest discharge capacity was achieved using  $\text{Li}(\text{CH}_3\text{COO})$  as a Li source of  $\text{LiFePO}_4$ , which was  $147 \text{ mA h g}^{-1}$ . On the other hand,  $\text{LiFePO}_4$  samples prepared from precursor solutions with  $\text{LiCl}$  and  $\text{LiOH}$  exhibited lower discharge capacities. As mentioned above, all  $\text{LiFePO}_4$  samples prepared by hydrothermal method in this study did not contain any impurities, so that all samples were expected to show discharge capacities near to the theoretical one ( $170 \text{ mA h g}^{-1}$ ). However, the discharge capacity depended on Li source utilized as a starting material for hydrothermal synthesis of  $\text{LiFePO}_4$ . The differences among three samples were particle size, particle shape, and crystal texture. Particle size of active material usually influences on charge-discharge performance,

because the  $\text{Li}^+$  ion diffusion and electronic conduction take place within the particle. In fact, as reducing the particle size, the diffusion length of  $\text{Li}^+$  ion and electronic conduction path are decreased, which reduce the diffusion resistance for  $\text{Li}^+$  ion and electrical resistance within the particle [11]. In the case of  $\text{LiFePO}_4$ , crystallographic phase transition takes place during charge and discharge, so that phase boundary diffusion may occur within the particle [16]. The rate of boundary diffusion depends on particle size and shape. By the way,  $\text{LiFePO}_4$  is an olivine-type compound, and anisotropic crystal structure is involved [23]. Consequently, the crystal orientation of  $\text{LiFePO}_4$  particle gives significant effects on its charge–discharge process. The  $\text{Li}^+$  ion diffusion takes place along *b*-axis in the crystal of  $\text{LiFePO}_4$  during charge and discharge [21–24]. Furthermore, the charge transfer ( $\text{Li}^+$  ion transfer) takes place mainly on the (020) plane [24]. Therefore, the electrode reaction rate of  $\text{LiFePO}_4$  can be improved by a preferential crystal orientation. If a tiny crystal with a (020) texture is obtained, faster electrochemical reaction can be achieved. In this way, the charge and discharge characteristics of  $\text{LiFePO}_4$  should be discussed considering at least two factors, i.e., crystal texture and particle size. The  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{Li}(\text{CH}_3\text{COO})$  had a larger particle size than that prepared from the precursor solution with  $\text{LiOH}$ . However, the  $\text{LiFePO}_4$  crystal prepared from the precursor solution with  $\text{Li}(\text{CH}_3\text{COO})$  had a preferred orientation with a (020) texture while the  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{LiOH}$  had random crystal orientations. The discharge capacity of  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{LiCl}$  was the smallest among the three  $\text{LiFePO}_4$  samples, due to the largest particle size and the (200) crystal texture. This crystal texture is not suitable for  $\text{Li}^+$  ion insertion and extraction, because the  $\text{Li}^+$  ion



**Fig. 3** Charge and discharge curves of  $\text{LiFePO}_4$  prepared from precursor solutions with  $\text{LiCl}$  (a),  $\text{Li}(\text{CH}_3\text{COO})$  (b), and  $\text{LiOH} \cdot \text{H}_2\text{O}$  (c). Charge and discharge measurements were carried out at 0.1 C rate



**Fig. 4** Charge and discharge curves of  $\text{LiFePO}_4$  prepared from precursor solutions with  $\text{Li}(\text{CH}_3\text{COO})$ . Charge and discharge measurements were carried out at various rates

diffusion scarcely occurs along  $a$ -axis and the charge transfer does not take place on the (200) plane but (020) [24].  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{LiOH}$  had the smallest particle size, however, the crystal texture of the sample was random. The smaller particle of the  $\text{LiFePO}_4$  is suitable for faster electrode reaction, but the poor (020) texture of  $\text{LiFePO}_4$  is not good. From these results, it can be said that the crystal texture of  $\text{LiFePO}_4$  particle is more dominant factor for the electrochemical performance. The crystal texture of  $\text{LiFePO}_4$  particle was strongly influenced by the Li source and/or pH of the precursor solution. It was revealed that the weak acidic condition ( $\text{pH} \approx 5$ ) was preferable to obtain flake-like crystals of  $\text{LiFePO}_4$  with a (020) texture, which showed high electrochemical reactivity.

Figure 4 shows charge and discharge curves of  $\text{LiFePO}_4$  prepared from the precursor solution with  $\text{Li}(\text{CH}_3\text{COO})$  at various charge and discharge rates. The discharge capacity decreased with increasing charge and discharge rate. This is due to polarization in cathode. At 2.0 C rate, the discharge capacity was  $32 \text{ mA h g}^{-1}$ . This is smaller value compared with those of other cathode materials at 2.0 C ( $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and so on) [26, 27]. The electronic

conductivity of  $\text{LiFePO}_4$  is smaller than those of other cathode materials. This property is not good for the high rate charge-discharge performance of lithium battery. In order to overcome this problem, smaller particles of  $\text{LiFePO}_4$  with a (020) texture should be prepared. The particle size of  $\text{LiFePO}_4$  does not only depend on Li source but also concentration of  $\text{Fe}^{2+}$  and  $\text{PO}_4^{3-}$  ions in the precursor solution. Further optimization of hydrothermal condition is now in progress in our group and will be reported in due course.

## Conclusion

$\text{LiFePO}_4$  was prepared by hydrothermal method using three different Li sources,  $\text{LiOH}$ ,  $\text{Li}(\text{CH}_3\text{COO})$ , and  $\text{LiCl}$ . The pH of the precursor solution varied depending on the Li source. The particle morphology and preferred crystal growth orientation of  $\text{LiFePO}_4$  were strongly influenced by Li source and/or pH of the precursor solution. The electrochemical performance of  $\text{LiFePO}_4$  depended on the crystal texture. The  $\text{LiFePO}_4$  crystal with a (020) texture exhibited the highest charge and discharge capacities among the three samples. The discharge capacity of  $\text{LiFePO}_4$  was  $147 \text{ mA h g}^{-1}$  measured at 0.1 C rate ( $17 \text{ mA g}^{-1}$ ), however, the discharge capacity decreased with increasing discharge rate and became less than  $40 \text{ mA h g}^{-1}$  at 2.0 C rate. This may be due to low electronic conductivity of  $\text{LiFePO}_4$ . In order to improve the electrochemical reactivity of  $\text{LiFePO}_4$ , smaller crystals with a (020) texture should be prepared by optimizing the hydrothermal condition.

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