Short communication

Cathode performance of olivine-type LiFePO$_4$ synthesized by chemical lithiation

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Abstract

Chemical lithiation with LiI in acetonitrile was performed for amorphous FePO$_4$ synthesized from an equimolar aqueous suspension of iron powder and an aqueous solution of P$_2$O$_5$. An orthorhombic LiFePO$_4$ olivine structure was obtained by annealing a chemically lithiated sample at 550 °C for 5 h in Ar atmosphere. The average particle size remained at approximately 250 nm even after annealing. The lithium content in the sample was quantitatively confirmed by Li atomic absorption analysis and ^{57}Fe Mössbauer spectroscopy. While an amorphous FePO$_4$/carbon composite cathode has a monotonously decreasing charge–discharge profile with a reversible capacity of more than 140 mAh g^{-1}, the crystallized LiFePO$_4$/carbon composite shows a 3.4 V plateau corresponding to a two-phase reaction. This means that the lithium in the chemically lithiated sample is electrochemically active. Both amorphous FePO$_4$ and the chemically lithiated and annealed crystalline LiFePO$_4$ cathode materials showed good cyclability (more than 140 mAh g^{-1} at the 40th cycle) and good discharge rate capability (more than 100 mAh g^{-1} at 5.0 mA cm^{-2}). In addition, the fast-charge performance was found to be comparable to that with LiCoO$_2$.
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1. Introduction

Ever since the commercialization of lithium-ion batteries using a layered rocksalt metal oxide cathode such as LiCoO$_2$ [1], these batteries have been widely used in 3C portable applications. On the other hand, rare-metal-free polyanionic cathode materials with a 3D framework have attracted much interest in large-scale energy conversion devices because of their low cost, low environmental impact, and high thermal stability, as shown in Table 1 [2–13]. Among these materials, ordered-olivine LiFePO$_4$ has attracted much attention because it has the highest energy density. However, a ferrous compound and ammonium phosphate are usually used as Fe and P sources. It is difficult to regard these materials as low-cost and environmentally friendly. On the other hand, olivine-related FePO$_4$ has the largest theoretical capacity, 177 mAh g^{-1} per lithium intercalation. We previously proposed an inexpensive low-temperature synthesis route from an aqueous suspension of iron powder and an aqueous solution of P$_2$O$_5$, and showed that it could work as a good cathode-active material not only for Li but also for Na cells [13]. All of the cathode materials in Table 1 are ferric compounds except the olivine-type LiFePO$_4$, and they can be synthesized in air, owing to the stability of Fe^{3+} in the matrix. However, these ferric compounds, such as FePO$_4$, have a serious drawback as cathode-active materials for Li-ion batteries, because they cannot work as a lithium source in the cell, even if they involve lithium such as Li$_3$Fe$_2$(PO$_4$)$_3$.

In this paper, we performed chemical lithiation with LiI in acetonitrile for amorphous FePO$_4$ synthesized from an equimolar aqueous suspension of iron powder and an aqueous solution of P$_2$O$_5$ in air. The electrochemical activity of the crystallized LiFePO$_4$ by annealing was investigated using a coin-type cell. The lithium content in the lithiated sample was quantitatively confirmed by Li atomic absorption analysis and ^{57}Fe Mössbauer spectroscopy. In addition, we investigated the fast-charge ability

Table 1
Typical rare-metal-free iron-based polyanionic cathode materials

Cathode	Material group	Average voltage vs. Li/Li$^+$ (V)	Capacity (mAh g^{-1}), reported/theoretical	Theoretical energy density (Wh kg^{-1})	References
$Fe_2(SO_4)_3$	NASICON	3.6	110/134	480	[2]
$Li_3Fe_2(PO_4)_3$		2.8	100/128	360	[3]
$LiFeP_2O_7$	Pyrophosphate	2.9	60/113	330	[4]
$Fe_4(P_2O_7)_3$		3.0	110/144	430	[4]
$LiFePO_4$	Olivine	3.4	165/170	580	[5]
$FePO_4$	Olivine related	3.0	155/178	530	[6–13]

of chemically lithiated $LiFePO_4$ in comparison with that of $LiCoO_2$.

2. Experimental

Amorphous $FePO_4$ was synthesized by a previously reported solution-based method [12,13]. X-ray amorphous phase is called simply as "amorphous phase" in this paper and the term is used for convenience hereafter. First, stoichiometric amounts of metallic iron powder and P_2O_5 (Wako Pure Chemical Industries, Ltd.) were reacted in water at room temperature. The precursor solution was mixed for 24 h by a planetary ball mill (200 rpm) and then annealed at various temperatures (100–650 °C) for 12 h in air. Then, to prepare $LiFePO_4$, chemical lithiation was performed for the amorphous $FePO_4$. Here, we used amorphous $FePO_4$ annealed at 350 °C in air. LiI was selected as a reducing agent [6–8]. We chose it because it is cheaper and easier to handle than more powerful reducing agents such as *n*-butyl lithium, which has a potential relative to pure lithium of around 1 V, although LiI's reducing power is not enough to reduce to Fe(II) completely [6,14]. The sample powder was stirred at 300 rpm for 24 h in 1 M solution of LiI (Wako Pure Chemical Industries, Ltd.) in acetonitrile (Li/Fe = 3/1 mole ratio). The solution was then filtered to remove the remaining LiI, which was then dried in a vacuum overnight. All chemically lithiated treatments were performed in an Ar-filled glovebox, because of the hygroscopic nature of LiI. Finally, the obtained powder was annealed at 550 °C for 5 h in Ar, according to the literature [7,8]. On the other hand, a mixture of a 3:2 molar ratio of Li_2CO_3 and Co_3O_4 (Wako Pure Chemical Industries, Ltd.) was sintered at 850 °C for 24 h in air to prepare $LiCoO_2$ (average particle size: 5 μm) as a standard cathode material.

The synthesized materials were identified by powder X-ray diffraction (XRD; Rigaku RINT2100HLR/PC) with Cu Kα radiation. We investigated the crystallization temperature of the amorphous material by TG–DTA (Rigaku Thermo Plus TG8210), which was heated at a rate of 5 °C min^{-1} up to 700 °C in an Ar atmosphere.

The amount of lithium ion chemically inserted into amorphous $FePO_4$ was confirmed by atomic absorption spectrometry (Hitachi Z-5310). In addition, to investigate the changes in the Fe oxidation state in the samples from before to after chemical lithiation, the ^{57}Fe Mössbauer spectrum was used. A constant acceleration method was performed using the Mössbauer spectrometer (Laboratory Equipment Corp.). As the Mössbauer source and the reference for the isomer shift we used, respectively, 370 MBq of ^{57}Co(Pd) and α-Fe foil enriched with ^{57}Fe. The morphology and particle size were observed by FE-SEM (JEOL JSM-6340F). The particle size distribution was also measured by a dynamic light-scattering particle size analyzer (Horiba LB-500X).

To improve the rate capability, the 70 w/o cathode powders (amorphous $FePO_4$ and lithiated $LiFePO_4$) were dry ball-milled with 25 w/o acetylene black (AB; Denki Kagaku Co. Ltd.). Moreover, the $LiFePO_4$/carbon composite powder ($LiFePO_4$/C hereafter) was annealed again at 500 °C for 1 h in Ar. On the other hand, 70 w/o $LiCoO_2$ and 25 w/o carbon were fully mixed by the conventional method using a mortar grinder. Cathode pellets were fabricated by mixing a 95 w/o cathode/carbon composite powder with a 5 w/o PTFE Teflon binder (Polyflon TFE F-103, Daikin Industry Ltd.) and punching the resulting material disks (ca. 30 mg in weight, 10 mm in diameter, and 250 μm in thickness). The disks were dried at 100 °C overnight in vacuum before use. The performance of each electrochemical cathode was evaluated by a 2032 coin-type Li cell with a nonaqueous electrolyte (1 M $LiPF_6$/EC:DMC = 1:1 vol.%, Tomiyama Pure Chemical Industries, Ltd.) and a polypropylene separator (Celgard 3501; Celgard LLC) against a Li metal anode. The coin-type cells were assembled in an Ar-filled glovebox. All cycle tests were performed at 25 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns for (a) the chemically lithiated sample, (b) the sample annealed at 550 °C for 5 h in Ar after chemical lithiation, and (c) the sample sintered at 800 °C for 36 h in Ar with a conventional solid-state reaction. There were no diffraction peaks in the chemically lithiated sample, while some diffraction peaks were observed in the annealed sample. All these peaks in Fig. 1(b) could be indexed as olivine-type $LiFePO_4$ with a *Pnma* space group (ICDD 40–1499). However, no diffraction peaks of trigonal $FePO_4$ could be seen in the XRD pattern. On the other hand, the annealed lithiated sample may have included some amount of unreacted amorphous $FePO_4$ phase, because the crystallization temperature of trigonal $FePO_4$ is 716 °C [7,8]. The refined cell parameters for the obtained olivine-type $LiFePO_4$ sample were $a = 10.332(9)$ Å, $b = 5.960(1)$ Å, $c = 4.701(4)$ Å, and volume = 289.54 Å^3. These values agree well with $LiFePO_4$ obtained by a solid-state reaction ($a = 10.324(4)$ Å, $b = 6.009(1)$ Å, $c = 4.687(6)$ Å,
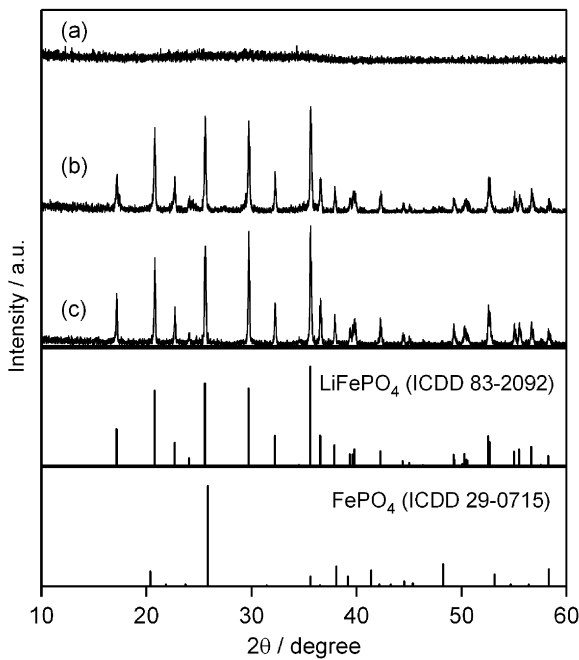
Fig. 1. XRD patterns for (a) amorphous LiFePO$_4$ obtained by chemical lithiation, (b) annealed LiFePO$_4$ after the chemical lithiation, and (c) olivine-type LiFePO$_4$ sintered by a conventional solid-state reaction.

Fig. 3. The ^{57}Fe Mössbauer spectra of (a) amorphous FePO$_4$ and (b) crystallized LiFePO$_4$ by annealing after chemical lithiation.

and volume = 290.82 Å^3). In addition, the obtained powder was gray, similar to the color of conventional olivine-type LiFePO$_4$.

The results of the TG–DTA measurements for amorphous FePO$_4$ and the lithiated sample are shown in Fig. 2. The weight loss observed below 200 °C corresponds to the dehydration by annealing. In addition, that of the lithiated sample was continuously observed until 300 °C. A small exothermic peak of amorphous FePO$_4$ in the DTA curve was observed at approximately 550 °C, and that of the lithiated sample was at 420 °C. These exothermic peaks were not accompanied by appreciable weight loss in the TG curve, and no symmetrical endothermic peaks were observed with decreasing temperature. The small exothermic peak of the amorphous FePO$_4$ seems to indicate
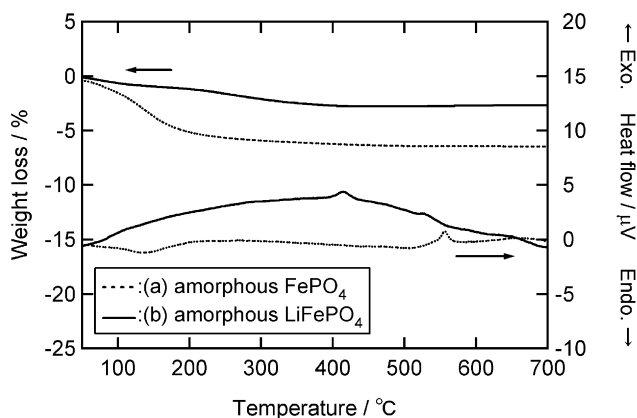
some structural transformation. Moreover, it transforms into trigonal FePO$_4$ (*P*321) at 716 °C, according to Refs. [7,9]. The trigonal FePO$_4$ consists of a corner-shared framework with FeO$_4$ tetrahedra and PO$_4$ tetrahedra. In contrast, the lithiated sample has a phase change to orthorhombic LiFePO$_4$ (*P*nma), which consists of an edge-shared and corner-shared framework with FeO$_6$ octahedra and PO$_4$ tetrahedra.

Fig. 3 shows the ^{57}Fe Mössbauer spectra for amorphous FePO$_4$ and olivine-type LiFePO$_4$ prepared by annealing at 550 °C for 5 h in Ar after chemical lithiation. The spectrum for amorphous FePO$_4$ exhibited one symmetric doublet with an isomer shift of 0.36 mm s^{-1}. This result indicates that the Fe oxidation state in the matrix is entirely Fe(III). In contrast, the spectra for LiFePO$_4$ prepared by chemical lithiation exhibited two symmetric doublets, with respective isomer shifts of 1.19 mm s^{-1} and 0.20 mm s^{-1}. The large symmetric doublet indicates that chemical lithiation changed the Fe oxidation state from Fe(III) to Fe(II). The small one indicates that the Fe oxidation state still kept Fe(III) without reacting. The Fe(II) content was found to be approximately 93% by calculating the intensity of each doublet. In addition, the amount of chemically inserted Li ions in the amorphous FePO$_4$ was found to be approximately 0.91 mol by atomic absorption spectrometry. These results are in good agreement. The ^{57}Fe Mössbauer spectroscopy and atomic absorption spectrometry revealed that the composition of the sample obtained by chemical lithiation was Li$_{0.9}$FePO$_4$, which is a two-phase 9:1 mixture with olivine-type LiFePO$_4$ and amorphous FePO$_4$.

Fig. 4 shows SEM images of amorphous FePO$_4$, olivine-type LiFePO$_4$ annealed at 550 °C for 5 h after the chemical lithiation, and standard olivine-type LiFePO$_4$ sintered at 800 °C for 36 h. In addition, the particle size distributions of amorphous FePO$_4$

Fig. 2. TG–DTA profiles for (a) amorphous FePO$_4$ and (b) amorphous LiFePO$_4$ obtained by chemical lithiation (heating rate: 5 °C min^{-1}; flow rate: 200 mL min^{-1}).
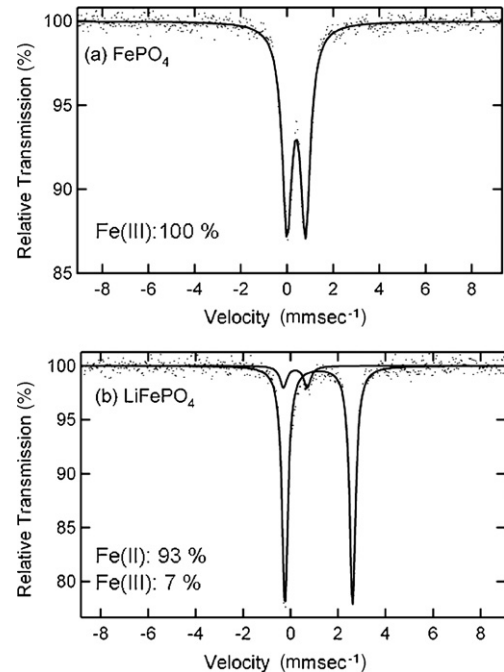
and chemically lithiated LiFePO$_4$ are shown in Fig. 5. For the measurement of particle size distribution, the powder was dispersed in ethanol to reduce the aggregation. It was confirmed that the minimum particle sizes of amorphous FePO$_4$ and chemically lithiated LiFePO$_4$ in Figs. 4 and 5 were 100 nm and that their average sizes were approximately 250 nm. The absence of a significant increase in particle size is due to the low annealing temperature—550 °C for 5 h. In contrast, the particle size distribution of a standard LiFePO$_4$ sample was beyond the scale range, between 3.0 nm and 6.0 μm. According to a geometrical estima-
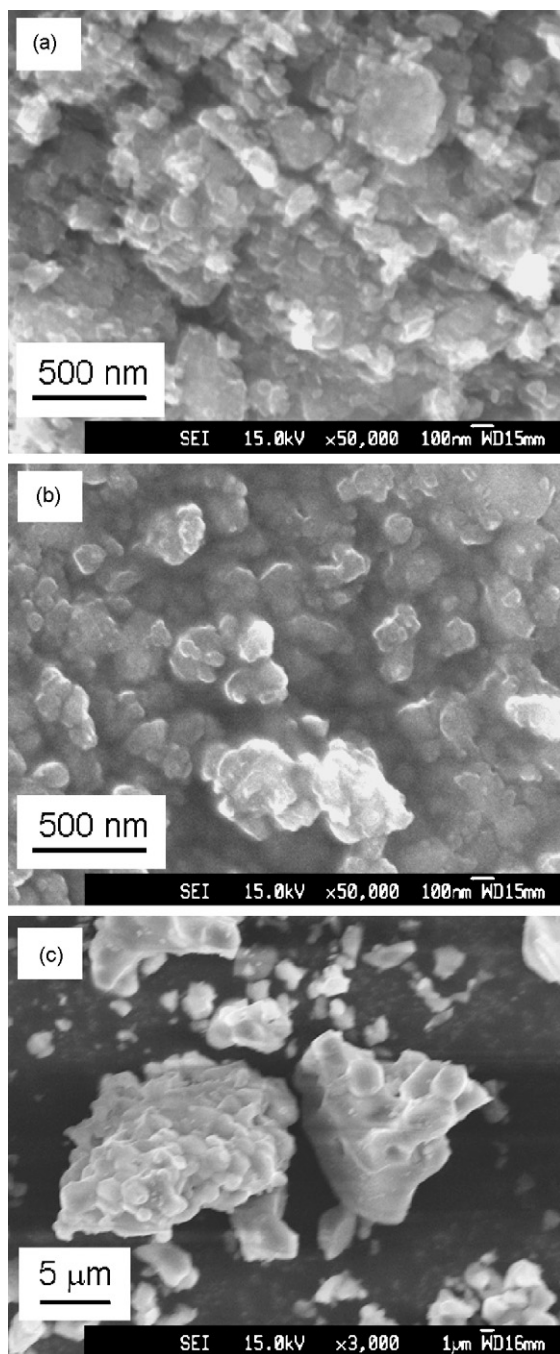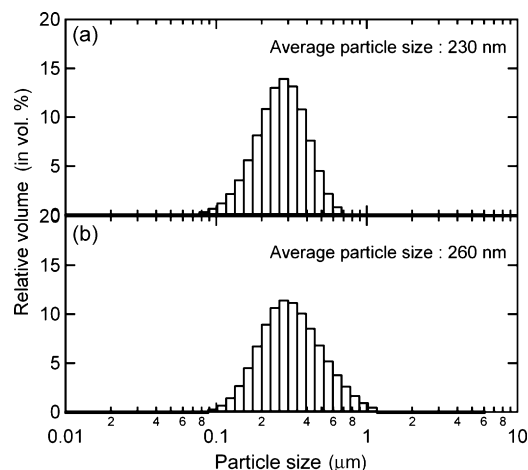

Fig. 5. The particle size distribution of (a) amorphous FePO$_4$ and (b) crystallized LiFePO$_4$ by annealing after chemical lithiation.

tion of the SEM images in Fig. 4, the average particle size of the standard sample was approximately 5 μm. It was found that the chemical lithiation of nano-sized FePO$_4$ is a useful method for synthesizing nano-sized olivine-type LiFePO$_4$.

Fig. 6 shows the charge/discharge profiles for the amorphous FePO$_4$/C and olivine-type LiFePO$_4$/C composite cathodes, respectively. FePO$_4$/C was cycled between 2.0 and 4.5 V, while LiFePO$_4$/C was between 2.0 and 4.0 V. The charge/discharge current for both cathodes was 0.2 mA cm^{-2}. The profiles of amorphous FePO$_4$/C each showed a single-phase reaction with an average voltage of ∼3.0 V, which is similar to that of the trigonal FePO$_4$ [12]. Although the first discharge capacity was 150 mAh g^{-1}, the second decreased to 140 mAh g^{-1} (80% of the theoretical capacity) because of an insufficiency in charging. In contrast, the profiles of LiFePO$_4$/C showed a two-phase reaction with a 3.4 V plateau, which is similar to that of olivine-
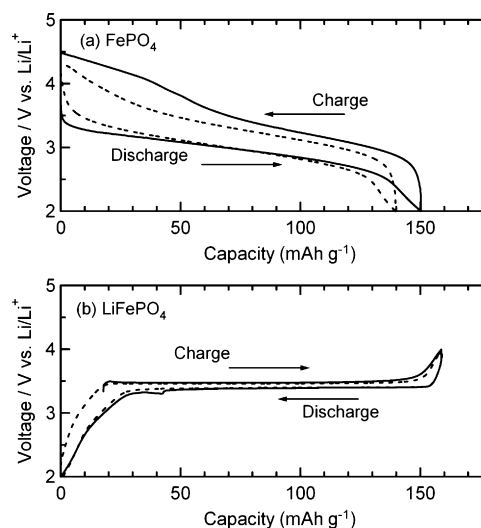

Fig. 4. SEM images of (a) amorphous FePO$_4$, (b) crystallized LiFePO$_4$ by annealing after chemical lithiation, and (c) olivine-type LiFePO$_4$ sintered by a conventional solid-state reaction.

Fig. 6. The charge/discharge profiles for (a) amorphous FePO$_4$/carbon composite and (b) chemically lithiated olivine-type LiFePO$_4$/carbon composite (continuous line: first cycle, dotted line: second cycle). The voltage range was 2.0–4.5 V for FePO$_4$/C and 2.0–4.0 V for LiFePO$_4$/C. The charge/discharge rate was 0.2 mA cm^{-2}.

type LiFePO$_4$ synthesized by a conventional solid-state reaction. These results indicate that the chemically lithiated LiFePO$_4$ is still electrochemically activated even after 550 °C annealing treatment. However, the first charge capacity (140 mAh g^{-1}) was found to be 90% smaller than the first discharge capacity (155 mAh g^{-1}), as shown in Fig. 5(b). The discrepancy between the charge/discharge capacity on the first cycle is consistent with the results of atomic absorption spectrometry and ^{57}Fe Mössbauer spectroscopy. In other words, the discrepancy can be explained by the incomplete chemical lithiation. The reversible capacity of the second cycle was 155 mAh g^{-1} (90% of the theoretical capacity) because the shortage of Li ion in the cathode matrix was compensated by the Li metal in the anode after the first cycle. Of course, the increase in lithiation time and temperature for the complete chemical lithiation of FePO$_4$ or the use of the stronger reducing agent should be considered, as such Li compensation cannot be expected in a practical Li-ion cell using a carbonaceous anode.

The cyclability for the amorphous FePO$_4$/C and that for the olivine-type LiFePO$_4$/C cathode are shown in Fig. 7. The charge/discharge condition was similar to that shown in Fig. 6. Both cathode materials showed good cyclability, although the discharge capacity of FePO$_4$/C was unstable during the first ten cycles. The discharge capacity was maintained at more than 150 mAh g^{-1} after the 40th cycle. Even at the 40th cycle, the profile of LiFePO$_4$/C prepared by chemical lithiation maintained a 3.4 V plateau, corresponding to a two-phase reaction, and there was no trace of a change to the trigonal FePO$_4$ on cycling.

Fig. 8 shows the discharge profiles at various current rates for the amorphous FePO$_4$/C and olivine-type LiFePO$_4$/C. The discharge current rate gradually increased from 0.2 to 1.0 mA cm^{-2}, while the charge current rate remained constant at 0.2 mA cm^{-2}. Here, the current density of 0.2 mA cm^{-2} corresponds to an approximately C/20 rate ($\sim$8.5 mA g^{-1}). Both cathode materials were cycled at a low rate several times before we evaluated the rate capability. The discharge and charge current rates were maintained at a discharge capacity greater than 150 mAh g^{-1} at 1.0 mA cm^{-2} without the capacity fading.
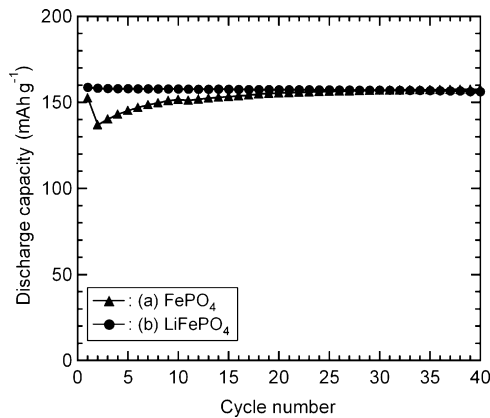

Fig. 8. The discharge rate capability for (a) amorphous FePO$_4$/carbon composite and (b) chemically lithiated olivine-type LiFePO$_4$/carbon composite. The charge current was kept constant at 0.2 mA cm^{-2}. The voltage range was 2.0–4.5 V for FePO$_4$/C and 2.0–4.0 V for LiFePO$_4$/C.

Although capacity did fade at higher discharge rates, the capacities were maintained at more than 140 mAh g^{-1} at 2.0 mA cm^{-2} and at more than 100 mAh g^{-1} even at 5.0 mA cm^{-2}. LiFePO$_4$/C showed a slightly better rate capability than amorphous FePO$_4$/C at more than 5.0 mA cm^{-2}.

The fast-charge capability of LiFePO$_4$/C at the 4.2 and 4.3 V cutoff conditions is shown in Fig. 9. As the standard cathode in Fig. 9, we used a normal micro-sized LiCoO$_2$ sintered at 850 °C in air. In the case of the 4 V-class cathodes, such as LiCoO$_2$, the voltage margin between the discharge voltage and oxidation potential of the nonaqueous electrolyte is usually less than 0.5 V, while in the case of LiFePO$_4$ it is larger than 1 V. Although the low electronic conductivity of LiFePO$_4$ has often been noted, we expect that the large voltage margin must be helpful for fast charging. In fact, Yamada et al. demonstrated the excellent fast-charging property of LiFePO$_4$ by potentiostatically stepwise charging [15,16]. To evaluate the rate capability of charging, the charge current rate was gradu-

Fig. 7. The cyclability for (a) amorphous FePO$_4$/carbon composite and (b) chemically lithiated olivine-type LiFePO$_4$/carbon composite. The voltage range was 2.0–4.5 V for FePO$_4$/C and 2.0–4.0 V for LiFePO$_4$/C. The charge/discharge rate was 0.2 mA cm^{-2}.

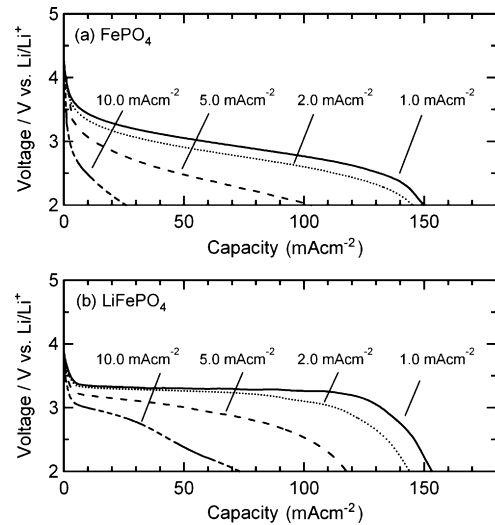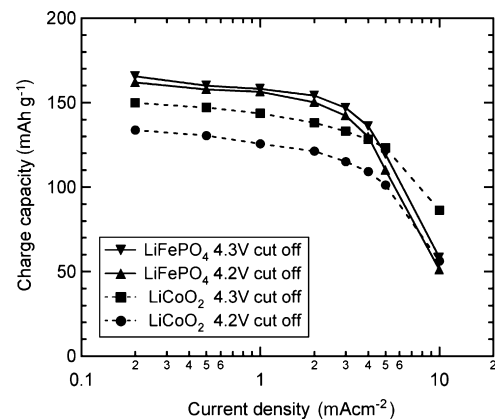Fig. 9. The fast-charge capability for LiFePO$_4$/carbon composite and LiCoO$_2$ at various charge cutoff voltages. The discharge current was kept constant at 0.2 mA cm^{-2}.

ally increased from 2.0 to $10.0\,\mathrm{mA\,cm^{-2}}$, while the discharge current rate was kept constant at $2.0\,\mathrm{mA\,cm^{-2}}$. In the case of 4.3 V cutoff charging at a rate of $10.0\,\mathrm{mA\,cm^{-2}}$, the charge capacity of $LiFePO_4/C$ was inferior to that of $LiCoO_2$. However, in the case of the 4.2 V cutoff, the fast-charge capability of $LiFePO_4/C$ was superior to that of $LiCoO_2$ between 0.2 and $10.0\,\mathrm{mA\,cm^{-2}}$. Moreover, considering the slight difference between the 4.2 and 4.3 V cutoffs, the results for $LiFePO_4$ mean that $LiFePO_4$ does not need a high cutoff voltage for fast charging. This facile comparison may not be suitable for the inherent kinetics of the cathodes, because of the differences in particle sizes and composite structures. However, it is found that the fast-charge performance of the nano-sized $LiFePO_4$/carbon composite is comparable to that of the conventional $LiCoO_2$.

4. Conclusions

Olivine-type $LiFePO_4$ was synthesized by annealing amorphous material obtained by the chemical lithiation of LiI to amorphous $FePO_4$. Atomic absorption spectrometry and ^{57}Fe Mössbauer spectroscopy revealed that the amount of chemically inserted Li was approximately 0.90 mol per $LiFePO_4$. The average particle size remained at about 250 nm before and after chemical lithiation and the following annealing treatment. The charge/discharge profile of prepared olivine-type $LiFePO_4/C$ exhibited a two-phase reaction with 3.4 V, similar to that of $LiFePO_4$ synthesized by the conventional solid-state reaction. The electrochemical activity of $LiFePO_4$ synthesized from $FePO_4$ was maintained after the annealing at $550\,^{\circ}C$ for 5 h in Ar. In addition, we confirmed that the fast-charging ability is comparable to that of a 4 V-class cathode on the market, although $LiFePO_4$ is not a conductive cathode.

$FePO_4$ is one of the highest cost-performance cathode-active materials because it can be obtained from an aqueous suspension of iron powder and an aqueous solution of P_2O_5 in air. Although it is not necessarily cheap to use LiI as a reducing agent and acetonitrile as a solvent, chemical lithiation is a useful method not only to convert $FePO_4$ to $LiFePO_4$, but also to obtain nano-sized $LiFePO_4$ with a good rate capability.

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