Short communication

FePO$_4$ cathode properties for Li and Na secondary cells

T. Shiratsuchi [a], S. Okada [a,*], J. Yamaki [a], T. Nishida [b]

[a] *Institute of Advanced Material Study, Kyushu University, Kasuga Koen 6-1, Kasuga 816-8580, Japan*
[b] *School of Humanity-oriented Science and Engineering, Kinki University, Kayanomori, Iizuka 820-8555, Japan*

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Abstract

Amorphous and crystalline FePO$_4$ were synthesized by annealing the precursor aqueous solution with P$_2$O$_5$ and iron powder in air. Although planetary ball milling is effective for reducing the synthetic time, it was confirmed that 15 days were sufficient reaction time, even at room temperature, to bring the same result without mixing. Annealing at over 500 °C in air resulted in trigonal FePO$_4$ with a $P321$ space group. Both amorphous and crystalline FePO$_4$ have a corner-shared matrix, and they showed similarly good capacity, not only for Li but also for Na anodes.
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1. Introduction

LiFePO$_4$ has drawn attention as the next-generation rare-metal-free cathode with the largest capacity [1,2]. However, divalent iron starting materials such as FeC$_2$O$_4$·2H$_2$O and (CH$_3$COO)$_2$Fe are expensive and toxic. In addition, the calcination process must be performed in an inert atmosphere. In order to keep production costs down, we changed the synthesis target from lithium iron(II) phosphate to iron(III) phosphate [3–7], which can be synthesized in air. Moreover, P$_2$O$_5$ and metallic iron powder were selected as inexpensive starting materials. In our previous paper, we reported on the cathode properties of the amorphous and crystalline trigonal FePO$_4$ in Li cells [8].

On the other hand, inexpensive and abundant sodium is an attractive anode for the next-generation batteries. However, the ionic volume of sodium is 2.5 times larger than that of lithium, and the cathode must include larger sites for Na$^+$ in the matrix. The trigonal FePO$_4$ with its corner-shared framework has a large bottleneck for guest diffusion. Although the density of this cathode is lower than the typical cathode materials in commercial Li-ion batteries, the sparse corner-shared matrix can be regarded as an ideal host structure for Na intercalation. Actually, the reversible insertion of various cations such as Na$^+$ or Mg^{2+} for FePO$_4$ has been tried by Tarascon and coworkers [9]. In this paper, the amorphous and crystalline FePO$_4$ cathode characteristics for Na anodes are unveiled using coin-type Na cells.

2. Experimental

We identified all the synthesized materials by XRD (Rigaku RINT2100HLR/PC), ICP-MS (Agilent Agilent7500c) and FT-IR (JASCO 680 plus). In addition, ^{57}Fe Mössbauer spectra were recorded at room temperature for FePO$_4$ cathode pellet, which was sealed in a laminate bag under argon atmosphere in the state after full discharge and charge. A constant acceleration method was used for the Mössbauer spectroscopy by spectrometer (Laboratory Equipment Corp.). Three hundred and seventy megabecquerel of ^{57}Co(Pd) and α-Fe foil enriched with ^{57}Fe were used as the Mössbauer source and the reference for isomer shift, respectively.

To improve the rate capability, the cathode powders were dry ball-milled with 25 (w/o) acetylene black (AB). Cathode pellets were then fabricated by mixing the powder with a 5 (w/o) PTFE Teflon binder (Polyflon TFE F-103, Daikin Industry Ltd.). We evaluated the electrochemical cathode performance in coin-type Na/Li cells using a nonaqueous electrolyte (1 M NaClO$_4$/PC, 1 M LiPF$_6$/EC:DMC = 1:1 vol.%, Tomiyama Pure Chemicals Co.) and a polypropylene separator (Celgard 3501) against a Na/Li metal anode.

3. Results and discussion

The P$_2$O$_5$ and metallic iron powders were reacted in water at room temperature. The precursor solution was mixed for 24 h by a planetary ball mill (200 rpm) and was dried at 100 °C for 24 h in air. The obtained powder was annealed at vari-

* Corresponding author. Tel.: +81 92 583 7841; fax: +81 92 583 7841.
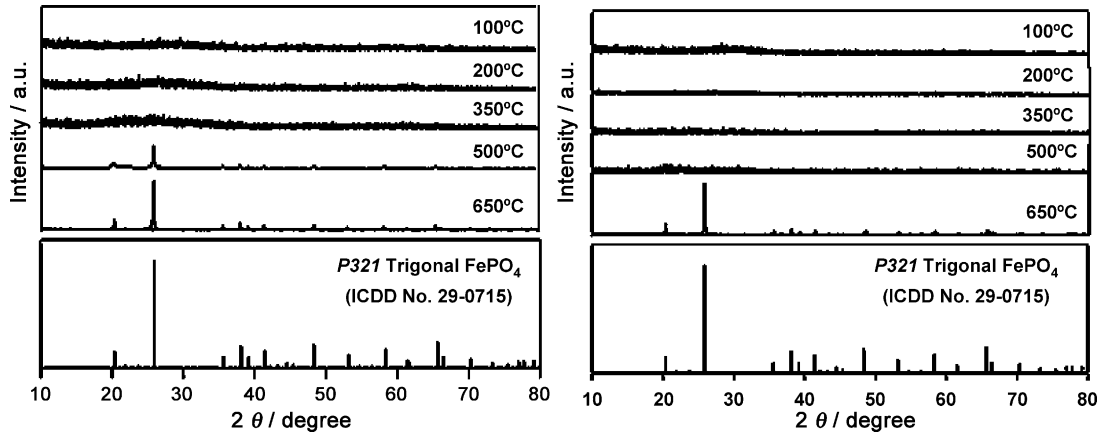*E-mail address:* s-okada@cm.kyushu-u.ac.jp (S. Okada).

Fig. 1. XRD profiles of FePO$_4$ annealed at a various temperature (left: with planetary ball milling and right: without planetary ball milling).
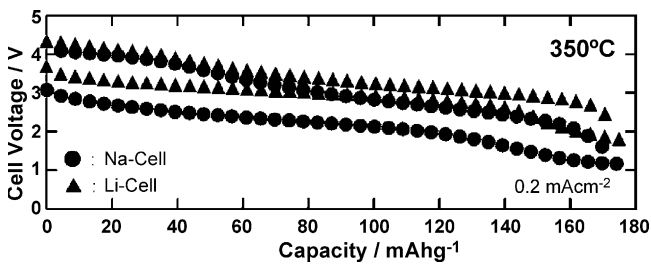

Fig. 2. QOCV profiles of amorphous FePO$_4$ annealed at 350 °C in Li and Na cells.

ous temperatures (100–650 °C) for 12 h in air. To reduce process cost for mixing, we also synthesized FePO$_4$ by keeping the reaction at room temperature for 15 days without mixing.

Fig. 1 shows the XRD profiles of the obtained materials with and without a planetary ball milling, respectively. The material annealed at 100–500 °C assumed an amorphous phase. The crystalline phase annealed at 650 °C was identified as trigonal
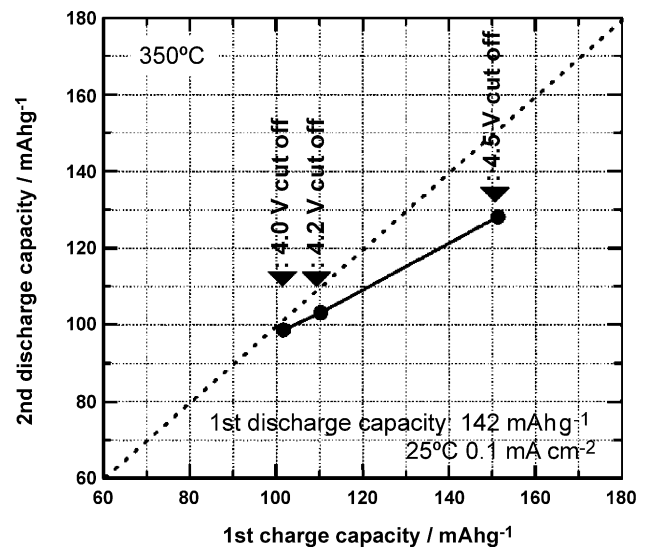

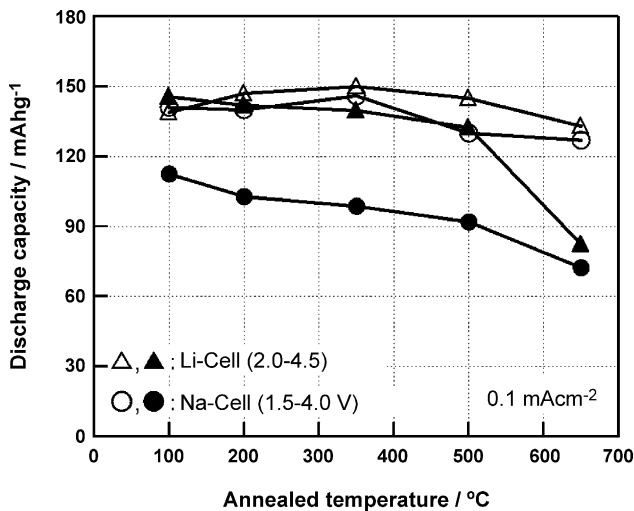Fig. 4. Charge cut-off voltage dependence of irreversibility in Na cell.

Fig. 3. Annealing temperature dependence of FePO$_4$ discharge capacity in Li and Na cells (open mark: first cycle and solid mark: second cycle).
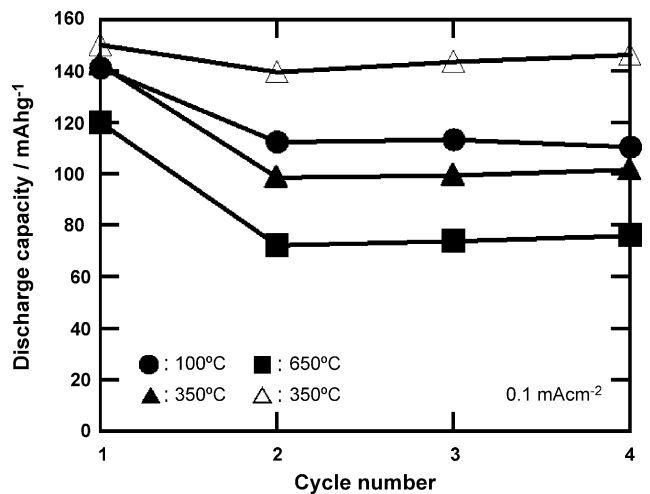

Fig. 5. Cycleability of FePO$_4$ annealed at various temperature in Li and Na cells (open mark: Li cell and solid mark: Na cell).
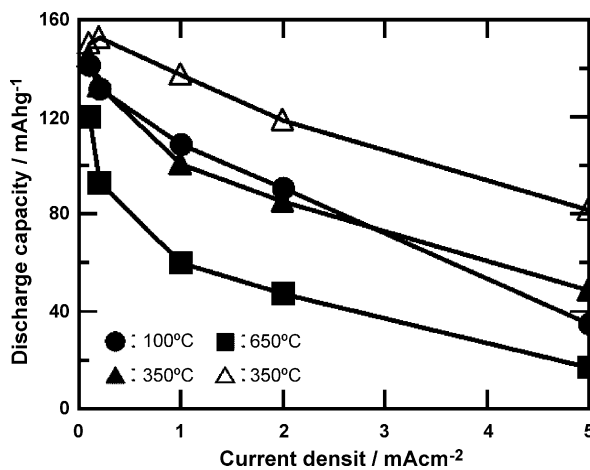
Fig. 6. Rate capability of FePO$_4$ annealed at various temperature in Li and Na cells (open mark: Li cell and solid mark: Na cell).
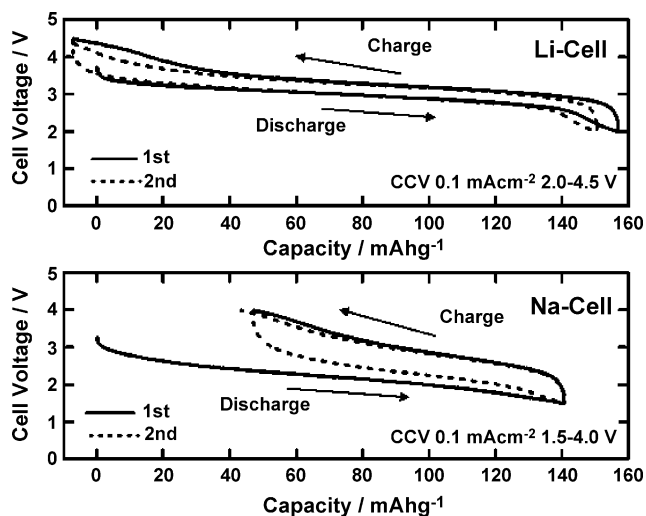

Fig. 7. First and second cycle profiles of amorphous FePO$_4$ obtained from solution without a planetary ball mill (top: Li cell and bottom: Na cell).

FePO$_4$ with a $P321$ space group (ICDD No. 29-0715). There was no clear difference in the XRD results between the two processes. The composition ratio, Fe/P, in amorphous FePO$_4$ was confirmed within 3% deviation by ICP-MS.

On the other hand, the FT-IR spectra showed that PO$_4$ tetrahedral units existed even in amorphous samples. An IR absorption peak around 1600 cm^{-1}, attributed to the H–O–H bending mode of crystal water, was detected in all samples except the crystalline sample [8].

3.1. FePO$_4$ obtained by a planetary ball mill

Fig. 2 shows QOCV profiles of amorphous FePO$_4$ annealed at 350 °C in Li and Na cells. The discharge–charge voltage profiles are lower by 0.5 V in the Na cell compared to the Li cell. This discrepancy is almost equal to the difference of standard oxidation reduction potential between Na/Na$^+$ and Li/Li$^+$. This suggests that the Na intercalation site in FePO$_4$ is same as that in the case of Li. Fig. 3 shows the dependence on the anneal-
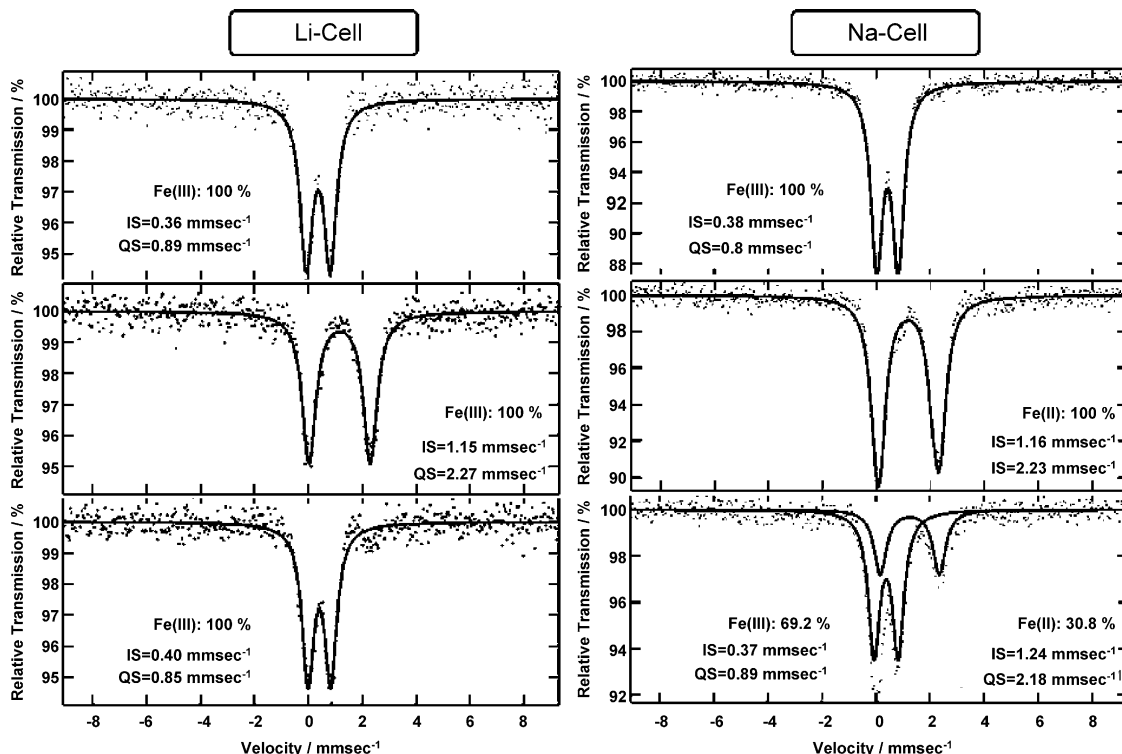

Fig. 8. Discharge–charge behavior of ^{57}Fe Mössbauer spectra of amorphous FePO$_4$ cathode pellets in Li and Na cells (top: initial, middle: after discharge and bottom: after charge).
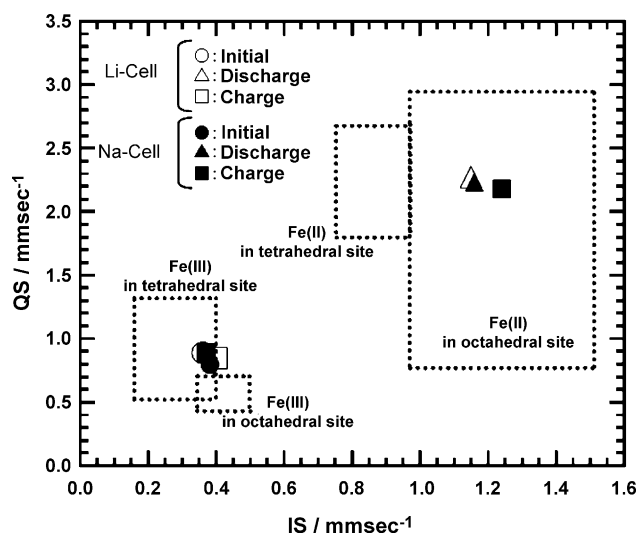
Fig. 9. Reversible behavior of iron valence states in amorphous $FePO_4$ matrix in Li and Na cells.

ing temperature of Li and Na cells. The voltage ranges of the cycle test were 2.0–4.5 V and 1.5–4.0 V for Li and Na cells, respectively. The best capacity (146 mAh g^{-1}) was obtained in amorphous $FePO_4$ annealed at 350 °C at a rate of 0.1 mA cm^{-2}. However, there was no great difference in first-cycle capacity between Li and Na cells. On the other hand, second discharge capacities of the Na cells showed a decrease, because the Na deintercalation is not sufficient under the 4.0 V charging condition. To improve the reversibility of the Na cell, we searched for the best charge cut-off voltage between 4.0 V and 4.5 V for amorphous $FePO_4$ annealed at 350 °C (Fig. 4). As the charge cut-off voltage increased to 4.5 V, not only the first charge capacity but also the second discharge capacity increased. However, the irreversible capacity also increased. The difference between the first charge capacity and second discharge capacity indicates electrolyte decomposition. According to the result of Fig. 4, we fixed the charge cut-off voltage for the cycle test of a Na//1 M NaClO$_4$/PC//FePO$_4$ system at 4.0 V. As shown in Fig. 5, there was no serious capacity fade after the second cycle even for the Na cell. Concerning the rate capability of the Na cell, amorphous $FePO_4$ was superior to crystalline $FePO_4$ (Fig. 6): with amorphous $FePO_4$ we could maintain a capacity of about 100 mAh g^{-1} at a rate of 1.0 mA cm^{-2}. The sparse amorphous matrix seems to be suitable for Na insertion than dense matrix of crystalline $FePO_4$.

3.2. FePO$_4$ obtained without a planetary ball mill

Fig. 7 shows the first and second cycle profiles of amorphous $FePO_4$ annealed at 100 °C. In the Li cell the reversible capacity was 156 mAhg^{-1}, while in the Na cell it was limited to 90 mAhg^{-1} at a rate of 0.1 mAcm^{-2}.

The ^{57}Fe Mössbauer spectra of the amorphous $FePO_4$ annealed at 100 °C indicated that the matrixes of the sample initially had high-spin Fe(III) at their tetrahedral sites. At the fully discharged state of the amorphous sample in the Li cell, the spectra indicated a change to Fe(II) at octahedral sites, then a return to Fe(III) at tetrahedral sites after charging, as shown in Figs. 8 and 9. However, in the Na cell, the Fe(II) state remained at about 30% up to the 4.0 V charged state. This must be the result of insufficient reversibility as shown in Fig. 5. Moreover, in the sample that was fully charged using a quasi-static QOCV mode, the Fe(II) component was reduced to 8%. The QOCV profile shows the fully charged state, but the existence of side reactions such as electrolyte decomposition must be accounted for when charging above 4 V.

4. Conclusions

We could obtain amorphous and crystalline $FePO_4$ from an aqueous solution of Fe and P_2O_5 both with and without ball milling. The XRD profiles and the cathode performances in the two synthesis processes are similar. The best capacity (156 mAh g^{-1}) for Li cell was obtained in amorphous $FePO_4$ annealed at 100 °C without a planetary ball mill at a rate of 0.1 mA cm^{-2}. In addition, it was confirmed that amorphous and crystalline $FePO_4$ could be good cathode using the Fe(III)/Fe(II) redox reaction not only for Li but also for Na cells. As a new inexpensive secondary battery system, we propose Na/amorfous $FePO_4$.

Acknowledgement

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