

New Simple Syntheses of Amorphous and Crystalline Iron Phosphate Cathodes

S. Okada, Y. Okazaki, T. Yamamoto, J. Yamaki and
T. Nishida*

Institute for Materials Chemistry and Engineering,
Kyushu University
6-1, Kasuga Koen, Kasuga 816-8580, Japan

*School of Humanity-oriented Science and Engineering,
Kinki University
Kayanomori, Iizuka 820-8555, Japan

Introduction

Ordered-olivine LiFePO₄ has attracted much attention as rare-metal free cathode [1, 2]. However, previous reports have described the use of such starting materials as FeC₂O₄·2H₂O or Fe(CH₃COO)₂ as Fe sources and (NH₄)₂HPO₄ or NH₄H₂PO₄ as P sources. It is difficult to regard these materials as low-cost and environmentally friendly. In this paper, we propose new methods to synthesize LiFePO₄ and FePO₄ using Fe or iron oxide. The former was obtained by high temperature melting synthesis and the latter by a low temperature soft chemistry method from the water solution. In this paper, the cathode characteristics of the synthesized LiFePO₄ and FePO₄ are investigated using coin cells.

Experimental

We identified all the synthesized materials by means of XRD (Rigaku RINT2100HLR/PC), FT-IR (JASCO 680 plus), and ICP (Agilent 7500C). In addition, we used TG-DSC (Rigaku Thermo Plus TG8110), GC/MS (Shimadzu), and ⁵⁷Fe Mössbauer spectroscopy (Laboratory Equipment Corporation) where needed.

The cathode pellets were fabricated by mixing the obtained samples, acetylene black (Denki Kagaku Co., Ltd.), and PTFE Teflon binder (Polyflon TFE F-103, Daikin Industry Ltd.) at a mass ratio of 70:25:5. We evaluated the electrochemical cathode performance in coin-type Li cells using a nonaqueous electrolyte (Mitsubishi Chemical Co., and Tomiyama Pure Chemicals Co.) and a polypropylene separator (Celgard 3501) against a Li metal anode.

Results and discussion

High temperature melting synthesis for LiFePO₄

In order to use low reactive iron oxide as starting material, FeO was melted with P₂O₅ and LiOH·H₂O at 1500 °C for a few minutes and cooled in an Ar atmosphere. The crystallinity of the obtained samples can be controlled by the cooling speed. Slow cooling in a furnace produced the olivine single phase, while on the other hand quenching in single roll quenching machine produced the amorphous phase. The slow-cooled sample with 140 mAh/g shows a similar profile to solid-state synthesized olivine LiFePO₄, though the quenched amorphous sample shows a monotonically decreasing discharge profile with poor capacity.

Low temperature soft chemistry method for FePO₄

In the use of low cost iron powder as a starting material, metallic iron powder and P₂O₅ were reacted in water at room temperature. The precursor solution was mixed for 24 hr by a planetary ball-mil (200 rpm) and annealed at various temperatures (100 - 650 °C) for 12 hr in air. The obtained ball-milled amorphous powders were

annealed for 12 hours at various temperatures (100 to 650 °C) in air. The crystallinity of the obtained samples can be controlled by the firing temperature. Although the IR spectra shows that PO₄ units exist even in the amorphous samples, an XRD peak was observed in the powder sample heated at 650 °C only (Fig.1). The crystalline phase was identified by XRD as trigonal FePO₄ with a P321 space group (ICDD29-0715). TG-DSC and FT-TR spectra proved that the amorphous sample included some crystal water in the matrix. Nevertheless, the reversibility of the amorphous sample is greater than that of the crystalline one. In both, the highest capacity was 153 mAh/g obtained by annealing at 500 °C.

The ⁵⁷Fe Mössbauer spectra of amorphous and crystalline FePO₄ indicate that both have Fe(II) in the tetrahedral site in the matrix in their initial states (Fig.2). The details of the Fe ion state in the matrix during cycling will be presented.

References

- [1] A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1188 (1997).
[2] A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1609 (1997).

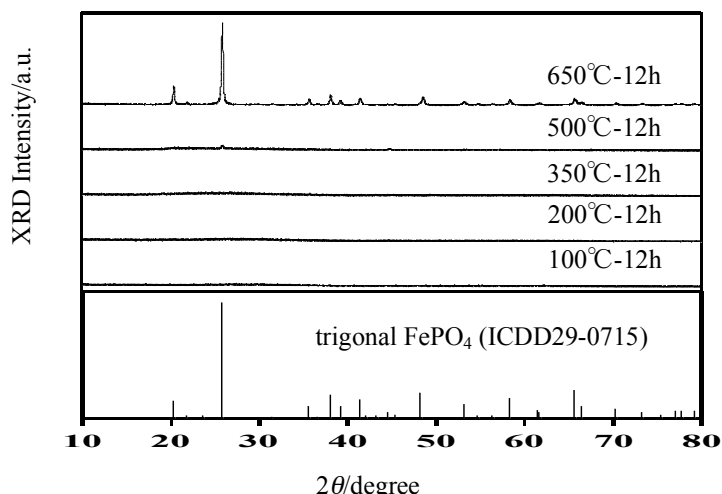


Fig.1 XRD profiles of FePO₄ samples annealed at various temperatures.

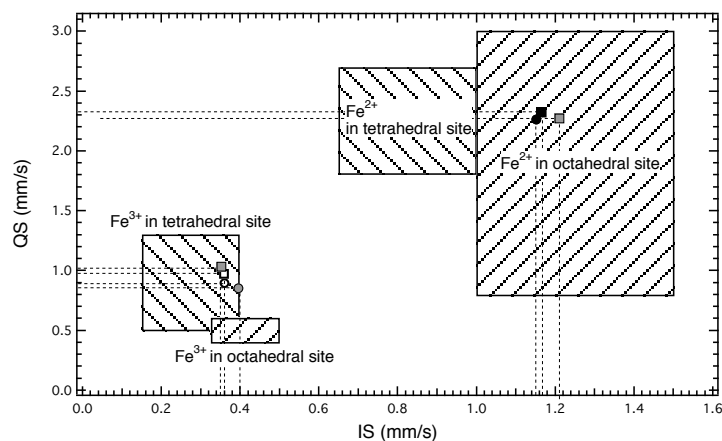


Fig.2 Iron valence states in an amorphous and crystalline FePO₄ matrix obtained from ⁵⁷Fe Mössbauer spectra.

- Open circle: initial amorphous FePO₄
- Solid circle: discharged amorphous FePO₄
- Grey circle: recharged amorphous FePO₄
- Open square: initial crystalline FePO₄
- Solid square: discharged crystalline FePO₄
- Grey square: recharged crystalline FePO₄