

New Lithium Iron Pyrophosphate as 3.5 V Class Cathode Material for Lithium Ion Battery

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Abstract: A new pyrophosphate compound $\text{Li}_2\text{FeP}_2\text{O}_7$ was synthesized by a conventional solid-state reaction, and its crystal structure was determined. Its reversible electrode operation at ca. 3.5 V vs Li was identified with the capacity of a one-electron theoretical value of 110 mAh g^{-1} even for ca. $1 \mu\text{m}$ particles without any special efforts such as nanosizing or carbon coating. $\text{Li}_2\text{FeP}_2\text{O}_7$ and its derivatives should provide a new platform for related lithium battery electrode research and could be potential competitors to commercial olivine LiFePO_4 , which has been recognized as the most promising positive cathode for a lithium-ion battery system for large-scale applications, such as plug-in hybrid electric vehicles.

The coming new energy economy must be based on a cheap and sustainable energy supply. Chemical energy storage using batteries can contribute to a potential solution, combined with sustainable sources such as wind and solar power. The lithium-ion battery is the most advanced chemical energy storage system, but its safety hazard and difficulty in cost reduction have prohibited large-scale applications.

Research in materials science is approaching a solution to these problems by a combination of abundant Fe and covalent $(\text{PO}_4)^{3-}$ units with fixed oxygen. This has led to the use of LiFe(II)PO_4 with olivine-type structure as a cathode material for lithium batteries.¹ Problems related to cost and safety can be solved with minimum expense to energy density by using Fe as a full $\text{Fe}^{3+}/\text{Fe}^{2+}$ one-electron redox center and fixing all oxygen atoms within the olivine framework *via* strong P–O covalent bonds.

In the search for new lithium-containing oxianion cathode materials with Fe(II), recent studies have focused on changing anions and identified lithium iron silicate, $\text{Li}_2\text{Fe(II)SiO}_4$ (160 mAhg^{-1} , 2.8 V vs Li);² fluorinated iron phosphate, $\text{Li}_2\text{Fe(II)PO}_4\text{F}$ (110 mAhg^{-1} , 3.4 V vs Li);³ and fluorinated iron sulfate $\text{LiFe(II)SO}_4\text{F}$ (140 mAhg^{-1} , 3.6 V vs Li)⁴ as alternative candidates. However, $\text{Li}_2\text{FeSiO}_4$ is unable to provide sufficient voltage, and the synthesis of fluorinated compounds requires complex routes, such as ion-exchange processes including ionothermal techniques with expensive ionic liquids.

Our principal concern is that the solution can be in the pyrophosphate-based composition $\text{Li}_2\text{Fe(II)P}_2\text{O}_7$, which has been neither synthesized nor documented in the materials database. The presently known lithium iron pyrophosphate is $\text{LiFe(III)P}_2\text{O}_7$ with space group $P2_1$ ($a = 4.8091(6) \text{ \AA}$, $b = 8.0574(9) \text{ \AA}$, $c = 6.928(1)$

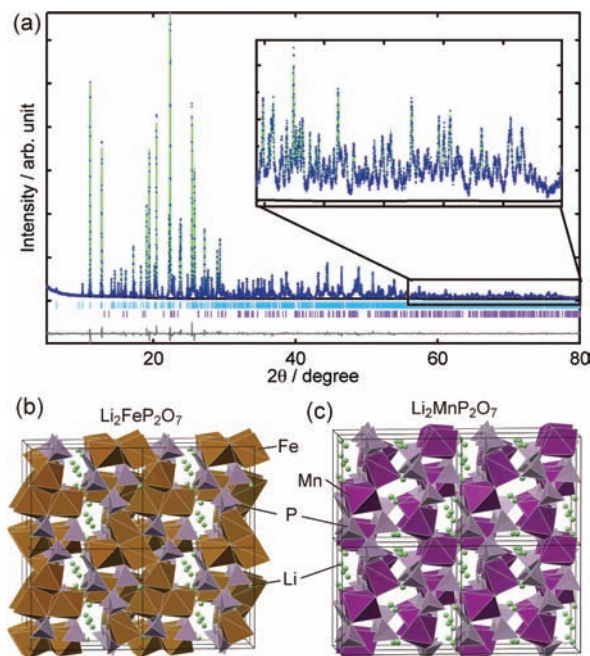


Figure 1. (a) Rietveld refinement pattern of high-resolution powder X-ray diffraction data for the $\text{Li}_2\text{FeP}_2\text{O}_7$; The observed and calculated intensity are represented by blue plus markers and green solid lines respectively. The bottom gray line shows the fitting residual difference. Bragg positions for $\text{Li}_2\text{FeP}_2\text{O}_7$ and impurity $\text{Fe}_2\text{P}_2\text{O}_7$ (~1%) are represented as light blue and purple tick marks respectively. (b) Crystal structure of $\text{Li}_2\text{FeP}_2\text{O}_7$. (c) Crystal structure of $\text{Li}_2\text{MnP}_2\text{O}_7$.

\AA , $\beta = 109.379(5)^\circ$) and had already been tested as a cathode material.⁵ Two major problems of the electrode reaction of LiFeP_2O_7 as a lithium-ion battery cathode are (i) the lack of lithium atoms that can be extracted and transferred to the anode during the initial charge process and (ii) the low voltage of $<3 \text{ V}$.⁵ A manganese analogue with the abovementioned ideal composition, $\text{Li}_2\text{Mn(II)P}_2\text{O}_7$, has recently been synthesized by Adam et al.,⁷ but no electrochemical data were reported. Its crystal structure was identified as having a different structural framework to that of LiFeP_2O_7 . Therefore, we then set $\text{Li}_2\text{FeP}_2\text{O}_7$ isostructural with $\text{Li}_2\text{MnP}_2\text{O}_7$ reported in ref 6 as the first target in the search for a new pyrophosphate based high-voltage cathode material. It would be expected that such an unreported compound would not be stable under conventional synthesis conditions and may, therefore, require a special synthetic technique. However, contrary to this expectation, the target $\text{Li}_2\text{FeP}_2\text{O}_7$ was easily obtained by heating a stoichiometric mixture of Li_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, and optional Ketjen Black at 873 K under Ar flow.

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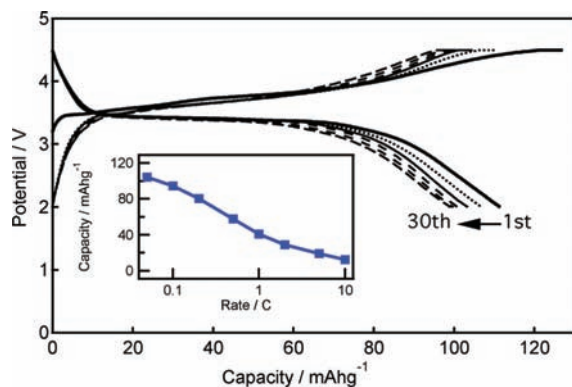


Figure 2. Galvanostatic charge–discharge curves for $\text{Li}_2\text{FeP}_2\text{O}_7$ up to 30 cycles measured at 298 K under a C/20 rate. For charging, after the voltage reached the cutoff voltage, the voltage was maintained at 4.5 V while the current decayed to the value corresponding to a C/200 rate. Inset shows discharge capacity under various current densities under identical charging conditions.

Figure 1 depicts a Rietveld refinement pattern for the high-resolution X-ray diffraction data measured at room temperature for $\text{Li}_2\text{FeP}_2\text{O}_7$. A small trace (ca. 1%) of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity was identified, and Mössbauer spectra were dominated by Fe(II) doublets for the major phase of $\text{Li}_2\text{FeP}_2\text{O}_7$ (see Supporting Information). The Bragg reflections were successfully indexed with space group $P2_1/c$ having a monoclinic unit cell with lattice parameters $a = 11.01847(4)$ Å, $b = 9.75536(3)$ Å, $c = 9.80517(3)$ Å, $\beta = 101.5416(2)^\circ$, $V = 1033$ Å³ (see Supporting Information). The fitting was satisfactory ($R_{\text{wp}} = 4.11\%$, $R_{\text{p}} = 3.21\%$, $R_{\text{Bragg}} = 1.03\%$, $\text{GOF} = 1.15$). The refined crystal structure of $\text{Li}_2\text{FeP}_2\text{O}_7$ is shown in Figure 2b. Details of the analysis and structural parameters are listed in the Supporting Information. Arrangement of the P_2O_7 unit is almost identical to that of $\text{Li}_2\text{MnP}_2\text{O}_7$ reported by Adam et al.⁷ However, the intensity ratio of the Bragg reflections showed a large difference, which was attributed to a disordered cation distribution, maintaining its stoichiometric composition. Fe atoms occupy three crystallographic sites, Fe1, Fe2 and Fe3. The Fe1 site is fully occupied, while Fe2 and Fe3 sites are statistically occupied by the remaining Fe atoms. Fe1 is coordinated as FeO_6 octahedra, and Fe2 and Fe3 are coordinated as distorted FeO_5 pyramids. Li atoms are coordinated as LiO_4 tetrahedra or LiO_5 trigonal bipyramids, forming a quasi-two-dimensional network along the b – c plane in the $P2_1/c$ setting, which provides a possible path for Li diffusion.

The electrochemical properties of a $\text{Li}_2\text{FeP}_2\text{O}_7$ with 13% w/w Ketjen Black were tested with a lithium metal anode in 2032-type coin cells at 298 K, with loadings of 3 mg of active material. Figure 2 shows the voltage–lithium composition trace cycled between 4.5 and 2.5 V measured at a C/20 rate (1 Li in 20 h), which indicates an electrochemical activity centered around 3.5 V vs Li and that is higher than the plateau voltage of Li_xFePO_4 . Thereby, the new pyrophosphate $\text{Li}_2\text{FeP}_2\text{O}_7$ offers the highest voltage among the known Fe-based phosphate cathodes. The initial reversible capacity

of ca. 110 mAh g^{-1} , which corresponds to a one-electron theoretical specific capacity, was reversible with steady capacity retention upon cycling. However, the initial charge curve showed a different shape from that of subsequent cycles, possibly due to the irreversible structural change. About 40% of the initial capacity can be delivered in 1 h (1C rate), and about 20% even in 6 min (10C rate) (Figure 2, inset), suggesting that such electrodes could sustain respectable rate capabilities. Note that such electrode activity was confirmed for a large particle of $\sim 1 \mu\text{m}$ size (see Supporting Information) and a electrode with no special effort for electron percolation such as carbon coating, indicating significant improvement is possible by further optimization.

In conclusion, a new pyrophosphate compound, $\text{Li}_2\text{FeP}_2\text{O}_7$, was successfully synthesized by a conventional solid-state reaction, and respectable cathode activity at 3.5 V vs Li was delivered without any technical effort such as nanosizing or carbon coating. Although the capacity of $\text{Li}_2\text{FeP}_2\text{O}_7$ is limited to a one-electron theoretical value of ca. 110 mAh g^{-1} , due to the relatively heavy weight of the pyrophosphate, the chemical composition $\text{Li}_{2-x}\text{MP}_2\text{O}_7$ is a two-electron reaction possibility between M^{2+} and M^{4+} ($0 < x < 2$), where the theoretical capacity would reach 220 mAh g^{-1} . The emerging rich chemistry in the novel $\text{Li}_{2-x}\text{MP}_2\text{O}_7$ compounds, combined with their ease of synthesis by conventional solid-state reaction, will inspire electrode optimization by application of alternative low-temperature synthetic routes to various $\text{Li}_2\text{MP}_2\text{O}_7$ derivatives, some of which may meet practical applications.

Acknowledgment. We gratefully acknowledge financial support from the cabinet office, government of Japan; the Funding Program for World-Leading Innovative R&D on Science and Technology, and the Ministry of Education, Culture, Sports, Science and Technology of Japan; Grant-in-Aid for Scientific Research (A) No. 19205027. The synchrotron XRD experiments were performed under KEK-PF user program No. 2009G092. The crystal structures were illustrated using the computer program VESTA.⁸

Supporting Information Available: Materials and methods; crystal structure information; Mössbauer spectra for oxidated and pristine samples; TG/DTA data for precursor. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA106297A