Improvement of electrochemical property of pyroxene-type LiFeSi$_2$O$_6$ and crystal-structure analysis

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Lithium iron metasilicate, LiFeSi$_2$O$_6$, was synthesized via a hydrothermal route and was identified as the pyroxene structure with space group C2/c using the synchrotron X-ray diffraction. Galvanostatic charge and discharge tests showed that the large charge and discharge capacities were obtained for the carbon-LiFeSi$_2$O$_6$ composite prepared by planetary ball-milling. The 10 wt% carbon-LiFeSi$_2$O$_6$ composite delivered a specific discharge capacity of 174 mAh·g$^{-1}$ at 25°C in the voltage range from 1.5 to 4.8 V because of the enhancement of the electric conductivity. The valence state of iron was estimated by the X-ray Absorption Near Edge Structure spectra, where the oxidation states changed from charge to discharge state. The Galvanostatic Intermittent Titration measurement was applied for LiFeSi$_2$O$_6$ and carbon-LiFeSi$_2$O$_6$ composite, and then the improved Li$^+$ diffusion was derived from the fully electron supply by the enhanced electric conductivity.

1. Introduction

Recently, the energy transformation and storage have been noticeable from the rapid development of solar power and hybrid electric vehicles. However, it is difficult to utilize the solar power and wind-power generation because of the unstable energy supply.$¹,²$ In addition, the huge power plants followed energy loss derived from the difficulty of the complete tune for power supply. Since the surplus energy must be stored, the large battery was strongly expected. However, the larger battery with extremely high safety and low cost is not found so far. Therefore, the cathode materials have been developed by using low cost elements, such as Mn and Fe, with high thermal stability in charge state.

The polyanion type structures consisted of the XO$_y$, e.g. PO$_4$, SiO$_4$, and BO$_3$, have been examined for the purpose of the safety enhancement. The inductive effect derived from the strong bond in polyanion XO$_y$ not only increased the voltages in the redox of the transition metals but suppressed the oxygen desorption from the host structure during the charge process.$³$ Especially, olivine-type LiFePO$_4$ consists mainly of major elements and exhibits high thermal stability due to the PO$_4$ tetrahedra. Although the practical application of the olivine-type LiFePO$_4$ was already performed, further stability for thermal runaway was needed. Whereas, the high capacity has been expected for Li$_2$MgSiO$_4$ (M = Mn, Fe, Ni, Co) with polyanion type cathode material. It has been noticed that the theoretical capacity of 330 mAh·g$^{-1}$ was not reversible but the high thermal stability resulted in the candidate of new cathode material.$⁴$ The replacement of the transition metals, M, has been examined to achieve the two-electron reaction by removal of all lithium atoms. However, the perturbation of structure accompanied with the delithiation and the irreversible two electron reaction has disturbed the practical application of Li$_2$FeSiO$_4$.$⁵$ Recently, the pyroxe type LiVSi$_2$O$_6$ and LiFeSi$_2$O$_6$ were reported with respect to the safety in the positive electrode material for Li-ion battery, LIB. The LiVSi$_2$O$_6$ showed the specific capacity of 85 mAh·g$^{-1}$ at 30°C and 181 mAh·g$^{-1}$ at 60°C, respectively. The higher capacity must be derived from the lithium-rich composition of Li$_{1.42}$VSi$_2$O$_6$ in the pyroxene structure.$⁶$ The LiFeSi$_2$O$_6$ has much attention for the low cost constituents, such as Fe and Si, with high Clarke number. The use of LiFeSi$_2$O$_6$ for cathode material in LIB was first reported and showed 78 mAh·g$^{-1}$ at room temperature.$⁷$ They revealed the crystal structure for the pristine LiFeSi$_2$O$_6$ by synchrotron XRD and neutron diffraction. The new material, pyroxene-type LiFeSi$_2$O$_6$, has not been investigated in the structural change during charge and discharge process. In addition, the discharge voltage was too low about 2.0 V and the discharge capacity was unsatisfactory for theoretical capacity of 125 mAh·g$^{-1}$. Therefore, the LiFeSi$_2$O$_6$ needed further investigation about the improvement of the electrochemical properties and the structure analysis during charge and discharge states.

This study focused on the pyroxene-type LiFeSi$_2$O$_6$ to develop the cathode materials with extreme high thermal stability. The composite with carbon and the pulverization of LiFeSi$_2$O$_6$ grains improved the electrochemical performance. The crystal structure change during charge and discharge were examined by the synchrotron XRD for the electrodes after electrochemical tests. This study revealed that the pyroxene-type structure was retained through the charge–discharge and accommodated the reversible lithium intercalation.

2. Experimental

2.1 Synthesis

The LiFeSi$_2$O$_6$ was prepared via hydrothermal process and followed by heat treatment. The LiOH·H$_2$O (98.0~102.0%, Wako Pure Chemical Industries, Ltd.) and Fe(COOH)$_2$·2H$_2$O (99%, Alfa Aesar) were dissolved into purified water, and then SiO$_2$ (99.0%, Wako Pure Chemical Industries, Ltd.) was added subsequently. The molar ratio of the Li:Fe:Si in the precursor

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² Preface for this article: DOI http://doi.org/10.2109/jcersj2.125.P4-1
solution was 1:1:2, then put into a Teflon-lined hydrothermal reactor, and the reactor was heated at 200°C in an oven for 72 h. After the hydrothermal reaction, the reactor was cooled down to room temperature. The precipitated powder was dried at 100°C for 24 h. Heat treatments for hydrothermally synthesized materials were carried out in a furnace at 950°C. For the improvement of the electrochemical properties, the as-prepared LiFeSi2O6 was mixed with carbon by planetary ball-milling (Pulverisette 6, Fritsch) with 1, 5, 10, 15, 20 wt% of acetylene black for 2 h in 300 rpm to obtain the C-LiFeSi2O6 composite.

2.2 Characterization and crystal structure

The crystalline phases were identified with X-ray diffraction (XRD, X’pert pro, PANalytical) with Cu Kα radiation. The measurements were scanning at 1°/min and operating at 45 kV and 40 mA with 2θ range from 10 to 70°. The morphology of particle was observed with a scanning electron microscope (SEM, S-2600N, Hitachi). Each specimen was holed on a conductive carbon tape and then sputtered by Au at 5 mA for 45 s.

The high resolution XRD data were collected by Synchrotron XRD at SPring-8 (BL14B2 beam lines). The diffracted patterns were analysed by Rietveld method using the Rietan-FP program (Ver 2.2). The data for composite electrodes were corrected for the background using data measured by the empty capillary. In the synchrotron sources, the X-ray absorption fine structures (XAFS) were also measured at BL14B2 beam line, and the data was analysed by the Athena program (Ver 0.8.056).

2.3 Electrochemical measurements

Electrochemical measurements were performed by HS cell (Hohsen Ltd.). The cathode was consisted of the prepared LiFeSi2O6 and conductive carbon back and PolyTetraFluoroEthylene (PTFE) with 5:5:1 weight ratios which were casted on an Al mesh at 20 MPa for 1 min. The composite powders and 5 wt% conductive carbon black were mixed in the cathode by using ball-mill. The composite with carbon was introduced to the glove box. The discharge and then charge were measured in an argon filled glove box. The measuring cells were disassembled in a glove box, and then the cathode was washed with DMC and was dried in vacuum at room temperature. Each measurement of open circuit voltages were the same voltage range and rested for 24 h.

3. Results and discussion

3.1 Characterization

Figure 1 showed the X-ray powder diffraction pattern for the synthesized LiFeSi2O6. The main peaks were attributed to the previously reported LiFeSi2O6 structure with C2/c space group. The lattice parameters of LiFeSi2O6 were determined as $a = 0.97010(14)$ nm, $b = 0.86749(8)$ nm, $c = 0.5320(1)$ nm and $\beta = 110.28(1)$° by using least square method. The minor peaks were identified as Fe2O3, Li2SiO3 and the cristobalite-type SiO2 phases.

To improve the low electric conductivity in the LiFeSi2O6, the conductive carbon black was fully mixed by using ball-mill. Figures 2(a) and 2(b) showed the morphologies for pristine powders and 5 wt% C-LiFeSi2O6 composite observed by SEM. The particle sizes were reduced from 1 μm to 300 nm after the composite with carbon by using ball-mill. The pulverization must introduce the short distance of lithium diffusion and then lower overvoltage.

3.2 Electrochemical property

Figure 3 showed the charge-discharge curves measured at 25°C and 60°C for synthesized LiFeSi2O6. There has been no significant change of the electrochemical property in the measured temperature. Figure 3(b) showed the charge-discharge curves for the composite C-LiFeSi2O6 with 1, 5, 10, 15, 20 wt% carbons at 25°C. In the case of the composite with 1 and 20 wt% carbons, the first charge was not achieved at upper voltage of 4.8 V, where the appropriate composite with carbon could not be performed. The overvoltage decreased with increasing the amounts of composite carbon, especially 10 and 15 wt%. The significant capacity below 2.0 V was not considered as essential but as the side reaction or the redox of the second phase, Fe2O3. In addition, the insertion amount of Li in the pyroxene structure...
behavior was obtained with 10 wt% C-LiFeSi$_2$O$_6$ whereas the charge voltage at fifth cycle could not rise up to upper voltage and 15 wt% C-LiFeSi$_2$O$_6$ broke down the voltage during charge. Thus, the best carbon amount in the composite was determined as 10 wt% in terms of the low overvoltage and high cycle performance.

### 3.3 Structural analysis
The synchrotron XRD for LiFeSi$_2$O$_6$ was performed to examine the structural change after charge and discharge. The quantitative phase analysis was also performed from the data using Rietveld method. The pyroxene-type structure with C$_2h$ space group was adopted to the initial structure models for Rietveld analysis. Each crystallographic site was occupied by two 4e sites for Li and Fe and two 8f sites for Si and O. Their site occupancies were fixed to agree with the chemical composition. All the present Rietveld fitting patterns were presented in Fig. 4. The crystal structure parameters and crystallographic data were summarized in Tables 1–3.

Since the impurity phases were detected in the synthesized powders, the second and third phases were assigned for Fe$_2$O$_3$ and Li$_2$Si$_2$O$_5$, respectively. Considering the multi-phase analysis, the relatively good fitting was obtained as the 4.3% in the $R_{wp}$. In the case of the electrodes after charge or discharge in Figs. 4(b) and 4(c), the Rietveld analyses were not achieved at good fitting results because of the large background derived from conductive carbon and binder. Each analyses for the electrodes converged below 10% in the $R_{wp}$ using pyroxene-type structure.

The valence states were examined by XAFS measurements. The Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectra were shown in Fig. 5 and confirmed around Fe$^{3+}$ for each specimens. The electrode of LiFeSi$_2$O$_6$ without composite with carbon did not show the peak shifts in the Fe K-edge XANES spectra. The tiny valence change was observed between after charge and discharge, which indicated the little change in the valence state of Fe in LiFeSi$_2$O$_6$. The diffraction patterns for the electrode of the C-LiFeSi$_2$O$_6$ composite after third charge were also affected for the large background by the carbon and/or binder [Figs. 4(d) and 4(e)]. The results of the Rietveld analysis for the LiFeSi$_2$O$_6$ indicated that the lattice constants increased from charge to discharge states due to becoming the larger ionic radii of Fe derived from the reduction accompanied by Li insertion. The redox of Fe was considered to contribute to the charge and discharge mechanism of LiFeSi$_2$O$_6$. The diffraction patterns certainly included the metallic iron and SiO$_2$ except for the main pyroxene phase, conductive carbon and binder. The metallic iron phase implied the reduction down to zero-valence of Fe by the discharge at relatively low voltage at 1.5 V. The previous report showed the plateau at 2.0 V, which might indicate the reduction of the zero-valence for Fe.

### 3.4 Chemical diffusion coefficient of Li$^+$

The composite with carbon for LiFeSi$_2$O$_6$ resulted in the appearance of 3.3 V plateau and capacity enhancement. The galvanostatic intermittent titration technique, GITT, measurements were performed to examine how the bottleneck in the electrical conductivity was eliminated by composite with carbon. The open circuit voltages were measured, and then the Li$^+$ diffusion coefficient was calculated by GITT technique. Tables 4(a) and 4(b) showed the results of the OCVs of LiFeSi$_2$O$_6$ and C-LiFeSi$_2$O$_6$ with 10 wt% carbon, respectively. The charge/discharge curves on the GITT were shown in Fig. 6(a) and the relaxation process was shown in Fig. 6(b).

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**Fig. 3.** (a) Charge and discharge profiles of LiFeSi$_2$O$_6$/Li cell measured at 25 and 60°C. (b) First charge and discharge profiles of C-LiFeSi$_2$O$_6$ composite with conductive carbon black with 5, 10 and 15 wt% versus Li cell measured at 25°C. (c) Charge and discharge profiles of C-LiFeSi$_2$O$_6$ composite conductive carbon black with 10 wt% versus Li cell for 2–5 cycles measured at 25°C. (Current density: 12.5 mA g$^{-1}$, Cut-off voltage: 1.5–4.8 V).
where \( R \) can be calculated using the following reaction (1) the chemical displacements and full occupancy for all sites are deviations of the last significant digits, and parameters without deviations and full occupancy for all sites are fixed. \( R \)-factors: \( R_{wp} = 4.36\% \), \( R_p = 3.14\% \), \( R_f = 1.58\% \). Lattice parameters: \( a = 0.966794(7) \) nm, \( b = 0.867141(5) \) nm, \( c = 0.529192(4) \) nm, \( \beta = 110.0941(6)^\circ \).

From GITT measurements, such as the previous study, in the following reaction (1) the chemical diffusion coefficient, \( D_{Li^{+}} \), can be calculated using the definition for Eq. (2) by Weppner and Huggins:

\[
\text{LiMO}_2 \rightleftharpoons \text{Li}_{1-x} \text{MO}_2 + x \text{Li}^+ + xe^- \tag{1}
\]

\[
D_{Li^+} = 4 \pi \left( \frac{V_m I_0}{FS_{Li^+} \int_a dE/\sqrt{F}} \right)^2 \tag{2}
\]

where \( D_{Li^+} \) is the chemical diffusion coefficient (cm²·s⁻¹), \( V_m \) the molar volume of active materials (cm³·mol⁻¹), \( I_0 \) the constant current (A), \( S \) the surface area of cathode (cm²), \( z_{Li} \) the valence state in electrode reaction, \( F \) the Faraday constant, \( dE/d\sqrt{F} \) the slope of the OCV curve, and \( dE_s/d\sqrt{F} \) the slope of the line in voltage versus square times. In the present study, the molar volume of LiFeSi₂O₆ was 62.71 cm³·mol⁻¹, the surface area of the cathode was 0.56 cm², the constant current of 2.0 × 10⁻⁵ A was operated and the valence of the electrode reaction was 1. The C-LiFeSi₂O₆ was flowed at constant current of 5.25 × 10⁻³ A and the other conditions were the same as those for the LiFeSi₂O₆.

The calculated Li⁺ diffusion coefficients were summarized in Tables 5(a) and 5(b) for LiFeSi₂O₆ and C-LiFeSi₂O₆ respectively. The plots of Li⁺ diffusion coefficients during discharging were shown in Fig. 7. The increase of diffusion coefficients was obtained for the C-LiFeSi₂O₆. For example, at \( x = 0.1 \) in the Li₁₋ₓFeSi₂O₆ diffusion coefficients were 9.55 × 10⁻¹² cm²·s⁻¹ for LiFeSi₂O₆ and enhanced for the 2.19 × 10⁻¹¹ cm²·s⁻¹ of C-LiFeSi₂O₆. The pyroxene-type LiFeSi₂O₆ was higher diffusion coefficient than olivine-type LiFePO₄ such reported as 6.77 × 10⁻¹⁶ cm²·s⁻¹.

4. Conclusion

The optimal condition of composite carbon was examined for LiFeSi₂O₆ for the purpose of the improvement of the electrochemical property. To analyze the crystal structure, the prepared LiFeSi₂O₆ and the electrodes after charge and discharge were performed by the synchrotron XRD and XAFS. The new plateau at 3.3 V was first reported by using ball-mill and then introduced.

**Table 1.** Refined structure parameters of Rietveld analysis for LiFeSi₂O₆ in space group C 2/c at room temperature. \( R \) is an isotropic atomic displacement parameter. Numbers in parentheses are estimated standard deviations of the last significant digits, and parameters without deviations and full occupancy for all sites are fixed.

† The curve at the bottom is a difference between the observed and calculated intensities in the same scale. (a) Before charge LiFeSi₂O₆, (b) After 1st charge LiFeSi₂O₆, (c) After 1st discharge LiFeSi₂O₆, (d) After 3rd charge C-LiFeSi₂O₆, (e) After 3rd discharge C-LiFeSi₂O₆.

Fig. 4. Rietveld refinement patterns of LiFeSi₂O₆ in space group C 2/c by synchrotron X-ray diffraction. Plus marks show observed synchrotron X-ray diffraction intensities and a solid line represents calculated intensities. The vertical marks indicate positions of allowed Bragg reflections. The curve at the bottom is a difference between the observed and calculated intensities in the same scale. (a) Before charge LiFeSi₂O₆, (b) After 1st charge LiFeSi₂O₆, (c) After 1st discharge LiFeSi₂O₆, (d) After 3rd charge C-LiFeSi₂O₆, (e) After 3rd discharge C-LiFeSi₂O₆.
Table 2. Crystallographic data for the electrodes after first charge and discharge for LiFeSi₂O₆ and after third charge and discharge for C-LiFeSi₂O₆

|                | LiFeSi₂O₆                                                                 | C-LiFeSi₂O₆                                                                 |
|----------------|---------------------------------------------------------------------------|---------------------------------------------------------------------------|
|                | pristine | 1st charge | 1st discharge | 3rd charge | 3rd discharge |
| a/Å            | 0.966794(7) | 0.96736(4) | 0.96750(4) | 0.9689(4) | 0.9671(3)     |
| b/Å            | 0.867141(5) | 0.86723(3) | 0.86721(3) | 0.8689(3) | 0.8673(3)     |
| c/Å            | 0.529192(4) | 0.52966(2) | 0.52967(2) | 0.5304(2) | 0.5297(2)     |
| β/degree       | 110.0941(6) | 110.113(3) | 110.133(3) | 110.24(3) | 110.24(3)     |
| Rwp/%          | 4.36     | 9.94     | 11.2      | 9.44      | 7.79          |
| Rf/%           | 1.58     | 1.82     | 1.68      | 1.96      | 1.95          |

Fig. 5. XANES spectra of Fe K-edge for LiFeSi₂O₆: (a) Fe₂O₃, (b) FeC₂O₄·2H₂O, (c) Before charge LiFeSi₂O₆, (d) After 1st charge LiFeSi₂O₆, (e) After 1st discharge LiFeSi₂O₆.

Fig. 6. Galvanostatic intermittent titration (a) curve vs. capacity and (b) curve vs. time for LiFeSi₂O₆.

Table 3. Molar ratio of multi-phase components estimated by the Rietveld refinement

|                | LiFeSi₂O₆ | C-LiFeSi₂O₆ |
|----------------|------------|-------------|
|                | pristine   | 1st charge  | 1st discharge | 3rd charge | 3rd discharge |
| LiFeSi₂O₆      | 93.5       | 92.2        | 90.4          | 55.3       | 61.7          |
| Li₂Si₂O₅       | 4.1        | 6.0         | 7.6           | 0          | 0             |
| Fe₂O₃          | 2.4        | 1.8         | 2.0           | 0          | 0             |
| SiO₂           | 0          | 0           | 0             | 22.1       | 0.7           |
| Fe              | 0          | 0           | 0             | 22.6       | 37.6          |

Table 4. Open circuit potentials of (a) Li₁₋ₓFeSi₂O₆ and (b) C-Li₁₋ₓFeSi₂O₆

|                | Li₁₋ₓFeSi₂O₆ | C-Li₁₋ₓFeSi₂O₆ |
|----------------|-------------|---------------|
|                | pristine    | 1st charge    | 1st discharge | 3rd charge | 3rd discharge |
| (a) x in Li₁₋ₓFeSi₂O₆ | Open circuit potentials/V vs. Li/Li⁺ |
| 0              | 2.774       | 2.616         |              |            |               |
| 0.05           | 3.367       | 2.624         |              |            |               |
| 0.10           | 3.597       | 2.797         |              |            |               |
| (b) x in C-Li₁₋ₓFeSi₂O₆ | Open circuit potentials/V vs. Li/Li⁺ |
| 0              | 2.415       | 2.280         |              |            |               |
| 0.1            | 2.840       | 2.313         |              |            |               |
| 0.2            | 3.148       | 2.461         |              |            |               |
| 0.3            | 3.344       | 2.680         |              |            |               |
| 0.4            | 3.556       | 2.943         |              |            |               |
| 0.5            | 3.737       | 3.167         |              |            |               |
| 0.6            | 3.869       | 3.387         |              |            |               |

Table 5. Chemical diffusion coefficients of Li⁺ of (a) Li₁₋ₓFeSi₂O₆ and (b) C-Li₁₋ₓFeSi₂O₆

|                | Li₁₋ₓFeSi₂O₆ | C-Li₁₋ₓFeSi₂O₆ |
|----------------|-------------|---------------|
|                | pristine    | 1st charge    | 1st discharge | 3rd charge | 3rd discharge |
| (a) x in Li₁₋ₓFeSi₂O₆ | DLi⁺/cm²s⁻¹ |
| 0              | 8.98 × 10⁻¹² | 8.28 × 10⁻¹³  |              |            |               |
| 0.05           | 8.87 × 10⁻¹² | 7.65 × 10⁻¹³  |              |            |               |
| 0.10           | 9.55 × 10⁻¹² | 2.11 × 10⁻¹³  |              |            |               |
| (b) x in C-Li₁₋ₓFeSi₂O₆ | DLi⁺/cm²s⁻¹ |
| 0              | 1.01 × 10⁻¹⁰ | 1.34 × 10⁻¹¹  |              |            |               |
| 0.1            | 2.19 × 10⁻¹¹ | 1.16 × 10⁻¹¹  |              |            |               |
| 0.2            | 2.89 × 10⁻¹¹ | 9.82 × 10⁻¹²  |              |            |               |
| 0.3            | 1.53 × 10⁻¹¹ | 9.79 × 10⁻¹²  |              |            |               |
| 0.4            | 1.01 × 10⁻¹¹ | 1.21 × 10⁻¹¹  |              |            |               |
| 0.5            | 9.49 × 10⁻¹² | 2.02 × 10⁻¹¹  |              |            |               |
| 0.6            | 9.91 × 10⁻¹² | 2.57 × 10⁻¹²  |              |            |               |
the high capacity. The appropriate carbon amounts in composite were determined as 10 wt\%. The XANES spectra showed that the redox of Fe might contribute to the charge and discharge reaction. The effect of carbon-LiFeSi₂O₆ composite on the electrochemical property clarified in the GITT technique for prepared LiFeSi₂O₆ and the composite with carbon. The chemical diffusivity of Li⁺ was promoted by one order of magnitude in the diffusion coefficient $D_{Li^+}$. Therefore, the present study concluded that the composite of conductive carbon and the pyroxene-type LiFeSi₂O₆ would be able to use as a cathode of LIB.

Acknowledgements  The authors appreciate Dr. C. Kim and Dr. K. Sugimoto (Japan Synchrotron Radiation Research Institute, SPring-8) for their help on synchrotron X-ray diffraction measurements at BL02B2 (proposal Nos. 2013B1120, 2014A1278, 2014B1457 and 2015A1541). The authors also acknowledge Dr. T. Homma (Japan Synchrotron Radiation Research Institute, SPring-8) for his help on synchrotron X-ray absorption fine structure measurements at BL4B2 (proposal No. 2015B1576).

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