Synthesis of \( \text{Li}_2\text{FeSiO}_4 \) nanoparticles/carbon composite for cathode materials by spray pyrolysis method

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\[ \text{Li}_2\text{FeSiO}_4 \] nanoparticles/carbon composite powders were synthesized using spray pyrolysis (SP), followed by heat treatment and grinding. Glucose, added to the precursor solution for SP, was used as the carbon source. Both \( \text{Li}_2\text{FeSiO}_4 \) nanoparticles and carbon were formed simultaneously during SP. The primary particle size of the \( \text{Li}_2\text{FeSiO}_4 \) powder obtained from this process was smaller than 20 nm. Graphitic carbon formation was inferred based on results obtained from FT-IR and Raman spectra.

1. Introduction

Rechargeable Li ion batteries are crucially important components for advanced energy storage in portable electronics and electric vehicles. Such applications commonly require excellent thermal and cycle stability, in addition to high electric capacity. Currently, Li-based oxide materials such as \( \text{LiCoO}_2 \), \( \text{LiNiO}_2 \), and \( \text{LiMnO}_2 \) are candidate materials for cathodes. However, these materials present safety risks because they release activated oxygen in cases of a deeply charged condition. That oxygen can lead to explosion.

Polyanion-type Li-based oxides such as \( \text{LiMPO}_4 \) and \( \text{Li}_{2/3}\text{MnSiO}_4 \) (M=Fe, Mn) are attracting great attention because of their high discharge capacity and stability by their strong covalent P-O or Si-O bonds. Especially, \( \text{Li}_{2/3}\text{MnSiO}_4 \) possesses high theoretical capacity (330 mAh·g\(^{-1}\)) by two electron reactions among \( \text{M}^{2+}/\text{M}^{3+}/\text{M}^{4+} \) various investigations have been conducted to date. However, practical reported values for this material are commonly 1 Li/unit or less, probably because of its low electric conductivity (10\(^{-12}\)-10\(^{-16}\) S·cm\(^{-1}\) order).\(^{3-5}\) Recently, some reports have described that discharge capacity higher than 1 Li/unit is feasible by decreasing the electron transfer distance through particle size reduction and mixture with conductive carbon.\(^{6-12}\)

Spray pyrolysis (hereinafter denoted as SP) is an efficient means of processing materials to prepare hybrid ceramic particles. Taniguchi et al. prepared a precursor powder of \( \text{Li}_2\text{MnSiO}_4 \) using this process. They prepared crystalline \( \text{Li}_2\text{MnSiO}_4 \) nanoparticles by subsequent annealing and ball-milling. Then they mixed the powder with a sucrose solution and annealed it again to prepare \( \text{Li}_2\text{MnSiO}_4 \)/carbon composite particles. Using this powder, they attained high initial discharge capacity [184 mAh·g\(^{-1}\)(1.14Li)].\(^{7}\) However, the discharge capacity decreased by more than 40% during only 20 cycles. Further improvement is necessary.

For this study, we used glucose as the carbon source. We added it to the precursor solution for SP to induce \( \text{Li}_2\text{FeSiO}_4 \) formation and carbon formation simultaneously in a single step. The obtained powder was milled and annealed. Then the relation among charge-discharge performance, carbon concentration, and crystallite size was investigated for this composite material.

2. Experimental

The precursor solution for SP was obtained by dissolving commercially available \( \text{LiNO}_3 \) (Kanto Chemical Co. Inc., Japan) and \( \text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O} \) (Kanto Chemical Co. Inc.), and by adding tetraethyl orthosilicate (TEOS; Shin-Etsu Chemical Co. Ltd., Japan) to distilled water in the stoichiometric atomic ratio for \( \text{Li}_2\text{FeSiO}_4 \). Concentration in the precursor solution was for 0.3 molar \( \text{Li}_2\text{FeSiO}_4 / \text{dm}^3 \). Then glucose (Gunze Chemical Industry Co., Ltd., Japan) was added to the precursor solution (58–100 g/dm\(^3\) ) to combine carbon with \( \text{Li}_2\text{FeSiO}_4 \). The precursor solution was atomized using an ultrasonic atomizer. The atomized mists for \( \text{Li}_2\text{FeSiO}_4 \) were introduced with the \( \text{N}_2 \) carrier gas into a furnace heated at 800°C. The obtained powder was annealed at 500°C for 10 h in a 1%H\(_2\)/Ar atmosphere. The annealed powder was ground using high-energy ball milling for 270 min. This process is designated as “the single process” hereinafter. For comparison, we also prepared the composite powder using a different process. First, \( \text{Li}_2\text{FeSiO}_4 \) powder was synthesized using SP without glucose addition. The powder was mixed with glucose in aqueous solution. The mixing molar ratio between \( \text{Li}_2\text{FeSiO}_4 \) and glucose was 2:1. The mixed sample was heated at 100°C for 1 h and in 500°C for 2 h in a 1%H\(_2\)/Ar atmosphere. We describe this process as “the separate process” in this report.

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The carbon contents in these powders were measured using a carbon/sulfur combustion analyzer (EMIA-320V; Horiba Ltd.). Crystalline phase in these powders was confirmed by X-ray powder diffraction (XRD, RINT Ultima II with D/teX Ultra; Rigaku Corp., Japan) with Cu-Kα radiation. The particle morphology was observed using transmission electron microscopy (TEM, H-9500; Hitachi Ltd., Japan). The organic functional groups in these powders were examined using infrared spectroscopy (FT-IR, FT/IR 6100; Jasco Corp., Japan) and Raman spectroscopy (NRS-5100; Jasco Corp., Japan).

The performance as a cathode material was evaluated using CR2032-typed coin cells at 25°C. A composite cathode was prepared by mixing 20 mg of active material (prepared carbon-hybridized Li₂FeSiO₄ powders) and 15 mg of conductive binder (treated acetylene black, TAB). The mixture was then pressed into a SUS-mesh, which plays the role of a current collector. The prepared electrodes were dried at 180°C for 12 h in a vacuum oven. The coin cell was made up of a cathode and Li metal sheet as anode. They were separated by a glass-wool sheet. The cells were prepared for charging and discharging up to 5.0 V on an electrochemical test instrument (BT2010 W; Nagano Keiki Co., Ltd., Tokyo, Japan). The coin cells were then assembled in an Ar atmosphere. The coin cells were charged under the delithiation of Li₂FeSiO₄ particles estimated from the full width at half maximum (FWHM) of the XRD and Debye-Scherrer formula were, respectively, 20 and 48 nm. The carbon contents of samples were, respectively, 8.2 and 8.8 mass%. The crystallite size corresponded to that found by TEM observation (Fig. 2).

Figure 3 presents the second charge and discharge curves of samples prepared using the single process and the separate process. Both samples were charged under the delithiation of 250 mAh·g⁻¹. Their second discharge capacities were, respectively, 219 mAh·g⁻¹ (single process) and 129 mAh·g⁻¹ (separate process). The powder produced using the single process provided better discharge capacity than that by the separate process. Figure 4(a) displays FT-IR spectra of the powder samples from these processes. Figure 4(b) shows Raman spectra of the powder samples from these processes and Li₂CO₃. The sample produced using the single process exhibits clear peaks at 1445 and 1505 cm⁻¹ in the IR spectra. The peaks around these wavenumbers are common in carbonate chemicals. They are generally attributed to the stretch vibration (ν₁-type) of carbonate ion. However, the symmetrical stretch vibration (ν₃-type) of carbonate ion, which provides a sharp peak at 1085 cm⁻¹ in the Raman spectra.

3. Results and discussion

Figure 1 displays the XRD patterns of Li₂FeSiO₄ samples: (a) the single process after SP, (b) the final powder from the single process, and (c) the final powder from the separate process. Immediately after SP, crystallinity of Li₂FeSiO₄ is very low, but it is increased by post-annealing at 500°C in Ar/H₂ atmosphere. It is noteworthy that the powder electrode of the single process exhibited a lower discharge performance, which indicates that Li₂FeSiO₄ was partially formed at this stage. The XRD pattern of the sample produced using the separate process (c) was assigned to monoclinic P2₁/n(γ) structure. Although some peaks are missing, probably because of the poor crystallinity, the XRD pattern of the sample by the single process (b) was assigned to orthorhombic Pmn2₁(β) structure. These structures are quasi-layered structures where Li⁺ ions occupy tetrahedral sites between layers comprising sheets of alternating corner-shared FeO₄ and SiO₄ tetrahedra. The crystallite size of Li₂FeSiO₄ particles estimated from the full width at half maximum (FWHM) of the XRD pattern and Debye-Scherrer formula were, respectively, 20 and 48 nm. The carbon contents of samples were, respectively, 8.2 and 8.8 mass%. The crystallite size corresponded to that found by TEM observation (Fig. 2).

Fig. 1. XRD patterns of Li₂FeSiO₄ samples: (a) single process after SP, (b) final powder from the single process, and (c) final powder from the separate process.

Fig. 2. TEM images of Li₂FeSiO₄ particles (circled) prepared using the single process.

Fig. 3. Discharge curves of Li₂FeSiO₄ prepared using (a) the single process and (b) the separate process. Straight lines are discharge curves. Dashed lines are charge curves.
of Li₂CO₃, was absent in the Li₂FeSiO₄ by these processes, suggesting the absence of remaining unreacted carbonates in the powder. The peaks around 1450 and 1500 cm⁻¹ in the IR spectra are commonly observed as the stretch vibration of the C–C bonds for aromatic carbons.¹⁶) The small peak around 1630 cm⁻¹ are attributed to vibrations from Si–O and COO or C–O groups (1260, and 1650 cm⁻¹) originated in carbonate ions.¹⁹),²⁰) Further investigation revealed that the Li₂FeSiO₄ produced using the single process is more hydrophilic than that produced using the separate process, which forms a graphitic carbon structure with high electric conductivity. Although the reason remains unclear, these results indicate that effective carbon formation on the powder surface produced using the single process engenders better discharge capacity with suppression of grain growth. Moreover, it provides excellent electric conductivity. It is noteworthy that the sample with a carbon concentration of 14.3 mass% exhibited the same discharge amount against initial charging conditions (250 mAh·g⁻¹), which indicates 100% Coulombic efficiency. A review of the literature revealed to us that this performance is the best ever reported for silicate materials with low electric conductivity. Further investigation revealed that this discharge capacity did not deteriorate even after 20 cycles (Figs. 7 and 8). It must be attributable to the relaxation of expansion and shrinkage in the process of charging and discharging because of its small particle size.

### 4. Conclusion

For this study, we used SP to prepare Li₂FeSiO₄ nanoparticles/carbon composite powders. Both Li₂FeSiO₄ nanoparticles and carbon were formed simultaneously by using glucose-added solution for SP. The carbon that formed actually suppressed grain growth effectively and provided electric conductivity to the powder. The Li₂FeSiO₄ nanoparticles/carbon composite powders exhibited excellent discharge capacity of 250 mAh·g⁻¹ and excellent cycle performance.

### Table 1

| Concentration of glucose solution (g/L) | 58 | 75 | 100 |
| Carbon content of Li₂FeSiO₄ (mass%) | 1.6 | 8.2 | 14.3 |
| Crystallite size (nm) | 22.5 | 19.6 | 11.8 |

### Figures

**Fig. 4.** (A) FT-IR spectra of Li₂FeSiO₄ prepared using (a) the single process and (b) the separate process. (B) Raman spectra of Li₂FeSiO₄ prepared using (a) the single process and (b) the separate process. (c) Li₂CO₃.

**Fig. 5.** XRD patterns of Li₂FeSiO₄ powders presented in Table 1: (a) 58 g/L, (b) 75 g/L, and (c) 100 g/L.

**Fig. 6.** Discharge curves of Li₂FeSiO₄ powders presented in Table 1: (a) carbon concentration = 1.6 mass% (58 g/L), (b) 8.2 mass% (75 g/L), and (c) 14.3 mass% (100 g/L). Straight lines are discharge curves. Dashed lines are charge curves.
Fig. 7. Cycle number dependence of the discharge capacity of the Li$_2$FeSiO$_4$ powder for which the carbon concentration was 14.3 mass%.

Fig. 8. Discharge curves of Li$_2$FeSiO$_4$ powders presented in Fig. 7 for 20th cycles.

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