High electrochemical performance of 3.9-V-LiFeSO$_4$F directly synthesized by scalable solid-state reaction within 1 h

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Supplementary information Fig. 1. XRD patterns of the two samples annealed at 250 °C for 15 h by simple solid-state reaction. (a) Sample 1 (LiF/ FeSO₄·H₂O) and (b) sample 2 (LiF/ FeSO₄). Red dots correspond to observed values and black lines are the calculated patterns, green lines indicate difference between the calculated and observed patterns. Each color bar corresponds to expected position of Bragg reflections of each phase.
Supplementary information Fig. 2. XRD patterns of the two samples annealed at 400 °C for 1 h under argon by simple solid-state reaction. (a) Sample 1 (LiF/FeSO₄·H₂O). (b) Sample 2 (LiF/FeSO₄. Black circle (symbol) indicates Li₂SO₄ impurity peak and triangle indicates Fe₃O₄ impurity.
Supplementary information Table 1. The refined lattice parameters of triplite from two samples. The refined parameters of sample 1 were that $R_{\text{expected}} = 3.154$, $R_{\text{profile}} = 7.2029$ and Weighted $R_{\text{profile}} = 11.456$ from X’pert High Score plus software. The refined parameters of sample 2 were that $R_{\text{expected}} = 5.532$, $R_{\text{profile}} = 9.30688$ and Weighted $R_{\text{profile}} = 12.76973$ from X’pert High Score plus software.

<table>
<thead>
<tr>
<th></th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β(°)</th>
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**Supplementary information Fig. 3.** XRD patterns and the derivative of voltage curve. (a) sample 2 (LiF+ FeSO₄) annealed at 350 °C during 1 hours by simple solid state synthesis. b) The differential capacity plot (-dq/dv) of sample 2 after annealing. Red dots correspond to observed values, and black lines are the calculated pattern, and green lines indicate the difference between the calculated and observed pattern. Each color bar corresponds to expected position of Bragg reflections of each phase.

XRD pattern in Supplementary information Fig. 3a shows that only triplite was formed with unreacted precursors as impurity phases without the formation of tavorite. Furthermore, ~ 3.9V redox potential of the sample in Supplementary information Fig. 3b clearly supports that only triplite was formed.
Supplementary information Fig. 4. X-ray diffraction pattern analysis of sample 1 (LiF/FeSO₄·H₂O) annealed at 250 °C for 15 h and then re-annealed at 400 °C for 1 h by simple solid-state reaction. Black triangle symbol (▼) symbol indicates Fe₃O₄ impurity.

Supplementary information Fig. 4 shows the XRD pattern of the sample that was annealed at 250 °C for 15 h and then re-annealed at 400 °C for 1 h under argon. The data clearly shows that the tavorite obtained at 250 °C was transformed to the triplite at 400 °C. The transformation of the tavorite in solid-state reaction was completed less than 1 h. This shortening phase transformation time can be the advantage of solid-state reaction over ionothermal or solvothermal process which
takes much longer time in phase transition. This transition data supports that the triplite is the most stable phase in LiFeSO$_4$F compounds while the tavorite is a metastable phase because it is synthesized only with FeSO$_4$ · H$_2$O at low temperature.
Supplementary information Fig. 5. X-ray diffraction pattern analysis of sample 2 (LiF/ FeSO$_4$) annealed at 400 °C for 45 min by simple solid-state reaction. Red dots correspond to observed values and black lines are the calculated patterns, green lines indicate difference between the calculated and observed patterns. Black circle symbol (●) indicates Li$_2$SO$_4$ impurity peak and black triangle symbol (▼) indicates Fe$_3$O$_4$ impurity.
Supplementary information Fig. 6. TEM image of the triplite LiFeSO$_4$F synthesized at 400 °C for 45min.

Supplementary information Fig. 6 clearly shows that the particle size of triplite synthesized at 400°C for 45min is about 150nm and it consistent with SEM analysis.
Supplementary information Fig. 7. X-ray diffraction pattern analysis of Li$_2$SO$_4$/FeF$_2$ mixture, annealed at 400 °C during 45 min by simple solid-state synthesis. Red dots correspond to observed values and black lines are the calculated patterns, green lines indicate difference between the calculated and observed patterns. Each color bar corresponds to expected position of Bragg reflections.

Supplementary information Fig. 7 clearly shows that triplite was formed irrespective of precursors. The Li$_2$SO$_4$/FeF$_2$ mixture also forms only triplite at 400 °C for 45 min by simple solid-state reaction. Main impurity phase was LiF which should be formed because of the excess of LiF.