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High electrochemical performance of 3.9-V-$LiFeSO_4F$ directly synthesized by scalable solid-state reaction within 1 h

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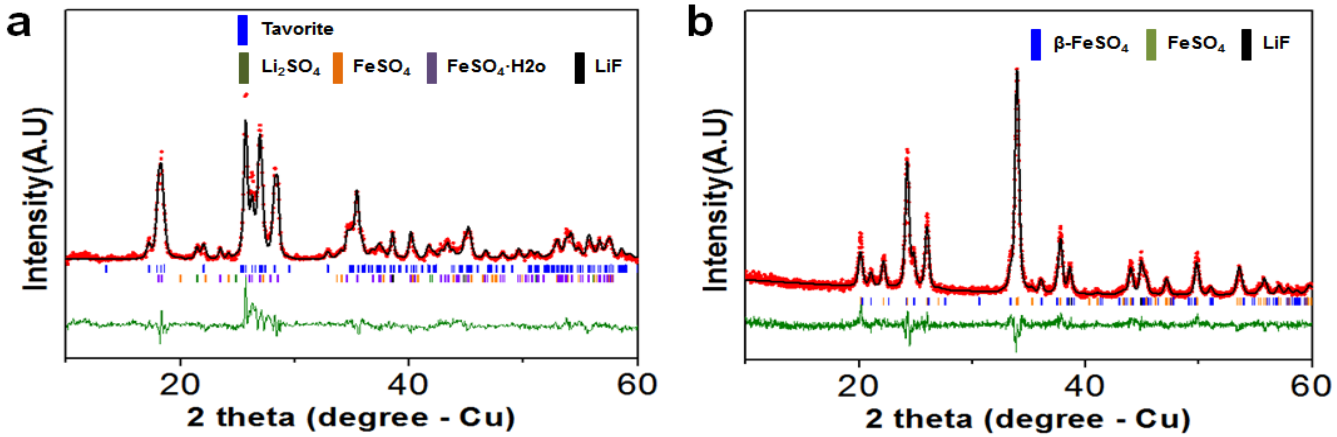
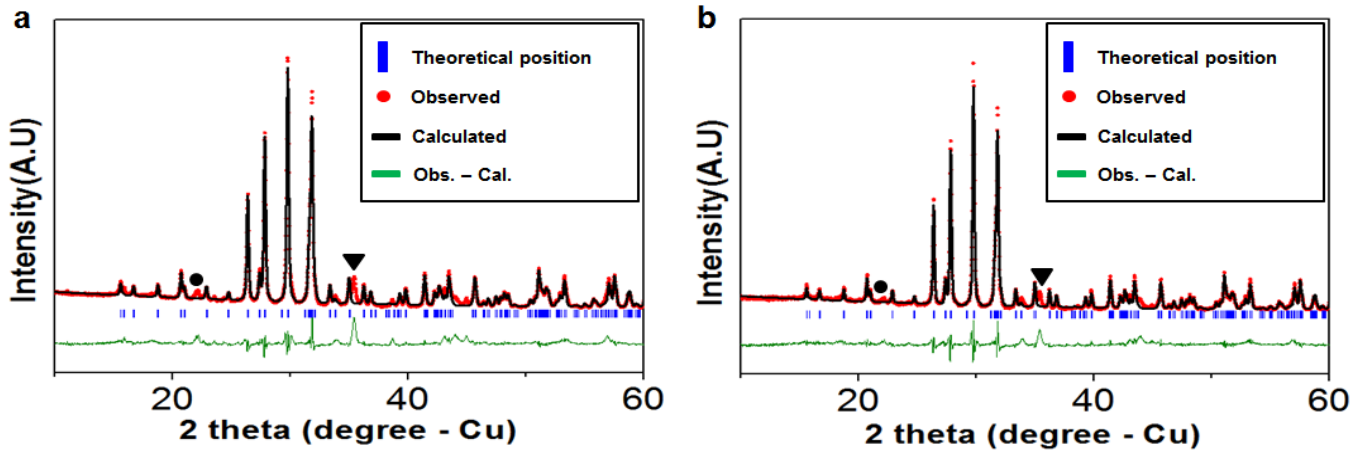
Supplementary information



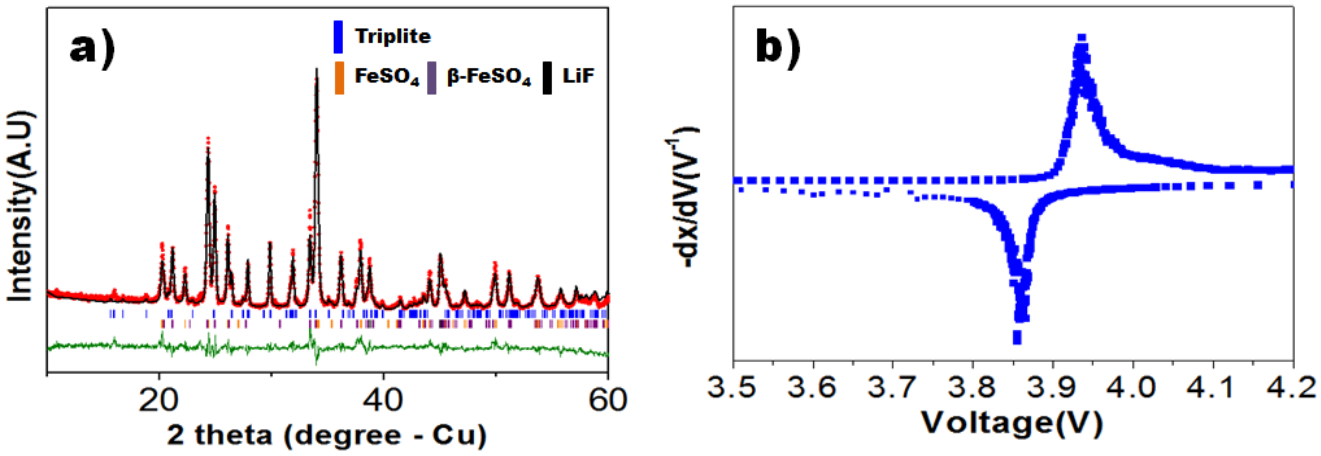
Supplementary information Fig. 1. XRD patterns of the two samples annealed at 250 °C for 15 h by simple solid-state reaction. (a) Sample 1 (LiF/ $FeSO_4 \cdot H_2O$) and (b) sample 2 (LiF/ $FeSO_4$). Red dots correspond to observed values and black lines are the calculated patterns, green lines indicate 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/ $FeSO_4 \cdot H_2O$). (b) Sample 2 (LiF/ $FeSO_4$. Black circle (symbol) indicates Li_2SO_4 impurity peak and triangle indicates Fe_3O_4 impurity.

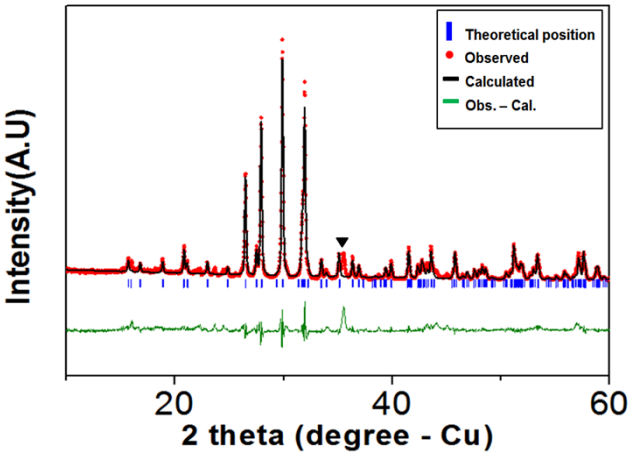
Supplementary information Table 1. The refined lattice parameters of triplite from two samples. The refined parameters of sample 1 were that $R_{expected}$ = 3.154, $R_{profile}$ = 7.2029 and Weighted $R_{profile}$ = 11.456 from X'pert High Score plus software. The refined parameters of sample 2 were that $R_{expected}$ = 5.532, $R_{profile}$ = 9.30688 and Weighted $R_{profile}$ = 12.76973 from X'pert High Score plus software.

	a(Å)	**b(Å)**	**c(Å)**	**β(°)**
Sample 1	13.0278	6.3931	9.8382	119.7192
Sample 2	13.0256	6.3928	9.8343	119.6968



Supplementary information Fig. 3. XRD patterns and the derivative of voltage curve. (a) sample 2 (LiF+ $FeSO_4$) 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.

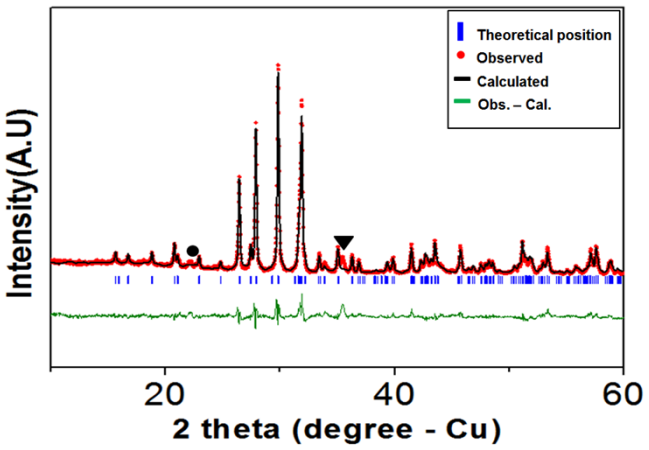
XRD pattern in Supplementary information Fig. 3a shows that only triplite was formed with unreacted precursors as impurity phases without the formation of tavorite. Furthermore, ~ 3.9V redox potential of the sample in Supplementary information Fig. 3b clearly supports that only triplite was formed.



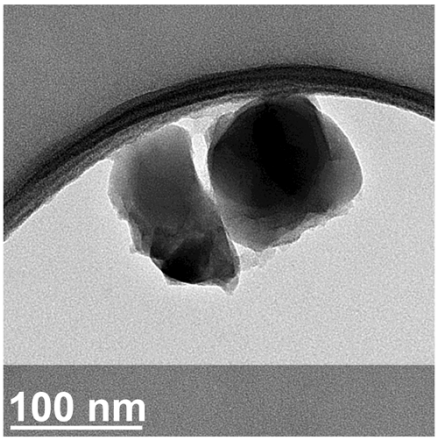
Supplementary information Fig. 4. X-ray diffraction pattern analysis of sample 1 (LiF/ $FeSO_4 \cdot H_2O$) annealed at 250 °C for 15 h and then re-annealed at 400 °C for 1 h by simple solid-state reaction. Black triangle symbol (▼) symbol indicates Fe_3O_4 impurity.

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 1h 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 tavortie 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 $LiFeSO_4F$ compounds while the tavorite is a metastable phase because it is synthesized only with $FeSO_4 \cdot H_2O$ at low temperature.

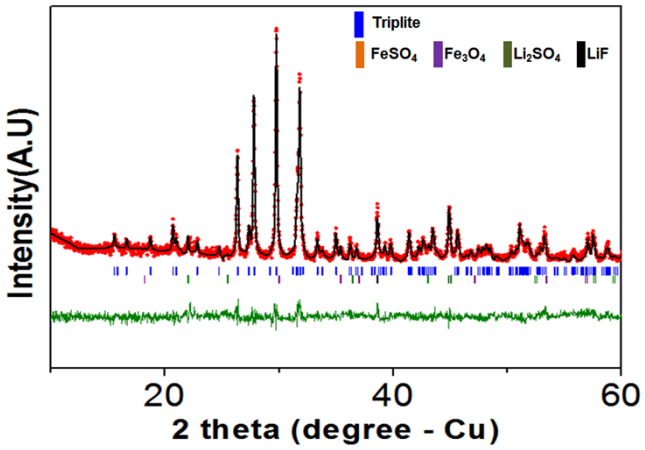


Supplementary information Fig. 5. X-ray diffraction pattern analysis of sample 2 (LiF/ $FeSO_4$) annealed at 400 °C for 45 min by simple solid-state reaction. Red dots correspond to observed values and black lines are the calculated patterns, green lines indicate difference between the calculated and observed patterns. Black circle symbol (●) indicates Li_2SO_4 impurity peak and black triangle symbol (▼) indicates Fe_3O_4 impurity.



Supplementary information Fig. 6. TEM image of the triplite $LiFeSO_4F$ 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_2SO_4/FeF_2 mixture, annealed at 400 °C during 45min 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_2SO_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.