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3.9V triplite $LiFeSO_4F$ was synthesized by scalable solid-state reaction within 1 h without undergoing phase transformation. The resulting material has nanosized particles that achieve almost full capacity and superior rate capability even at 10C (6 min).

Journal Name

ARTICLE

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

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Fe-based polyanion materials such as LiFePO$_4$ or LiFeBO$_3$ are safe and can achieve high energy density, so they have been considered as cathode materials for large-scale lithium ion batteries. Among these compounds, LiFeSO$_4$F achieves the highest voltage (3.9 V) among Fe^{2+}/Fe^{3+} redox couples, and therefore can have higher energy density than LiFePO$_4$. However, full utilization of 3.9V-LiFeSO$_4$F is severely limited by its non-scalable synthesis process and poor electrochemical activity. Here, we report a method to synthesize 3.9 V-LiFeSO$_4$F by a scalable solid-state reaction within 1 h by understanding thermodynamic stability of 3.9V LiFeSO$_4$F. The resulting material shows the best electrochemical performance reported to date. The process yields nanosized particles that achieve almost full capacity, 140 mAh/g, which is 93% of the theoretical capacity, and that retain excellent capacity, ~ 75 mAh/g at 1C for 150 cycles and high rate capability even at 10C (6 min). This scalable solid-state reaction for 3.9V-LiFeSO$_4$F makes it a plausible replacement for LiFePO$_4$ in the next generation of lithium ion batteries.

Introduction

Rechargeable Li ion batteries are widely used as power sources for portable electric and electronic devices. Recently, use of Li ion batteries has been extended to large-scale applications such as electrical vehicles and energy storage systems. In these large scale applications, the energy density and safety of the battery as well as low cost are important. Fe-based polyanion compounds[1] such as LiFePO$_4$[2-6], or LiFeBO$_3$[7-9], or Li$_2$FeSiO$_4$[10, 11 12, 13] have been considered as cathode materials for large scale applications. Especially, LiFePO$_4$ has been attracted a lot of attention because of excellent capacity retention with very high rate capability.[2-5] However, LiFePO$_4$ has a low operating voltage leading to relatively low energy density.[3] Efforts to increase the operating voltage of polyanion-based compounds have been tried by exploiting an inductive effect.[14, 15] Triplite LiFeSO$_4$F[16] is a promising cathode material because it exhibits an open-circuit voltage (OCV) of 3.9 V vs Li$^+$/Li^0, which is the highest potential among Fe^{2+}/Fe^{3+} redox couples in Fe-based compounds; it also has a theoretical capacity of 151 mAh/g. Because of this high energy density, triplite LiFeSO$_4$F will be a promising candidate in the cathode of Li ion batteries and can be a plausible replacement for LiFePO$_4$. However, use of triplite LiFeSO$_4$F for this purpose is severely limited by an impractical synthesis process and poor electrochemical properties.

The existing complicated process to synthesize triplite LiFeSO$_4$F exploits the phase transformation of tavorite, which is another polymorph of LiFeSO$_4$F and exhibits an OCV of

3.6V. This phase transformation process takes up to 14 day[17] to form triplite because the transformation is driven by entropy from Li/Fe disordering at octahedral sites; this entropy is not large in typical synthesis conditions.[18] For instance, the tavorite is first formed using an ionothermal or solvothermal process, then transformed at ~300 °C, however, it takes a long time to obtain well-crystallized triplite.[17] The long synthesis time makes triplite LiFeSO$_4$F less practical. Furthermore, the existing synthesis process uses FeSO$_4$ · H$_2$O, which is a typical starting precursor in solid-state reactions with pressure vessels.[19, 20] FeSO$_4$ · H$_2$O in solid-state reaction kinetically stabilizes tavorite LiFeSO$_4$F because of structural similarity of FeSO$_4$ · H$_2$O with tavorite.[19] As a result, the solid-state reaction with FeSO$_4$ · H$_2$O also requires prolonged phase transformation of the tavorite to form triplite.

The phase transformation of tavorite to form triplite can be accelerated by two methods: increasing the driving force by introducing surface defects or disordered tavorite.[21, 22] The microwave-assisted solvothermal is also used for heavily-disordered tavorite.[22] Still these approaches require a phase transition of tavorite to form triplite. Recently, triplite can be synthesized by special process such as SPS (Spark Plasma Sintering) process.[21] To fully utilize triplite, a scalable and direct synthetic process that uses a solid-state reaction should be developed.

The structural features cause poor electrochemical activity of triplite LiFeSO$_4$F. Triplite consists of two metal sites that are octahedrally coordinated by four oxygen atoms and two fluorine atoms. In the crystal form of triplite, Li and Fe are statistically distributed in the two octahedral sites, therefore;

triplite does not have an apparent long-range Li diffusion channel in the structure that leads to sluggish lithium diffusion. Furthermore, metal octahedra (MO_4F_2) in the triplite are connected by edge-sharing chains;[23] edge-sharing between Fe can result in strong electrostatic repulsion during extraction of Li, especially during full delithiation, so Fe octahedra restrict full utilization of triplite. These structural disadvantages of triplite can cause poor electrochemical activity. Furthermore, the prolonged synthesis process originated from slow phase transformation of tavorite can result in the formation of large particles, which may contribute to low electrochemical activity under these structural disadvantages. These difficult synthesis procedures and unfavorable structural characteristics impede the development of triplite that achieves its theoretical capacity and shows good electrochemical performance. Therefore, development of scalable synthesis process and improvement of triplite's electrochemical properties are vital in using $LiFeSO_4F$ as a cathode material. Here, we report that the triplite $LiFeSO_4F$ can be directly synthesized with scalable solid-state reaction at 400 °C because triplite is a thermodynamically stable phase irrespective of precursors or the phase transformation. Furthermore, the scalable solid-state reaction yields nanosized $LiFeSO_4F$ particles that can help to improve electrochemical activity. The resulting material achieves almost full capacity, and superior rate capability even with 10C (6 min) discharge rate and excellent capacity retention at 1C for 150 cycles.

Experimental

Synthesis

To prepare Sample 1 (LiF/ $FeSO_4 \cdot H_2O$), $FeSO_4 \cdot 7H_2O$ was annealed at 150 °C for 1 h under Ar atmosphere to synthesize the monohydrate $FeSO_4 \cdot H_2O$. After preparing monohydrate $FeSO_4 \cdot H_2O$, $FeSO_4 \cdot H_2O$ and LiF (mole ratio of LiF: $FeSO_4 \cdot H_2O$ = 1: 1) were ball milled with various diameter zirconia balls for 48 h in acetone. The mixture of precursors was dried and then formed into pellets (5-mm radius) under 5 metric tons of pressure. Then the pellet was annealed at various experiment conditions in a covered alumina crucible. To prepare Sample 2 (LiF/ $FeSO_4$), $FeSO_4 \cdot 7H_2O$ was annealed at 390 °C for 1 h under Ar atmosphere to synthesize anhydrous $FeSO_4$. After preparing $FeSO_4$, $FeSO_4$ and LiF (mole ratio of LiF: $FeSO_4$ = 1: 1) were ball milled with various diameter zirconia balls for 48 h in acetone. The mixture of precursors was dried and then formed into pellets (5-mm radius) with 5 metric tons of pressure. Then the pellet was annealed at various experiment conditions in a covered alumina crucible. Especially during annealing at 350 °C, $FeSO_4$ was manually mixed with LiF to investigate the synthesis route by slowing down the formation of triplite.

X – ray diffraction pattern (XRD)

XRD patterns were obtained using a Rigaku MAX-2500 equipped with a Cu-Kα source operating at 40 kV with a current of 100 mA. The scan range was from 10° to 60° over 2θ at 2° min-1.

Chemical delithiation & ICP (Inductively coupled plasma)

The chemical delithiation was performed by treating the triplite (LiF/ $FeSO_4$, annealed at 400 °C for 45 min) with an oxidizing agent, NO_2BF_4 in acetonitrile solvent for overnight. ICP was measured using an ICP-Spectrometer (SPECTRO) at a wavelength of 670.754 nm.

TGA (Thermogravimetric Analysis) & SEM (Scanning Electron Microscopy)

TGA was performed in the temperature range 25 - 600 °C with an SDT Q 600 (T_A instruments) at a heating rate of 3.3 °C/min under Ar.

SEM was conducted with an XL30S FEG (PHILPS ELECTRON OPTICS B.V) electron microscope (5 kV) operating under low-vacuum conditions. The samples were coated with Pt to avoid a charging effect.

Electrochemical characterization

Electrochemical tests were performed in a Swagelok-type half-cell with Li metal anode. Electrodes were prepared by mixing an active material, carbon (Super P, Timcal) and binder (Polyvinylidene fluoride, KUREHA, KF7208) in a weight ratio of 65: 30: 5, respectively. The cells were assembled in an Ar-filled glove box and tested on a Maccor Series 4000 operating in galvanostatic mode using non-aqueous electrolyte (1M-LiPF$_6$ in EC: DEC (1:1) from Panaxetec), and Celgard 2400 as separator. All cells were tested at room temperature. The loading density of the electrode was ~ 2 mg/cm^2.

Results

a. **Thermogravimetric Analysis (TGA) data: $FeSO_4 \cdot H_2O$ with LiF shows quite different reaction pathway compared to $FeSO_4$ with LiF.**
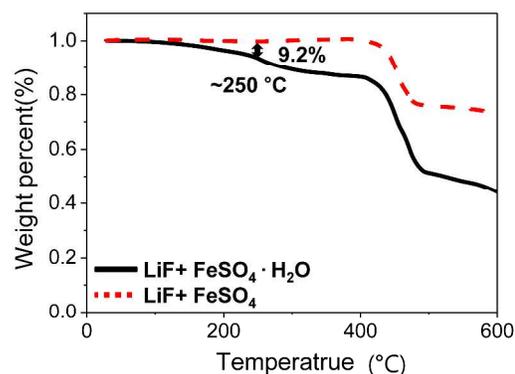

Fig. 1. TGA measurements of LiF/ $FeSO_4 \cdot H_2O$ (Sample 1) and LiF/ $FeSO_4$ (Sample 2). Black line indicates TGA result of Sample 1 (LiF+ $FeSO_4 \cdot H_2O$) and red dotted line indicates TGA result of Sample 2 (LiF+ $FeSO_4$)

To understand how $FeSO_4 \cdot H_2O$ affects the formation of the triplite in a solid-state reaction, LiF/ $FeSO_4 \cdot H_2O$ (Sample 1) and LiF/ $FeSO_4$ (Sample 2) were prepared by using solid-state reaction at different annealing temperatures (T_A). TGA results (Fig. 1) suggest that the two samples have quite different reaction pathways. Sample 1 lost ~ 9.2% of its weight at T_A = ~ 250 °C that is theoretical value from the loss of H_2O from LiF/$FeSO_4 \cdot H_2O$. Further weight loss in Sample 1 occurred until T_A = ~300 °C. Larger weight loss than ~9.2 wt% can be explained by the addition of H_2O in handling sample because of instability of $FeSO_4 \cdot H_2O$ compared to $FeSO_4 \cdot 7H_2O$; Sample 2 did not lose any weight until T_A = 400 °C. At T_A > 400 °C, both samples lost substantial weight, possibly due to decomposition

of LiFeSO$_4$F.[20] Considering that the tavorite can be formed by topotactic reaction of FeSO$_4$ · H$_2$O with LiF because of the structural similarity of FeSO$_4$ · H$_2$O with tavorite,[24] the loss of H$_2$O can indicate that tavorite starts to form at T$_A$ = 250 °C. To observe phase evolution, both samples were annealed at 250 °C under Ar for 15 h.

b. **XRD data at 250 °C: tavorite forms at 250 °C only with FeSO$_4$ · H$_2$O and the formation of the tavorite depends on the precursor.**

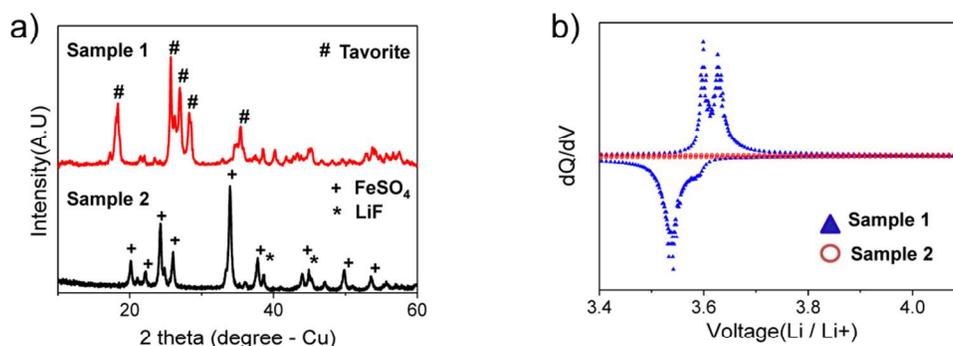**Fig. 2.** XRD patterns of the two samples and the differential capacity plots of the two samples. (a) XRD patterns of Sample 1 (LiF/ FeSO$_4$·H$_2$O) and Sample 2 (LiF/ FeSO$_4$) annealed at 250 °C during 15 hours by simple solid-state reaction. '#' symbols correspond to the patterns of the tavorite. '+' symbols correspond to the patterns of FeSO$_4$ and '*' symbols correspond to the patterns of LiF. b) The differential capacity plots (-dq/dv) of Sample 1 and Sample 2.

XRD patterns of the two samples annealed at 250 °C under Ar for 15 h (Fig. 2a and Supplementary information Fig. 1) indicate that the main phase of LiF/ FeSO$_4$·H$_2$O (Sample 1) was tavorite but that LiF/ FeSO$_4$ (Sample 2) did not show any tavorite phase or any reaction. Both samples retained unreacted precursors (Sample 1: LiF and FeSO$_4$ · H$_2$O; Sample 2: LiF, FeSO$_4$, and β - FeSO$_4$, which might be a result of phase transition of FeSO$_4$).[24]

The presence of H$_2$O in Sample 1 caused it to show different phase evolution from Sample 2. Unlike in Sample 2, tavorite started to appear at T$_A$ = 250 °C only in Sample 1. This suggests that the loss of H$_2$O observed in TGA measurement may be related to the formation of the tavorite and that the existence of H$_2$O can critically affect only the formation of tavorite. At T$_A$ = 250 °C. This observation is consistent with earlier observations that tavorite can be obtained by the presence of H$_2$O in wet chemical processes.[16, 24, 25] In solid-state reaction, the formation of the tavorite depends on the precursors, indicating that tavorite is not thermodynamically stable at T$_A$ = 250 °C.

The use of FeSO$_4$ · H$_2$O as a starting precursor results in formation of tavorite at low T$_A$ and requires a phase transformation to form triplite. Therefore the formation of triplite may be irrelevant to the phase transformation of tavorite if the starting precursors are different.

Electrochemical evaluations (Fig. 2b) of the two samples annealed at 250 °C confirmed that Sample 1 formed tavorite, while Sample 2 did not. Characteristic redox potential of Fe^{2+}/Fe^{3+} couple in tavorite, ~ 3.6V vs. Li$^+$/Li^0 was observed in Sample 1. However Sample 2 did not show any redox reaction behavior in the same potential window. These XRD patterns and electrochemical evaluations indicate that tavorite was synthesized at 250 °C only when FeSO$_4$·H$_2$O precursor was used with LiF. Tavorite can be metastable depending on the

starting precursor used. The requirement of phase transformation from tavorite to form triplite is due to the use of FeSO$_4$ · H$_2$O as a starting precursor, not to thermodynamic stability of tavorite over triplite.

c. **At 400 °C, triplite forms irrespective of precursors and is the most stable phase of LiFeSO$_4$F compounds.**
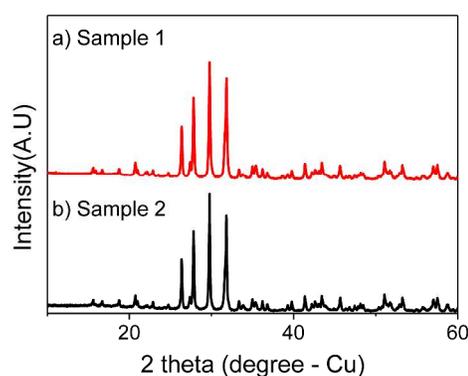
Fig. 3. XRD patterns of the two samples annealed at 400 °C for 1 hour under Ar. (a) Sample 1 (LiF/ FeSO$_4$·H$_2$O) and (b) Sample 2 (LiF/ FeSO$_4$).

The formation of LiFeSO$_4$F compounds at T$_A$ = 250 °C depends on the precursors used. To observe the phase evolution of the two samples at high temperature, the annealing temperature of the two samples under Ar was increased to 400

°C for 1 h. However, the annealing time was limited to <1 h because LiFeSO$_4$F can decompose at 400 °C (Fig. 1).

XRD patterns (Fig. 3 and Supplementary information Fig. 2) show that both samples annealed at 400 °C consisted of high purity triplite ($\geq$ 95 wt %); the main impurities were Fe$_3$O$_4$ and Li$_2$SO$_4$, which may be decomposition products of LiFeSO$_4$F. Formation of the triplite in both samples was completed within 1 h at T$_A$ = 400 °C. This formation time is much shorter than that observed in previous approaches such as ionothermal or solvothermal processes. The short synthesis time in this simple solid-state reaction is a crucial advantage compared to other processes, thus, enables practical use of triplite LiFeSO$_4$F. Even though triplite formed within 1 h, it had good crystallinity in both samples (Fig. 3), with lattice parameters similar to previous reports[16, 22] (Supplementary information Table. 1).

Triplite formed at T$_A$ = 400 °C is stable irrespective of starting precursors. The formation of the triplite depends on the temperature rather than on the precursors. The stability of triplite over tavorite at high temperature is consistent with a recent calorimetric measurement result[18].
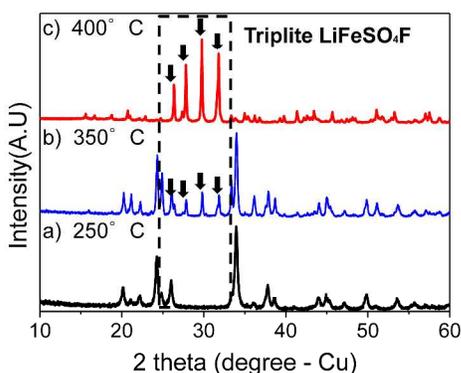

Fig. 4. XRD patterns of the Sample 2 (LiF/ FeSO$_4$) annealed at various annealing temperatures. (a) 250 °C for 15 hours, (b) 350 °C for 1 hour, and (c) 400 °C for 1 hour by simple solid-state reaction. The triplite is indicated by arrows gradually increases without the formation of the tavorite as the heating temperature increases.

In solid-state reaction, triplite can be directly synthesized from LiF/ FeSO$_4$ without undergoing the phase transition of tavorite. Sample 2 (LiF/ FeSO$_4$) was annealed at different T$_A$ and observed using XRD to determine how T$_A$ affects this phase evolution. At T$_A$ = 250 °C (Fig. 4a), unreacted precursors remained without forming other phases for the full 15 h. However, at T$_A$ = 350 °C, a small amount of triplite was formed, but no tavorite formed (Fig. 4b). Furthermore, electrochemical evaluation (Supplementary information Fig. 3) of the sample annealed at 350 °C showed the characteristic redox potential (3.9 V vs. Li$^+$/Li^0) of Fe^{2+}/Fe^{3+} in triplite. This observation indicates that only triplite formed at T$_A$ = 350 °C. At T$_A$ = 400 °C, the formation of the triplite by reaction of precursors was almost complete within 1 h. XRD patterns according to T$_A$ show that triplite was formed without formation of tavorite. Considering that the amount of triplite at 400 °C for 1 h significantly increased compared to 350 °C for 1 h, temperature strongly affects the kinetic of triplite formation.

Furthermore, the phase transformation of the tavorite to the triplite was quickly completed when T$_A$ > 250 °C. The tavorite synthesized at T$_A$ = 250 °C was transformed to the triplite at T$_A$ = 400 °C within 1 h (Supplementary information Fig. 4). These results indicate that the tavorite can only form from FeSO$_4$·H$_2$O at low T$_A$. Triplite is the most stable phase of LiFeSO$_4$F at high temperature, 400 °C. In short, triplite can be directly synthesized within 1 h without undergoing the phase transition from tavorite or can be synthesized by fast phase transformation of tavorite at high temperature such as 400 °C.

d. Electrochemical properties of triplite LiFeSO$_4$F synthesized by scalable solid-state reaction
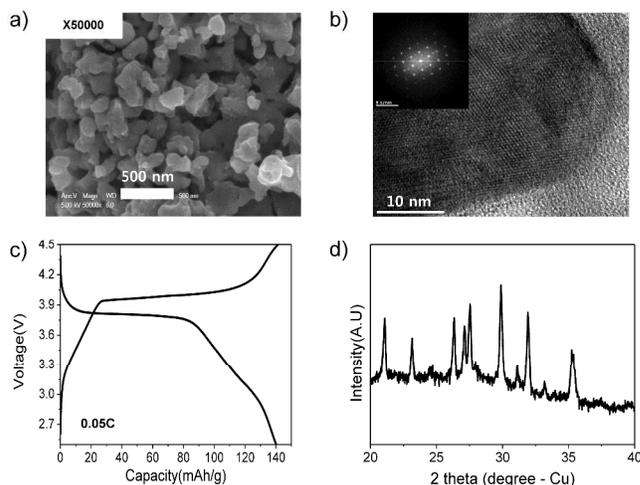

Fig. 5. SEM & TEM image and Electrochemical properties of the triplite LiFeSO$_4$F and XRD pattern of chemically delithiated FeSO$_4$F of the triplite LiFeSO$_4$F synthesized at 400 °C for 45min. (a) SEM image, (b) TEM image, (c) Voltage curve of the LiFeSO$_4$F at C/20 and (d) XRD pattern of chemically delithiated FeSO$_4$F.

The triplite is easily synthesized by short solid-state reaction and does not require prolonged phase transformation of the tavorite. Short solid-state reaction also leads to beneficial features to the particle size. Fig. 5a shows SEM image of the sample 2 (LiF/ FeSO$_4$) annealed at 400 °C for 45 min that shows the triplite in Supplementary information Fig. 5. The particle size of the triplite synthesized at 400 °C for 45 min is about 100 ~ 200 nm. Furthermore, TEM image of the sample 2 (LiF/ FeSO$_4$) in Fig. 5b and Supplementary information Fig. 6 confirms the particle size and then shows well-crystalized particles with lattice fringe even at 45 min annealing time. These nanosized particles shorten Li diffusion length, eventually increasing electrochemical activity of the triplite LiFeSO$_4$F. It is worth nothing that there is no residual carbon or carbon coating in the triplite synthesized at 400 °C because of utilizing carbon-free precursors.

Fig. 5c shows the electrochemical properties of the triplite LiFeSO$_4$F at C/20 rate. A rate of n·C corresponds to a full discharge in 1/n hr. It exhibits the characteristic redox potential of Fe^{2+}/Fe^{3+} in the triplite, 3.9V (Li$^+$/Li^0). The triplite LiFeSO$_4$F can deliver 140 mAh/g, which is 93% of theoretical capacity (151 mAh/g). This is the first electrochemical data to show that triplite can achieve almost full capacity. The best capacity reported to date is 80 % of theoretical capacity.[22] The chemical delithiation of triplite LiFeSO$_4$F further corroborates that the triplite can achieve the theoretical capacity. Fig. 5d shows the

XRD pattern of the chemically delithiated $FeSO_4F$. This indicates that the triplite $LiFeSO_4F$ can be fully delithiated by using chemical method. The amount of lithium (94%) in the chemically delithiated $FeSO_4F$ was also confirmed by ICP (Inductively coupled plasma) measurement. Through these electrochemical properties, we first show that the triplite can achieve full capacity. The nanosized particles of $LiFeSO_4F$ can really help to achieve better electrochemical properties. However, carbon-free precursors were used in this case, therefore; it was deduced that improvement of electrochemical activity can be from material's properties.
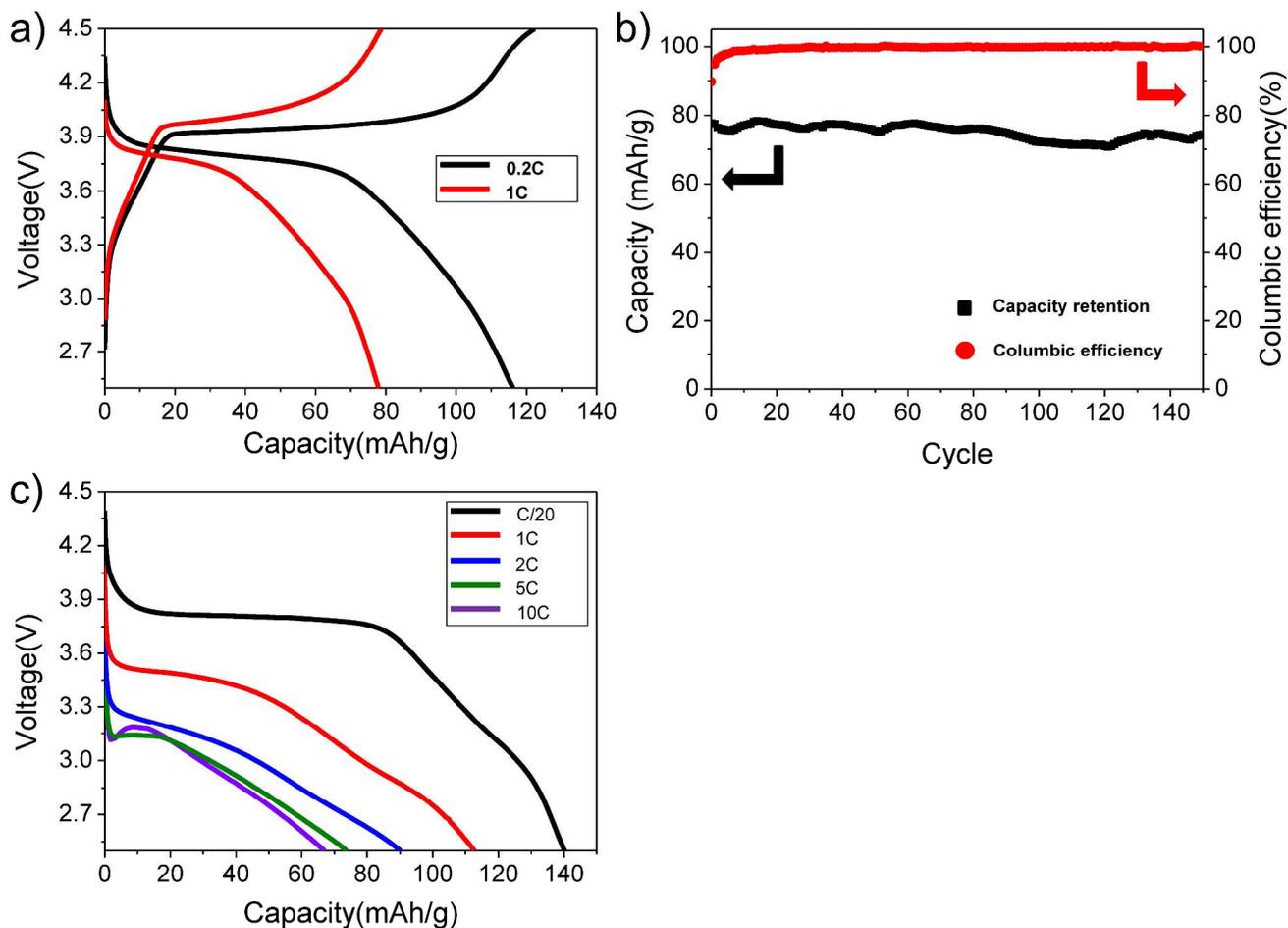

Fig. 6. Electrochemical properties of the triplite $LiFeSO_4F$ synthesized at 400 °C for 45min. (a) Galvanostatic charging and discharging profiles at a rate of C/5 and 1C rate (b) Capacity retention (left y-axis) and columbic efficiency (right y-axis) at 1C rate (c) The rate capability of the sample at different rates. The charging rate is C/20 without a voltage hold and then the discharging rates are various from C/2 to 10C. The voltage window of the electrochemical test is from 2.5V to 4.5V.

Fig. 6 shows electrochemical properties of the triplite $LiFeSO_4F$ synthesized at 400 °C for 45 min. The material shows capacity of 120 mAh/g at C/5 rate. Furthermore, the capacity of ~ 75 mAh/g at 1C charge and 1C discharge rate is maintained for 150 cycles without significant capacity degradation. The columbic efficiency holds nearly 100% at 1C rate up to 150 cycles except for a first few cycles. The best capacity retention reported to date was 25 cycles at C/20.[26] Fig. 6c shows the rate capability of the triplite $LiFeSO_4F$. The sample shows capacity of 140 mAh/g at C/20 rate, which is 93 % of theoretical capacity. When the current was further increased, ~ 112 mAh/g (82% of the capacity at C/20) can be delivered at 1C rate. Even at 10C rate, corresponding to a time of 6 min to fully discharge, the material achieves about 50% of the capacity at C/20 as shown in Fig. 6c. The triplite synthesized at 400 °C for 45 min shows excellent capacity retention and high rate capability. These superior electrochemical properties suggest that the triplite synthesized by solid-state reaction at 400 °C may have facile lithium transport even though the disordering of Li and Fe may exist in the structure. Scalable solid-state reaction makes triplite $LiFeSO_4F$ suitable for practical implementation by achieving full utilization of its energy density.
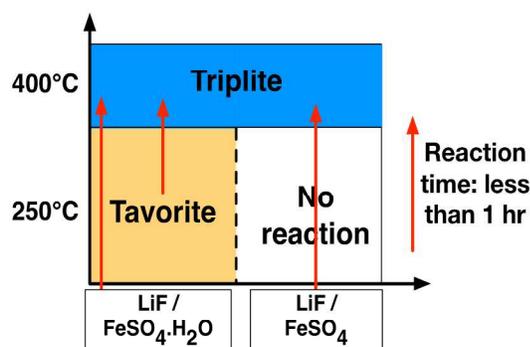
Discussion

Fig. 7. Schematic diagram of the relationship of the two phases with respect to experimental parameters.

In this study, we found that triplite is the most stable phase at high temperature such as 400 °C and can be synthesized directly using a simple solid-state reaction without undergoing phase transition from tavorite. In contrast, the formation of tavorite depends on precursors and temperatures; this dependence indicates that tavorite can be a metastable phase. The relationship (Fig. 7) between tavorite and triplite depends on experimental parameters such as temperatures and precursors. Tavorite is only synthesized by using LiF/ $FeSO_4·H_2O$ at low temperature. The main driving force of tavorite formation is the structural similarity with $FeSO_4·H_2O$. When the Sample 1 (LiF/ $FeSO_4·H_2O$) was annealed at 250 °C, H_2O in the $FeSO_4·H_2O$ started to evaporate. During this process, two possible reactions can occur: the formation of $FeSO_4$ and topotactic reaction of LiF/ $FeSO_4·H_2O$. The former requires severe structural change because $FeSO_4$ has a very different crystal structure than that of $FeSO_4·H_2O$.[27, 28] The latter is facilitated by the structural similarity between $FeSO_4·H_2O$ and tavorite $LiFeSO_4F$. Therefore, the topotactic reaction may be more kinetically favorable than the formation of $FeSO_4$. This topotactic reaction may explain why tavorite formed only when $FeSO_4·H_2O$ with LiF is used. This observation is consistent with recent data.[24] When the annealing temperature (T_A) increased to 400 °C, tavorite was quickly transformed to triplite (Supplementary information Fig. 4). This fast phase transition at high temperature suggests that tavorite is not the most stable phase of $LiFeSO_4F$. The stability of triplite over tavorite is consistent with recent thermochemical studies.[18] Use of $FeSO_4·H_2O$ as a starting precursor makes tavorite kinetically stable and requires phase transformation from tavorite to obtain triplite. The speed of the phase transition from tavorite depends on the temperature.[22] It is worth noting that the solid-state reaction in this study did not yield high-purity tavorite.

In contrast, the formation of the triplite does not depend on the starting precursors. With Sample 2 (LiF/ $FeSO_4$), triplite formed directly without intermediate phases or the tavorite phase at low temperature. Formation of triplite depends on the temperature, not on the precursors. At high T_A ~ 400 °C, triplite is the most stable phase irrespective of precursors or the presence of phase transition. Therefore, a key factor that influences the formation of triplite is thermal energy. This

finding is compatible with the driving force of the formation of the triplite, i.e., the entropy that originates from the Li/Fe disordering in octahedral sites in the triplite structure.[18] At high temperature, the entropy will be maximized, thereby causing triplite to be more thermodynamically stable than tavorite. Therefore, triplite can be synthesized with various precursors at high temperature. For instance, Li_2SO_4/FeF_2 easily formed triplite without forming tavorite (Supplementary information Fig. 7). However, cautions should be excised when synthesizing triplite because triplite $LiFeSO_4F$ can be easily decomposed at high temperature > 400 °C, as does in $LiVPO_4F$.[15]

The developed scalable solid-state reaction at high temperature, 400 °C, has several advantages over previous approaches that take prolonged time to synthesize triplite at low temperature, 300 °C. The solid-state reaction is fast because triplite can be synthesized directly or formed by fast phase transition; the reaction is also scalable because triplite is the most stable phase of $LiFeSO_4F$ and thus can be synthesized from various precursors at high temperature. The solid-state reaction also yields nanosized $LiFeSO_4F$ particles. They can achieve good capacity retention at 1C charge and 1C discharge rate for 150 cycles and high rate capability even at 10C rate (Fig. 6) even though structural disadvantages originated from the Li/Fe disordering can degrade electrochemical properties during charging/discharging.[16] This superior electrochemical performance indicates that the developed scalable solid-state reaction can electrochemically activate the triplite by mitigating the effect of structural disadvantages. The electrochemical performance of the triplite can be improved by influencing the distribution of Li/Fe by providing high thermal energy and by using nanosized particles to mitigate the structural disadvantages.

High temperature in the developed solid-state reaction may affect the distribution of Li/Fe, alleviating the effects that the structural disadvantages of triplite impose on the electrochemical activity. Recent calculation results[23, 29] report that the thermodynamically stable structure of triplite in the ground state may have corner-sharing Fe octahedra that provide facile Li diffusion channels. High temperature or large thermal energy in the solid-state reaction may help the $LiFeSO_4F$ to achieve the thermodynamically stable triplite structure as predicted by theoretical calculations. Typically, High temperature is an effective way to control cation disordering. For example, Li/Fe anti-site defects in $LiFePO_4$ compound are easily cured by annealing at high temperature such as 500 °C[30], thereby facilitating lithium diffusion[30]. Since 400 °C in the triplite synthesis can be enough to affect Li/Fe disordering, the triplite synthesized at 400 °C may have facile lithium transport because of favorable change of the Li/Fe disordering.

The particle size of the triplite will have a critical impact on its electrochemical activity because triplite does not have any apparent long-range Li diffusion channels and follows the two-phase reaction during charging/discharging.[19] The developed solid-state reaction easily yields nanosized particles. Firstly, the nanosized particles shorten Li diffusion length and consequently improve transport of Li and result in good electrochemical activity. The nanosized triplite particles can achieve high rate capability up to 10C (6 min) (Fig. 6) even with the lack of any apparent long-range Li diffusion channel. Secondly, the nanosized particles in the triplite can mitigate structural changes associated with insertion/extraction of lithium. As a result, the triplite can achieve almost full capacity and excellent capacity retention up to 150 cycles (Fig. 6).

Structural changes in the triplite $LiFeSO_4F$ and strong electrostatic repulsion between edge-shared Fe octahedra can be worsen by phase-separating behavior during charging/discharging.[19] In phase-separating compounds, mechanical strain and structural changes induced by insertion/extraction of lithium can be accumulated and can severely degrade electrochemical properties.[31] Therefore, the minimization of the particle size in the triplite $LiFeSO_4F$ can be a critical step toward improving its electrochemical performance, as is observed with nanosized particles of $LiFePO_4$, which is a well-known phase-separating compound; the resulting material can achieve excellent electrochemical performance because nanosized particles by themselves induce less mechanical changes than large particles and can facilitate phase transition during charging/discharging.[32, 33] The developed solid-state reaction can help triplite $LiFeSO_4F$ to achieve excellent electrochemical performance because of its nanosized particles and lessening structural disadvantages.

Conclusion

The results of this study suggest that triplite can be directly synthesized from various precursors due to its thermodynamic stability over tavorite, and that the structural disadvantages due to Li/Fe disordering in octahedral sites can be alleviated by using nanosized particles and annealing at high temperature. The triplite material is easily prepared using a solid-state reaction, which can be easily scaled up. The resulting material achieves almost full capacity and high rate capability. We have demonstrated that triplite $LiFeSO_4F$ synthesized by scalable solid-state reaction is a promising cathode material because it has superior electrochemical performance and high energy density. We strongly believe that our findings lay an important ground and will stimulate further research on the promising 3.9V $LiFeSO_4F$ cathode material.

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Notes and references

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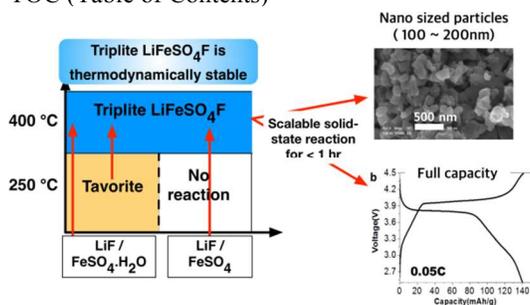
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TOC (Table of Contents)

3.9V triplite LiFeSO$_4$F was synthesized by scalable solid-state reaction within 1 h without undergoing phase transformation. The resulting material has nanosized particles that achieve almost full capacity and superior rate capability even at 10C (6 min).