

Cite this: *J. Mater. Chem. A*, 2015, 3, 7583

High electrochemical performance of 3.9 V LiFeSO₄F directly synthesized by a scalable solid-state reaction within 1 h†

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Fe-based polyanion materials such as LiFePO₄ or LiFeBO₃ 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, LiFeSO₄F achieves the highest voltage (3.9 V) among Fe²⁺/Fe³⁺ redox couples and therefore can have higher energy density than LiFePO₄. However, full utilization of 3.9 V LiFeSO₄F is severely limited by its non-scalable synthesis process and poor electrochemical activity. Here, we report a method to synthesize 3.9 V LiFeSO₄F by a scalable solid-state reaction within 1 h by understanding the thermodynamic stability of 3.9 V LiFeSO₄F. The resulting material shows the best electrochemical performance reported to date. The process yields nanosized particles that achieve almost full capacity, 140 mA h g⁻¹, which is 93% of the theoretical capacity and that retain excellent capacity, ~75 mA h g⁻¹ at 1 C for 150 cycles and high rate capability even at 10 C (6 min). This scalable solid-state reaction for 3.9 V LiFeSO₄F makes it a plausible replacement for LiFePO₄ in the next generation of lithium ion batteries.

Received 24th December 2014

Accepted 23rd February 2015

DOI: 10.1039/c4ta07095j

www.rsc.org/MaterialsA

Introduction

Rechargeable Li ion batteries are widely used as power sources for portable electric and electronic devices. Recently, the use of Li ion batteries has been extended to large-scale applications such as electric 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 compounds¹ such as LiFePO₄,^{2–6} LiFeBO₃,^{7–9} or Li₂FeSiO₄^{10–13} have been considered as cathode materials for large scale applications. Especially, LiFePO₄ has attracted a lot of attention because of its excellent capacity retention with very high rate capability.^{2–5} However, LiFePO₄ 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 LiFeSO₄F¹⁶ is a promising cathode material because it exhibits an open-circuit voltage (OCV) of 3.9 V vs. Li⁺/Li⁰, which is the highest potential among Fe²⁺/Fe³⁺ redox couples in Fe-based compounds; it also has a theoretical capacity of 151 mA h g⁻¹. Because of its high energy density, triplite LiFeSO₄F will be a promising candidate as a cathode of Li ion batteries and can be

a plausible replacement for LiFePO₄. However, the use of triplite LiFeSO₄F for this purpose is severely limited by its impractical synthesis process and poor electrochemical properties.

The existing complicated process to synthesize triplite LiFeSO₄F exploits the phase transformation of tavorite, which is another polymorph of LiFeSO₄F and exhibits an OCV of 3.6 V. This phase transformation process takes up to 14 days¹⁷ to form triplite because the transformation is driven by entropy from Li/Fe disordering at octahedral sites; this entropy is not large under typical synthesis conditions.¹⁸ For instance, 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 LiFeSO₄F less practical. Furthermore, the existing synthesis process uses FeSO₄·H₂O, which is a typical starting precursor in solid-state reactions with pressure vessels.^{19,20} FeSO₄·H₂O in solid-state reactions kinetically stabilizes tavorite LiFeSO₄F because of its structural similarity to tavorite.¹⁹ As a result, the solid-state reaction with FeSO₄·H₂O also requires prolonged phase transformation of 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 method is also used for heavily disordered tavorite.²² Still these approaches require a phase transition of tavorite to form triplite. Recently, triplite has been synthesized by a special process such as the 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.

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† Electronic supplementary information (ESI) available: XRD patterns and refinement values of each sample, annealed under various conditions. The differential capacity plot of sample 2, after annealing at 350 °C. See DOI: 10.1039/c4ta07095j

The structural features of triplite LiFeSO_4F cause poor electrochemical activity. 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 triplite are connected by edge-sharing chains;²³ edge-sharing between Fe can result in strong electrostatic repulsion during the 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 originating from slow phase transformation of tavorite can result in the formation of large particles, which may contribute to low electrochemical activity with these structural disadvantages. These difficult synthesis procedures and unfavorable structural characteristics impede the development of triplite from achieving its theoretical capacity and showing good electrochemical performance. Therefore, development of a scalable synthesis process and improvement of triplite's electrochemical properties are vital for using LiFeSO_4F as a cathode material. Here, we report that triplite LiFeSO_4F can be directly synthesized by a 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 the electrochemical activity. The resulting material achieves almost full capacity and superior rate capability even at 10 C (6 min) discharge rate and excellent capacity retention at 1 C for 150 cycles.

Experimental

Synthesis

To prepare sample 1 ($\text{LiF}/\text{FeSO}_4 \cdot \text{H}_2\text{O}$), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was annealed at 150 °C for 1 h under an Ar atmosphere to synthesize monohydrate $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. After preparing monohydrate $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and LiF (mole ratio of $\text{LiF} : \text{FeSO}_4 \cdot \text{H}_2\text{O} = 1 : 1$) 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 under various experimental conditions in a covered alumina crucible. To prepare sample 2 (LiF/FeSO_4), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was annealed at 390 °C for 1 h under an Ar atmosphere to synthesize anhydrous FeSO_4 . After preparing FeSO_4 , FeSO_4 and LiF (mole ratio of $\text{LiF} : \text{FeSO}_4 = 1 : 1$) 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) under 5 metric tons of pressure. Then the pellet was annealed under various experimental 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-K α 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)

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 overnight. ICP was conducted 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 of 25–600 °C with an SDT Q 600 (TA instruments) at a heating rate of 3.3 °C min^{-1} under Ar.

SEM was conducted with an XL30S FEG (PHILIPS 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 a 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 a non-aqueous electrolyte (1 M LiPF_6 in EC : DEC (1 : 1) from Panaxetec) and Celgard 2400 as a separator. All cells were tested at room temperature. The loading density of the electrode was $\sim 2 \text{ mg cm}^{-2}$.

Results

Thermogravimetric analysis (TGA) data: $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ with LiF shows quite different reaction pathways compared to FeSO_4 with LiF

To understand how $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ affects the formation of triplite in a solid-state reaction, $\text{LiF}/\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (sample 1) and LiF/FeSO_4 (sample 2) were prepared by using the 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 $\sim 9.2\%$ of its weight at $T_A = \sim 250$ °C that is the theoretical value from the loss of H_2O from $\text{LiF}/\text{FeSO}_4 \cdot \text{H}_2\text{O}$. Further weight loss in sample 1 occurred up to $T_A = \sim 300$ °C. Larger weight loss than $\sim 9.2 \text{ wt}\%$ can be explained by the addition of H_2O in handling the sample because of the instability of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ compared to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; sample 2 did not lose any weight up to $T_A = 400$ °C. At $T_A > 400$ °C, both samples lost a substantial amount of weight, possibly due to the decomposition of LiFeSO_4F .²⁰ Considering that tavorite can be formed by a topotactic reaction of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ with LiF because of the structural similarity of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ to tavorite,²⁴ the loss of

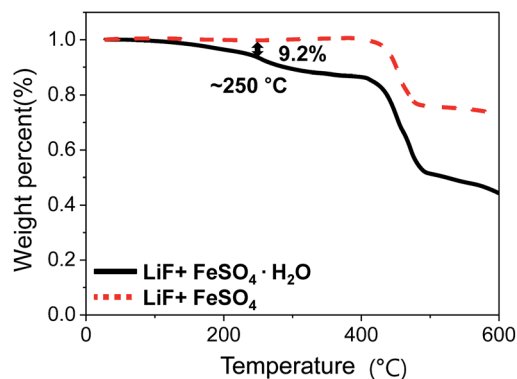


Fig. 1 TGA measurement results of LiF/FeSO₄·H₂O (sample 1) and LiF/FeSO₄ (sample 2). The black line indicates TGA results of sample 1 (LiF + FeSO₄·H₂O) and the red dotted line indicates TGA results of sample 2 (LiF + FeSO₄).

H₂O can indicate that tavorite starts to form at $T_A = 250$ °C. To observe the phase evolution, both samples were annealed at 250 °C under Ar for 15 h.

XRD data at 250 °C: tavorite forms at 250 °C only with FeSO₄·H₂O and the formation of tavorite depends on the precursor

XRD patterns of the two samples annealed at 250 °C under Ar for 15 h (Fig. 2a and ESI Fig. 1[†]) indicate that the main phase of LiF/FeSO₄·H₂O (sample 1) was tavorite but that LiF/FeSO₄ (sample 2) did not show any tavorite phase or any reaction. Both samples retained unreacted precursors (sample 1: LiF and FeSO₄·H₂O; sample 2: LiF, FeSO₄, and β -FeSO₄, which might be a result of phase transition of FeSO₄).²⁴

The presence of H₂O in sample 1 made it show phase evolution different from sample 2. Unlike in sample 2, tavorite started to appear at $T_A = 250$ °C in sample 1. This suggests that the loss of H₂O observed in TGA measurements may be related to the formation of tavorite and that the existence of H₂O can critically affect only the formation of tavorite at $T_A = 250$ °C. This observation is consistent with previous observations that

tavorite can be obtained in the presence of H₂O in wet chemical processes.^{16,24,25} In solid-state reactions, the formation of tavorite depends on the precursors, indicating that tavorite is not thermodynamically stable at $T_A = 250$ °C.

The use of FeSO₄·H₂O as a starting precursor results in the 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. A characteristic redox potential of the Fe²⁺/Fe³⁺ couple in tavorite, ~ 3.6 V vs. Li⁺/Li⁰, 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 the FeSO₄·H₂O 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 FeSO₄·H₂O as a starting precursor, not due to the thermodynamic stability of tavorite over triplite.

At 400 °C, triplite forms irrespective of precursors and is the most stable phase of LiFeSO₄F compounds

The formation of LiFeSO₄F 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 LiFeSO₄F can decompose at 400 °C (Fig. 1).

XRD patterns (Fig. 3 and ESI Fig. 2[†]) show that both samples annealed at 400 °C consisted of high purity triplite (≥ 95 wt%); the main impurities were Fe₃O₄ and Li₂SO₄, which may be decomposition products of LiFeSO₄F. The formation of 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

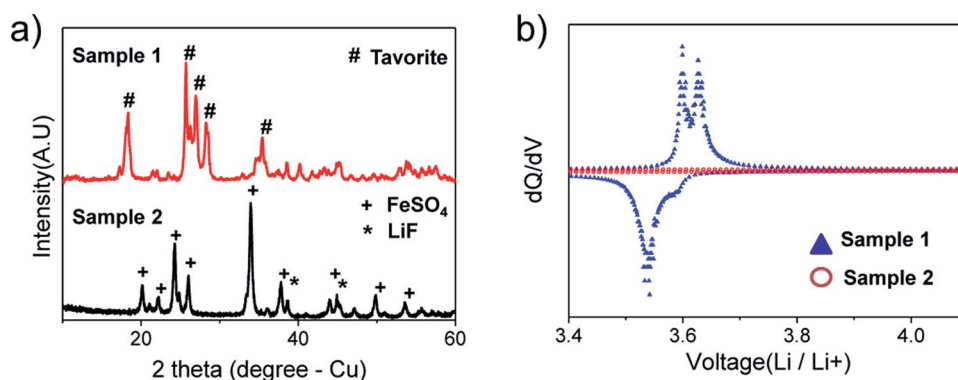


Fig. 2 XRD patterns of the two samples and the differential capacity plots of the two samples. (a) XRD patterns of sample 1 (LiF/FeSO₄·H₂O) and sample 2 (LiF/FeSO₄) annealed at 250 °C for 15 hours by a simple solid-state reaction. '#' symbols correspond to the patterns of tavorite. '+' symbols correspond to the patterns of FeSO₄ and '*' symbols correspond to the patterns of LiF. (b) The differential capacity plots ($-dq/dv$) of sample 1 and sample 2.

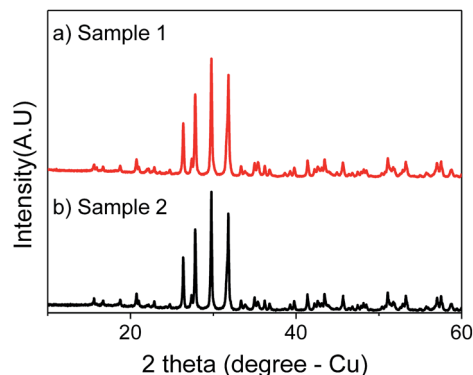


Fig. 3 XRD patterns of the two samples annealed at 400 °C for 1 hour under Ar. (a) Sample 1 (LiF/FeSO₄·H₂O) and (b) sample 2 (LiF/FeSO₄).

short synthesis time in this simple solid-state reaction is a crucial advantage compared to other processes, thus, enabling practical use of triplite LiFeSO₄F. 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} (ESI Table 1†).

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

In solid-state reactions, triplite can be directly synthesized from LiF/FeSO₄ without undergoing the phase transition of tavorite. Sample 2 (LiF/FeSO₄) 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 was formed (Fig. 4b). Furthermore, electrochemical evaluation (ESI Fig. 3†) of the sample annealed at 350 °C showed the characteristic redox potential (3.9 V vs. Li⁺/Li⁰) of Fe²⁺/Fe³⁺ in triplite. This observation indicates that only triplite formed at $T_A = 350$ °C. At $T_A = 400$ °C, the formation of

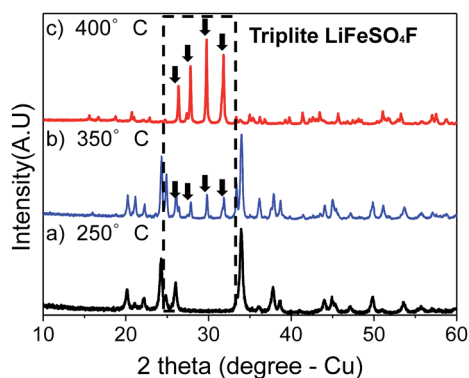


Fig. 4 XRD patterns of sample 2 (LiF/FeSO₄) annealed at various annealing temperatures. (a) 250 °C for 15 hours, (b) 350 °C for 1 hour, and (c) 400 °C for 1 hour by a simple solid-state reaction. The triplite, indicated by arrows, gradually increases without the formation of tavorite as the heating temperature increases.

triplite by the reaction of precursors was almost complete within 1 h. XRD patterns according to T_A show that triplite was formed without the formation of tavorite. Considering that the amount of triplite at 400 °C for 1 h significantly increased compared to that at 350 °C for 1 h, temperature strongly affects the kinetics of triplite formation.

Furthermore, the phase transformation of tavorite to triplite was quickly completed when $T_A > 250$ °C. The tavorite synthesized at $T_A = 250$ °C was transformed into triplite at $T_A = 400$ °C within 1 h (ESI Fig. 4†). These results indicate that tavorite can only form from FeSO₄·H₂O at low T_A . Triplite is the most stable phase of LiFeSO₄F 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.

Electrochemical properties of triplite LiFeSO₄F synthesized by the scalable solid-state reaction

Triplite is easily synthesized by a short solid-state reaction and does not require prolonged phase transformation of tavorite. A short solid-state reaction also leads to beneficial features to the particle size. Fig. 5a shows the SEM image of sample 2 (LiF/FeSO₄) annealed at 400 °C for 45 min that shows the triplite in ESI Fig. 5.† The particle size of the triplite synthesized at 400 °C for 45 min is about 100–200 nm. Furthermore, the TEM image of sample 2 (LiF/FeSO₄) in Fig. 5b and ESI Fig. 6† confirm the particle size and show well-crystallized particles with lattice fringes even at 45 min annealing time. These nanosized particles shorten the Li diffusion length, eventually increasing the electrochemical activity of triplite LiFeSO₄F. It is worth noting that there is no residual carbon or carbon coating in the triplite synthesized at 400 °C because of the utilization of carbon-free precursors.

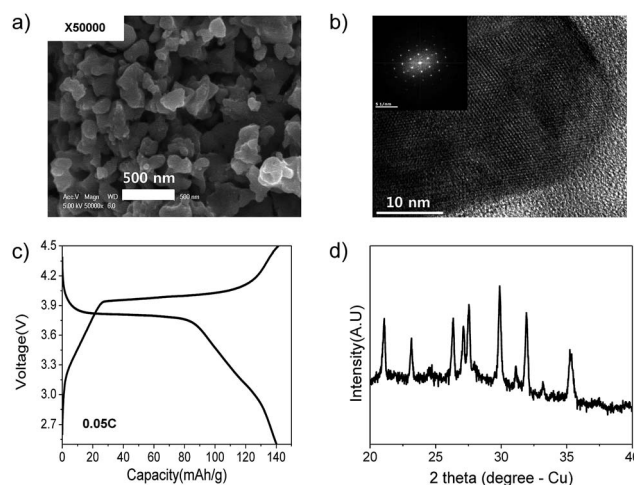


Fig. 5 SEM & TEM images, electrochemical properties of triplite LiFeSO₄F and the XRD pattern of chemically delithiated FeSO₄F of triplite LiFeSO₄F synthesized at 400 °C for 45 min. (a) SEM image, (b) TEM image, (c) voltage curve of LiFeSO₄F at C/20 and (d) XRD pattern of chemically delithiated FeSO₄F.

Fig. 5c shows the electrochemical properties of triplite LiFeSO_4F at C/20 rate. A rate of $n\text{C}$ corresponds to a full discharge in $1/n$ h. It exhibits the characteristic redox potential of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the triplite, 3.9 V (Li^+/Li^0). Triplite LiFeSO_4F can deliver 140 mA h g^{-1} , which is 93% of theoretical capacity (151 mA h g^{-1}). These are 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_4F further corroborates that triplite can achieve the theoretical capacity. Fig. 5d shows the XRD pattern of chemically delithiated FeSO_4F . This indicates that triplite LiFeSO_4F can be fully delithiated by using a chemical method. The amount of lithium (94%) in chemically delithiated FeSO_4F was also confirmed by ICP (inductively coupled plasma) measurements. Through these electrochemical properties, we first show that 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 shows electrochemical properties of the triplite LiFeSO_4F synthesized at 400°C for 45 min. The material shows a capacity of 120 mA h g^{-1} at C/5 rate. Furthermore, a capacity of $\sim 75 \text{ mA h g}^{-1}$ at 1 C charge and 1 C discharge rates is maintained for 150 cycles without significant capacity degradation. The coulombic efficiency holds nearly 100% at 1 C 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 triplite LiFeSO_4F . The sample shows a capacity of 140 mA h g^{-1} at C/20 rate, which is 93% of theoretical capacity. When the current was further increased, $\sim 112 \text{ mA h g}^{-1}$ (82% of the capacity at C/20) can be delivered at 1 C rate. Even at 10 C 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 the solid-state reaction at 400°C may have facile lithium transport even though the disordering of Li and Fe may exist in the structure. The scalable solid-state reaction makes

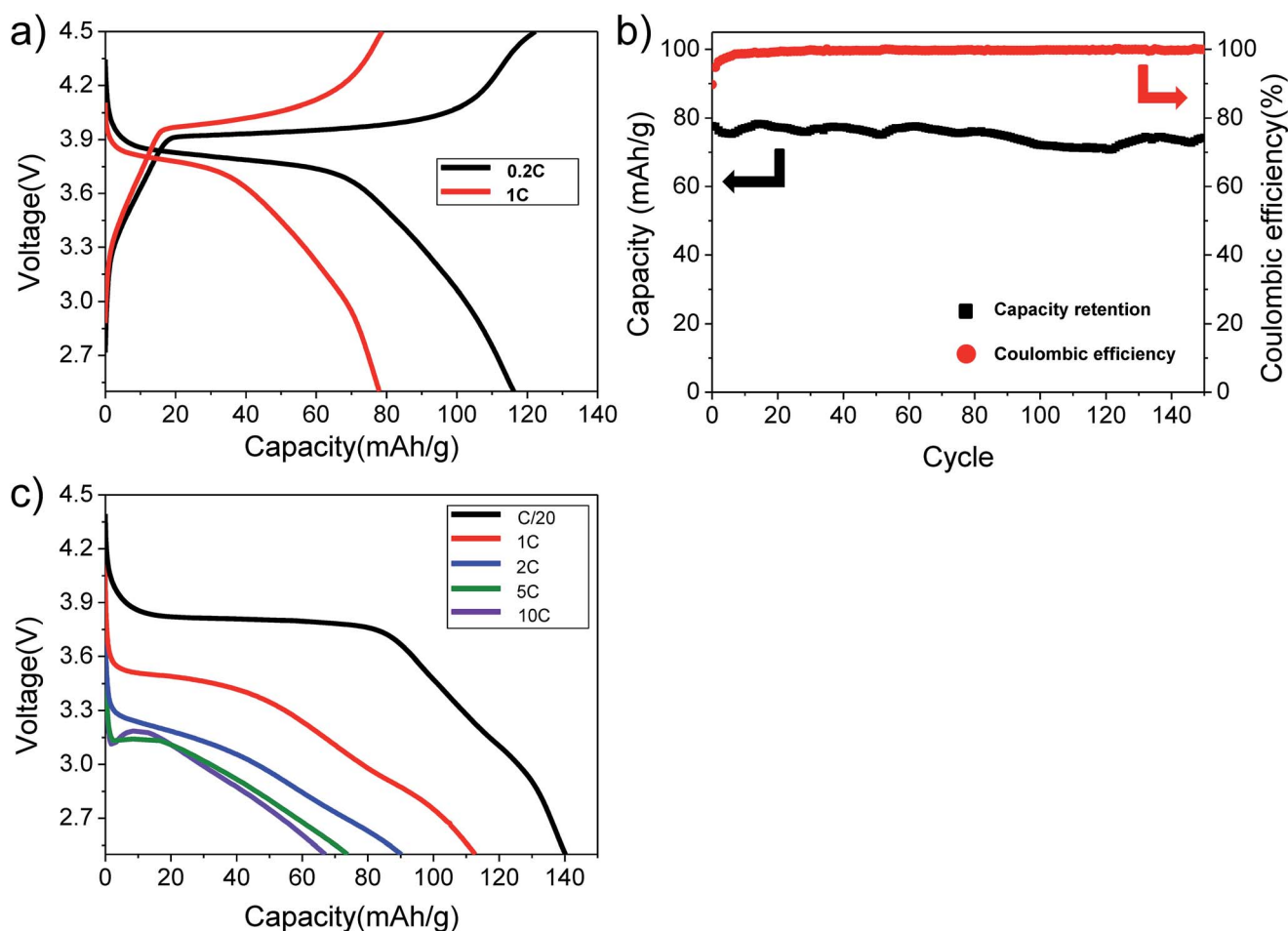


Fig. 6 Electrochemical properties of the triplite LiFeSO_4F synthesized at 400°C for 45 min. (a) Galvanostatic charging and discharging profiles at a rate of C/5 and 1 C, (b) capacity retention (left y-axis) and coulombic efficiency (right y-axis) at 1 C rate and (c) the rate capability of the sample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

triplite LiFeSO_4F suitable for practical implementation by achieving full utilization of its energy density.

Discussion

In this study, we found that triplite is the most stable phase at high temperature such as $400\text{ }^\circ\text{C}$ 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 $\text{LiF}/\text{FeSO}_4\cdot\text{H}_2\text{O}$ at low temperature. The main driving force of tavorite formation is the structural similarity of tavorite to $\text{FeSO}_4\cdot\text{H}_2\text{O}$. When sample 1 ($\text{LiF}/\text{FeSO}_4\cdot\text{H}_2\text{O}$) was annealed at $250\text{ }^\circ\text{C}$, H_2O in the $\text{FeSO}_4\cdot\text{H}_2\text{O}$ started to evaporate. During this process, two possible reactions can occur: the formation of FeSO_4 and topotactic reaction of $\text{LiF}/\text{FeSO}_4\cdot\text{H}_2\text{O}$. The former requires a severe structural change because FeSO_4 has a very different crystal structure than that of $\text{FeSO}_4\cdot\text{H}_2\text{O}$.^{27,28} The latter is facilitated by the structural similarity between $\text{FeSO}_4\cdot\text{H}_2\text{O}$ 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 $\text{FeSO}_4\cdot\text{H}_2\text{O}$ with LiF is used. This observation is consistent with recent data.²⁴ When the annealing temperature (T_A) increased to $400\text{ }^\circ\text{C}$, tavorite quickly transformed into triplite (ESI 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 The use of $\text{FeSO}_4\cdot\text{H}_2\text{O}$ 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 triplite does not depend on the starting precursors. In the case of sample 2 (LiF/FeSO_4), triplite formed directly without intermediate phases or the tavorite phase at low temperature. The formation of triplite depends on

the temperature, not on the precursors. At high $T_A \sim 400\text{ }^\circ\text{C}$, 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 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 from various precursors at high temperature. For instance, $\text{Li}_2\text{SO}_4/\text{FeF}_2$ easily formed triplite without forming tavorite (ESI Fig. 7†). However, caution should be exercised when synthesizing triplite because triplite LiFeSO_4F can be easily decomposed at high temperature $>400\text{ }^\circ\text{C}$, as does in LiVPO_4F .¹⁵

The developed scalable solid-state reaction at high temperature, $400\text{ }^\circ\text{C}$, has several advantages over previous approaches that take prolonged time to synthesize triplite at low temperature, $300\text{ }^\circ\text{C}$. 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 1 C charge and 1 C discharge rates for 150 cycles and high rate capability even at 10 C rate (Fig. 6) even though structural disadvantages originating 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 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 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 compounds are easily cured by annealing at high temperature such as $500\text{ }^\circ\text{C}$,³⁰ thereby facilitating lithium diffusion.³⁰ Since $400\text{ }^\circ\text{C}$ in the triplite synthesis can be sufficient to affect Li/Fe disordering, the triplite synthesized at $400\text{ }^\circ\text{C}$ may have facile lithium transport because of the 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

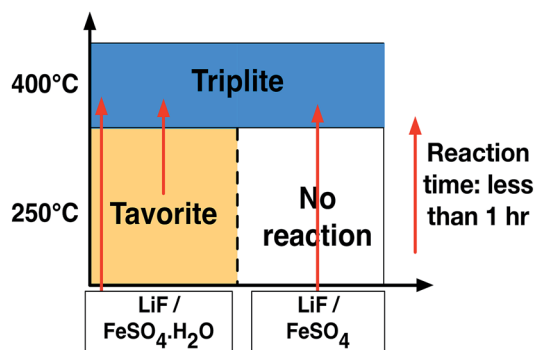


Fig. 7 Schematic diagram of the relationship between the two phases with respect to experimental parameters.

nanosized particles shorten the Li diffusion length and consequently improve the transport of Li and result in good electrochemical activity. The nanosized triplite particles can achieve high rate capability up to 10 C (6 min) (Fig. 6) even with the lack of any apparent long-range Li diffusion channels. 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 triplite LiFeSO_4F and strong electrostatic repulsion between edge-shared Fe octahedra can be worsened 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 the electrochemical properties.³¹ Therefore, the minimization of the particle size of 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 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 less 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 a 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 3.9 V LiFeSO_4F cathode material.

Acknowledgements

We thank Prof. J. M. Tarascon for his insightful discussions. This research was supported by the Center of Futuristic Material-system of the Brain Korea 21 Project.

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