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Authors

Seo, Dong-Hwa
Park, Kyu-Young
Kim, Haegyeom
[et al.](#)

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Approaching one Li extraction/reinsertion in triplite LiFeSO_4F cathode for lithium rechargeable batteries

Dong-Hwa Seo,^{1 †} Kyu-Young Park,^{2 †} Haegyeom Kim,^{2 †} Sung-Kyun Jung,² and Kisuk Kang^{2,3 *}

1. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

2. Department of Materials Science and Engineering, Research Institute of Advanced Materials (RIAM), Seoul National University, Gwanak-ro 599, Gwanak-gu, Seoul 151-742, Republic of Korea

3. Center for nanoparticle research, Institute for Basic Science (IBS), Seoul National University, Gwanak-ro 599, Gwanak-gu, Seoul 151-742, Republic of Korea

[†]These authors equally contribute to this work.

Corresponding Author. Tel.: +82-2-880-7088 Fax.: +82-2-885-9671 E-mail address: matlgen1@snu.ac.kr

1. Introduction

Lithium-ion batteries (LIBs) technology has attracted considerable attention with growing demand for emerging large scale energy storage devices such as electric vehicles (EVs) and energy storage systems (ESS) for electric grid¹. To satisfy the requirements of those applications, current LIB system needs better performing electrode materials by optimizing various factors including safety, sustainability, economy, energy density, and power density. Thus, considerable efforts have been continuously devoted to the development on new electrode materials¹⁻⁵, especially, Fe-based polyanionic compounds have been intensively studied as promising candidates as cathode materials for LIBs because of their environmental and economic advantages compared to other transition metal-based compounds⁶⁻¹³. Furthermore, another major merit of these polyanionic compounds is that the operating potential is potentially tunable through inductive effects from the polyanionic bonding, which can increase the relatively low redox potential of Fe²⁺/Fe³⁺ in simple oxides systems such as pyrophosphate (Li₂FeP₂O₇)⁹, silicate (Li₂FeSiO₄)¹⁰, borate (LiFeBO₃)¹², fluorophosphates (Li₂FePO₄F)¹³, and fluorosulfate (LiFeSO₄F)¹⁴.

One of the most important new Fe-based polyanionic cathode materials, tavorite LiFeSO₄F, delivers relatively high redox potential ~ 3.6 V (vs. Li/Li⁺), which is even higher than that of the olivine structured

LiFePO₄ (~ 3.4 V vs. Li/Li⁺), with high reversible capacity putting it as a promising cathode candidate¹⁴. It triggered intensive research interests in developing Fe-based high voltage cathode materials, as efforts to achieve this goal, LiFe_{1-x}Mn_xSO₄F with triplite structure with unforeseen high Fe²⁺/Fe³⁺ redox potential with ~3.9 V (vs. Li/Li⁺) was developed by Barpanda *et al*⁷. Since then, it has aroused considerable recent interests in the 3.9 V class Fe-based cathode, triplite LiFeSO₄F, optimization and investigation on its electrochemical properties have intensively conducted.²¹⁻²⁶

While the triplite LiFeSO₄F possesses significant potential as a next-generation cathode due to its unprecedented high Fe²⁺/Fe³⁺ redox potential, slow kinetics of the triplite LiFeSO₄F is problematic and hinders its applications²³. A previous theoretical study suggested that the triplite LiFeSO₄F has three dimensional Li transportation network with relatively low activation energies below ~ 700 meV²⁷, but the utilization on of triplite LiFeSO₄F has been experimentally limited to a substantially lower than one Li per LiFeSO₄F even at very low current rates. Even today, the origin of slow kinetics remains poorly understood. Herein, we carefully investigate the local crystal structure and possible diffusion paths in the triplite LiFeSO₄F using transmission electron microscope (TEM) analysis combined with theoretical first principles study, demonstrating that local disordered Li/Fe configuration of triplite become a bottleneck for Li transports. Based on this result, we proposed an approach to utilizing one Li in triplite LiFeSO₄F, wherein the reduction of particle size of LiFeSO₄F in triplite

structure smaller than the domain size could significantly improve rate capability and therefore realize extraction/insertion of one Li in the triplite LiFeSO_4F .

2. Results and discussion

The crystal structure of electrode material primarily determines Li ion diffusion, thus, it is important to understand the slow kinetics of triplite LiFeSO_4F in structural point of view. Here, the LiFeSO_4F powder was synthesized through a conventional solid-state method to observe local crystal structures⁷ (The details of synthesis conditions are described at experiment section). We confirmed that the prepared triplite LiFeSO_4F is well synthesized while a little impurity of $\text{Fe}_2(\text{SO}_4)_2$ is detected by a full pattern matching method with measured X-ray diffraction patterns (Fig. 1 (a)). The structural parameters of the triplite LiFeSO_4F are obtained to $a = 13.041(1) \text{ \AA}$, $b = 6.397(2) \text{ \AA}$, $c = 9.834(2) \text{ \AA}$ and $\beta = 119.766(2)^\circ$, respectively, which is in a good agreement with previous reports²³. We further investigated the particle size and local structure of LiFeSO_4F using a high resolution transmitted electron microscopy (HR-TEM), in which a single crystalline triplite LiFeSO_4F with $\sim 200 \text{ nm}$ size was observed (Fig. 1 (b)). Interestingly, it is observed that the prepared triplite shows some distorted crystalline signals with a 10-20 nm domain size along [010] zone axis as shown in Figure 1(c). In addition, (-200) dark field image along a [010] zone axis also demonstrates that the distorted signals are widely dispersed in a single triplite particle. (Figure 1. (d)) Note that the distorted

signals with domains are not shown in specific particles but observed in almost particles (See Fig. S1).

For further investigation on the origin of distorted crystal structure, more precise structural analysis was carefully conducted using the 80 kV high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) at the certain boundary between domains. In this experiment, the specimen was prepared using the focused ion beam (FIB) technique to avoid the specimen-thickness effect. The HAADF-STEM generally depicts the Z-contrast of atoms that provide direct position of relatively heavy elements²⁸, thus the bright signals are mainly from Fe atoms due to their much higher atomic mass than those of Li, S, O and F atoms in the LiFeSO_4F triplite. The HAADF-STEM image within [010] zone axis (Fig. 1 (e)) clearly shows that each regions marked by dash lines contains quiet different local atomic configurations. The arrangements of Fe atoms in region 1 and 3, which are corresponding with the nano-domains, are almost identical with a hexagon pattern as shown in blue and green inset of Fig. 1(e), however, the small region 2 (boundary between the region 1 and 3, red dashed line and red inset figure) contains additional bright signals at right of center of the hexagon patterns (marked sites with arrows. See red inset figure of Fig 1 (e)), indicating that the additional Fe ions exist in the area. The line scanning measurement between A and B points in Fig. 1(e) also proves the additional signals (black arrows in Fig. 1 (f)) and the lattice distances in region 2 are 0.519 nm, which is different with those in region 1 (0.584 nm), indicative of

different atomic configurations of the region 2.

The triplite LiFeSO_4F has two different octahedral sites, M1 and M2 sites as shown in S Fig. 1, coordinated with four oxygen and two fluorine atoms²⁵. In this structure, fluorine atoms are arranged with *cis* type in MO_4F_2 , whereas those adopt *trans* arrangement in tavorite LiFeSO_4F . The M1 sites are interconnected with M2 sites by two F-O edges and with M1 sites by one F-F edge and one O-O edge. Sulfur atoms are occupied in tetrahedral site which are corner shared with four M1 and four M2 sites. The reported results of the refinements of X-ray and neutron diffraction revealed that the two different cation sites (M1 and M2) are randomly filled with a equivalent amount of Fe and Li (50:50)⁷, indicating that various possible Li/Fe orderings can be coexisted within the triplite framework. The plausible local Li/Fe arrangements can be classified by the local connections between same cations, such as corner-shared (F-corner) and edge-shared (F-F edge, F-O edge, and O-O edge, **see supplementary Fig. S2**). It is important to know how Li and Fe ions are locally arranged in the triplite LiFeSO_4F because it inherently affect the Li diffusion and its electrochemistry, thus, several researches has attempted to reveal the overall Li/Fe arrangements of triplite. Among them, Yahia *et al.* successfully proved that the triplite LiFeSO_4F mainly formed with the corner-shared Li/Fe arrangement rather than edge-shared ones, claiming that the corner-shared Li/Fe ordering is thermodynamically more favorable than the other configurations when considering entropy term in room temperature. In addition, they showed that the theoretical redox voltage

of Fe ions (~ 3.9 V vs. Li) and simulated XRD pattern of the corner-shared arrangement have a better agreement with experiments than other arrangements²⁵.

Our TEM results are also coincidence with the previous literature that the synthesized LiFeSO_4F is mainly structured with the corner-shared configuration, which is depicted as the Fe-hexagon patterns at the HADDF-STEM analysis, as observed at the region 1 and 3 (See Figs 1 (e) and (h)). However, some small local areas, such as region 2, have additional Fe ions within the each Fe-hexagon rings, and we find out that the additional sites are well corresponding with the edge-shared Fe arrangements²⁵. (Hereinafter, the corner-shared, edge-shared, and mixed corner-/edge-shared Li/Fe arrangements are denoted as corner, edge and corner-edge mixed configuration, respectively, for convenience) The Figure 1(h) show a schematic Fe octahedral framework of the corner (left side) and corner-edge mixed configurations (overlapped configuration along the [010] axis, right side) **axis**. The Fe ions of edge configuration (deep-purple octahedral site in Figure 1 (h)) is positioned at the right center of hexagon Fe arrangement, which schematic well matched with the HADDF-STEM results of the additional Fe atom signals as shown in the inset of Figure 1 (e). It indicates that the 'boundary' between the pure corner configuration domains composed with the combination of corner- and edge-configurations, suspected as the origin of distorted structure signals due to lattice misfit between the corner and edge configurations (Fig. S2). Considering that the distorted signals are widely spread in almost particles

(See Fig. S1) and the $dq\ dV^{-1}$ analysis of triplite slightly shows ~ 4.1 V (vs. Li/Li⁺) peak (See Fig. S3), which is electrochemical signature of edge-shared configuration redox potential²⁵, the triplite particles are likely to contain considerable amount of edge configuration in their crystal structure. We conjectured that the local corner-edge mixed configuration is formed because of its little difference formation energies between edge- and corner-shared configurations²⁵, resulting in unexpected nano-domains in triplite crystalline.

It is well known that even a small amount of locally disordered atomic configuration or impurities sensitively affects the ionic mobility of electrode materials. For example, local Fe_{Li}-Li_{Fe} anti-site defects in LiFePO₄ impedes the movement of lithium ion, lowering their ionic diffusivity or resulting in capacity dead zone during cycling²⁹. Reflecting back on our observations, the local corner-edge mixed configuration also affect the overall Li ion mobility of LiFeSO₄F, thus, we calculated the activation barriers for Li migration in various configurations based on the TEM results (Fig. 2 and **Fig. S4**). In this calculation, we considered the corner configuration and three different edge configurations, edge#3, edge#4 and edge#5, as denoted by Yahia *et al.*²⁵. In the edge#3 configuration, same Li/Fe cations are interconnected by F-O edges, while the Fe atoms fully occupied either the M1 sites or M2 sites and those are one-dimensionally interconnected through the F-F and O-O edges in the edge#4 and edge#5 cases. Figure 2 shows the activation barriers for Li migration along various pathways in the corner, edge#3, edge#4 and

edge#5 configurations. The calculated activation barriers for Li migration along three dimensional pathways in the corner configuration are lower than 600 meV, similar to previous literature²⁷. Especially, one dimensional diffusion pathways along (110) and (1-10) have very low activation barriers (~ 350 meV), which is a comparable value with the LiFePO₄ electrode material, expecting that the pure corner-shared triplite can show relatively fast rate capability. On the other hand, most of Li migration pathways in the edge configurations have relatively higher activation barriers than those of corner one. For example, in the cases of edge#4 and edge#5 configurations, the activation barriers for Li migration along Li octahedral chains are higher than ~ 700 meV arisen from that the Li ion should pass through the F-F or O-O edges to avoid the strong electrostatic repulsion from Fe^{2+/3+} ions. Moreover, the activation barrier for Li migration across Li octahedral chains is even higher than 1200 meV account of strong electrostatic repulsion forces from Fe^{2+/3+} ions (**See Fig X**). Considering that the ionic diffusivity is inversely exponential to the activation barrier, it is expected that the edge configurations of LiFeSO₄F has much lower ionic diffusivity then that of the corner configuration. The activation barriers of Li migration within corner-edge mixed configuration can be approximated by those within edge configurations because hopping to edge configuration is likely to be a rate-limiting step for Li mobility within corner-edge configuration. According, our *ab initio* calculations indicates that Li ions can easily migrate inside the domains of the corner configuration, but those are hard to migrate across the domain

'boundaries' structured with the corner-edge mixed configurations, impeding the extraction and re-insertion of Li ions in the triplite LiFeSO_4F structure.

On the basis of the theoretical works in the previous section, we can infer that the local corner-edge mixed configuration can emerge the slow kinetic of triplite due to their relatively high diffusional activation barriers. Then, if we synthesize the pure corner-shared triplite or reduce the particle size of the particles to the nanoscale, Li transport kinetics would be significantly improved owing to the absence or less effect of local corner-edge configuration impeding the Li ion diffusion. Based on this simple idea, we prepared very fine triplite LiFeSO_4F nanoparticles *via* a simple mechanochemical method to verify the utilization of one Li extraction and insertion in the triplite LiFeSO_4F . The triplite LiFeSO_4F nanoparticles were fabricated by mixing and milling FeSO_4 and LiF at 400 RPM for 48 hours (see details in the experimental section), which can provide energy to nucleate nanosized LiFeSO_4F from FeSO_4 and LiF (Figure 3a). The obtained LiFeSO_4F was refined using Rietveld method and the detailed refinement results were shown in Figure 3b. The refined lattice parameters were in a good agreement with the triplite phase in the literature and other crystalline impurities were not observed²³. We further confirmed that no residual precursors and impurities in amorphous phase exist in the prepared powder using FT-IR analysis (Figure 3c). Also, no noticeable FT-IR vibration mode was observed at 1000 cm^{-1} , which is a characteristic feature of tavorite LiFeSO_4F ³⁰, indicating that the triplite

LiFeSO₄F was well obtained by the simple mechanochemical method. The as-synthesized LiFeSO₄F nanoparticles were characterized using TEM analysis, shown in Figure 3d. The particle size of the triplite LiFeSO₄F was about 5 nm, which is much smaller than the local corner-shared domain size of triplite synthesizing through the conventional solid-state method. From that, we expect there would be significantly less local Li/Fe domain boundaries in the nanoparticles or, at least, the effect of the local mixed configuration would be minimized.

Figure 3e shows the typical charge/discharge profile of nanosized LiFeSO₄F in triplite structure, wherein ~0.95 Li can be reversibly utilized delivering a capacity of ~143 mAh g⁻¹ at C/50 (1 C = 150 mA g⁻¹). The slope profile of nanosized LiFeSO₄F is attributable to the very fine particle size accompanying with structural defects which could be generated by the mechanochemical reaction²⁴. The atoms at the very surface can be rearranged because of the high surface energy, and the chemical potential of Li can vary significantly depending on the atomic arrangements and electronic defects. While it is possible to utilize almost one Li in the LiFeSO₄F nanoparticles with ~5 nm size (see red line in Figure 3e), only ~0.67 Li could be utilized when the particle size increases to >30 nm (see blue line in Figure 3e). In the nanosize of >30 nm, the utilization of Li ions in the triplite LiFeSO₄F is considerably inhibited. It should be noted that the sample of >30 nm was obtained by a heat treatment of the nanosized triplite LiFeSO₄F to grow particle size (see Fig. S5). The heat treatment temperature was controlled below the decomposition

temperature of the triplite LiFeSO_4F . Most notable here is that the increase in particle size significantly decreases the utilization of Li ions in the triplite LiFeSO_4F even if the increased particle size is still in nanoscale. Possible explanation is that the local corner-edge mixed configuration blocks the Li transport paths in the sample of >30 nm. When we simply assume the particle has a spherical shape with a diameter of 30 nm, there should be more than 70 local Li/Fe domains with a diameter of 7 nm (on the basis of the observations in the previous section). As a result, the increase in particle size of the triplite LiFeSO_4F can predominantly restrict the Li ion utilization for battery operations.

The electrochemical properties of the triplite LiFeSO_4F nanoparticles were further characterized as shown in Figure 3f-h. The triplite LiFeSO_4F nanoparticles deliver stable cycle life up to 40 cycles without noticeable capacity decay with high coulombic efficiency near 100 % and energy efficiency of ~ 93 % (Figure 3f and inset therein). Excellent electrochemical performance of the triplite LiFeSO_4F nanoparticles is more highlighted in rate capability (Figure 3g). The triplite LiFeSO_4F nanoparticles can retain ~ 80 mAh g^{-1} at 1C and ~ 60 mAh g^{-1} at 5 C. While the reversible capacity of the triplite LiFeSO_4F has been limited less than 120 mAh g^{-1} (~ 0.8 Li in the triplite LiFeSO_4F), to the best our knowledge, this work demonstrates for the first time the utilization of almost one Li extraction and insertion in the triplite LiFeSO_4F (Figure 3h). Because slightly slope profiles in our sample can deteriorate the energy density, we compared the energy density of our sample with those of previous literatures (Fig. S6). However,

the triplite LiFeSO_4F nanoparticles can approach to $\sim 500 \text{ Wh kg}^{-1}$ at C/50 and deliver higher energy density than literatures. This result demonstrates that our approach to reduce particle size smaller successfully improve the kinetics of the title compound and therefore its rate capability.

Conclusion.

In summary, we observed that the triplite LiFeSO_4F prepared through the conventional solid-state method contains some distorted crystal structures, revealing that it attributed from the local corner and edge mixed configurations using the HADDF-STEM analysis. The DFT calculation demonstrates that the edge-configurations of triplite have relatively higher Li ion diffusional activation barriers than that of corner-configuration, thus, even a small amount of edge-configuration can emerge the slow kinetic issue of triplite. On the basis of the conclusion, we adapt the nano-sizing strategy into triplite to avoid bottleneck effect arisen from edge configurations through the simple mechanochemical method. Notably, the nano-sized triplite LiFeSO_4F is, for the first time, utilized with almost one Li extraction and reinsertion, showing unprecedented high rate capability than previously available. Our results suggest that extraction and insertion of one Li in LiFeSO_4F , which is one of promising cathode materials with a high energy density, can be delivered with reducing the possibility of Li ion diffusion path crossing over to edge-configuration.

3. Experiments

3.1. Synthesis of bulk LiFeSO₄F

FeSO₄·7H₂O (99%, Aldrich) was heated at 100 °C for 3 hours (5% H₂/95% Ar mixture) to dehydrate and form FeSO₄·H₂O. Then, LiF and FeSO₄·H₂O (Fe/Li = 1/1.1 in molar ratio) were mixed by planetary ball milling at 300 RPM for 3 hours. Every 30 minutes, the planetary ball milling was stopped and rested for 10 minutes not to overheat the sample. As-obtained mixture was pelletized and heated at 350 °C for 24 hours under pure N₂ atmosphere (99.999%)

3.2. Fabrication of triplite LiFeSO₄F nanoparticles by mechanochemical method

Mechanochemical synthesis of triplite LiFeSO₄F was conducted using planetary milling (Fritsch, Pulverisette7). LiF (99%, Aldrich) and FeSO₄ were used as precursors. FeSO₄ was obtained by the dehydration of FeSO₄·7H₂O (99%, Aldrich) at 400 °C for 12 h under ambient argon. LiF and FeSO₄ were put into the container (Fe/Li = 1/1.2 in molar ratio), and the container was sealed in an argon-filled glove box. The powders were homogeneously mixed in the container using planetary milling at 400 RPM for 48 hours. The sample powder was mixed once more with graphite as a conductive carbon by planetary milling to increase the electronic conductivity at 400 RPM for 48 hours (graphite/sample = 1/5 in weight ratio).

3.3. Material characterization

The structure of sample was analyzed with an X-ray diffractometer (XRD, D2PHASER) using Cu K α radiation and a fourier transform infrared spectroscopy (FT-IR, Hyperion 3000). Structural parameters of sample was confirmed with a full pattern matching method using Fullprof programs³⁶. The morphology of the samples was verified by the means of high resolution transmission electron microscope (HR-TEM, JEM-2100F). HADDF-STEM images are obtained using Cs-corrected TEM (ARM 200F).

3.4. Electrochemical measurements

The LiFeSO₄F-graphite mixture (84 wt%), conductive carbon (6 wt%), and a polyvinylidene fluoride (PDVF) binder (10 wt%) were mixed in N-methyl-2-pyrrolidone (Aldrich, 99.5%) into a slurry. The slurry was casted onto aluminum foil and dried for use as a test electrode. A CR2016-type coin cell was assembled using the test electrode, an elemental lithium counter electrode, a separator (Celgard 2400), and an electrolyte of 1M LiPF₆ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 in volume ratio). The assembled cell was electrochemically tested using a battery cyler (WonA Tech, WBCS 3000) at a voltage range of 2.5-4.5V.

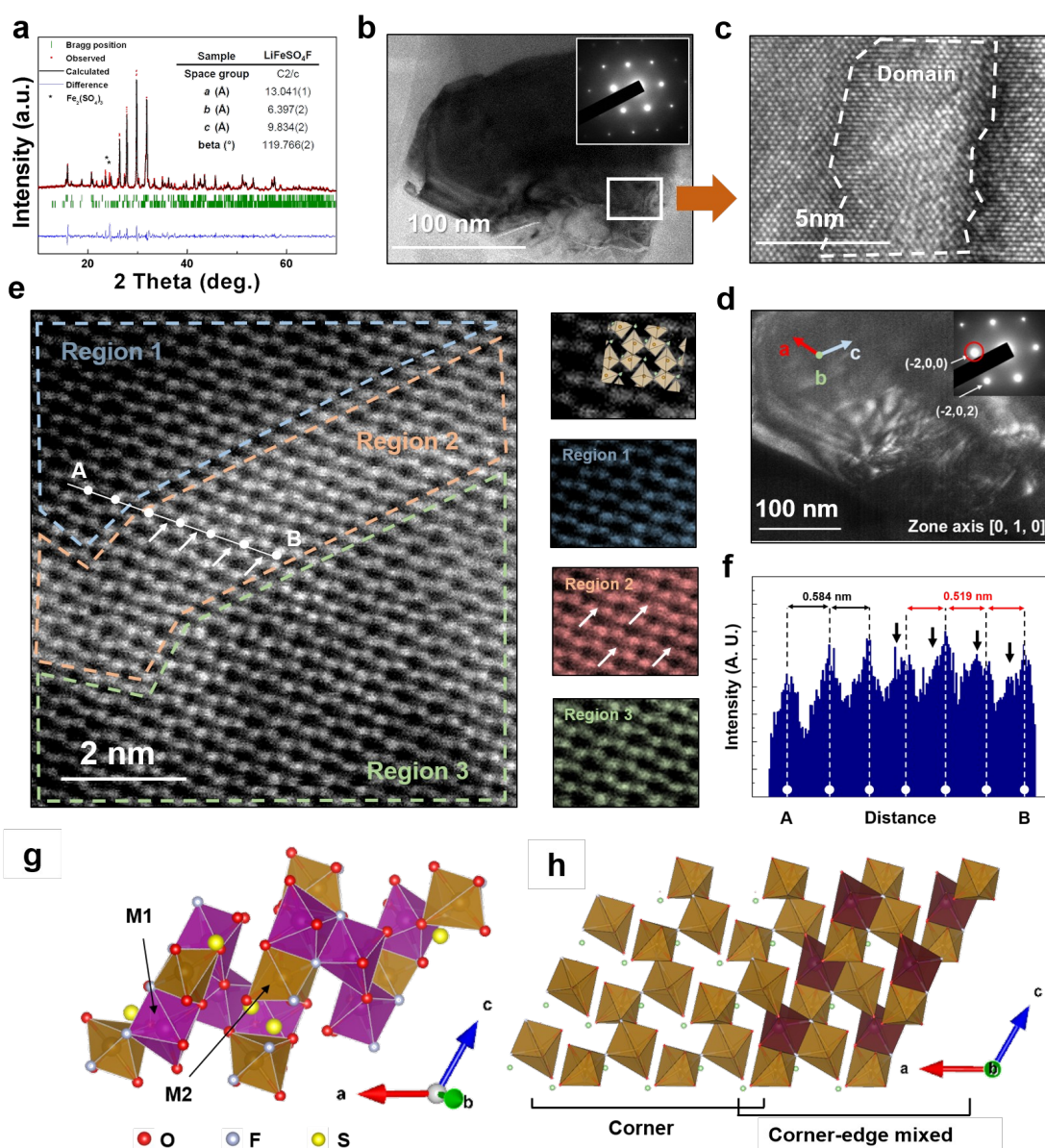


Figure 1. Structural characterizations of triplite synthesized by solid-state method (a) Full pattern matching results of prepared triplite powder with lattice parameters. (b) Single crystalline triplite TEM image with diffraction pattern. (c) HR-TEM image and (d) dark filed TEM image of [-200] zone of triplite. (e) HADDF-STEM image of triplite. Each regions exhibit quietly difference atomic structure as shown in inset figures. (f) Lattice signal from A to B in figure (e). The region 2 shows narrowed atomic distances and additional lattice signals. (g) M1 and M2 octahedral

framework of triplite. **(h)** Schematic of the domain boundary between corner and corner-edge mixed configurations of triplite-LiFeSO₄F. The brown and deep-purple octahedral sites indicate the corner Fe framework and additional Fe site from mixed Li/Fe ordering, respectively.

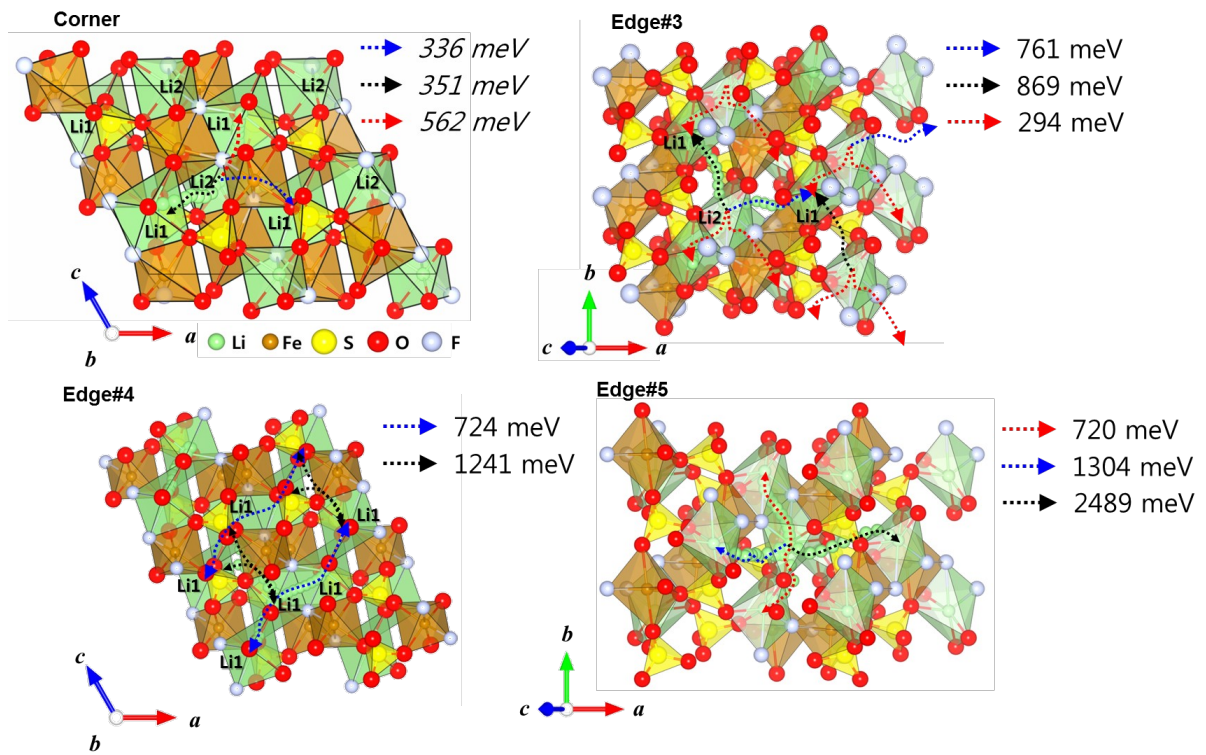


Figure 2.

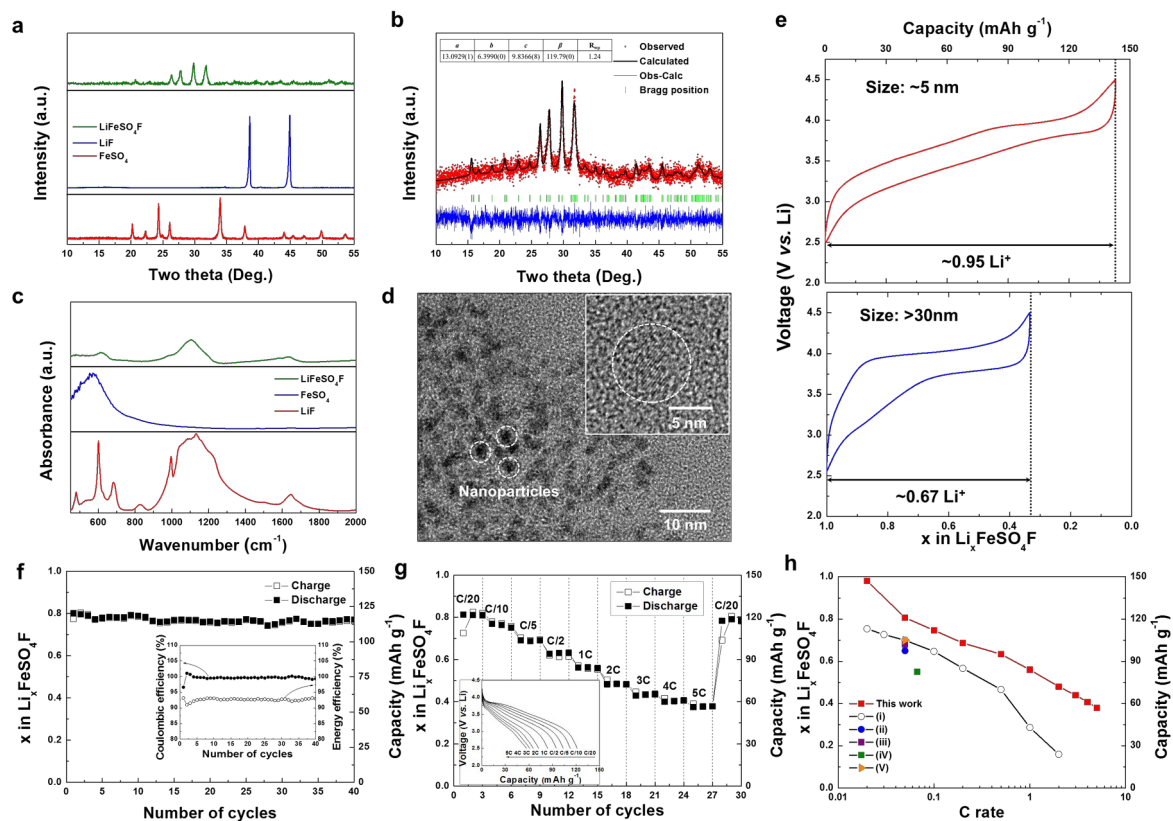


Figure 3. Characterization of the triplite LiFeSO_4F nanoparticles.

(a) XRD patterns of FeSO_4 (red), LiF (Blue), and the triplite LiFeSO_4F (green). **(b)** Rietveld refinement result. **(c)** FT-IR spectra of FeSO_4 (red), LiF (Blue), and the triplite LiFeSO_4F (green). **(d)** TEM image of the triplite LiFeSO_4F nanoparticles. **(e)** Typical charge/discharge profiles of the triplite LiFeSO_4F nanoparticles (~ 5 nm) and the triplite LiFeSO_4F obtained by the post heat treatment (>30 nm). **(f)** Cycle stability measurements (inset: coulombic and energy efficiency) **(g)** Rate capability (inset: charge/discharge profiles at various current rates) **(h)** Electrochemical performance comparison with literatures. (i) Ionic thermal method²³ (ii) spark plasma sintering synthesis²⁴ (iii) ultra-rapid microwave synthesis²¹ (iv) ionic thermal method (Zn-doped triplite)³⁵ (v) Solid-state method⁷.

References.