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Tavorite-type LiFeSO₄F is used to demonstrate the inherent moisture sensitivity issue of sulfate-based materials for Li-ion batteries.
Introduction

Commercialized by Sony in 1990, Li-ion batteries have transformed the global market for portable electronics. However, there is still an appreciable gap for Li-ion batteries to replace gasoline and conquer the automobile industry. Hence, research towards high energy density batteries with environmentally benign and inexpensive electrode materials has been urgently pursued. Today’s layered LiCoO2 and its derivative Li(Ni1/3Mn1/3Co1/3)O2, termed Li-NMC, are the industry leading positive electrode materials for most electronic gadgets because they offer the highest energy density; however, in large volume electric vehicle (EV) or grid applications, the implementation of these cathode materials will be hindered by materials abundance issues. The polyanionic compound LiFePO4 has received unprecedented attention as an alternative to layered oxide electrodes, and is becoming the most praised material for powering the next generation EVs because it provides safety, cost, and material abundance advantages.

However, due to its low voltage redox potential (3.45 V), the energy density of LiFePO4 cannot fully satisfy the requirement of energy-demanding applications. To partially alleviate this issue and enhance the potential of the Fe2+/Fe3+ redox couple, researchers successfully investigated the joint effect of adding electronegative F and replacing PO43− by a more electronegative sulfate polyanion SO42− to prepare a new LiFeSO4F phase. This phase shows polymorphism; depending on the synthesis conditions LiFeSO4F crystallizes either in theavorite or triplite structures, showing redox potentials of 3.6 and 3.9 V for the Fe2+/Fe3+ redox couple, respectively.4,5 Because of these elevated redox voltages, LiFeSO4F can rival LiFePO4.

Theavorite LiFeSO4F phase was synthesized by reacting FeSO4·H2O with LiF via a topotactic reaction (Eq. 1). Such a reaction, which preserves the structural framework of FeSO4·H2O, enlists the replacement of the water molecules by fluorine and the consequent ingress of Li+ in the open cavities to preserve electroneutrality.

\[
\text{FeSO}_4 \cdot \text{H}_2 \text{O} + \text{LiF} \rightarrow \text{LiFeSO}_4 \cdot \text{F} + \text{H}_2 \text{O}
\]

(1)

Since the compound is soluble in water, several water-free synthesis protocols have been reported, including solid-state, solvothermal,6,7 ionothermal,1 and so forth. Among them the ionothermal process based on the use of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-TFSI) is so far the best option to reproducibly synthesizeavorite LiFeSO4F with a reversible capacity approaching 140 mAh g−1 at a current density of C/10 (charge or discharge 1 Li+ in 10 hours). In the presence of ionic liquids, the water departure from FeSO4·H2O is postponed by the hydrophobic ionic liquid so as to cope with dissociation kinetics of LiF for enabling the proper reactivity rate of both F− and Li+ species with the precursor phase. To combat the high cost of ionic liquids, a solvothermal alternative was proposed that consists of using tetraethylene glycol (TTEG) as the solvent. It is
believed that using hydrophilic TTEG, in contrast to hydrophobic ionic liquid, can help improve the solubility of LiF at elevated temperatures, which is key to the success of the reaction.\(^9\) The tavorite LiFeSO\(_4\)F powders synthesized at 220°C via the easily scalable TTEG approach were shown to deliver a reversible capacity of 130 mAh g\(^{-1}\) at C/10 current density, which is lower than the 140 mAh g\(^{-1}\) obtained by the ionothermal route. Although other solvothermal synthetic approaches of LiFeSO\(_4\)F were also reported, observed electrode performances were rather inconsistent, indicative of a missing link hindering mastery of the synthesis of this fluorosulfate.\(^{6,9}\)

Previously, Ati and co-workers noticed the retro-conversion from LiFeSO\(_4\)F to FeSO\(_4\)·H\(_2\)O and LiF when trace amount of water was present in organic solvents when assembling batteries,\(^2\) but no detailed mechanism was provided. This phase instability reminds us of another member of the fluorosulfate family, LiZnSO\(_4\)F, which rapidly decomposes into ZnSO\(_4\)·H\(_2\)O and LiF in open environment. Both of these examples are pointing towards limited stability of these phases towards water. Moreover, sulfate-based electrode materials have long been criticized for their low moisture resistivity in general,\(^10,11\) but comprehensive understanding towards the structural evolution, and more importantly the corresponding changes in electrochemical performance have not been revealed. Thus, we decided to embark on a detailed study of the moisture effect on the synthesis, handling, and performances of tavorite LiFeSO\(_4\)F. Herein, we report the structural and electrochemical behaviors of LiFeSO\(_4\)F to be strongly dependent upon the room temperature relative humidity (RH), namely an increasing deterioration with increasing RH, and demonstrate that this finding can be generalized to other attractive sulfate-based electrodes whether they contain Li or Na as guest species. Through this study we also provide evidence for the electrochemically-driven \textit{in situ} formation of the already reported tavorite-type (Li)FeSO\(_4\)OH phase.

**Synthesis and characterization**

Equimolar amounts of FeSO\(_4\)·H\(_2\)O and LiF precursors were used to prepare tavorite LiFeSO\(_4\)F. Owing to both the extremely low solubility of LiF in organic solvents and the large particle size of commercial LiF powders (~10 µm), we decided to synthesize LiF powders via a precipitation method. NaF (Riedel-de Haën, 99%) and LiOH·H\(_2\)O (Sigma-Aldrich, 98%) solutions were used to precipitate LiF. The white powders were characterized by X-ray diffraction (XRD) for phase purity and by scanning electron microscopy (SEM) for morphology. The precipitates were single-phased LiF, as deduced from XRD data recorded from a Philips PW1830 powder X-ray diffractometer (Almelo, Netherlands) equipped with a Cu K\(\alpha\) radiation source (\(\lambda = 1.5406 \text{ Å}\)) and a graphite monochromator. From SEM data collected using a JEOL JEM 6700F field-emission scanning electron microscope (Tokyo, Japan) equipped with a cold emission gun and an energy-dispersive X-ray spectrometer, we could deduce that our LiF powders consist of ~1 µm diameter particles as compared to 5-10 µm for commercial LiF (Fig. S1 Electronic Supplementary Information). Therefore, owing to its highly divided character, this homemade LiF was adopted as the source of Li and F in the following synthesis.

Equally, owing to the importance of having base-forming precursors free of Fe\(^{3+}\) we synthesized our monohydrate FeSO\(_4\)·H\(_2\)O precursor following a routine protocol reported elsewhere.\(^1\) Commercial FeSO\(_4\)·7H\(_2\)O (Sigma-Aldrich, 99%) powders were re-precipitated in water-ethanol with the presence of ascorbic acid to remove Fe\(^{3+}\) ions. The recuperated powders were immersed in excess amount of ionic liquid EMiTFSI (C\(_3\)H\(_7\)N\(_2\)O\(_3\)S\(_2\), Shanghai Chengjie, \(\geqslant 98\%\)) and the temperature was slowly increased to and maintained at 100 °C for 2 hours to allow the formation of FeSO\(_4\)·H\(_2\)O. The recovered white powders were identified as pure FeSO\(_4\)·H\(_2\)O by XRD and confirmed to be free of Fe\(^{3+}\) as deduced by Mössbauer spectrum recorded in the transmission geometry in the constant acceleration mode.

Turning to the synthesis of tavorite-type LiFeSO\(_4\)F, the solid-state reaction was excluded from this investigation, with efforts focused instead on revisiting the less energy-intensive solvothermal and ionothermal synthesis protocols, owing to the difficulties encountered in routinely reproducing them. We surveyed various parameters, including solvent type, reaction time, and reaction temperature. Equimolar amounts of FeSO\(_4\)·H\(_2\)O and LiF were intimately mixed and placed in a 125 mL Teflon-lined stainless steel autoclave with 30 mL of TTEG (C\(_2\)H\(_5\)OH, Sigma-Aldrich, 99%) or 5 mL of EMiTFSI depending on the synthesis route. The autoclave was sealed under Ar and placed in a muffle furnace. The temperature was raised to 160 °C at 5 °C min\(^{-1}\) and then to desired temperatures (220-250 °C for solvothermal reaction and 280-310 °C for ionothermal reaction) at 1 °C min\(^{-1}\) for a predefined time (12-60 hours). When the reaction was completed, the furnace was cooled down to room temperature. The product was separated by centrifugation, washed several times with acetone or dichloromethane, and dried under vacuum at 50 °C overnight prior to being characterized for phase purity and oxidation state of iron.

The corresponding XRD patterns are shown in Fig. 1 (a)-(b). For the solvothermal reaction, phase-pure LiFeSO\(_4\)F could not be formed in 24 hours below 250 °C because of a sluggish reaction rate, while the formation of FeSO\(_4\) impurity can be observed when the temperature was too high. Similar phenomena were also observed in ionothermal syntheses, with tavorite-type LiFeSO\(_4\)F only forming in a very narrow temperature range. Improper reaction setting would inevitably lead to FeSO\(_4\)·H\(_2\)O or FeSO\(_4\) impurity phases whose characteristic peaks are located at 23.6° and 34.1°, respectively. No Fe\(^{3+}\) ion was detected by Mössbauer spectroscopy, implying the high purity of the as-prepared LiFeSO\(_4\)F samples. This survey shows that the best experimental condition for producing phase-pure LiFeSO\(_4\)F free of Fe\(^{3+}\) is to heat the precursors at 230 °C for 60 hours in TTEG, or at 305 °C for 24 hours in EMiTFSI. Such conditions were systematically used to prepare single-phased tavorite-type LiFeSO\(_4\)F powders to be studied in this paper.

Previous reports have mentioned that LiFeSO\(_4\)F could not be synthesized by hydrophilic ionic liquids such as 1-butyl-3-methylimidazolium trifluoromethanesulphonate (bmim-TFSI),\(^4\) and the difficulties in maintaining the low water content in highly hydrosopic TTEG. At this stage an obvious extension of our work was to check the impact of the reacting media water content on the progress of the topotactic reaction leading to the formation of LiFeSO\(_4\)F. LiFeSO\(_4\)F syntheses were conducted by i) systematically controlling the water content of both TTEG and EMiTFSI reacting media using a Metrohm 831 Karl Fischer coulometer (Ionenstrasse, Switzerland), and ii) monitoring the room temperature (25 °C) RH of the working place which is geographically dependent and can easily reach more than 80% in certain places (e.g. Hong Kong, where most of this work was carried out). In practice, moist Ar gas was bubbled into TTEG to increase its water content from 540 to 3100 ppm according to Karl Fischer measurements. As was anticipated, we were unable to synthesize phase-pure LiFeSO\(_4\)F when the solvent water content was increased, specifically at contents greater than 1200 ppm. A significantly reduced reaction rate was observed, which signified the strong impact of water content of the reaction media on the synthesis of LiFeSO\(_4\)F. This parameter has not adequately captured researchers’ attention, which explains why the reported data are limited and inconsistent.
Electrochemical performance

The electrochemical performance of as-synthesized LiFeSO₄F powders was assessed in both 2025-type coin cells and Swagelok-type cells. To prepare coin cell electrodes, 70 wt% of active material was mixed with 20 wt% of conductive carbon Super P and 10 wt% of polyvinylidene fluoride (PVDF) binder in 1:2 w/w N-methyl-2-pyrrolidinone (NMP) solution by planetary ball-milling at 400 rpm for 2 hours. The resultant slurry was cast on Al foils in a room without specific humidity control. To prepare Swagelok cathodes, 80 wt% of LiFeSO₄F and 20 wt% of carbon Super P (denoted hereafter as LiFeSO₄F-C) were intimately mixed by ball-milling in Ar. Both type of cells were assembled in an Ar-filled glovebox with O₂ and H₂O contents less than 1 ppm, using cast Al foil (coin cell) or composite powders (Swagelok) as the cathode, metallic Li as the anode, 1 M of LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) as the electrolyte, and Celgard 2325 membrane (coin cell) or two pieces of Whatman GF/D glass fiber (Swagelok) as the separator. Cells were cycled on a LAND membrane (coin cell) or two pieces of Whatman GF/D glass fiber in galvanostatic mode between 4.5 and 2.2 V vs. Li at 25 °C using a current density of C/20.

Fig. 1 XRD screening of synthesis conditions of tavorite-type LiFeSO₄F by (a) solvothermal and (b) ionothermal methods, and particle morphology of samples synthesized by optimized (c) solvothermal and (d) ionothermal protocols.

Fig. 2 First cycle performance of ionothermal (black) and solvothermal (red) samples at a current density of C/20 (a) in Swagelok-type cells and (b) in coin cells.

Fig. 2 (a) compares the performances of LiFeSO₄F samples prepared via ionothermal and solvothermal routes in Swagelok-type cells. The ionthermally-obtained sample outperforms the solvothermally-prepared sample, which can be well explained from morphology and conductivity perspectives. As compared in Fig. 1 (c)-(d), the as-synthesized ionothermal sample has a much smaller average particle size (~300 nm) than the solvothermal one (~850 nm). Smaller particles lead to a shortened diffusion path for Li⁺ and to better electrode kinetics in agreement with our experimental results. Another possibility to account for such a difference could be the presence of an EMI-TFSI grafting layer at the surface of LiFeSO₄F which will enhance the ionic conductivity, as previously reported for LiZnSO₄F. This would contrast with an ionic blocking thin layer of TTEG at the surface of LiFeSO₄F made in glycol-based media, although such a possibility is therefore quite unlikely given that repeatedly washing the sample yielded no changes in performance.

A similar trend in the electrochemical performance between ionothermal and solvothermal samples was found as expected when the tests were performed using coin cells. In contrast, their poor overall performances (limited reversible capacity, larger polarization) as compared to Swagelok hardware came as a total surprise. It should be noted that the RH was not strictly controlled in the course of coin cell assembly, which further implicates the limited chemical stability of LiFeSO₄F against water.

To shed some light on this issue we decided to study the effect of water on the structural stability of LiFeSO₄F when aged in various RH. Thus we quantitatively mimicked humid environments using saturated salt solutions that are commonly known to produce stable RH at certain temperatures in a closed system. LiFeSO₄F powders were left for various amounts of time in desiccators containing Mg(NO₃)₂, NH₄NO₃, NaCl, and KCl saturated solutions with autogenous equilibrium RH of 53%, 62%, 75%, and 85%, respectively at 25 °C as determined by a hygrometer within an accuracy of ±1%. Fig. 3 shows the evolution of the XRD patterns of powders left for 36 hours under different RH. Strikingly, we noted a rapid disappearance of the Bragg peaks pertaining to the tavorite phase with increasing humidity so that by 75% RH LiFeSO₄F has totally decomposed. At this stage it is worth mentioning that a significantly accelerated decomposition rate was found for ball-milled LiFeSO₄F-C electrodes due to their highly divided nature. XRD patterns of the fully transformed samples indicate the coexistence of multiple hydrated sulfate phases (FeSO₄·nH₂O, with n =1, 4, and 7). Their relative amounts, quantified by Rietveld...
refinement\textsuperscript{16} performed with the FullProf suite\textsuperscript{17} (Fig. S2), were found to depend upon the exposure time to humidity, with the $n = 7$ member dominating at longer exposures.

Swagelok-type cells containing LiFeSO$_4$F samples aged under various RH were assembled and their performances are shown in Fig. 4. For fresh composite powders without any contact to moisture, the voltage composition curve and its accompanying derivative in Fig. 4 (a) indicate, in agreement with the literature, a 3.6 V vs. Li plateau which corresponds to the reversible uptake of ~0.85 Li$^+$. This drastically contrasts with the sloping voltage profile recorded for LiFeSO$_4$F-C powders left in 85\% RH for 2 hours in Fig. 4 (b). Upon cycling, the derivative curve (Fig. 4 (b) right) shows the onset of two additional redox pairs located near 3.3 and 3.1 V. Whether purely coincidental or not, such peaks were found to correspond to the electrochemical signatures of tavorite-type (Li)FeSO$_4$OH vs. Li,\textsuperscript{18} hence suggesting the \textit{in situ} formation of the electrochemically active (Li)FeSO$_4$OH during the cycling of LiFeSO$_4$F samples exposed to highly humid environment. This does not come as a full surprise since both OH$^-$ and F$^-$ species share various similarities and can co-exist in minerals such as triplite (Mg,Fe)$_2$(PO$_4$)(F,OH), creedeite Ca$_3$Al$_2$SO$_4$(F,OH)·2H$_2$O, and norbergite Mg$_3$(SiO$_4$)(F,OH)$_2$.

Nevertheless, the mechanism of this transformation calls for better understanding of the stability of the tavorite LiFeSO$_4$F phase.

To grasp further insight into the \textit{in situ} formation of (Li)FeSO$_4$OH and test whether F$^-$ was involved in this process we performed a similar experiment using a F$^-$-free sulfate electrode exposed to the same degree of RH (85\%) as previously described for LiFeSO$_4$F. We selected FeSO$_4$ since we experienced its progressive capture of water when placed in high RH environment. Fig. 5 shows the electrochemical performance of electrodes that were made out of this sample and tested in coin cells. The cells were started on charge. The voltage increased continuously up to 4.5 V. In contrast, the discharge curve shows a step-wise profile with the appearance of the 3.3 and 3.1 V plateaus corresponding to (Li)FeSO$_4$OH. The subsequent curves mirror nicely the first discharge but drastically deviate from the first charge, suggesting that the electrode has undergone major structural/compositional change during the first charge. Once this transformation is done, the electrode shows a sustained reversibility of ~100 mAh g$^{-1}$ while maintaining the characteristics of (Li)FeSO$_4$OH, hence providing an irreproducible proof for its \textit{in situ} formation. It is worth noting that similar charge and discharge profiles were also observed by two other groups,\textsuperscript{19,20} but neither of them checked the moisture sensitivity issue nor reported the signature of (Li)FeSO$_4$OH in their voltage curves.
This is indicative of a better resistance of the tavorite phase against moisture, in good agreement with calorimetry measurements which have shown that among the two polymorphs the triplite phase disappeared after 8 and 200 hours, respectively while the triplite transforms into successive hydrated iron sulfate phases. Fig. 6 XRD patterns of (a) tavorite and (b) triplite LiFeSO₄ powders left in 85% RH at 25 °C as a function of time.

The aforementioned XRD and electrochemical studies strongly indicate that a pre-requisite for achieving optimized performance with tavorite-type LiFeSO₄F is to operate in a dry reaction media (water content < 1000 ppm). At this stage, a legitimate question is whether the triplite polymorph, which offers a 300 mV advantage in methodology and found a similar behavior with a lower degradation rate as shown by the XRD patterns collected as a function of time in 85% RH. Rietveld refinements indicate that both compounds transforms into successive hydrated iron sulfate phases. Note that for 85% (Fig. 6) and 62% RH (Fig. S3), the tavorite phase fully disappeared after 8 and 200 hours, respectively while the triplite phase was still present. This is indicative of a better resistance of the triplite phase against moisture, in good agreement with calorimetry measurements which have shown that among the two polymorphs the triplite phase is thermodynamically more stable. We also generalized our study to other Li(Na)-based sulfate phases (LiFeSO₄OH₂, FeSO₄OH, Fe₂O(SO₄)₂, Li₂FeSO₄O₂) polymorphs and NaFe₂(SO₄)₄ (Fig. 7). Apart from the Fe₂O(SO₄)₂ oxysulfate, the others were shown to react with water as well with different degrees of severity depending upon their structure and state of division, thus leading to the general conclusion that moisture sensitivity is inherent to sulfate-based electrodes. This does not come as a surprise as sulfates are known to be soluble in water, because oxygen atoms in both SO₄²⁻ and H₂O have comparable Lewis basicity (~0.17 v.u.), which is for instance not the case for phosphates (~0.25 v.u.). The insolvency of the oxysulfate Fe₂O(SO₄)₂ may therefore be explained by the presence of an oxygen atom that does not belong to any sulfate group, which therefore presents a different Lewis basicity and limits its moisture sensitivity.

Discussion and conclusion

We have reported the extreme sensitivity of LiFeSO₄F and sulfates in general to moisture, and revealed the feasibility to electrochemically trigger the in situ formation of (Li)FeSO₄OH. An understanding of the mechanism(s) by which such compounds react with water is a critical step towards proposing solutions for their practical use as electrodes. Similarly, identifying the reacting steps involved in the formation of (Li)FeSO₄OH could enable us to prepare other novel materials. Both of these points are discussed below.

Let’s first turn to the synthesis of tavorite LiFeSO₄F that relies on a topotactic reaction enlisting a quasi-equilibrium state between FeSO₄·H₂O and LiFeSO₄ (Eq. 1). When H₂O is present in great excess, according to Le Chatelier’s principle, the backward reaction (Eq. 2) is preferred with LiF precipitated as dead weight. In addition, Mitchell has discovered that when the RH is higher than 65%, FeSO₄·H₂O will spontaneously absorb water at 25 °C (Eqs. 3 and 4) to respectively form FeSO₄·4H₂O and FeSO₄·7H₂O. Thus, the continuous consumption of FeSO₄·H₂O further promotes the spinodal decomposition of LiFeSO₄F, as illustrated in Fig. 8. Lastly, based on the tiny amount of Li₂SO₄·H₂O observed among the decomposition products, the feasibility of having a competing degradation path in accordance with Eq. 5 cannot be fully disregarded.
When electrodes made out of these water-bearing LiFeSO$_4$F materials are placed in contact with electrolyte, H$_2$O molecules released from i) surface adsorption and ii) FeSO$_4$·4H$_2$O and FeSO$_4$·7H$_2$O dehydration will induce LiPF$_6$ decomposition and HF formation.$^{29,30}$ This corrosive species will attack the electrode, leading to metal dissolution and performance degradation. Although switching to LiClO$_4$ electrolytes may prevent HF formation, the degradation of the cathode material at highly humid environment is always irreversible. A detailed analysis on water content is provided in the supporting information (Fig. S4).

From this study, two RH domains appear critical for handling LiFeSO$_4$F: for RH ≤ 50% spinodal decomposition is retarded, whereas decomposition occurs at an exceedingly fast rate for RH ≥ 65%. Therefore, the RH should be strictly controlled when processing LiFeSO$_4$F in order to retain good electrode performance. Alternatively, coating a protective layer on particle surfaces may also improve moisture resistivity. Hence, it does not come as a surprise that enrobing the powder by a layer of conductive polymer poly-3,4-ethylenedioxythiophene (PEDOT) has led to enhanced performance for this material.$^9$ We performed preliminary polymer coating on tavorite LiFeSO$_4$F, and confirmed, using a similar test protocol a lower decomposition rate compared to the pristine sample. Another option is to incorporate the tavorite LiFeSO$_4$F phase with carbonaceous materials, such as hierarchical graphene-nanostructuring$^{31}$ and low temperature carbon coating.$^{32}$ We effectively experienced that these treatments can help mitigate the impact of moisture.

Lastly, to shed light on the formation of the F-free (Li)FeSO$_4$OH, we examined the role of H$_2$O and here we provide a possible interpretation. Introduction of H$_2$O to non-aqueous}

$$\text{LiFeSO}_4\text{F} + \text{H}_2\text{O} \rightarrow \text{FeSO}_4\cdot \text{H}_2\text{O} + \text{LiF}$$

$$\text{FeSO}_4\cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow \text{FeSO}_4\cdot 4\text{H}_2\text{O}$$

$$\text{FeSO}_4\cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O} \rightarrow \text{FeSO}_4\cdot 7\text{H}_2\text{O}$$

$$2\text{LiFeSO}_4\cdot \text{F} + 2\text{H}_2\text{O} \rightarrow \text{Li}_2\text{SO}_4\cdot \text{H}_2\text{O} + \text{FeSO}_4\cdot \text{H}_2\text{O} + \text{FeF}_3$$

$\text{Fig. 8 Schematic illustration of the decomposition & hydration processes of LiFeSO}_4\text{F} in humid environment (RH > 65%), and the dehydration of FeSO}_4\cdot 7\text{H}_2\text{O} in the electrolyte.}$
(Li)FeSO$_4$OH from both differential capacity curves and Mössbauer spectra.

In conclusion, we have reported reproducible production of phase-pure tavorite LiFeSO$_4$F using both solvothermal and ionothermal methods, and demonstrated via XRD that the phase is extremely sensitive to moisture. While the material remains intact for several months when the RH is below 50%, there is a full and rapid decomposition of LiFeSO$_4$F into FeSO$_4$$\cdot$H$_2$O ($n$ = 1, 4, 7) and LiF in highly humid environment (>62% RH at 25 °C). Special cares will have to be exercised in processing sulfates for large-scale applications. Water sources along the synthesis and processing of LiFeSO$_4$F electrodes should be maximally eliminated. Nevertheless, such manufacturing difficulties can be mitigated via the use of surface modified particles with PEDOT, carbon coating, hierarchical nanostructuring, or other techniques that remain to be designed. This moisture reactivity, including both decomposition and hydration reactions, is applicable to sulfate-based electrode materials in general; the only exception we found is the oxysulfate phase, Fe$_2$(O$_2$SO$_4$)$_3$, which does not react with moisture. Lastly, the feasibility to electrochemically form (Li)FeSO$_4$OH in an in situ way, offers another approach to stabilizing metastable phases that has been poorly explored to date.

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**Notes and references**