



## Formation of *tavorite*-type $\text{LiFeSO}_4\text{F}$ followed by *in situ* X-ray diffraction



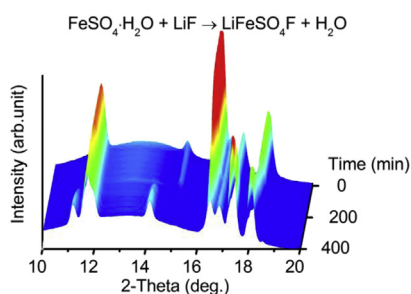
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### HIGHLIGHTS

- *In situ* XRD was used to follow the formation of *tavorite*  $\text{LiFeSO}_4\text{F}$  in a glycol medium.
- Two different precursor mixtures,  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{LiF}$ , and  $\text{Li}_2\text{SO}_4 + \text{FeF}_2$ , were used.
- The formation of *tavorite*  $\text{LiFeSO}_4\text{F}$  always occurs through  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ .

### GRAPHICAL ABSTRACT



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### ABSTRACT

The *tavorite*-type polymorph of  $\text{LiFeSO}_4\text{F}$  has recently attracted substantial attention as a positive electrode material for lithium ion batteries. The synthesis of this material is generally considered to rely on a topotactic exchange of water ( $\text{H}_2\text{O}$ ) for lithium (Li) and fluorine (F) within the structurally similar hydrated iron sulfate precursor ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ) when reacted with lithium fluoride (LiF). However, there have also been discussions in the literature regarding the possibility of a non-topotactic reaction mechanism between lithium sulfate ( $\text{Li}_2\text{SO}_4$ ) and iron fluoride ( $\text{FeF}_2$ ) in tetraethylene glycol (TEG) as reaction medium. In this work, we use *in situ* X-ray diffraction to continuously follow the formation of  $\text{LiFeSO}_4\text{F}$  from the two suggested precursor mixtures in a setup aimed to mimic the conditions of a solvothermal autoclave synthesis. It is demonstrated that  $\text{LiFeSO}_4\text{F}$  is formed directly from  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and LiF, in agreement with the proposed topotactic mechanism. The  $\text{Li}_2\text{SO}_4$  and  $\text{FeF}_2$  precursors, on the other hand, are shown to rapidly transform into  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and LiF with the water originating from the highly hygroscopic TEG before a subsequent formation of  $\text{LiFeSO}_4\text{F}$  is initiated. The results highlight the importance of the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  precursor in obtaining the *tavorite*-type  $\text{LiFeSO}_4\text{F}$ , as it is observed in both reaction routes.

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## 1. Introduction

The increasing interest in exploitation of renewable energy sources, such as solar and wind power, as well as the shift towards electric transportation technologies for decreased  $\text{CO}_2$  emissions, have significantly intensified the academic and industrial

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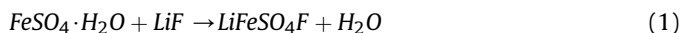
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development of suitable energy storage systems. For mobile applications in particular, lithium ion (Li-ion) batteries represent one of the most promising alternatives due to their high gravimetric and volumetric energy/power densities. However, to meet the demands on safety, cost, cycling life time and green chemistries, the research on new battery components with improved properties is constantly on-going.

The development of *olivine*-type  $\text{LiFePO}_4$  [1] represented a significantly improved alternative as positive electrode material based on the electrochemical behavior and the improved safety performance compared to the conventionally employed  $\text{LiCoO}_2$ ,  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$ . Moreover, it triggered a shift of focus towards insertion materials based on “polyanionic” frameworks, which has led to the discovery of several other interesting compounds such as  $\text{Li}_2\text{FeSiO}_4$  [2],  $\text{LiFeBO}_3$  [3],  $\text{LiVPO}_4\text{F}$  [4], and more recently,  $\text{LiFeSO}_4\text{F}$  [5]. The latter has attracted attention among battery scientists as a result of its interesting structural and electrochemical characteristics [5–13], and depending on the synthesis conditions the material crystallizes in either a meta-stable *tavorite* or the thermodynamically favored *triplite*-type structure [14,15]. Both polymorphs display promising electrochemical performance with record-high potentials for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple at 3.6 and 3.9 V (vs.  $\text{Li}/\text{Li}^+$ ) in the *tavorite* and *triplite* structure-type, respectively [5–7,10].

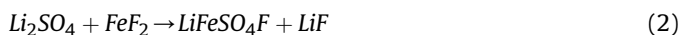
Focusing now solely on the *tavorite*-type  $\text{LiFeSO}_4\text{F}$  (named after the eponymous mineral with the composition  $\text{LiFePO}_4\text{OH}$  [16]), the synthesis of this polymorph is generally considered to rely on a kinetically controlled topotactic reaction, observed when starting from the precursors  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{LiF}$  [5,8] as described by the following reaction scheme:



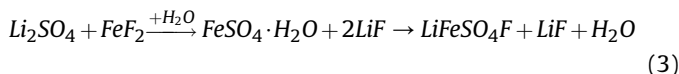
The feasibility of this reaction path has been suggested to be rooted in the strong structural resemblance between the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  precursor and the final product  $\text{LiFeSO}_4\text{F}$  [5,8], as illustrated in Fig. 1. It is claimed that if the rate of water removal from  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  is

slower than the process of topotactic insertion of  $\text{LiF}$ , the overall structural features of the former precursor will be preserved and promote the formation of the *tavorite*-type  $\text{LiFeSO}_4\text{F}$  [5,8]. If, on the other hand, the water removal from the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  precursor is too fast, the compound will collapse into anhydrous  $\text{FeSO}_4$  which can no longer be utilized to obtain the *tavorite*-type polymorph due to their structural differences [8]. The rate of dehydration is effectively controlled by the applied temperature to the reaction mixture in combination with the nature (degree of hydrophilicity) of the utilized reaction medium, where ionic liquids [5], glycols [8], and polymers [17] all have been shown to be viable alternatives. These solvent assisted syntheses routes typically require reaction times in the range of 7–60 h. Solid-state preparations have also been successful, but requires even longer reaction times of about 72 h as well as a large excess of the  $\text{LiF}$  precursor [18].

In addition to the reaction mechanism described above, a recent report [15] suggested that the *tavorite* polymorph of  $\text{LiFeSO}_4\text{F}$  can also be formed through a non-topotactic reaction, involving dissolution-precipitation of the precursors  $\text{Li}_2\text{SO}_4$  and  $\text{FeF}_2$  when heated in tetraethylene glycol (TEG) as reaction medium, as described by the following reaction scheme:



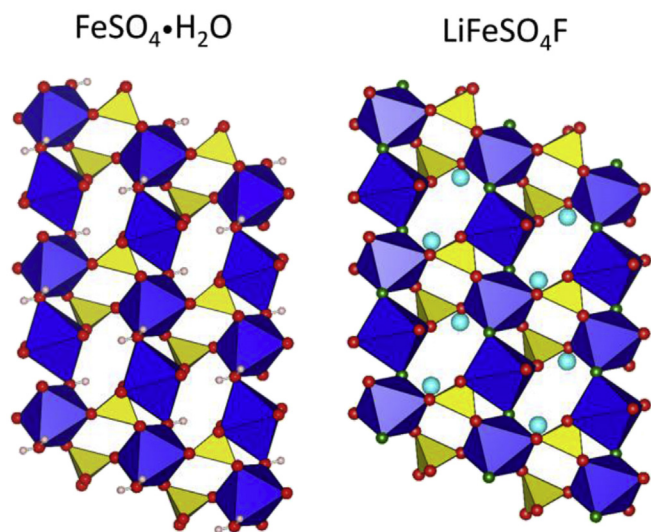
It was thus claimed that there was no role of water in this reaction mechanism, in contrast to the profound role it plays in the topotactic alternative. Shortly thereafter, another report [14] questioned the non-topotactic reaction mechanism as *ex situ* X-ray diffraction analyses at different time intervals during the reproduction of this synthesis route showed the formation of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  as an intermediate phase together with  $\text{LiF}$  before reaching the  $\text{LiFeSO}_4\text{F}$  product, indicating that reaction scheme (2) should instead be described as:



The water was believed to be introduced to the reaction environment either through the highly hygroscopic precursors or the TEG reaction medium. This hypothesis was strengthened by the inability to succeed with the reaction in solid state under dry conditions [14]. Thus, it was highlighted that the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  precursor has a critical role in the growth of *tavorite*-type  $\text{LiFeSO}_4\text{F}$ .

Since *ex situ* X-ray diffraction (XRD) only provides structural information about the starting precursors and intermediates/products at ambient conditions, *in situ* studies are necessary to obtain information about the reaction process in actual synthesis conditions. Such *in situ* XRD studies are fairly uncommon within the research field of Li-ion batteries, but a few recent reports have demonstrated the possibility of probing phase transitions in solution-assisted reactions during the synthesis of electrode materials such as  $\text{BiFeO}_3$  [19] and  $\text{LiFePO}_4$  [20,21]. In the case of  $\text{LiFePO}_4$ , the *in situ* XRD study enabled identification of a new intermediate phase,  $\text{FeC}_2\text{O}_4 \cdot \text{C}_2\text{H}_6\text{O}_2$ , formed during a solvothermal reaction between  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{LiH}_2\text{PO}_4$  in ethylene glycol [21]. Thus, the study exemplifies the benefits and importance of using *in situ* techniques, as such a mechanism could be difficult to discover by *ex situ* characterizations alone.

In the light of the above presented debate regarding the synthesis of  $\text{LiFeSO}_4\text{F}$ , we are here taking a closer look into the reaction processes with *in situ* X-ray diffraction (XRD) using a synchrotron radiation source. This is carried out by reacting the proposed precursor mixtures,  $\text{FeSO}_4 \cdot \text{H}_2\text{O} + \text{LiF}$ , and  $\text{Li}_2\text{SO}_4 + \text{FeF}_2$ , respectively, in a setup mimicking the conditions of a conventional solvothermal



**Fig. 1.** The illustration highlights the strong structural similarities between the *tavorite*-type  $\text{LiFeSO}_4\text{F}$  product and the  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  precursor involved in the topotactic reaction route. The  $\text{SO}_4$  tetrahedra are colored in yellow, oxygen atoms in red, hydrogen atoms in white, fluorine atoms in green, and lithium atoms in turquoise. The iron atoms are located in the center of the blue octahedra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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