

A Mössbauer spectroscopy study of polyol synthesized *tavorite* LiFeSO₄F

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Abstract The *tavorite* polymorph of LiFeSO₄F has attracted considerable attention as a cathode material for lithium ion batteries due to interesting structural and electrochemical characteristics. For the analysis of such iron-based electrode materials, Mössbauer spectroscopy has become an important and highly useful tool. In this work, we perform a detailed Mössbauer study of pristine *tavorite* LiFeSO₄F prepared by an optimized synthesis in tetraethylene glycol as reaction media. In contrast to many reported results, we demonstrate the use of an asymmetric fitting model for the inner doublet of the spectrum, which is coupled to the structural properties of the compound. Moreover, we discuss a new approach of ascribing the Fe²⁺-doublets to the two distinct crystallographic iron sites of *tavorite* LiFeSO₄F by comparing the Mössbauer signal intensities with the expected *f*-factors for the corresponding iron atom.

Keywords Lithium ion battery · *Tavorite* LiFeSO₄F · Mössbauer spectroscopy

1 Introduction

The inevitable need to decrease the global dependence on fossil fuels for a more sustainable future has significantly intensified the development of renewable energy systems, such as wind and solar power, as well as driven the shift towards electrical transportation. In such applications, rechargeable lithium ion (Li-ion) batteries are currently representing one of the most promising strategies for large scale energy storage. These outlooks have triggered an increased activity to further develop the

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battery components, where research on new electrode materials has been a major focus.

The class of iron-based cathode materials containing polyatomic anions was introduced with the discovery of LiFePO_4 [1], which showed electrochemical activity at 3.45 V for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple against Li/Li^+ , with good reversibility and improved safety compared to conventional metal oxide compounds such as LiCoO_2 . Lately, the discovery of LiFeSO_4F [2] has demonstrated the possibility of raising the potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple within Li-insertion compounds even higher. The two known polymorphs of pure LiFeSO_4F [2–4], isostructural with the minerals *tavorite* and *triplite*, are operating at 3.6 V and 3.9 V vs. Li/Li^+ , respectively. Despite having the lower potential, the *tavorite* polymorph is particularly interesting from an electrochemical point of view due to its three-dimensional channel framework facilitating fast lithium transport, which is suitable for high rate applications. The synthesis of *tavorite* LiFeSO_4F relies on a kinetically controlled topotactic reaction [2, 5] between the structurally similar $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ precursor and LiF , which can be carried out in different reaction media, including ionic liquid [2], polymers [6], and glycol [7], or by a solid-state preparation [8].

In studies of iron-based compounds, ^{57}Fe Mössbauer spectroscopy (MS) is an ideal characterization tool for quantifying the purity of synthesized materials, probing the changes of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ -ratio during battery operation, and retrieving qualitative information about chemical environments and atomic order. Several Mössbauer studies have been carried out on *tavorite* LiFeSO_4F [8–10] and closely related materials [11, 12]. While the overall quality and features of the reported spectra have varied, they have generally been fitted with a similar standard model consisting of two symmetrical doublets. Different strategies have also been proposed to ascribe the Mössbauer doublets to the crystallographic iron sites of the structure based on the average bond distances within, and the distortion of, the iron-ligand polyhedra, and on the iron-lithium distances [8, 12].

In this study, we discuss the details of the Mössbauer spectrum of pristine *tavorite* LiFeSO_4F prepared by an optimized synthesis in tetraethylene glycol (TEG), and couple these to the crystal structure of the compound. We demonstrate that this synthesis method generates well ordered samples with sharp and resolved spectral peaks, where a modified fitting model is needed compared to previously published studies. Moreover, we propose a different approach of ascribing the Mössbauer doublets to the crystallographic iron sites, not earlier discussed for this compound.

2 Experimental details

2.1 Sample preparation

LiFeSO_4F samples were prepared by using a low temperature solvothermal approach [7]. First, commercially available $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, >99 %) was partially dehydrated under constant flow of N_2 at 100 °C for 3 h to produce phase pure $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. The $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ precursor was then mixed with a slight excess (1.15:1) of LiF (Alfa Aesar, >99 %) by ball-milling for 1 h in acetone. Batches of approximately 1 g of this powder mixture were then dispersed in 30 mL of TEG by stirring for 30 min. The dispersions were then heated in 45 mL Teflon-lined steel

autoclaves (Parr Instruments) using different temperature programs depending on the desired purity of the final product. To obtain phase pure LiFeSO₄F, avoiding the common impurities FeSO₄ and FeSO₄·H₂O, an optimized program was used where the reactant dispersion was heated with a slow temperature ramp (RT–200 °C at 1.5 °C/min and 200–220 °C at 0.07 °C/min), kept at 220 °C for 50 h, and finally ramped to 230 °C (0.17 °C/min) before allowing a slow cooling. LiFeSO₄F containing intentional FeSO₄·H₂O impurity was prepared in a similar way, but was kept at 220 °C for only 20 h, and was then slowly cooled to RT without employing the last temperature ramping step. The products, having an ivory white color, were then collected by centrifugation, washed with acetone, dried at room temperature under N₂ flow, and finally stored under Ar atmosphere. In addition, anhydrous FeSO₄ was prepared for a Mössbauer reference measurement by dehydration of FeSO₄·7H₂O under a constant flow of N₂ at 300 °C for 3 h.

2.2 Mössbauer spectroscopy

The Mössbauer spectra were collected in a transmission mode using a computerized spectrometer of constant acceleration type with a ⁵⁷CoRh source. The unfolded data was stored using 1024 memory cells. The absorbers were prepared by mixing ~30 mg of active material with a suitable amount of boron nitride, which was then spread evenly over a absorber disc (13 mm in diameter). The amount of active material was chosen to give optimal thicknesses, resulting in maximal signal-to-noise ratios. Due to the moisture sensitivity of the studied compound, the absorbers were kept under a flow of N₂ during the measurements. The folded spectra, covering a velocity span of ±5 mm/s, were Lorentzian line least-square fitted using the "Recoil" software [13]. The center shift, CS, being the sum of the true isomer shift and the second order Doppler shift, is given relative to metallic iron (α -Fe) at room temperature. The magnitude of the quadrupole splitting, |QS|, is given as the peak separation in the doublet, and the line width, *w*, is the experimental FWHM of the spectral peaks.

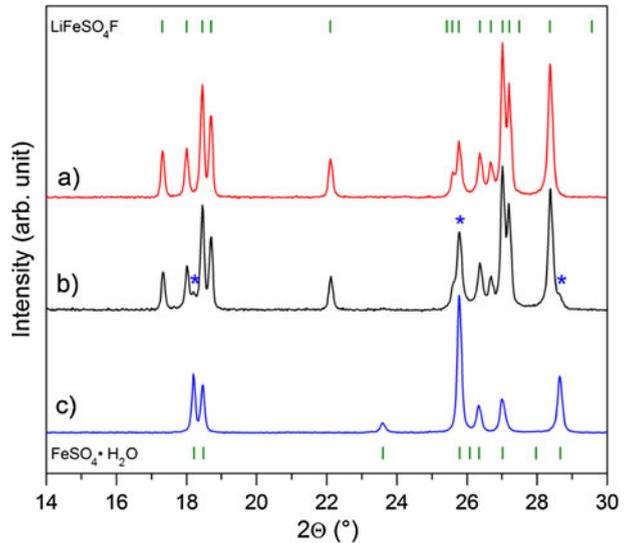
2.3 X-ray diffraction

Powder X-ray diffraction patterns were collected on a Bruker D8 equipped with a Lynxeye linear detector with fluorescence suppression, using CuK α radiation ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54439 \text{ \AA}$).

3 Results and discussion

In this work, a series of five batches, denoted as as-prepared LiFeSO₄F, were produced using the optimized temperature program described in the experimental section. All of these samples were characterized by X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) showing very similar results, indicating a good reproducibility. The diffraction pattern and Mössbauer spectrum of the "as-prepared LiFeSO₄F", presented below, are results for one sample representative for the series. The presented Mössbauer hyperfine parameters, however, are the average values from the entire series of five samples, for better statistics.

Fig. 1 X-ray diffraction patterns of **a** as-prepared LiFeSO_4F , **b** LiFeSO_4F containing significant amounts of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ impurity (the most prominent contributing reflections from $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ are marked with blue stars), and **c** phase pure $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ synthesis precursor



The XRD pattern of the as-prepared LiFeSO_4F (Fig. 1a) confirms a phase pure product in the *tavorite* structure, with no indications of crystalline impurities besides expected traces of excess LiF precursor (not seen in the presented two-theta range). A full pattern Rietveld refinement on a comparably phase pure sample, produced by us in a similar way, is presented elsewhere [14]. The XRD pattern is in good agreement with previously reported results for this compound [2].

The Mössbauer spectrum of the same sample (Fig. 2a) shows two sets of sharp and well resolved doublets, as expected for the two distinct crystallographic iron sites in LiFeSO_4F , $\text{Fe}(1)$ and $\text{Fe}(2)$, with unequal environments [2, 15]. The hyperfine parameters, presented in Table 1, correspond well with Fe^{2+} in a high spin coordination. No detectable traces of Fe^{3+} could be observed. While the overall characteristics of the spectrum are in good agreement with that presented in other Mössbauer studies of this compound, we do notice details that have either not been observed or discussed before, to the best of our knowledge. To begin with, we consistently obtain a higher intensity for the inner doublet in our fittings, averaging 52.5(1.0) % for the produced batches. At a first glance, this appears surprising due to the equally populated iron sites in LiFeSO_4F , as suggested by diffraction studies [2, 15]. However, thorough Rietveld refinements of high resolution neutron diffraction data reveal differences in the isotropic displacement factors, B , which were determined to 0.77(4) and 0.66(5) Å^2 for the $\text{Fe}(1)$ and $\text{Fe}(2)$ site, respectively [15]. The vibration magnitude does in turn affect the recoil-less fraction of the atoms, i.e. the f -factor, in accordance with the following equation:

$$f = e^{-\frac{B}{2\lambda^2}} \quad (1)$$

The expected f -factor ratio for the two iron sites can thus be calculated by:

$$\frac{f_2}{f_1} = e^{-\frac{B_2 - B_1}{2\lambda^2}} \quad (2)$$

Fig. 2 Mössbauer spectra of **a** as-prepared LiFeSO_4F , and **b** LiFeSO_4F containing $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ impurity

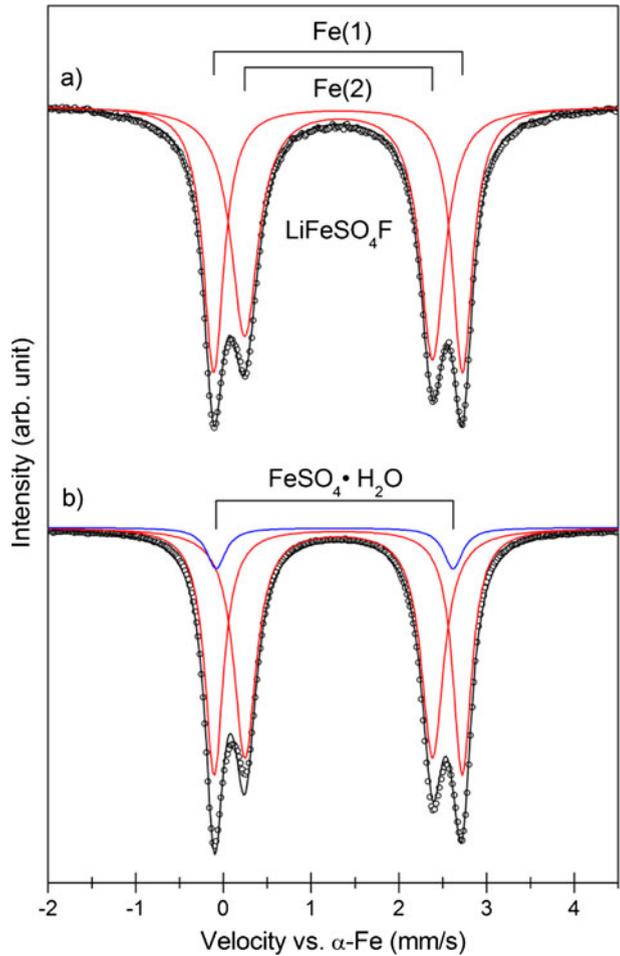


Table 1 Hyperfine parameters for the prepared samples, including the center shift, CS, quadrupole splitting, QS, line width for the right peak of the doublet, w_+ , and the line width ratio of the left and the right peak of the doublet, w_-/w_+ (* = fixed value)

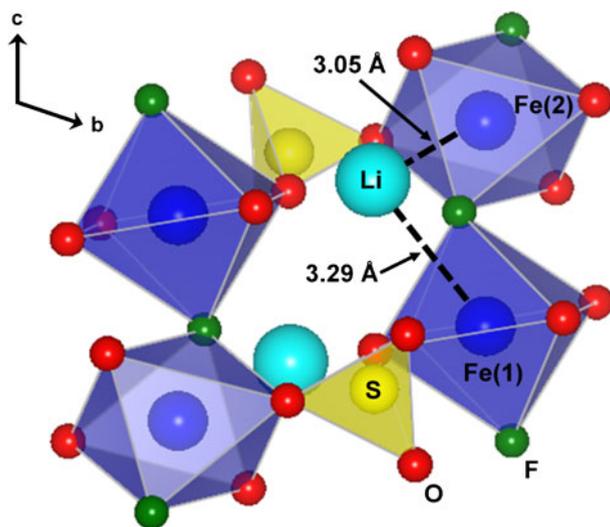
Sample		CS (mm/s)	QS (mm/s)	w_+ (mm/s)	w_-/w_+
As-prepared	Outer doublet Fe(1)	1.308(10)	2.83(1)	0.235(10)	1.00(1)
LiFeSO_4F	Inner doublet Fe(2)	1.313(10)	2.15(1)	0.256(10)	1.13(4)
$\text{FeSO}_4 \cdot \text{H}_2\text{O}$		1.268(10)	2.70(1)	0.259(10)	1.00*
FeSO_4		1.280(10)	3.10(1)	0.263(10)	1.00*

Given a 14.4 keV Mössbauer source ($\lambda = 0.8616 \text{ \AA}$), as used in this study, the above mentioned isotropic displacement factors used in (2) give an f -factor ratio of $f_2/f_1 = 1.077 (\pm 0.037)$. With equally populated iron sites in the *tavorite* LiFeSO_4F structure, this results in expected Mössbauer signal intensities of 48.1 and 51.9 % for the Fe(1) and Fe(2) site, respectively. This is in good agreement with the intensities obtained from the Mössbauer fittings of our produced materials, averaging

47.5(1.0) and 52.5(1.0) % for the outer and inner doublet, respectively. Thus, by this approach, we can ascribe the outer and the inner doublet to the Fe(1) and Fe(2) site, respectively, as indicated in Fig. 1a. This is in good agreement with a previously proposed assignment based on comparing the hyperfine parameters with the average iron-ligand bond distances within the FeO_4F_2 octahedra, and the iron-lithium distances [8]. Moreover, this information can be useful in quantifying the purity of synthesized LiFeSO_4F , as it suggests that one should expect the Mössbauer spectrum of phase pure samples to display differences in the doublet intensities, in accordance to the discussion above.

Another observed detail in the Mössbauer spectrum for the as-prepared LiFeSO_4F is a significant asymmetry in the line width of the inner Fe(2) doublet. This is very obvious from a visual survey of the spectrum, comparing the left and right half of the signal. The outer Fe(1) doublet is, however, much more symmetric. Generally, there are several possible explanations for asymmetries of Mössbauer doublets; (i) texture effects (i.e. preferred orientation of the crystals/particles in the prepared absorber), (ii) the Goldanskii-Karyagin effect, (iii) impurities, or (iv) simply a natural feature due to the properties of the crystal structure. It is quite unreasonable to expect texture effects for the as-prepared LiFeSO_4F due to the rather isotropic particle shape (representative scanning electron microscopy images are presented elsewhere [14]). Moreover, both texture effects and the Goldanskii-Karyagin effect should cause areal asymmetries to both doublets, rather than a line width asymmetry to one of the doublets [16, 17], as observed in this study. Additionally, both these effects could be unambiguously ruled out by a Mössbauer measurement at the “magic angle” [16] of 54.7° between the γ -beam and the normal to the absorber plane, showing no significant differences in the spectrum. When it comes to impurities, the XRD pattern of the as-prepared LiFeSO_4F (Fig. 1a) showed no detectable amounts of unwanted crystalline phases except for LiF, as mentioned above. However, since the sensitivity of Mössbauer spectroscopy is generally greater than that for X-ray diffraction, it could simply be so that possible impurities were not detected by the latter. The two most probable impurities that may be obtained due to a poorly optimized synthesis of *tavorite* LiFeSO_4F are FeSO_4 and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. The former is facilitated by a faster dehydration step than insertion of LiF in the topotactic reaction, usually due to a too high reaction temperature. The latter is obtained due to an overall incomplete reaction. Both phase pure FeSO_4 and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ were prepared and characterized by XRD (the latter presented in Fig. 1c) and MS, and their hyperfine parameters are presented in Table 1. It becomes clear that the asymmetry of the Fe(2) doublet is not likely to be a result of the presence of FeSO_4 , since its hyperfine parameters differ compared to those of LiFeSO_4F to such an extent that the Mössbauer signals cannot superimpose without being able to identify the signal of FeSO_4 as a shoulder on the left hand side of the spectrum. However, the hyperfine parameters of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ are closer to those of the Fe(1) and Fe(2) doublets in LiFeSO_4F , and are more likely to completely overlap. To investigate the effects of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ impurities on the LiFeSO_4F spectrum, a sample with intentional impurities was prepared (described in the experimental section) and characterized. The XRD pattern of this sample (Fig. 1b) indeed confirms a significant presence of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. The Mössbauer spectrum (Fig. 2b) was fitted with symmetrical Fe(1) and Fe(2) doublets, and by locking the hyperfine parameters for $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, except for the intensity. From the spectrum, it is evident that the

Fig. 3 Illustration of the local structure around the Li-ions in *tavorite* LiFeSO_4F , generated from published neutron diffraction refinement data [15]



$\text{FeSO}_4 \cdot \text{H}_2\text{O}$ impurity is affecting the Fe(1) doublet more than the Fe(2), and by comparing the experimental data with the calculated fit it is clear that its presence cannot explain the asymmetry to the LiFeSO_4F signals, and can thus be ruled out as an explanation. No other possible impurities with hyperfine parameters that would likely cause the observed features could be found in the literature.

Thus, this leaves us to consider whether the asymmetry can be a natural feature of the LiFeSO_4F material. It was recently proposed [15] that the lithium ions in *tavorite* LiFeSO_4F fully occupies only one crystallographic site, located in between the two partially occupied sites that were previously suggested [2]. The lithium ions are situated significantly closer to the Fe(2) than to Fe(1) site, as illustrated in Fig. 3, causing the former to be more prone to variations in the chemical environment as the lithium ions are moving. This is seen as a systematically higher line width (and larger sensitivity to the synthesis conditions) of the inner doublet in the literature [8, 10], in good agreement with what we obtain here. However, to obtain an asymmetry in the line width such that $w_-/w_+ > 1$, there must be a negative correlation between the center shift, CS, and the quadrupole splitting, QS. In this case, it is not unreasonable to picture such a situation. If the positively charged Li-ion moves towards the Fe(2) site, one can expect it to attract the electron cloud of the iron. Such an attraction leads to a decrease of the s-electron density at the Fe nucleus causing an increase of the CS. At the same time, the QS will decrease due to an increased ligand contribution opposite to the major valence contribution to the QS. If the Li-ion moves away from the Fe(2) site, the CS and QS will be affected in the opposite way. Thus, the observed line width asymmetry of the Fe(2) doublet in *tavorite* LiFeSO_4F can be explained by the structural properties. The reason why this feature is much more pronounced in our spectra compared to previous studies [8, 10] can possibly be explained by the more ordered samples that are obtained through our optimized synthesis, as seen on the exceptionally narrow peak widths for both doublets of the as-prepared sample.

4 Conclusion

In this work, we have prepared *tavorite* LiFeSO_4F in TEG using optimized synthesis conditions, resulting in phase pure and well ordered samples showing sharp and resolved Mössbauer doublets, with narrow line widths. We have observed a consistently higher intensity for the inner doublet of the spectrum, which is attributed to a lower displacement factor, B, for the Fe(2) than for the Fe(1) site. Thus, we use this information to ascribe the inner and outer doublet to the Fe(2) and Fe(1) site, respectively, as a complementary method to previously suggested approaches of assigning the spectral peaks. Moreover, we demonstrate the need of using an asymmetric line width fitting model for the Fe(2) doublet, such that $w_-/w_+ > 1$, and propose this feature to be a natural result of the crystal structure properties. This type of asymmetry is explained by a negative correlation between the center shift and the quadrupole splitting caused by the movement of the Li-ion in the vicinity of the Fe(2) site.

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