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Supporting Information for

# Sodium Iron Sulfate Alluaudite Solid Solution for Na-ion Batteries: Moving Towards Stoichiometric Na<sub>2</sub>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

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The present Supporting Information file contains results and experimental details on

- (S1) Rietveld refinements,
- (S2) Mössbauer spectra,
- (S3) operando X-ray diffraction
- (S4) solvent selection

# S1 – Rietveld Refinements

#### Summary

The refinements of all diffractograms (Figures S1-1 and S1-2) are in good agreement with the model proposed by Oyama *et al.*<sup>1</sup> for the alluaudite sulfate phase. The refined positions are close to those from this model and show that the structures are closely related, even in the case of sample S-2h. Thus, apart from the occupancies, the stoichiometric phase is very similar to the reported Na-rich phase, which suggests that it should display similar properties in terms of electrochemistry and ion mobility.

The high value of  $B_{iso}$  for Na3 can be related to the high mobility of the Na<sup>+</sup> ion on this site, as suggested by BVS and DFT calculations.<sup>2,3</sup> The experimental peak profiles of the first two reflections are not well reproduced by the calculated curve. However, the observed and calculated intensities (= peak areas) are in good agreement.



Figure S1-1. Rietveld refinement results of the X-ray diffraction patterns of sample R-2h.



Figure S1-2. Rietveld refinement results of the X-ray diffraction patterns of sample S-2h.

## **Crystallographic data**

	Sample R-2h	Sample S-2h	
Chemical formula	Na <sub>2.50</sub> Fe <sub>1.75</sub> (SO <sub>4</sub> ) <sub>3</sub>	Na <sub>2</sub> Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	
Mr	443.4	445.9	
Crystal system, Space group	Monocli	nic, C2/c	
Temperature (K)	30	00	
Z		4	
a (Å)	12.6469(4)	12.6376(6)	
b (Å)	12.7694(4)	12.7325(3)	
c (Å)	6.5126(2)	6.4939(3)	
α, β, γ (°)	90, 115.514(3), 90	90, 115.494(3), 90	
V (Å <sup>3</sup> )	949.17(6)	943.17(8)	
Radiation type	Cu-Kα, λ = 1.540560 Å (67%) and 1.544390 Å (33%)		
R <sub>Bragg</sub>	5.12 5.39		

Table S1-1: Crystal data and refinement indices for X-ray diffraction data.

 Table S1-2: Calculated parameters from the refinement data.

	Sample R-2h	Sample S-2h
Net charge	-0.07(9)	-0.06(8)
Calculated stoichiometry	0.26(4)	0.06(3)
Measured stoichiometry (ICP)	0.25(2)	0.05(2)

 Table S1-3: Fractional atomic coordinates and isotropic displacement parameters for X-ray diffraction on sample R-2h.

Site	X	У	Ζ	B <sub>iso</sub> (Ų)	Occ. (abs.)
Na1	0	0.7321(15)	1⁄4	3.2(5)	1
Na2	0	1/2	0	1.7(1.0)	0.59(3)
Na3	0	0.012(4)	1⁄4	11(2)	0.62(4)
Fe1	0.2700(5)	0.3423(4)	0.3528(10)	1.16(14)	Fe: 1.72(3) – Na: 0.28(3)
S1ª	0	0.27645(12)	1⁄4	1.23(15)	1
O11ª	0.0851(2)	0.3461(2)	0.2163(4)	1.8(2)	2
O12ª	0.0523(2)	0.20898(19)	0.4515(4)	1.8(2)	2
S2ª	0.23815(10)	0.10296(8)	0.1312(2)	1.23(15)	2
O21ª	0.23453(18)	0.16857(19)	0.3162(4)	1.8(2)	2
O22ª	0.1783(2)	0.0029(2)	0.1223(4)	1.8(2)	2
O23ª	0.3603(2)	0.0865(2)	0.1693(5)	1.8(2)	2
O24ª	0.3263(2)	0.3416(2)	0.0856(4)	1.8(2)	2

<sup>a</sup>Positions from *Oyama et al.*<sup>1</sup>

 Table S1-4: Fractional atomic coordinates and isotropic displacement parameters for X-ray diffraction on sample S-2h.

Site	x	У	Ζ	B <sub>iso</sub> (Ų)	Occ. (abs.)
Na1	0	0.736(2)	1⁄4	3.3(7)	1
Na2	0	1/2	0	3.0(1.2)	0.66(4)
Na3	0	0.006(6)	1⁄4	9(3)	0.44(5)
Fe1	0.2707(6)	0.3436(5)	0.3538(12)	0.92(13)	1.92(3)
S1	0	0.2771(12)	1⁄4	1.37(18)	1
011	0.0862(17)	0.3462(17)	0.222(4)	1.5(3)	2
012	0.0546(17)	0.2094(16)	0.450(4)	1.5(3)	2
S2	0.2416(10)	0.1042(8)	0.133(2)	1.37(18)	2
021	0.2350(17)	0.1724(16)	0.319(4)	1.5(3)	2
022	0.1831(16)	0.0035(19)	0.120(3)	1.5(3)	2
023	0.365(2)	0.0905(17)	0.179(4)	1.5(3)	2
024	0.3254(18)	0.3408(16)	0.084(4)	1.5(3)	2

## **Experimental details**

Powder X-ray diffraction (XRD) was performed on a Bruker D8 diffractometer with a Cu-K $\alpha$  radiation and a Lynxeye XE-T 1D detector (192 strips). Diffractograms were collected in the 10-130° 2 $\theta$ -range with a 0.007° step size and a 0.2 s/strip step time. Rietveld refinements of the diffractograms were conducted using the FullProf Suite, in the *C2/c* spacegroup proposed by Barpanda *et al.*<sup>4</sup>

The peak shape function was described using the TCH pseudo-Voigt function with Finger's treatment of the axial divergence. The instrumental function was determined from XRD data on LaB<sub>6</sub> collected in the same conditions. The background was described with a 4<sup>th</sup>-order Chebyshev polynomial, with an additional 1/x term.

As the diffraction data used in this study originates from a home-laboratory diffractometer, the total number of refined parameters was kept reasonably low by applying some constraints. It must be noted that the stoichiometry of the phases was not set as a constraint. For both samples, it is in good agreement with the experimental measurements (Table S1-2).

For sample R-2h, the net charge was restrained to  $0 \pm 0.01$ . The occupancy of Na1 was set to 1.0 and the Fe1 site was set fully occupied with a mix of Na and Fe. The  $B_{iso}$  for the S atoms were refined as a single value, as well as the  $B_{iso}$  for the O atoms and the  $B_{iso}$  for the Na and Fe atoms on site Fe1. For sample S-2h, the same constraints were used, except the Fe1 site was only composed of Fe, which was necessary to obtain a sensible stoichiometry.

The starting models were taken from *Oyama et al.*<sup>1</sup> and the following parameters were refined sequentially: occupancies of the Na and Fe atoms,  $B_{iso}$  of the Na and Fe atoms,  $B_{iso}$  of the S and O atoms, positions of the Na and Fe atoms. For sample S-2h, the positions of the S and O atoms were further refined.

## S2 – Mössbauer Spectroscopy

## Summary

The spectra for all samples (Figure S2-1) can be fitted using two doublets with hyperfine parameters corresponding to those reported previously<sup>4</sup>.

 $\alpha$ -FeSO<sub>4</sub> exhibits quite strong quadrupole splitting (3.08 (2) mm/s) and the isomer shift (1.27 (1) mm/s) corresponds to Fe(II). The obtained hyperfine parameters are close to the reported values for FeSO<sub>4</sub><sup>5</sup>.

In the case of S-2+12h, the presence of  $\alpha$ -FeSO<sub>4</sub> shows that sample S-2h decomposes upon heating, evidence of its metastability. Sample R-2+12h does not contain this  $\alpha$ -FeSO<sub>4</sub> secondary phase, showing that sample R-2h is stable, as expected.



Figure S2-1. Room-temperature <sup>57</sup>Fe Mössbauer spectra of (a) S 2h, (b) S 2+12h, (c) R-2h and (d) R-2+12h.

**Table S2-1.** Hyperfine parameters<sup>a</sup> of the room-temperature <sup>57</sup>Fe Mössbauer spectra of all samples.

Sample	Туре	δ (mm/s)	Δ (mm/s)	Г (mm/s)	Area (%)
S-2h	Fe"(1)	1.277(4)	2.34(1)	0.36(1)	50(1)
	Fe"(2)	1.275(4)	2.01(1)	0.39(1)	50(1)
	Fe"(1)	1.273(4)	2.39(1)	0.37(1)	42(1)
S-2+12h	Fe"(2)	1.284(4)	2.00(1)	0.40(1)	42(1)
	α-FeSO <sub>4</sub>	1.27(1)	3.08(2)	0.40(1)	16(1)
R-2h	Fe"(1)	1.275(4)	2.43(1)	0.37(1)	50(1)
	Fe"(2)	1.288(4)	2.06(1)	0.39(1)	50(1)
R-2+12h	Fe"(1)	1.270(3)	2.43(1)	0.40(1)	50(1)
	Fe"(2)	1.289(3)	2.06(1)	0.42(1)	50(1)

<sup>a</sup>δ, isomer shift referred to α-iron at 295 K; Δ, quadrupole splitting; Γ, line width.

#### **Experimental details**

<sup>57</sup>Fe Mössbauer spectra were acquired in transmission mode on a constant-acceleration spectrometer with a <sup>57</sup>Co(Rh) source at room temperature, in the ±12 mm/s and ±4 mm/s velocity ranges. The samples were prepared with about 30 mg of NFS material mixed with boron nitride. The spectrometer was calibrated using a high-purity  $\alpha$ -Fe foil as a reference absorber. The spectra were fitted using Lorentzian doublets with the Fullham program to extract the hyperfine parameters. The quality of the fitting procedure was judged on the basis of minimizing the number of parameters and  $\chi^2$  values.

## S3 – Operando X-ray diffraction

#### Summary

As also observed for the S-2h sample (Figure 7 in the main article), the whole intensity of the  $(\overline{1}12)$  peak of R-2h is shifted during cycling, indicating that all the material probed by the X-ray diffraction measurement is electrochemically active at the low cycling rate. In the case of this Na-rich sample, comparison is possible with the synchrotron *in situ* diffraction study reported by Oyama et al.<sup>6</sup> and the cell parameters extracted from our operando data for the R-2h sample (see Figure S3-1a) are in good agreement with these reference data.



**Figure S3-1.** a) Comparison of the evolution of the cell parameters upon cycling between sample R-2h and results from a synchrotron study by Oyama *et al.*<sup>6</sup> Parameter b in sample R-2h could not be reliably determined in the charged state due to peak superposition and broadening upon cycling and a low signal-to-noise ratio in our data. b) XRD patterns of R-2h in the electrochemical cell at the start, after one charge and after one discharge. The  $\mathbf{\nabla}$  symbol and the vertical dotted lines mark the peaks from the electrochemical cell. c) Close-up view of the dotted parts of the XRD patterns from b).

#### **Experimental details**

For the operando XRD experiments, the active material was mixed with 20 wt% carbon black. The *operando* cell with a beryllium window was assembled with a sodium Whatman glass-fiber separator, 1 M NaPF<sub>6</sub> dissolved in propylene carbonate as an electrolyte, and Na metal as counter and reference electrode. Figure S3-2 highlights which peaks are due to the electrochemical cell. Besides, it shows that in the case of the operando measurement, the smaller step time and the presence of the beryllium window increase the background signal. The absorption by the beryllium window is more severe at lower 20 angles because the X-ray path through the window material is longer at lower incidence angles.



**Figure S3-2.** X-ray diffractograms of the S-2h sample in a normal sample holder (red) and in the electrochemical cell (blue). The diffractogram of the empty cell is shown in black. The ▼ symbol and the vertical dotted lines mark the peaks from the electrochemical cell.

## S4 – Solvent selection

After a first evaluation based on handbooks, experimental solubility tests were carried out on the following solvents.

	Dissolves	Dissolves	
Solvent	Na <sub>2</sub> SO <sub>4</sub> ?	FeSO₄?	
H <sub>2</sub> O	$\checkmark$	~	Rejected: formation of Na <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O
Ethylene glycol	×	$\checkmark$	
Glycerol	$\checkmark$	$\checkmark$	Selected as solvent
EtOH	×	×	
iPrOH	×	×	Selected as anti-solvent

## References

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