

## ***Kröhnkite-type Na<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O as a novel 3.25 V insertion compound for Na-ion Batteries***

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### ***Structural characterization***

X-ray diffraction patterns of polycrystalline powder samples were acquired by a Rigaku RINT-TTR III powder diffractometer equipped with a Cu-K $\alpha$  radiation source ( $\lambda_1 = 1.5405 \text{ \AA}$ ,  $\lambda_2 = 1.5443 \text{ \AA}$ ) operating at 50 kV and 300 mA. Typical scans were performed in the  $2\theta$  range of 8~90° (step size = 0.028°.s<sup>-1</sup>). Synchrotron X-ray diffraction (S-XRD) was conducted on the Powder Diffraction beamline at BL-10 of the Australian Synchrotron (Clayton, Australia) using radiation source of wavelength ( $\lambda = 0.82550 \text{ \AA}$ , calibrated against a LaB<sub>6</sub> standard). For S-XRD, the powder samples were loaded inside glass capillaries ( $\varnothing = 0.3 \text{ mm}$ ) inside an Ar-filled glovebox. Rietveld analysis<sup>1</sup> of the S-XRD data was performed using the GSAS program<sup>2</sup> with EXPGUI front-end<sup>3</sup>, taking into account the zero-shifts, scale factors, background corrections and pseudo-Voigt peak shape parameters.

### ***Physical characterization***

Mössbauer characterization was conducted with a Topologic System Inc. unit having a <sup>57</sup>Co  $\gamma$ -ray source duly calibrated with an  $\alpha$ -Fe foil as standard. Around 0.1 g

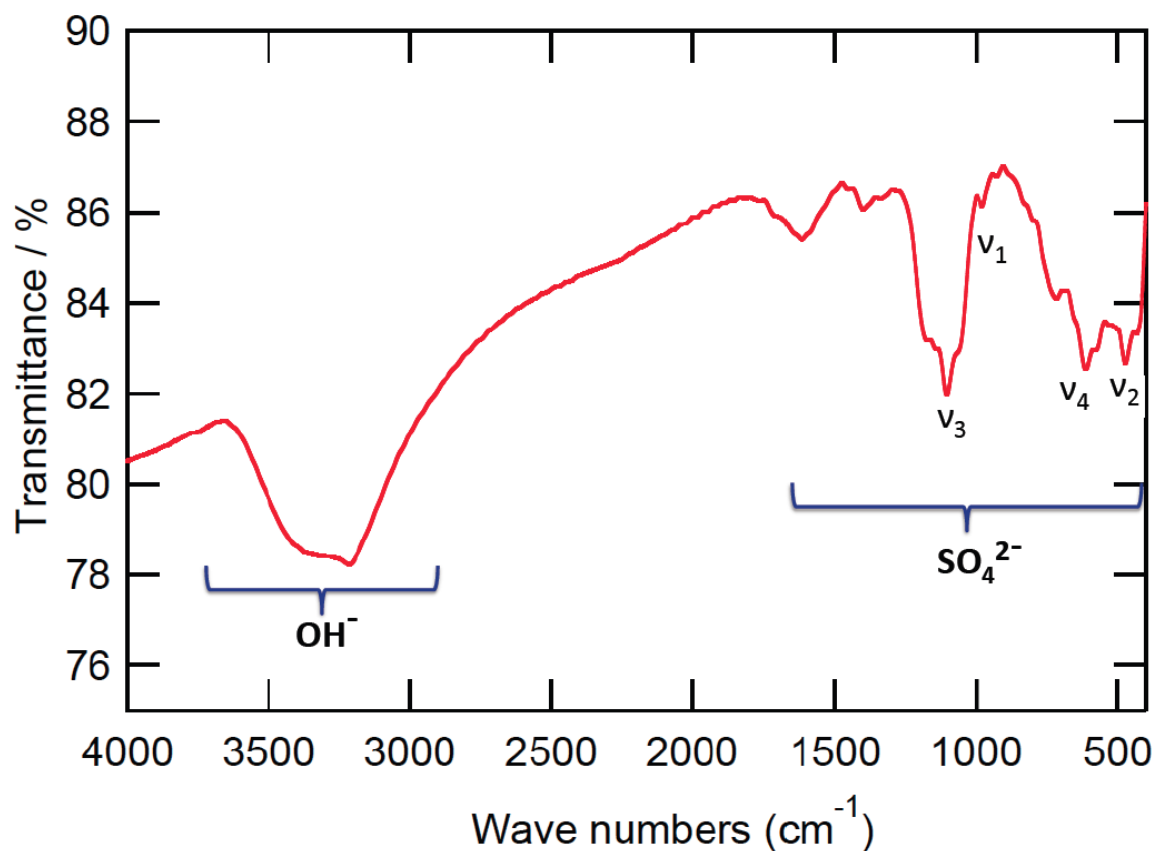
powder sample was sealed inside a Pb sample holder by polyethylene films. The spectra were collected for over 10 h in transmission mode and were fitted by MossWinn3.0 program. Infrared spectra were acquired using KBr pellets containing powder samples in the wavelength range of 400 ~ 4000  $\text{cm}^{-1}$  with a JASCO FT/IT-6300 unit. Thermal analysis was performed in RT ~ 500  $^{\circ}\text{C}$  temperature range (heating rate = 5  $^{\circ}\text{C}\cdot\text{min}^{-1}$ ) with a Rigaku ThermoPlus DSC 8230 unit operating under steady Ar flow. Scanning electron microscopy was conducted on powder samples mounted on conducting carbon tape by a Hitachi S-4800 FE-SEM unit operating at 5 kV.

### ***Electrochemical characterization***

To gauge the feasibility of Na (de)insertion, the working electrode was formulated by mixing 80 wt% active material  $\text{Na}_2\text{Fe}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$ , 15 wt% acetylene carbon black and 5 wt% of polyvinylidene fluoride (PVdF) binder in NMP (*N*-methylpyrrolidone) solvent. The resulting slurry was cast on an Al film acting as current collector. Post overnight drying at 120  $^{\circ}\text{C}$  in vacuum, 20  $\mu\text{m}$  thick cathode disks ( $\text{O} = 18 \text{ mm}$ ) were punched out with a average cathode loading of  $\sim 3 \text{ mg}\cdot\text{cm}^{-2}$ . 2032-type coin cells were assembled inside an Ar-filled glove box using these cathode disks as working (+ve) electrodes, Na metal foil as counter (-ve) electrodes separated by polypropylene films soaked with 1 M  $\text{NaClO}_4$  dissolved in propylene carbonate (PC) acting as electrolyte. These coin cells were subjected to galvanostatic cycling with a TOSCAT-3100 battery tester (Toyo system) in the voltage range of 2.0-4.0 V (at 25  $^{\circ}\text{C}$ ).

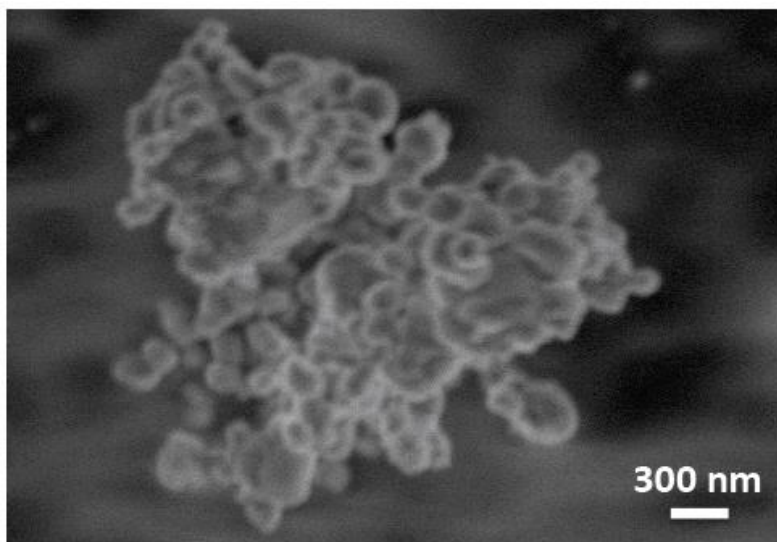
### **References**

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2. Larson, A. C.; Von Dreele, R. B. General Structure Analysis System (GSAS); Los Alamos National Laboratory Report, LAUR 86-748: Los Alamos National Laboratory: Los Alamos, NM, 1994.
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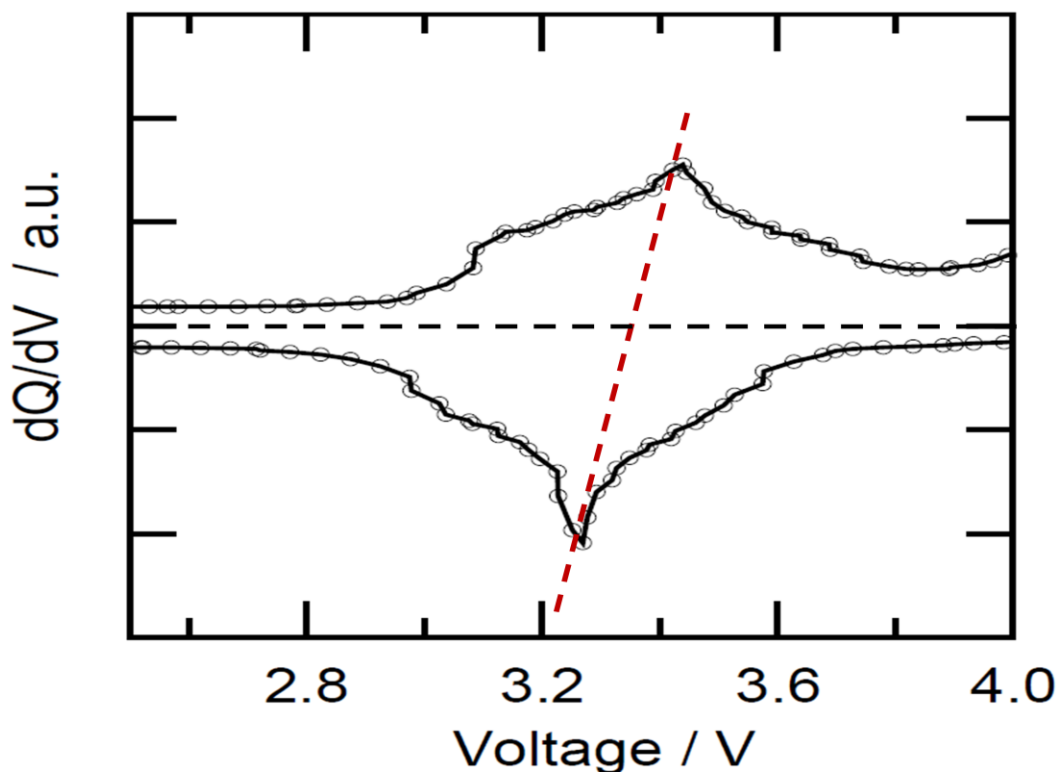


**Figure S1:** FT-IR spectrum of  $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  phase depicting the vibration bands corresponding to constituent  $\text{SO}_4$  and  $\text{H}_2\text{O}$  units.

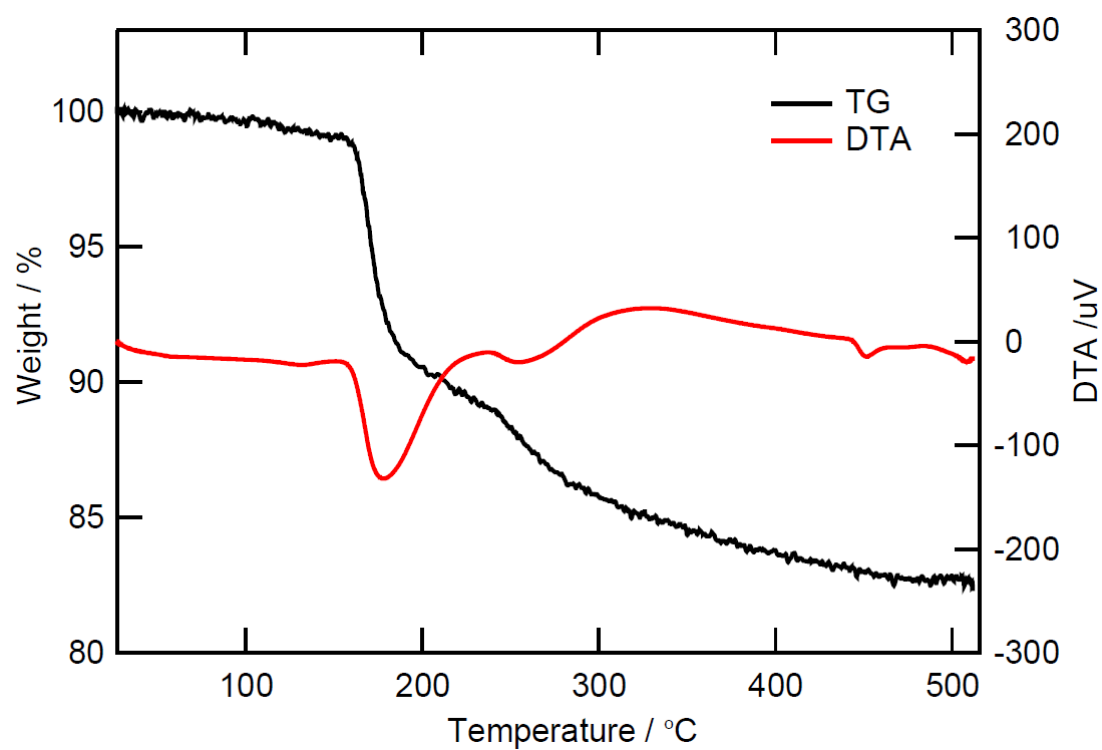
The constituent bonded and free  $\text{SO}_4^{2-}$  anions delivers several IR peaks in the low wavenumber window ( $400\text{-}1700\text{ cm}^{-1}$ ) (Figure S1). The asymmetric  $\text{SO}_4$  tetrahedra further leads to degeneration in these principal IR peaks. Four main internal modes are observed, which can be described as: (a) the symmetric stretching mode  $\nu_1$ , (b) the symmetric bending mode  $\nu_2$ , (c) the asymmetric stretching mode  $\nu_3$ , and (d) the asymmetric bending mode  $\nu_4$ . Owing to the overall asymmetry in  $\text{SO}_4$  arrangement, the asymmetric stretching and bending mode ( $\nu_3$  and  $\nu_4$ ) undergo severe degeneration leading to multiple bands around  $1105\text{ cm}^{-1}$  and  $611\text{ cm}^{-1}$ . Additionally, broad and distinct peak at high wavenumber window ( $3200\text{-}3600\text{ cm}^{-1}$ ) is observed arising from the symmetric/asymmetric stretching of  $\text{OH}^-$  anions of the structural  $\text{H}_2\text{O}$  component.



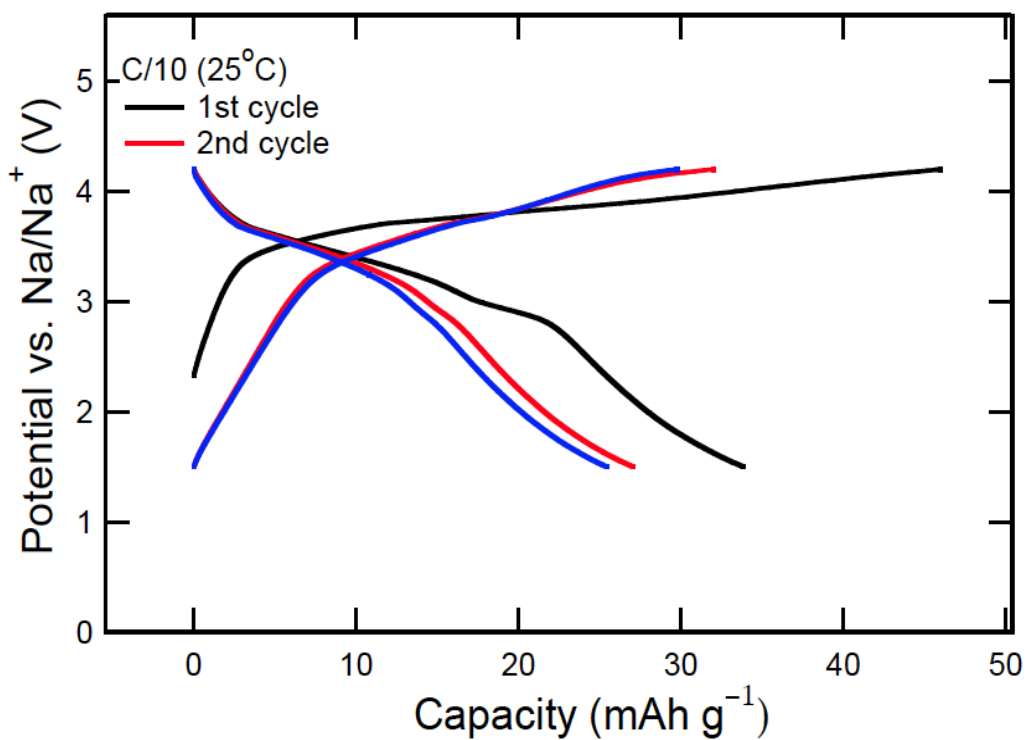
**Figure S2:** Representative SEM image of as-synthesized  $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  compound showing micrometric (secondary) agglomerates consisting of primary nanoparticle of size range 100-300 nm.



**Figure S3:** Differential ( $dQ/dV$ ) curve of charge-discharge profile of  $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  *krohnkite* phase. The average redox potential is centered around 3.25 V.



**Figure S4:** Thermal analyses (TG-DTA) profiles of  $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  *krohnkite* phase. The dehydration occurs in multiple steps between 170-300 °C. The final product was  $\text{Na}_6\text{Fe}(\text{SO}_4)_4$ .



**Figure S5:** Charge-discharge profile of  $\text{Na}_6\text{Fe}(\text{SO}_4)_4$  phase showing 3.4 V redox activity.