**Kröhnkite-type Na$_2$Fe(SO$_4$)$_2$.2$H_2$O as a novel 3.3 V insertion compound for Na-ion batteries**

Prabeer Barpanda,*,†,‡ Gosuke Oyama,§ Chris D. Ling,‡ and Atsuo Yamada*,†,§

† Metallurgical Engineering and Materials Science (MEMS), Indian Institute of Technology Bombay (IITB), Powai, Mumbai 400076, India
‡ Department of Chemical System Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
§ School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia
¶ Unit of Element Strategy Initiative for Catalysts & Batteries, ESICB, Kyoto University, Kyoto 615-8510, Japan

Supporting Information Placeholder

**ABSTRACT:** Solid-state sulfate chemistry continues to yield promising high-voltage polyanianic cathode materials for rechargeable batteries (cf. fluorosulfates and bisulfates). As part of our ongoing exploration of new sulfate chemistry, here we report a new candidate cathode material for sodium-ion batteries, Na$_2$Fe(SO$_4$)$_2$.2$H_2$O. Prepared by conventional low temperature (ca. 80 °C) dissolution and precipitation route, it stabilizes in a monoclinic unit cell with $P2_1$/$c$ (#14) symmetry, isostructural to the mineral kröhnkite. Its crystal structure has refined against synchrotron X-ray diffraction. This bihydrated compound demonstrates reversible Na (de)insertion with a capacity exceeding 70 mAh/g, involving Fe$^{3+}$/Fe$^{2+}$ redox activity centered at 3.25 V (vs. Na/Na$^+$). The synthetic, structural and electrochemical details of this new low-cost insertion compound are presented.

**KEYWORDS.** Sodium-ion battery, cathode, Na$_2$Fe(SO$_4$)$_2$.2$H_2$O, kröhnkite, synchrotron X-ray.

The need for electrochemical energy storage devices (i.e., batteries) for portable consumer electronics, hybrid vehicles and (remote-area) grid-power storage continues to grow exponentially. This has led to world-wide efforts to build better batteries, tailor-made for specific applications, the design parameters of which are not necessarily limited to electrochemical performance (capacity, voltage and rate kinetics) but also include cost, operational safety, sustainable usage and recyclability. The battery research community is under particular pressure to develop more economical materials and processing routes.1

This situation is especially pronounced in case of sodium-ion batteries. The growing consumption of lithium for batteries in portable devices and automobiles is beginning to have an impact on Li resources, which has inspired materials chemists to explore alternative sodium-based chemistry for applications not limited by mass or volume power density, such as batteries connected to renewable energy generators and large-scale grid-power storage. Aware of the fact that the cathode accounts for large portion of the net cost of a battery, numerous alternative oxide and polyanianic-based cathode chemistries have been explored of late.2 Parallel to the Li-ion battery case, a large effort on the Na-ion battery research focus on unraveling new ‘polyanianic’ cathodes with tunable structures, rich polymorphism and varied redox potential.

Phosphate PO$_4^3-$-based compounds have been shown to represent a large family of viable cathodes materials, some examples being NaFePO$_4$, Na$_2$FePO$_4$F, Na$_2$MP$_2$O$_7$ (M = Fe/Cr/Mn), and Na$_2$Fe$_2$(PO$_4$)$_3$(P$_2$O$_7$).3 Following our groups’ recent efforts in the relatively abundant Na–M–P–O (phosphate/pyrophosphate) systems,4–6 in an effort to discover new cathodes with lower cost and higher redox potential, we are now focusing our attention on sulfate (SO$_4^2-$) chemistry, including fluorosulfates [AMSO$_4$F, A = Li/Na/K] and bisulfates [Li$_2$M(SO$_4$)$_3$].7–9 Although various SO$_4^2-$-based cathodes have been reported as viable candidates for Li-ion batteries, no such success has been reported for Na-ion batteries. To fill this gap, here we report a new compound Na$_2$Fe(SO$_4$)$_2$.2$H_2$O as the first reversible SO$_4^2-$-based positive insertion compound suitable for use in rechargeable sodium-ion batteries.

As well as the cheap and abundant elements in the Na–Fe–S–O–H system, this compound has the advantage that it can be prepared at low temperature (ca. 80 °C) by a one-step dissolution and precipitation method. Adopting a monoclinic structure in the kröhnkite mineral family, it shows a relatively high Fe$^{3+}$/Fe$^{2+}$ redox potential (ca. 3.3 V vs. Na/Na$^+$) with a reversible capacity in excess of 70 mAh/g. Although its commercial prospects would be hindered by its low capacity, it paves way for discovery of dehydrated derivatives [i.e., Na$_2$Fe(SO$_4$)$_2$] and other new SO$_4^2-$-based cathode materials for large-scale Na-ion battery applications.
NaFe(\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\) was prepared via a classical dissolution and precipitation route by (i) dissolving equimolar quantities of commercially procured Na\(\text{SO}_4\) (Wako, 99%) and Fe\(\text{SO}_4\cdot7\text{H}_2\text{O}\) (Wako, 99%) precursors in minimal amount of distilled water, (ii) adding a pinch of ascorbic acid (\(\text{C}_6\text{H}_6\text{O}_6\), Wako, 99%) to avoid Fe\(^{3+}\)\(\rightarrow\)Fe\(^{2+}\) oxidation and (iii) drying the resulting solution at 70-80 °C with steady stirring to remove any excess water. The final white powder was collected, ground and dried at 70 °C for 1 hour for further characterization. This low-temperature synthesis is energy efficient and easily scalable with no need for careful handling. It is important to note that when precipitation was conducted in alcohol (e.g. ethanol) media, it formed NaFe(\(\text{SO}_4\)\(\cdot\)4\(\text{H}_2\text{O}\). Our attempts to synthesize the dehydrated version, i.e. NaFe(\(\text{SO}_4\))\(\cdot\), via several routes failed repeatedly, instead forming NaFe(\(\text{SO}_4\)\(\cdot\)4\(\text{H}_2\text{O}\) as an impurity (phase-pure NaFe(\(\text{SO}_4\))\(\cdot\) can be prepared by solid-state synthesis using 3:1 mixture of Na\(\text{SO}_4\) and Fe\(\text{SO}_4\)). From a synthetic point of view, the thermodynamic stability order of these anhydrous and hydrated sulfate compounds is:

NaFe(\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\) (least stable) < NaFe(\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\) < NaFe(\(\text{SO}_4\)\(\cdot\)4\(\text{H}_2\text{O}\) < NaFe(\(\text{SO}_4\))\(\cdot\) (most stable).

The details of characterization methods (structure/ electrochemical) are provided in the Supplementary Information.

In our exploration of sulfate chemistry for sodium-ion batteries we have been able to take advantage of an extensive database of known minerals, particularly the hydrated sulfate derivatives such as bloedite, mohrite, darapskite, chalcantinite, antlerite etc. One such mineral is kröhnkite, with the general chemical formula \(A_2(\text{XO}_2)(\text{H}_2\text{O})_2\), including Na\(_2\)Cu(SO\(_4\))\(\cdot\)2H\(_2\)O.\(^{10}\) Noting that its structure contained possible Na-ion diffusion channels, we attempted to design a kröhnkite insertion compound for sodium batteries. Mindful of the fact that Na\(_2\)M(SO\(_4\))\(\cdot\)2H\(_2\)O is a limited family with only three known compositions ([M = Cu, Cd, Mn])\(^{11}\) and Fe-based homologue offers best electrochemical activity, we synthesized the previously unknown NaFe(\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\) compound. Starting with a polyhydrate precursor (i.e., Fe\(\text{SO}_4\cdot7\text{H}_2\text{O}\) in solution, the dissolution and precipitation reaction proceeds through dehydration and the formation of new structural H\(_2\)O. The final number of structural H\(_2\)O can be manipulated by controlling the reacting media. If the final precipitation is carried out by adding excess (hydrophobic) alcoholic media (e.g. ethanol), it hinders structural water removal giving rise to well-known bloedite NaFe(\(\text{SO}_4\)\(\cdot\)4\(\text{H}_2\text{O}\) product. However, when the precipitation is carried out just by progressive heating of precursor solution, it facilitates a higher degree of structural water removal resulting in kröhnkite-type Na\(_2\)Fe(\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\). This low temperature (70-80 °C) synthesis is sustainable and easily scalable.

The presence of structural water molecules is known to grossly modify the final crystal structure [e.g. tavorite NaFe\(\text{SO}_4\)\(\cdot\)12\(\text{H}_2\text{O}\) \(\rightarrow\) ukolsonitve NaFe\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\)]. Simultaneously, we observed the structure of NaFe(\(\text{SO}_4\)\(\cdot\)2\(\text{H}_2\text{O}\) differs from bloedite NaFe(\(\text{SO}_4\)\(\cdot\)4\(\text{H}_2\text{O}\). Synchrotron X-ray powder diffraction (S-XRD) data collected on the Powder Diffraction beamline of the Australian Synchrotron at a wavelength \(\lambda = 0.58966 \ \text{Å}\) indicated the formation of kröhnkite monoclinic structure (space group = \(P2_1/c\), #14) with lattice parameters \(a = 5.76386(5)\), \(b = 12.97517(10)\), \(c = 5.44923(4) \ \text{Å}\), \(\beta = 105.9675(3)\). The Rietveld-refinement of a kröhnkite-type structure model against S-XRD data led to the fit shown in Figure 1. For the final refinement, all atomic positions and atomic displacement parameters could be freely refined except for the hydrogen atoms, as expected for x-ray diffraction data, which were refined by treating the sole crystallographically unique H\(_2\)O molecule as a rigid body (the orientation of which was refined). The structural details are deposited as a CIF file. A minor (14.42(8) wt%) impurity of NaFe(\(\text{SO}_4\)\(\cdot\)4\(\text{H}_2\text{O}\) evident in the S-XRD data was accounted for in the refinement. The Mössbauer spectrum (Figure 1, inset), which can be fitted with model using one Fe doublet, confirms that only Fe\(^{3+}\) is present with no Fe\(^{2+}\) impurities (despite the synthesis in aqueous media and air exposure).

The crystal structure is illustrated in Figure 2. It consists of Fe(\(\text{SO}_4\))\(\cdot\)\(\text{H}_2\text{O}\): building blocks, in which FeO\(_6\) octahedra are alternately bridged by SO\(_4\) tetrahedra to form continuous chains parallel to \(c\)-axis. For each FeO\(_6\) octahedron, four of the coordinating O atoms are shared with neighboring SO\(_4\) units, while the other two O atoms (located in \(cis\)-position) are part of structural H\(_2\)O molecules. Note that the data were of sufficient quality to refine the orientation of H\(_2\)O, giving a chemically reasonable structure evidently stabilized by hydrogen bonding (1.86 Å) to neighboring SO\(_4\) units. Na atoms occupy interstitial positions among the chains to form alternating modulated layers of Fe(\(\text{SO}_4\))\(\cdot\)\(\text{H}_2\text{O}\) and Na atoms along the \(a\)-axis. These [Fe(\(\text{SO}_4\))\(\cdot\)(\(\text{H}_2\text{O}\))]\(\cdot\)\(\text{Na}^+\) chains are in turn linked by Na\(^+\) cations (Na-O bonds) and H\(^+\) cations (hydrogen bonds) to form a pseudo-layered framework. The SO\(_4\) tetrahedral and FeO\(_6\) octahedral units are highly symmetrical, with the SO\(_4\) units acting as polydentate (connecting) ligands. Convoluted channels along the \(b\)-axis present a diffusion pathway for the Na (de)insertion reactions.
The feasibility of Na’-diffusivity in the as-synthesized Na$_2$Fe(SO$_4$)$_2$:2H$_2$O bihydrous phase was tested in a standard Na half-cell setting (Figure 3). Without any further particle size and material conductivity optimization, galvanostatic cycling at a rate of C/20 (at 25 °C) delivers reversible discharge capacity approaching 70 mA h/g, which is >90% of its 1-electron theoretical capacity of 81.4 mA h/g. It undergoes a Fe$^{3+}$/Fe$^{2+}$ redox reaction located at an average potential of 3.25 V (vs. Na/Na’). From the perspective of sodium-ion batteries, most of the known cathodes for which work at ~3 V, the current material offers a relatively high redox potential that appears to arise due to the presence of two electronagative SO$_4$-units. Recently, the bloedite-type Na$_2$Fe(SO$_4$)$_2$:4H$_2$O phase was shown to have Fe$^{3+}$/Fe$^{2+}$ redox reaction at 3.3 V, but having very low capacity (ca. 51 mA h/g) even at a slow rate of C/50 and bad reversibility. The structural difference as a function of structural water content alters their final electrochemical properties. Unlike the bloedite case, the current krohnkite cathode offers excellent reversibility as shown for the first 20 cycles (Figure 3). This is the first example of highly reversible Na extraction from any sulfate-based cathode for sodium-ion batteries. While it has limited theoretical capacity, it opens up possible routes to the discovery of new sulfate cathode chemistry. The most obvious is to simply remove the structural water to obtain a dehydrated Na$_2$Fe(SO$_4$)$_2$ cathode. Our attempts in this direction have so far failed, resulting in the formation of the more thermodynamically stable Na$_2$Fe(SO$_4$)$_3$ (which was also found to be redox active with a Fe$^{3+}$/Fe$^{2+}$ potential at 3.4 V – see Supporting Information). Nevertheless, exploring sulfate battery further, we have discovered a novel high-rate 3.55 V cathode for Na battery that will be reported shortly.

In summary, we have discovered a novel krohnkite-type Na$_2$Fe(SO$_4$)$_2$:2H$_2$O compound with a pseudo-layered monoclinic structure, offering convoluted Na’-diffusion channels that permit Na (de)insertion reactions. The Fe$^{3+}$/Fe$^{2+}$ redox potential is 3.25 V and the reversible discharge capacity is 70 mA h/g. This is the first example of a reversible Na (de)intercalation cathode among all SO$_4$ based and bihydrous compounds for sodium-ion batteries. It can be the first step towards further exploration of sulfate-based chemistry to realize novel cathode materials for sodium batteries.

ASSOCIATED CONTENT

Supporting Information. Details of the structural, physical and electrochemical characterization of Na$_2$Fe(SO$_4$)$_2$:2H$_2$O, the FT-IR spectrum, thermogravimetric analysis, and battery cycling of Na$_2$Fe(SO$_4$)$_3$. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Authors
* Phone: +81-3-5841-7295. Fax: +81-3-5841-7488. E-mail: pra-beer@iith.ac.in; yamada@chemsys.t.u-tokyo.ac.jp

ACKNOWLEDGMENT

We acknowledge financial support from MEXT-Japan under the ‘Element Strategy Initiative for Catalysts & Batteries’ (ESICB) project. PB is thankful to the Japan Society for the Promotion of Sciences and IIT Bombay for generous financial support. GO is grateful to JSPS for financial support. CDL thanks the Australian Research Council for financial support (#DP110102662). Crystal structures were illustrated using the VESTA software.

REFERENCES

(2) Palomares, V.; Casas-Cabanas, M.; Castillo-Martínez, E.; Han, M. H.; Rojo, T. Energy Environ. Sci. 2013, 6, 2312-2337.


