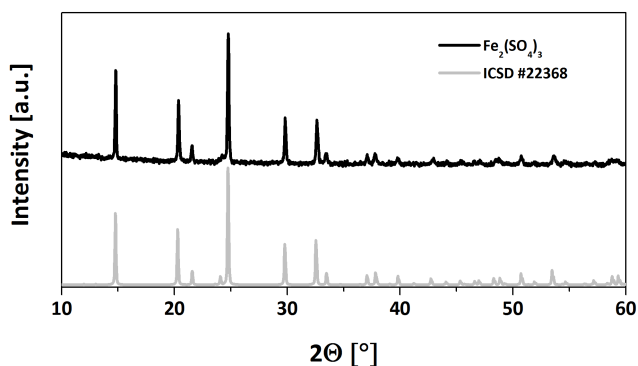


# Iron (III) Sulfate: A Stable, Cost Effective Electrode Material for Sodium Ion Batteries

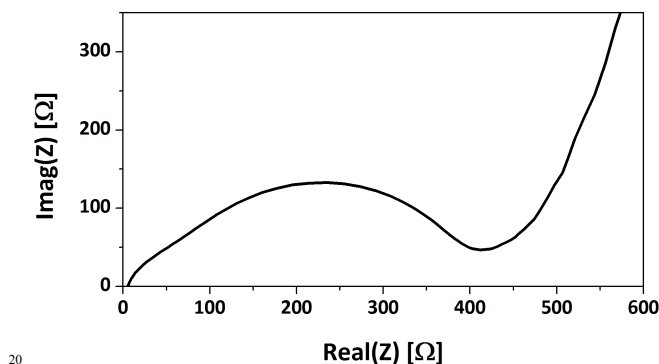
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## Supporting Information

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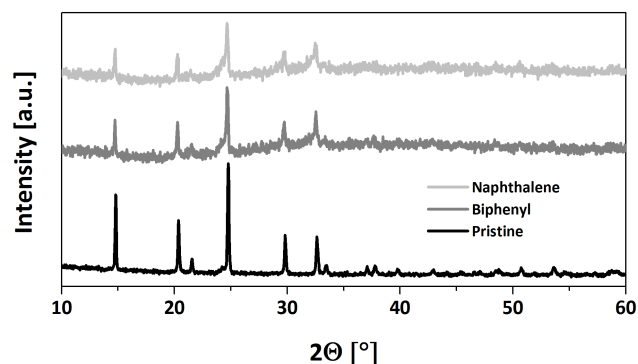


ESI Figure 1. Powder X-Ray Diffraction (XRD) Pattern of Rhombohedral Ferric Sulfate.

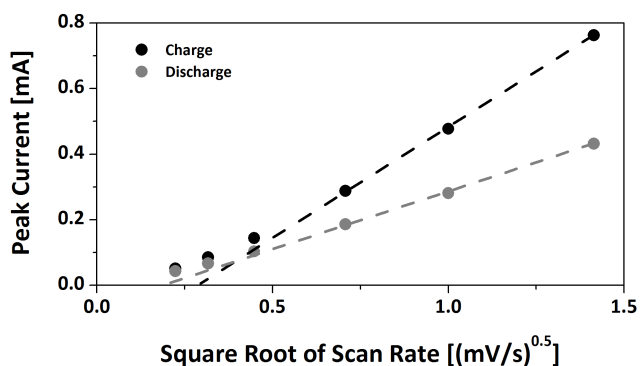


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ESI Figure 4. Representative PEIS Scan taken at charged state after one full discharge/charge cycle. 10mV amplitude.



ESI Figure 2. Powder XRD pattern of pristine and chemically sodiated materials of 1:1 molar ratios active material to sodium.



ESI Figure 3. Demonstration of system diffusion limitations at high CV scan rates.

## Experimental

25 Anhydrous ferric sulfate (Aldrich) was heated in air to 525 °C in a Carbolite Box Furnace for 12h and transferred to an argon-filled chamber before cooling to 200 °C. This heat treatment ensures the removal of all water and crystallization in the rhombohedral phase.<sup>1</sup> All subsequent steps occurred under Argon atmosphere. The material was ball-milled with carbon (Super P) in a tungsten carbide container using a Fritsch planetary ball mill for 4 hours at 400 rpm, with a 40:1 ball to powder ratio. This was to enhance the mixing between the active material and carbon. The slurry was prepared in a 70/20/10 ratio of  $\text{Fe}_2(\text{SO}_4)_3$ /carbon/PVDF(HSV900). The material was stirred overnight with N-Methyl-2-pyrrolidone (NMP), then coated with a 75 $\mu\text{m}$  doctor blade on 15 $\mu\text{m}$  etched aluminium, dried, and finally compressed with an MTI roll press. Electrodes of 2  $\text{cm}^2$  were stamped, with active material loading varied between 1.0-1.5  $\text{mg}/\text{cm}^2$ .

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40 CR2016-type coin cells were used for all electrochemical testing. Sodium metal was used as both a counter and reference electrode in these cells, while Whatman GF/F glass microfiber filters were used as separators. 1M  $\text{NaClO}_4$  in EC:PC (1:1 v/v) was chosen for the electrolyte. An Arbin BT2000 battery tester was used for galvanostatic studies, while a Biologic VMP3 performed cyclic voltammetry and impedance spectroscopy. C-rate corresponds to full charge or discharge in one hour, assuming 134  $\text{mAh}\cdot\text{g}^{-1}$  theoretical capacity (2  $\text{Na}^+$ ). Room temperature was 24 °C throughout tests. For galvanostatic and voltammetry analysis, it was found the material could be discharged further to 1.5V, but this added only a few more units of capacity, while causing additional degradation over the long term. Thus 2.0V cutoff was used for the majority of these tests. For GITT and EIS, cells were discharged and charged fully once to establish the first cycle irreversibility in which  $\frac{1}{2}\text{Na}^+$  is left in the

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system after full charge. GITT analysis was carried out using Matlab based on equations previously described.<sup>2</sup> BET surface area was 30.603 m<sup>2</sup>/g. For potentiostatic electrochemical impedance spectroscopy (PEIS) analysis, only the semicircle region was analyzed on the Nyquist plot. The model used as follows for fitting:  $R_s + R_{CT(Counter)}/Q_{DL(Counter)} + R_{CT(Working)}/Q_{DL(Working)}$ .

The series resistance,  $R_s$ , had a constant value of  $\sim 5\Omega$  throughout tests with various states of charge/discharge. The sodium metal counter also had a constant  $R_{CT}$  of  $\sim 50\Omega$ , corresponding to the first semicircle region. Lastly, both constant phase element values,  $Q_{DL}$ , also remained relatively constant throughout the process. Both GITT and PEIS graphs were converted from the amount of intercalated sodium (in moles of Na vs.  $Fe_2(SO_4)_3$ ), to percentage. This provides a better understanding to the reader of the material's properties, irrespective first cycle irreversibility. Chemical sodiation of iron (III) sulfate was carried out in 1:1 and 1:2 molar ratio (active to sodium), for one day with two different reducing agents. These were prepared by careful dissolution of sodium bits in 0.5M naphthalene/THF and 0.5M biphenyl/DME solutions. The obtained sodiation reagents were aged with constant agitation for 24h before being used.

The powder X-ray diffraction (PXRD) pattern was obtained using a Bruker D8 with  $Cu-K\alpha$  (1.54Å) radiation. A Quantachrome Nova 1200 pore analyser was used to carry out  $N_2$  physisorption at 77 K, with 200 mg material.

## References

1. P. G. Coombs and Z. A. Munir, *Journal of Thermal Analysis*, 1989, **35**, 967-976.
2. W. Weppner and R. A. Huggins, *Journal of The Electrochemical Society*, 1977, **124**, 1569-1578.