

Electronic Supplementary Information

Direct hydrofluorothermal synthesis of sodium transition metal fluorosulfates as possible Na-ion battery cathode materials.

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(1) Synthesis

All starting materials used in the synthesis were purchased from Sigma-Aldrich® (UK) with reagent grade that did not require further purification.

Warning! Caution should be taken due to the potentially violent nature of the reactions, with the possible generation of HF gas (very toxic by inhalation, in contact with skin and if swallowed) as a side product.

$\text{Na}_3\text{FeF}_2(\text{SO}_4)_2$ (I) was prepared via hydrofluorothermal process. Stoichiometric amounts of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ (0.112 g, 0.671 mmol), H_2SO_4 (98% wt, 0.073 mL 1.342 mmol) and NaOH (50% wt, 0.106 mL 2.013 mmol) were mixed thoroughly in a 23 mL capacity Teflon™-lined Parr autoclave. The molar ratio of the Fe:S:Na was 1:2:3. The autoclave was sealed and heated at 175 °C for 3 days and then cooled to room temperature. The pink single phase product was collected by suction filtration with deionized water and dried in air.

$\text{Na}_3\text{MnF}_2(\text{SO}_4)_2$ (II) synthesis. Stoichiometric amounts of MnF_3 (0.0611 g, 0.546 mmol), H_2SO_4 (98% wt, 0.0594 mL 1.092 mmol), and NaOH (50% wt, 0.0865 mL 1.638 mmol) were mixed thoroughly in 23 mL capacity Teflon™ lined Parr autoclave, with molar ratio of Mn:S:Na was 1:2:3. The autoclave was sealed and then heated at 200 °C for 3 days and then cooled to room temperature. Dark brown product with minor phase was collected as (I).

$\text{Na}_3\text{VF}_2(\text{SO}_4)_2$ (III) synthesis, Stoichiometric amounts of VF_3 (0.0432 g, 0.4 mmol), H_2SO_4 (98% wt, 0.0435 mL 0.8 mmol), and NaOH (50% wt, 0.0634 mL 1.201 mmol) were mixed thoroughly in 23 mL capacity Teflon™ lined Parr autoclave, with molar ratio of V:S:Na was 1:2:3. The autoclave was sealed and then heated at 175 °C for 4 days and then cooled to room temperature. Olive green single phase product was collected as (I).

$\text{Na}_2\text{FeF}_3\text{SO}_4$ (IV) was prepared via hydrofluorothermal process. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.212 g, 0.763 mmol), hydrofluoric acid (45% wt, 0.0295 mL, 0.763 mmol) and NaF (0.048 g, 1.445 mmol) were mixed thoroughly in 23 mL capacity Teflon™ lined Parr autoclave. The autoclave was sealed and then heated at 175°C for 2 days before cooling slowly to room temperature. Light green major phase product was collected as (I).

$\text{Na}_5\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}\text{F}_4(\text{SO}_4)_2$ (V) was synthesized through hydrofluorothermal process. MnF_3 (0.0611 g, 0.546 mmol), H_2SO_4 (98% wt, 0.0594 mL, 1.092 mmol), NaF (0.0688 g, 1.638 mmol) were mixed thoroughly in 23 mL capacity Teflon™ lined Parr autoclave. The autoclave was sealed and then heated at 180°C for 3 days before cooling slowly with ramp of 0.2 °C/min to room temperature. Dark brown product with major phase was collected as (I).

$\text{Na}_{12}\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}\text{F}_8(\text{SO}_4)_6$ (VI) was synthesized through hydrofluorothermal process. MnF_2 (0.0712 g, 0.766 mmol), H_2SO_4 (98% wt, 0.0833 mL, 1.532 mmol), NaF (0.0965 g, 2.299 mmol), were mixed thoroughly in 23 mL capacity Teflon™ lined Parr autoclave. The autoclave was

sealed and then heated at 180°C for 3 days before cooling slowly with ramp of 0.2 °C/min to room temperature. Pink product with minor phase was collected as (I).

(2) Structure determination

X-ray diffraction characterization Single-crystal X-ray diffraction (SXD) data was collected for all samples at 120 K on a Rigaku FR-E+ ultra-high flux diffractometer, using Mo-K α ($\lambda=0.71073$ Å) radiation, Structure were solved using the WinGX suite of programmes,^{E1} utilizing XPREP^{E2} and SHELX-97,^{E3} to solve the structure by direct methods.^{E4} Full information of single crystal data are summarized in Table 1 (main text) and in the deposited CIFs. CCDC numbers 424955-424960.

References

- E1. L. J. Farrugia, *Journal of Applied Crystallography*, 1999, **32**, 837-838.
- E2. G. Sheldrick, *XPREP. Space Group Determination and Reciprocal Space Plots*, 1991.
- E3. G. M. Sheldrick, *Release 97-2, University of Göttingen, Germany*, 1997.
- E4. G. M. Sheldrick, *Acta Crystallographica Section A*, 1990, **46**, 467-473.

(3) Powder X-ray Diffraction and SEM/EDAX analysis of Na₃FeF₂(SO₄)₂ (I) and Na₃VF₂(SO₄)₂ (III)

(a) Na₃FeF₂(SO₄)₂ (I)

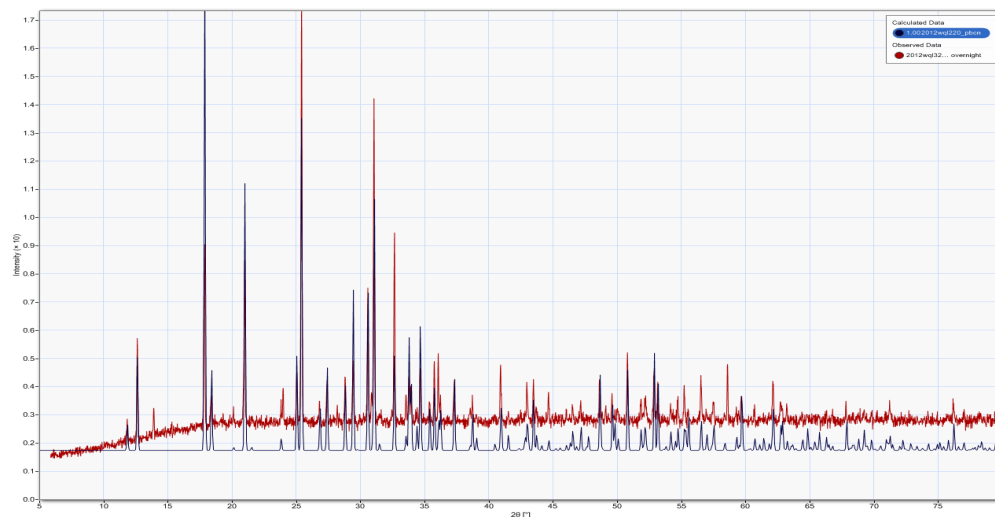
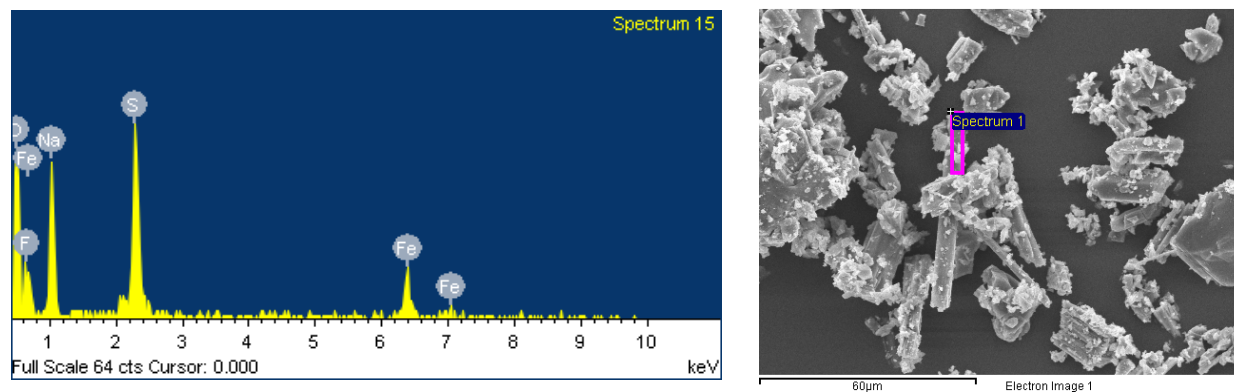


Fig 1. Powder X-ray diffraction comparison of Na₃FeF₂(SO₄)₂. Collected experimental data (Red) is shown in comparison with the calculated, from SXD data, pattern (Blue).



Elements	Theoretical Atomic Ratio	Experimental Atomic %	Experimental Atomic Ratio
Na	3	15.73	2.59
Fe	1	6.07	1
S	2	11.92	1.96

(b) $\text{Na}_3\text{VF}_2(\text{SO}_4)_2$

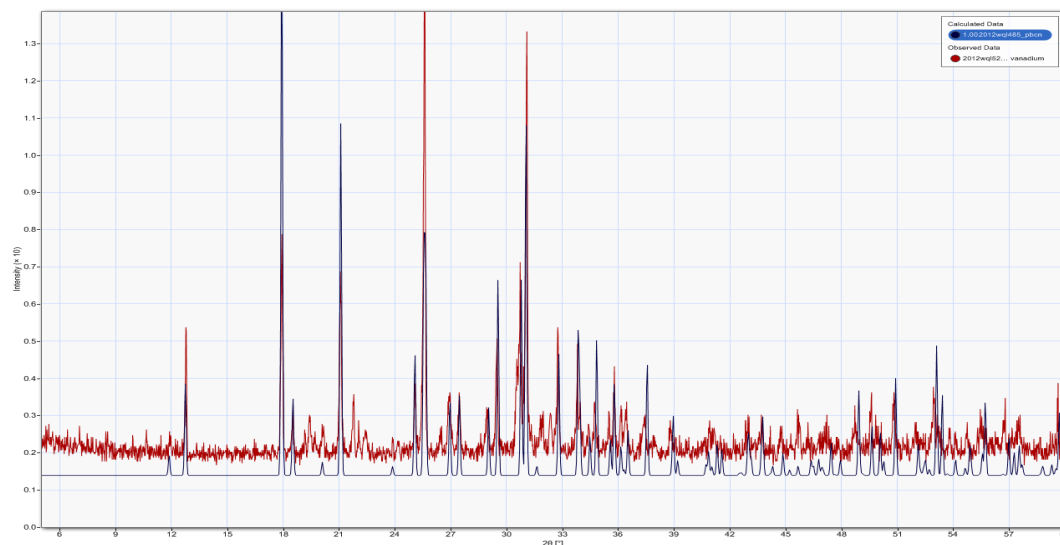
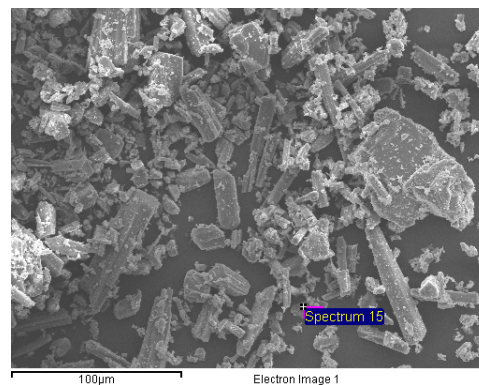
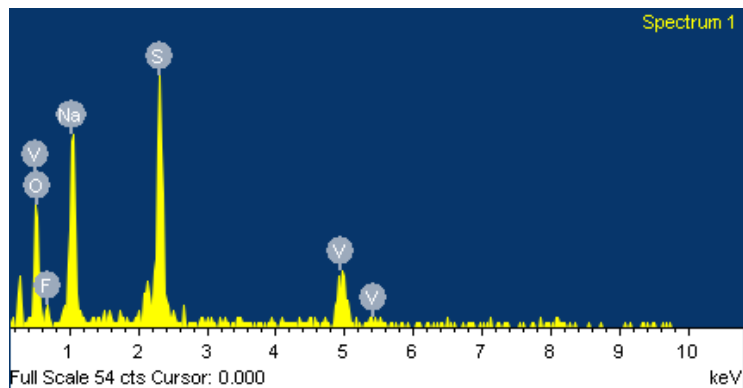


Fig 2. Powder X-ray diffraction comparison of $\text{Na}_3\text{VF}_2(\text{SO}_4)_2$. Collected experimental data (Red) is shown in comparison with the calculated, from SXD data, pattern (Blue).

EDX-SEM compound III: $\text{Na}_3\text{VF}_2(\text{SO}_4)_2$



Elements	Theoretical Atomic Ratio	Experimental Atomic %	Experimental Atomic Ratio
Na	3	16.08	3.12
V	1	5.16	1
S	2	14.17	2.75

(4) Electrochemistry

Experimental details

$\text{Na}_3\text{VF}_2(\text{SO}_4)_2$ and $\text{Na}_3\text{FeF}_2(\text{SO}_4)_2$ were used as the active materials for electrochemical sodium insertion/extraction experiments. 75 % by weight active material was combined with 20 % by weight dry acetylene black (Shawinigan Black, *Chevron Phillips*) in a pestle and mortar and ground until a homogenous mixture was produced. 5% by weight dry PTFE (6C-N, *Dupont*) was then added to the mixture, and worked into a single solid lump. The cathode material was calendared using a rolling mill (*Durston*) to produce an 80 μm thick uniform film. Cathode pellets with a diameter of 8mm were produced from the film using a punch and dried under vacuum at 120 °C overnight.

Electrochemical testing of material was carried out using PFA Swagelok type cells with 1.0 M NaPF_6 (98%, *Sigma-Aldrich*) in PC (*Sigma-Aldrich*) soaked glass fibre separators and sodium foil (ACS grade, *Sigma-Aldrich*) negative electrodes assembled under an inert argon atmosphere. The water content of the electrolyte was tested using the Karl Fischer technique was found to contain less than 10 ppm of moisture. A potentiostat (VMP1, *Bio-Logic*) was used to cycle the cells under constant current conditions at a C-rate of 0.1 assuming one electron transfer per formula unit of active material.

Results and discussion

The open circuit of the pristine $\text{Na}_3\text{FeF}_2(\text{SO}_4)_2$ was measured at 2.88 V vs. Na metal. The cell was cycled twice under galvanostatic conditions to give the results shown in Figure E1. The upper potential limit was set at 4.0 V during the first anodic half cycle to avoid any likelihood of electrolyte decomposition. A plateau near 3.5 V, leading to a significant rise to the limiting potential after passage of 65 mAh g^{-1} suggests an almost complete oxidation of Fe^{III} to Fe^{IV} with a theoretical capacity of 75 mAh g^{-1} for the extraction of one electron and one sodium ion per structural unit. However, a low capacity of 3 mAh g^{-1} during the cathodic half cycle showed a strong resistance to any re-insertion as the potential reduced to the negative limit of 2.0 V, presumably due to the blocking of sodium ion diffusion pathways following a structural change that occurred during the extraction of sodium.

The potential limit was raised to 4.5 V on the second cycle, expanding the potential window to investigate reactions at higher potential due to further oxidation. On the second charge, the voltage increases sharply until 4.2 V where a further irreversible oxidation process occurs. Since it has recently been shown that NaPF_6 can be stable above 4.5 V vs. Na in this solvent^{E5}, the observed current is here attributed to further oxidation of the sample by extraction of sodium. However, oxidation of Fe^{IV} to Fe^{V} is unlikely, and therefore the evolution of oxygen, as previously demonstrated for high voltage lithium cathodes such as $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ is a more likely explanation.^{E6}

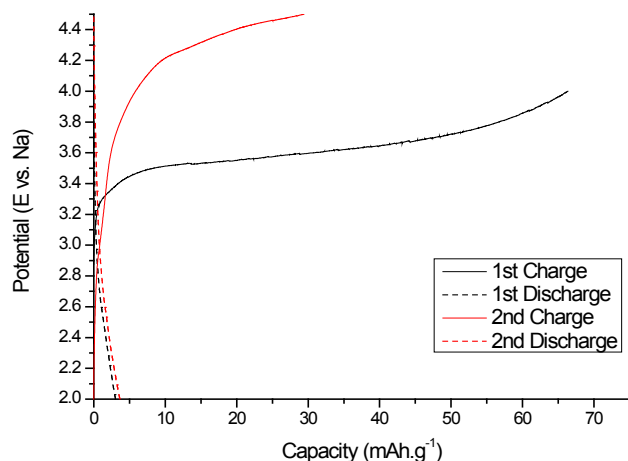


Figure E1. Galvanostatic cycling of $\text{Na}_3\text{FeF}_2(\text{SO}_4)_2$ vs. Na metal with 1.0 M NaPF_6 in PC at 7.6 mA g^{-1} , i.e. approximately 0.1 C assuming a theoretical capacity of 76 mAh g^{-1} .

The results $\text{Na}_3\text{VF}_2(\text{SO}_4)_2$ positive electrode material tested in the same way as $\text{Na}_3\text{FeF}_2(\text{SO}_4)_2$ are shown in Figure E2. The open circuit of the pristine cell was measured at 2.68 V vs. Na metal. A gradual rise in potential around 3.6 V, becoming steeper near 4.0 V after the passage of the oxidation 101 mAh g^{-1} (c.f. 77 mAh g^{-1} for a one-electron transfer) suggests rather more than a single oxidation from V^{III} to V^{IV} , and more than one sodium atom extracted, with the possibility of some V^{V} being produced. The cathodic half-cycle showed 6.5 mAh g^{-1} , which is possible evidence of re-insertion of sodium to a small extent.

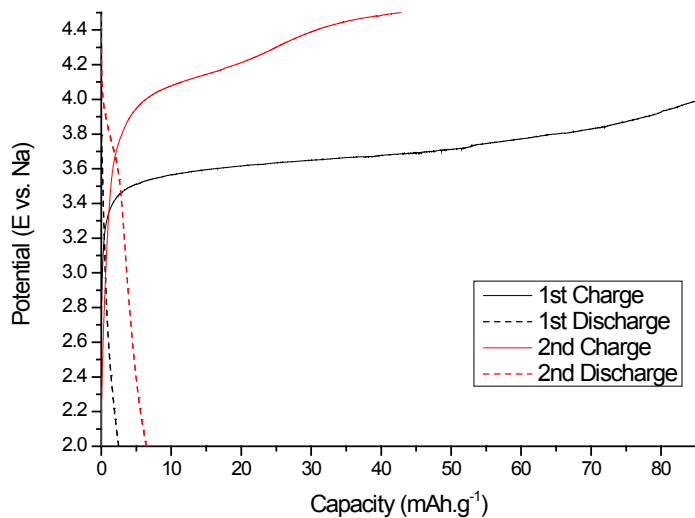


Figure E2. Galvanostatic cycling of $\text{Na}_3\text{VF}_2(\text{SO}_4)_2$ vs. Na metal with 1.0 M NaPF_6 in PC at 7.7 mA g^{-1} , i.e. approximately 0.1 C assuming a theoretical capacity of 77 mAh g^{-1} .

References

- E5 Ponrouch, A.; Marchante, E.; Courty, M.; Tarascon, J.-M.; Palacín, M. R. *Energy & Environmental Science*, **2012**, 5, 8572.
- E6 Johnson, C. S.; Kim, J.-S.; Lefief, C.; Li, N.; Vaughey, J. T.; Thackeray, M. M. *Electrochemistry Communications*, **2004**, 6, 1085–1091.