Fe-based $\text{SO}_4$-$\text{PO}_3$F heteropolyanionic cathodes
for sodium-ion batteries

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Limited uneven distribution and high cost of lithium resources raise serious concerns about the future of the currently dominating lithium-ion battery. In the quest for new battery technologies, sodium-ion batteries (SIB) have become an attractive alternative. The abundance of sodium and its affordable price render SIBs an interesting option for large-scale energy storage systems.

Intensive research efforts have been dedicated to the development of suitable cathode materials for SIBs. For instance, polyanions came into focus in terms of their cycling stability, safety and low cost. Especially sulfate-based compounds such as $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ present high redox potentials caused by the strong inductive effect of the $\text{SO}_4^{2-}$ group and thus emerged as promising cathode materials.$^{[1,2]}$

In an attempt to find new high-voltage cathodes, we explore heteropolyanionic systems to enhance the degree of freedom. As a starting point, we chose sodium iron sulfate $\text{Na}_2\text{Fe}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}[^3]$, where $\text{SO}_4^{2-}$ is partially substituted by the isovalent fluorophosphate $\text{PO}_3\text{F}^2$. Since $\text{PO}_3\text{F}^2$ has not been studied so far as a polyanion for cathode materials, our interest lies especially in the exploration of its effect on the electrochemical performance as compared to the pure sulfate-based compound. In this work, the heteropolyanionic system $\text{Na}_2\text{Fe}(\text{SO}_4)_{2-x}(\text{PO}_3\text{F})_x\cdot 2\text{H}_2\text{O}$ was synthesized following the previous work of Driscoll et al.$^{[4]}$ (Figure 1), and its electrochemical properties were studied. The similar operating potential of the solid-solution phases as compared to the $\text{Na}_2\text{Fe}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$ end-member suggests that $\text{PO}_3\text{F}^2$ can compete with the elevated inductive effect of $\text{SO}_4^{2-}$ opening the door to novel high-voltage cathode materials.

![Figure 1](image)

Figure 1: Schematic representation of the formation of the solid-solution $\text{Na}_2\text{Fe}(\text{SO}_4)_{2-x}(\text{PO}_3\text{F})_x\cdot 2\text{H}_2\text{O}$.

References: