Fe-based SO_4-PO_3F 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 $Na_2Fe_2(SO_4)_3$ present high redox potentials caused by the strong inductive effect of the 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 $Na_2Fe(SO_4)_2 \cdot 2H_2O$[3], where SO_4^{2-} is partially substituted by the isovalent fluorophosphate PO_3F^{2-}.[4] Since PO_3F^{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 $Na_2Fe(SO_4)_{2-x}(PO_3F)_x \cdot 2H_2O$ 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 $Na_2Fe(SO_4)_2 \cdot 2H_2O$ end-member suggests that PO_3F^{2-} can compete with the elevated inductive effect of SO_4^{2-} opening the door to novel high-voltage cathode materials.

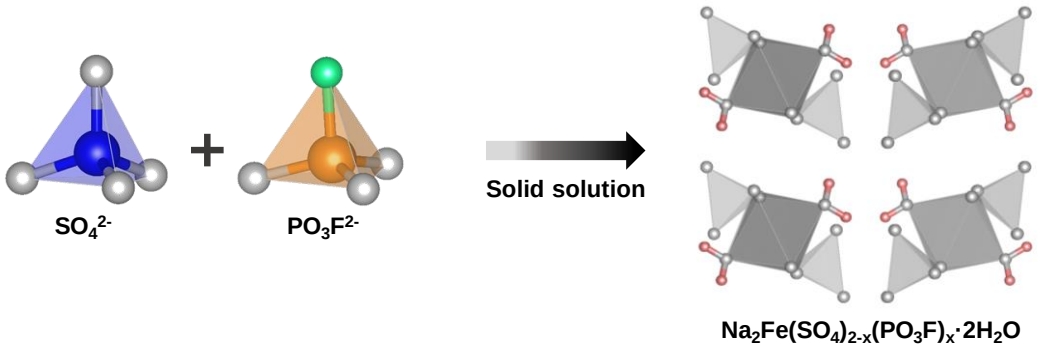

Figure 1: Schematic representation of the formation of the solid-solution $Na_2Fe(SO_4)_{2-x}(PO_3F)_x \cdot 2H_2O$.

References:

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