Crystal Structure in Bringing Excellent Electrochemical Properties in Alluaudite Type Sodium Insertion Materials

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To meet the global energy demand, efficient energy generation and storage are counted as savours. Here, electrochemical energy storage in general and rechargeable batteries in particular is the most efficient form of energy storage and (mobile) delivery. In this regard, lithium-ion batteries have ushered the wireless revolution over the last three decades. But, the ever growing concerns over natural lithium reserves has stimulated major interest in sodium-ion batteries as economic alternatives, particularly for large-scale storage applications. At this stage, be it Li-ion or Na-ion technologies, both need to be improved in order to match the energy density, operational safety and sustainability as required by myriad of energy hungry applications. Addressing such challenges - “Energy Storage (R)Evolution” vastly relies on innovation of new cathode materials along with the optimization of existing ones. One of the popular way of navigating such materials is via the ideas of crystallography.

A crystallographer of battery materials looks for channels (open paths) that can store and transport alkali ions. In this prospect, inorganic materials with three dimensional polyanionic framework materials such as borates, phosphates, fluorophosphates, pyrophosphates, silicates, sulfates, fluoroanhydride are viable battery materials as they provide open channels with structural stability. Among them, sulphate based materials attests highest voltage due to the presence of electron withdrawing group. One of most cited example was NASICON type Fe₂(SO₄)₃, which can intake multiple Na⁺ ions to form Na₂Fe₂(SO₄)₃. In a recent breakthrough, a completely different polymorph of Na₂Fe₂(SO₄)₃ was discovered adopting alluaudite mineral structure. It has benchmarked the highest ever Fe³⁺/Fe²⁺ redox potential (ca. 3.8 V vs. Na⁺/Na°) with excellent cyclability and rate kinetics.

The origin of such high redox voltage is alluring, which can be correlated to its crystal structure. Na₂Fe₂(SO₄)₃ stabilizes into a monoclinic framework (s.g. C2/c), which is built from unique edge sharing of transition metal octahedra (TM₂O₆) that are in turn interconnected by SO₄ tetrahedral units. This renders large open channels along b axis for sodium (de)insertion. Inspired by this beautifully channelized crystal structure of Na₂Fe₂(SO₄)₃, in the present study, we have extended the alluaudite family by discovering isostructural Na₂Mn₂(SO₄)₃ and Na₂Co₂(SO₄)₃ analogues. Synergizing X-ray diffraction, Rietveld refinement, bond valence sum analysis and electrochemical measurements, we have identified the Na-ion migration pathways that enable these alluaudite materials to act as superior cathodes for next generation rechargeable sodium batteries. We will describe the synthesis and structural aspects of various SO₄-based alluaudites and compare them with PO₄-based and MoO₄-based alluaudite cathodes.