Independent of any source of energy, all of them require efficient energy storage and that is where rechargeable batteries emerge as efficient, economical and sustainable devices for energy storage. Being the lightest element with small cation size, lithium offers the highest energy density and therefore commands a sizeable market in portable electronics sector. The increasing demand of lithium-based systems has put a humongous pressure on lithium producing industries, as the global lithium reserves are limited. Moreover, cost and transport restrictions associated with lithium have forced us to look for an alternate chemistry, where sodium-ion batteries have emerged as viable electrochemical energy storage devices.

The performance parameters of batteries such as voltage, capacity, energy density etc. depend on the electrochemical activity of the alkali-ion involved in diffusion. In the past decade or so there has been huge uprising in the study of cathode materials for sodium batteries starting from layered oxides to polyanionic frameworks. In recent time, fluorine based materials have been gradually finding a prominent place in energy storage and conversion, resulting in enhanced performance of batteries. Although they are poor electronic conductors than their oxide counter-parts, they exhibit higher potential owing to larger ionicity of M-F bond than M-O bond. Hence, fluorophosphates class of polyanionic cathodes has garnered great interest. Transition metal-based fluorophosphates can be used in both Li- and Na-based architecture, as shown in case of Na₂FePO₄F. This material has an orthorhombic structure with Pbcn space group, which is isostructural to both Na₂FePO₄OH and Na₂CoPO₄F consisting of biocathedral Fe₂O₇F₂ units having face sharing FeO₄F₂ octahedra connected via bridging F atoms to form chains. These chains are abridged by PO₄ tetrahedra to form [FePO₄F] infinite layers with twodimensional pathways for sodium ion migration. Efficient Li insertion (at 3.6 V vs. Li/Li⁺) and Na insertion (at 3.0 V vs. Na/Na⁺) have been reported in Na₂FePO₄F with excellent reversibility.

Reversible Li⁺ (de)insertion has also been observed in variety of LiMPO₄F fluorophosphates (M= Fe, V, Ti, Co, Cr). Depending upon the synthesis conditions and constituent transition metals, they can show rich polymorphism, multiple electron redox processes and tunable redox potentials. These Li-based and Na-based fluorophosphates can be prepared by conventional solid-state synthesis as well as variety of solvothermal routes. The current work will describe (i) tavorite structured fluorophosphates, (ii) polymorphism in A₂MPO₄F (A = Li/Na, M = Fe, Co, Mn), (iii) diffusion migration pathways and (iv) electrochemical performance of several alkali metal fluorophosphate battery insertion materials.


Keywords: Batteries, Fluorophosphates, Polymorphism