Electrochemical storage has become an indivisible part of our mobile society and energy grid systems. In future, Li-ion and Na-ion batteries are poised to conquer electric vehicles (EV) and grid storage markets. Batteries with high-performance and environmentally benign materials are widely pursued for large scale dissemination. This calls for research at the material level. Currently battery researchers are focusing their attention to design polyanionic electrodes made up of earth abundant elements. Three-dimensional framework compounds comprising polyanions (e.g. SO$_4^{2-}$, PO$_4^{3-}$ etc.) have been designed as viable alternatives to oxide-based electrode materials (LiM$_{x}$O$_y$). Fe-based polyanionic compounds are promising, where LiFePO$_4$ is a pioneer candidate offering decent redox potential (3.45 V versus Li$^+$/Li$^-$), chemical/thermal stability and flat discharge profile. To increase the Fe$^{3+}$/Fe$^{2+}$ redox potential (and thereby energy density) of polyanionic compounds, more electronegative polyanionic species can be used. By replacing PO$_4^{3-}$ with the more electronegative SO$_4^{2-}$, together with optional addition of highly electronegative F$^-$ ions, higher energy density can be achieved with higher redox potential. In this work we will explain our approach focusing on novel families of sulfate-based polyanionic cathode systems: (i) bisulfate Li$_2$Fe(SO$_4$)$_2$ and (ii) fluorosulfate AFeSO$_4$F (A=Li, Na, K).

We will discuss the energy-savvy soft chemical synthesis approach for these compounds. Li$_2$Fe(SO$_4$)$_2$ exists in two polymorphs (i) marinite phase (monoclinic: C2/m symmetry) and (ii) orthorhombic phase (Pbca symmetry) as a result of varying ball milling time. Marinite phase stabilizes with short duration ball milling ($\leq$ 1 hour) followed by calcination in inert atmosphere, whereas orthorhombic phase requires long duration milling. Both structures consist of a 3D framework of FeO$_6$ and SO$_4$ groups, where the FeO$_6$ octahedra are isolated from each other and only linked through the SO$_4$ tetrahedra via oxygen corner-sharing. The key difference between the structures of Li$_2$Fe(SO$_4$)$_2$ polymorphs is the way in which the FeO$_6$ and SO$_4$ polyhedra are interconnected. Marinite phase reveals electrochemical activity at 3.83 V, whereas orthorhombic phase shows activity close to 3.73 V and 3.85 V involving biphasing redox behaviour. Orthorhombic phase delivers excellent cycling stability and rate kinetics than its marinite counterpart.

Alkali metal fluorosulphates, AFeSO$_4$F (A=Li, Na, K), form a structurally rich family of compounds. LiFeSO$_4$F can be prepared in two distinct polymorphs both built with FeO$_4^-$ octahedra and SO$_4^{2-}$ tetrahedra, namely, the tavorite (triclinic: P-1) and the triplite (monoclinic: C2/c) structures. Triplite phase of LiFeSO$_4$F displays the highest potential ever reported among all known Fe-based compounds (ca. 3.9 V vs Li/Li$^+$). While NaFeSO$_4$F assumes a maxweillite structure, KFeSO$_4$F forms KTiOPO$_4$-type orthorhombic structure. It contains MO$_4^-$ octahedra linked by F atoms in the vertices and neighbouring MO$_4^-$ units are connected to two SO$_4^{2-}$ units to create buckling in chains along [010] and [100] directions. The crystal structure, polymorphism and final electrochemical performance of various SO$_4^{2-}$ containing high-voltage cathodes will be described.


Keywords: batteries, bisulfates, fluorosulfates