

**Synthesis, Structure and Properties of LiMSO_4F
Phases (M = 3d metal) as Positive Electrode
Materials for Li-ion Batteries**

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Over the last two decades, energy storage devices have observed a steadily growing demand by virtue of their potential implementation for automotive applications (PHEV and HEV). Such a new market has boosted research for new and efficient electrodes materials in terms of power and energy densities. In fact, the last decade has observed commercialization of polyanionic compounds such as *Olivine* LiFePO_4 .^[1] The latter remains as the most desired electrode material for the next generation of Li-ion batteries.

By substituting PO_4^{3-} with SO_4^{2-} along with the addition of F^- , our group recently prepared the *Tavorite* LiFeSO_4F compound,^[2] which shows sustained reversible capacity of 140mAh/g at a voltage of 3.6V vs. Li and relies on the use of abundant resources. Moreover, its synthesis is straightforward and its electrode processing is quite simple. Therefore, we investigated the other members of this family by varying the 3d metals (Co, Ni, Mn and Zn). This investigation revealed that both LiMnSO_4F and LiZnSO_4F crystallize in two different structure types namely *Triplite* and *Sillimanite*, respectively. This motivated our study of the solid solutions of $\text{LiFe}_{1-y}\text{M}_y\text{SO}_4\text{F}$ (M = Mn or Zn).^[3]

Through this study, we observed an increase in the redox potential from 3.6 to 3.9V by going from the *Tavorite* to the *Triplite* structure. The *Sillimanite* did not show any increase in redox potential compared to *Tavorite*. Using *in situ* Mössbauer and XANES studies, the electroactivity was confirmed to be from the iron redox couple ($\text{Fe}^{3+}/\text{Fe}^{2+}$) only in these solid solutions.

These results motivated the preparation of *Triplite* LiFeSO_4F (Mn and Zn-free).^[4] Since, we encountered several difficulties in reproducing the synthesis products, we conducted isothermal calorimetric measurements to understand the relative thermodynamic stabilities of these two polymorphs (*Tavorite* vs. *Triplite*). The results of which showed the *Triplite* LiFeSO_4F to be more stable than the *Tavorite*, due to increased entropy.^[5]

New synthetic approaches (SPS and mechanical alloying) were utilized to prepare the *Triplite* LiFeSO_4F and the phase transformation from *Tavorite* to *Triplite* was observed by simple aging or by increasing local disorder. Further, the synthesis procedures were adapted to prepare a new family of lamellar hydroxysulfates as potential positive electrode materials for Li-ion batteries.^[6]

References:

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