
Conclusions

We had started our work to increase the energy density of the cathode by modifying $\text{Na}_{1+x}\text{Fe}_2(\text{SO}_4)_2\text{PO}_4$ intending to increase the specific capacity by increasing x , i.e., increasing the number of sodium-ions taking part in the intercalation/deintercalation process, and a capacity equivalent to 75mAh/g capacity was achieved. Due to Strong coulombic interaction, and SEI formation, we were not able to utilize or realize the theoretical capacity of the material.

Further, I tried to improve Capacity by increasing the potential window of the operating voltage of the electrode by the inclusion of high energy redox couple of $\text{Mn}^{2+/3+}$, $\text{Ni}^{2+/3+}$, and inactive Mg^{2+} redox. We successfully achieved the increase in operating potential vs. Na/Na^+ for the doped electrode, but at the same time, we lost the capacity due to the catalytic oxidation activity of Ni, Mn that may lead to degradation of electrolyte at higher voltages.

The further high ionic character of SO_4 ligand also results from partial solubility of the electrode in a high dielectric liquid electrolyte. The dielectric constant of EC: DEC electrolyte is close to 55, and water has a dielectric constant close to 80. Thus, a high ionic character that is responsible for voltage up-gradation resulted in partial solubility of the material into the electrolyte solution. This has resulted in material instability and huge capacity loss. Thus, we cannot go above 3.5V in $\text{Na}_{1+x}\text{Fe}_2(\text{SO}_4)_2\text{PO}_4$ system with doping with Ni, Mn, Mg.

Further, to confirm our hypothesis of high ionic character leading to voltage up-gradation and creating material instability, we synthesized $\text{NaCr}(\text{SO}_4)_2$ into Eldfellite structure to utilize the redox couple of $\text{Cr}^{3+/4+}$ and ionic character of only SO_4^{2-} ligand. The charge-discharge profile showed voltage up-gradation or realization $\text{Cr}^{3+/4+}$ couple

vs Na/Na⁺ above 4V followed by oxidation of electrolyte. To our surprise, on discharge, redox of Cr^{3+/2+} was observed below 1V. Generally, Cr³⁺ → Cr²⁺ reduction doesn't happen easily as Cr²⁺ band lies close to the conduction band of Cr metal. Thus, the high ionic character of SO₄²⁻ ligand shifted Cr^{3+/2+} redox couple also, and a reversible intercalation/de-intercalation of Na⁺ ion followed with a stable capacity equivalent to ~75 mAh/g was realized. The strong Na⁺-Na⁺ coulombic interaction seems to play an important role in lowering the capacity of the materials. Further, NCS/Li cell resulted in a stable capacity equivalent to 150 mAh/g at C/10 current rate. Higher capacity was realized due to the absence of Na⁺-Na⁺ ion coulombic interactions.

Therefore, we decided to shift from a highly ionic SO₄²⁻ ligand to a more covalent polyphosphate ligand and then enhance voltage using high-energy redox couples. We choose polyhedral P₂O₇ and P₂O₁₁ units to achieve higher energy capacity as well as the high-power density of the electrode. We have started with Mo₂P₂O₁₁ to utilize Mo^{4+/6+} couple similar to Cr^{4+/6+} and realized a capacity of 89mAh/g and energy density of 267Wh/Kg at an operating voltage of 3.0V w.r.t. Na/Na⁺. The reversible storage capacity is realized with a phase transformation from Mo₂P₂O₁₁ to Na_{1±x}Mo₂P₂O₁₁ that has made the reversible intercalation/de-intercalation possible

Suggestions for Future Work

- ❖ Move away from highly ionic SO_4^{2-} polyhedra in a high dielectric constant electrolyte system.
- ❖ Prefer to work with Phosphate polyhedra for a highly stable electrode system.
- ❖ Need to explore $\text{Mo}^{4+/3+}$ redox couple in detail for the Sodium-ion battery system.
- ❖ Structural engineering with NaMP_2O_7 ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{Cr}$, and a mixture thereof) to develop a novel cathode to access $\text{M}^{3+/4+}$ redox couple for high-capacity sodium-ion battery.