

## Abstract

A small technological revolution was started when Sony launched their rechargeable battery in 1991. Since then, the rechargeable battery has become a household item for almost everyone on the planet. This is because the Li-ion technology vastly outperformed its rechargeable predecessors, i.e. the nickel cadmium and Ni-metalhydride, in terms of voltage and specific energy density. Some of the most utilized battery chemistries for commercial rechargeable Li-ion batteries have glaring issues. They have decreased safety due to low thermal runaway temperatures and use costly low abundance elements such as Ni and Co whose price is not only subject to supply-and-demand but also geopolitical issues. Battery chemistries of the future should be cheaper, safer and more environmentally friendly while being tailored to the specific need of the application. The aim of this project is to investigate how changing the intercalation ion (Li and Na), the electrochemically active species (first row transition metals) and/or the framework component of crystalline phosphate-based cathode materials affects the electrochemical performance and the structural electrochemically-driven phase transformation during cycling.

It was also found that by varying the synthesis conditions, the morphology of  $\text{Fe}_{2-y}\square_y(\text{PO}_4)(\text{OH})_{3-3y}(\text{H}_2\text{O})_{3y-2}$  particles could be fine-tuned by controlling the pH, synthesis time and addition of surfactant in the hydrothermal synthesis. This made it possible to tune the overpotential and improving the capacity by reduction of the particle size. Through SR-PXRD, it was found that  $\text{Fe}_{2-y}\square_y(\text{PO}_4)(\text{OH})_{3-3y}(\text{H}_2\text{O})_{3y-2}$  undergoes a complete solid solution phase transformation over the entire xLi and xNa compositional range.  $\text{Fe}_{2-y}\square_y(\text{PO}_4)(\text{OH})_{3-3y}(\text{H}_2\text{O})_{3y-2}$  was found to perform well as a cathode material for both Li-ion and Na-ion intercalation.

Chemically delithiated phospho-olivine  $\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$  ( $y = 0.0, 0.1, 0.2, 0.4, 0.6$  and  $0.8$ ) was found to be a very versatile cathode material as it exhibits great electrochemical performance during Na-ion intercalation at low Mn substitution. 10 – 20 % Mn substitution of Fe in the phospho-olivine structure yields >15 % higher capacities compared to Mn-free  $\text{FePO}_4$  against Na with  $\text{Mn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$  exhibiting the highest capacity of 145 mAh g<sup>-1</sup>. Even with substitution of Fe by Mn, it was found that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple can be split into two steps with the formation of a  $\text{Na}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$  ( $x > y$ ) intermediate as observed in Mn-free  $\text{FePO}_4$  vs. Na. Operando SR-PXRD showed that low Mn substitution leads to lowering of the lattice misfit whereas higher Mn substitution leads to higher lattice misfits revealing a capacity-misfit correlation for  $\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$  against Na. Thus, the effect of substituting Mn into the phospho-olivine structure is stronger than that of introducing the larger Na-ion.

Furthermore, mixed transition metal phospho-olivines ( $\text{LiMn}_{0.5-0.5y}\text{Fe}_{0.5-0.5y}\text{M}_y\text{PO}_4$ , M = first row transition metal) was investigated as cathode materials, a combined PXRD-XRF-mapping study about aging in commercial  $\text{LiFePO}_4$  was investigated and in another study a route for optimization of electrode performance was devised.