

Crystal Structures and Electrochemical Properties of the Battery Materials $\text{Na}_x\text{M}_3(\text{PO}_4)_3$

Hamdi Ben Yahia¹, Rachid Essehli¹, Ilias Belharouak¹

¹*Qatar Environment And Energy Research Institute, Hamad Bin Khalifa University, Doha, Qatar*

E-mail: Hyahia@qf.org.qa

Polyanionic Transition-metal phosphates with open-framework structures have been subject to growing scientific interest as electrode materials for sodium-ion batteries. This is mainly due to the remarkable structural and thermal stabilities of this class of materials. In particular, iron-based phosphate compounds such as, NaFePO_4 , FePO_4 , $[\text{Na}_{1-x}\text{Li}_x]\text{MnFe}_2(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}_{3-x}\text{Mn}_x(\text{PO}_4)_3$, $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$, $\text{Na}_2\text{Fe}(\text{P}_2\text{O}_7)$, $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$, $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$, $\text{Na}_2\text{Fe}(\text{PO}_4)\text{F}$, $\text{Na}_{6.24}\text{Fe}_{4.88}(\text{P}_2\text{O}_7)_4$, and $\text{Na}_{3.12}\text{Fe}_{2.44}(\text{P}_2\text{O}_7)_2$, have been intensively studied as positive electrode materials for sodium-ion batteries (NIBs). These compounds have been chosen because they are anticipated to be low cost materials, with enhanced safety and high energy density.

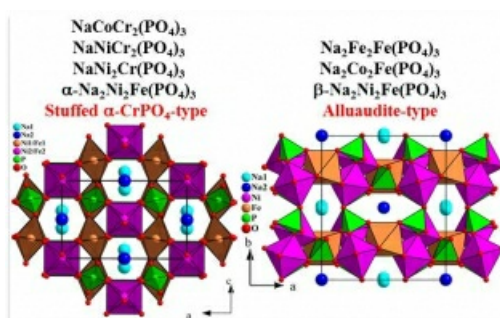
Recently, we have tested new phosphates $\text{Na}_x\text{M}_2\text{T}(\text{PO}_4)_3$ ($1 \leq x \leq 2$, $\text{M} = \text{Co}$ and Ni ; $\text{T} = \text{Cr}$ and Fe) as dual anode/cathode materials for sodium-ion batteries [1-3]. These materials, which have been prepared by different reaction routes, exhibited promising electrochemical properties. They crystallize with the -CrPO₄- and alluaudite-type structures. Furthermore, it is possible to replace Co, Ni, and Cr by Fe. In this case, the alluaudite structure is preserved and the resulting phase $\text{Na}_2\text{Fe}_3(\text{PO}_4)_3$ exhibited interesting sodium intercalation properties. Depending upon the synthesis route chosen, the morphology of $\text{Na}_{2-x}\text{M}_2\text{Fe}(\text{PO}_4)_3$ changes inducing differences in the electrochemical properties. Moreover, the refinement of the structures by the Rietveld method using synchrotron and neutron powder diffraction data revealed a decrease of the sodium content due to a slight oxidation of Fe²⁺ to Fe³⁺.

Detailed study on the mechanism of sodium removal/insertion will be presented using X-ray, galvanometric cycling, and cyclic voltammetry techniques.

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Keywords: [Powder Diffraction](#), [Sodium Ion Batteries](#), [Phosphates](#)