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, NaFePO₄, FePO₄, [Na₁₋ₓLix]MnFe₂(PO₄)₃, Na₂Fe₃₋ₓMnx(PO₄)₄, Na₂Fe(P₂O₇), Na₄Fe₃(PO₄)₂(P₂O₇), Na₃Fe(PO₄)(CO₃), Na₂Fe(PO₄)F, Na₆.24Fe₄.88(P₂O₇)₄, and Na₃.12Fe₂.₄₄(P₂O₇)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 NaₓM₂T(PO₄)₃ (1≤x≤2, M = Co and Ni; T = 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 crystalize 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 Na₂Fe₃(PO₄)₃ exhibited interesting sodium intercalation properties. Depending upon the synthesis route chosen, the morphology of Na₂-xM₂Fe(PO₄)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.


Keywords: Powder Diffraction, Sodium Ion Batteries, Phosphates