

Solid state electrochemistry: a tool for synthesis and characterization of solids

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Researches on battery materials has considerably increased during the last 30 years due to the huge development of lithium-ion batteries for portable devices (laptops, cellular phones, ...) and more recently with the need to store energy in order to optimize its consumption. The next goal is the development of batteries for electric vehicles and their use into the grid. In most of the batteries, the intercalation (deintercalation) of monovalent cations (H^+ , Li^+ , Na^+) and electrons is the basic electrochemical reaction. The cell voltage is equal to the difference in Fermi level between the two electrodes. If one electrode exhibits a constant voltage it can act as reference and therefore, the cell voltage reflects all structure modifications which occur on the material upon intercalation. The change in cell voltage depends on: (i) the electronic band filling, (ii) the change in the band structure due to change in composition, (iii) the modification of the Madelung energy. For the solid state chemist the studies of the electrochemical reaction using a battery open new possibilities to determine phase diagrams at RT, but also to synthesize new metastable phases from a precursor made by classical solid state chemistry.

In this presentation we report about the Na_xVO_2 , and $Na_x(Fe,Mn)O_2$ systems with a special focus on the phase diagram. Depending on the composition and the experimental conditions O3 or P2 structures are obtained for the layered starting phases. The structures of all starting materials were determined by Rietveld refinement of their X-Ray diffraction patterns. As the transformation between O3 and P2 structural types would require M-O bond breaking, the O3 and P2 systems present different behaviors although they have the same chemical formulae

Three different phases were obtained for the $Na_{1/2}VO_2$ composition depending on the packing of the starting material. These phases exhibit very similar sodium ordering in the interslab space but very different vanadium ordering in the VO_2 slab. Depending on the oxygen packing the vanadium ions can be isolated or can form pairs or trimers within the VO_2 slab.

The study of the $Na_x(Fe,Mn)O_2$ systems for several Fe/Mn ratios leads either to O3 or P2 type phases depending on the sodium amount and the Fe/Mn ratio. Depending on the compositions either the Mn^{3+}/Mn^{4+} or the Fe^{3+}/Fe^{4+} redox couples can be involved. The participation of iron has been proved by ex situ and in situ XAS and Mossbauer spectroscopy.

A general overview of the properties of these materials will be presented with a special focus on structures and properties.