Experimental Report

Proposal: **5-24-525** **Council:** 10/2012

Title: Na3V2(PO4)2F3 as positive electrode for Li-ion batteries: investigation of the Na/Li ion-exchange and ofthe phase diagram upon cycling

This proposal is a new proposal

Researh Area: Chemistry

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Samples: (Na,Li)3-xV2(PO4)2F3

Instrument	Req. Days	All. Days	From	To
D2B	3	3	04/04/2013	07/04/2013

Abstract:

The development of new materials for high energy density batteries takes an important part of academic and industrial research in the field of positive electrode materials for lithium-ion batteries. The energy density of positive electrode materials can be improved through an increase in its gravimetric or volumetric capacity and/or in the value of the redox couple Mn+1/Mn vs. Li. Recently we focused our interest on Na3V2(PO4)2F3 4 as a positive electrode material for Li and Na-ion batteries as more than one electron per transition metal is expected to be reversibly exchanged at a high voltage. The aim of the study proposed here is to get more insight into the Na+/Li+ ion exchange reaction occurring upon cycling of Na3V2(PO4)2F3 in lithium cells, but also to characterize the phase diagrams stabilized depending on the potential window used.

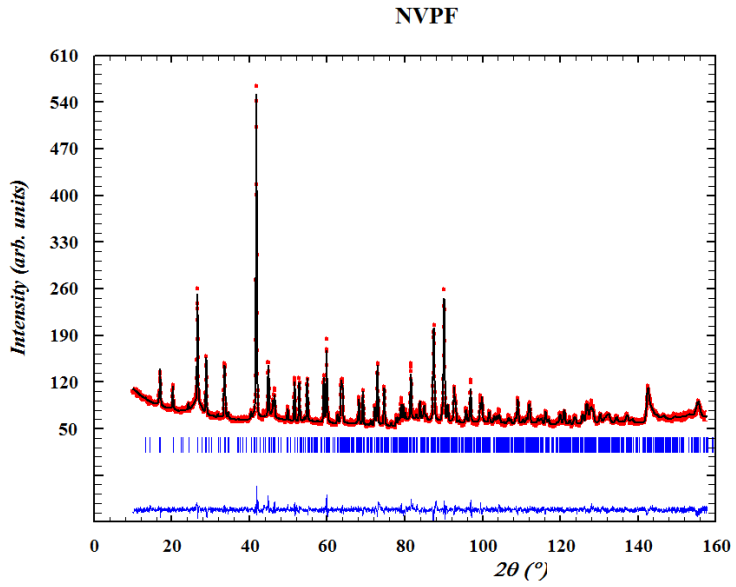
Experimental report for the proposal 5-24-525:

Na3V2(PO4)2F3 as positive electrode for Li-ion batteries: investigation of the Na/Li ion-exchange and of the phase diagram upon cycling

The proposal dealt with the study of different phases prepared thorough chemical desodiation from the sodium insertion material $Na_3V_2(PO_4)_2F_3$. As described in the proposal's abstract, the pristine material had been chemically oxidized to prepare 6 phases $Na_xV_2(PO_4)_2F_3$ (with x = 2.5, 2, 1.5,1,0 and 3 (after a complete cycle)). Unfortunately, the phase Na=0 revealed way more difficult than expected to prepare because of an amorphisation of the material. Therefore, the study of the phase Na=0 and the one that was supposed to be prepared from it, i.e. Na=3 after sodium re-insertion, were not conducted.

During the 3 days on D2B we measured therefore at 1.59 A the pristine material (about 6 hours), the phases Na = 2.5, 2, 1.5 and 1 (12 hours each since they cannot be prepared in high amounts (about 200 mg of each). With the remaining hours we measures another sample of composition Na = 2.5, but this time prepared electrochemically instead than chemically, to compare the two and see if any difference was present.

The performance of the instrument was absolutely satisfactory and all the recovered powder patterns of good quality. At present the study of the pristine material has been done, together with synchrotron data on the same material. In particular, the structure and space group were already known, but thanks to our data a different space group was found. The Rietveld refinement of the neutron data for $Na_3V_2(PO_4)_2F_3$ in the new orthorhombic proposed space group is reported in the figure below.



Regarding the desodiated phases, only a preliminary study of the data has been done up to now; the goal is in particular a detailed analysis that involves the parallel study of in-situ data acquired again at synchrotron facilities on the same material.

A paper regarding the structure and electrochemical properties of $Na_3V_2(PO_4)_2F_3$ is in preparation and it will be submitted soon.