Experimental Report

Proposal: **5-21-1076** **Council:** 10/2012

Title: Ex situ and In Situ structural investigation of Li+ staging in LixVOPO4-type electrodes for Li batteries

This proposal is a new proposal

Researh Area: Materials

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Samples: LiVOPO4
VOPO4
Li2VOPO4
Li1.5VOPO4
Li1.75VOPO4

Instrument	Req. Days	All. Days	From	To
D2B	2	2	18/07/2013	21/07/2013
D20	2	2	19/07/2013	22/07/2013

Abstract:

The present proposal deals with the precise investigation of the various crystalline forms of LixVOPO4 that can be obtained electrochemically through Li+ insertion or extraction into/from LiVOPO4. This material shows indeed an unprecedented succession of phase transitions upon Li+ insertion/extraction towards definite compositions that are still not resolved structurally.

To fully understand this fascinating electrochemical system, into which possible charge ordering on vanadium might occur, we intend to perform two kinds of experiments at ILL:
• Isolate / prepare intermediate LixVOPO4 compositions (~200-300 mg for each composition x = 0-0.5, 1, 1.5, 1.7, 2) through slow electrochemical cycling in order to perform high resolution acquisition on the diffractometer D2B.
• Use this model system as a first example of insitu neutron diffraction experiments within the electrochemical cell under development in the frame of the recently awarded (starting Sept 2012) PhD-ILL grant of Matteo Bianchini.

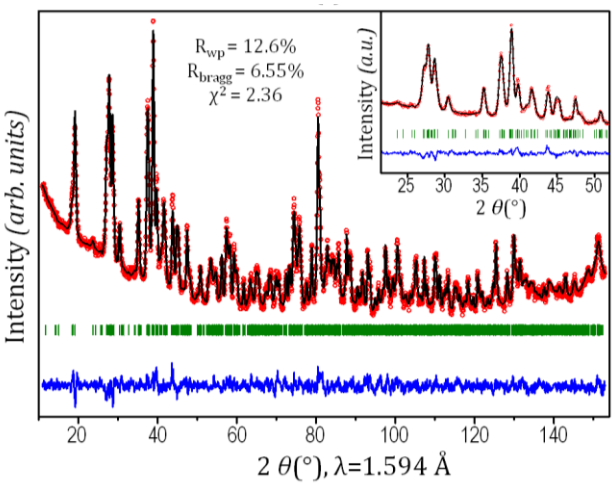
Experimental report for the proposal 5-21-1076:

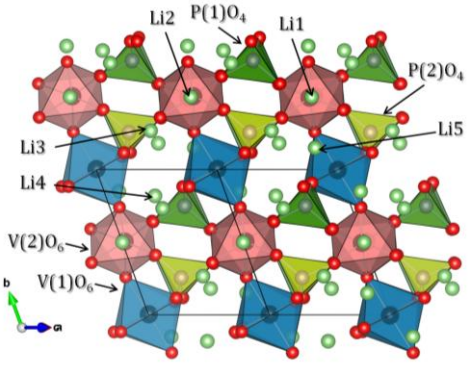
Ex situ and In Situ structural investigation of Li+ staging in

LixVOPO4-type electrodes for Li batteries

The proposal dealt with two different but related goals. On one side, it was the study ex-situ and in-situ of the crystalline phases obtained from the pristine material $LiVPO_4O$ via lithium insertion and extraction. On the other side, the main goal was the validation of the electrochemical cell developed in the context of the PhD grant of Matteo Bianchini. Such a cell is intended to combine good electrochemical properties and the ability to extract neutron powder diffraction patterns of good quality to be exploited for Rietveld refinements.

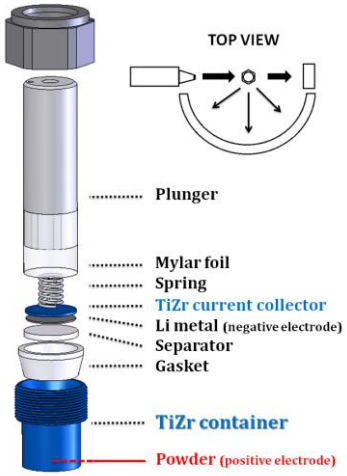
Regarding the ex-situ study, in particular, samples Li_xVPO_4O with x=0, 1.5, 1.75 and 2 were prepared chemically from $LiVPO_4O$ and they were used for powder diffraction measurements performed on D2B at 1.59 A. The crystal structure of the initial phase and of the x=0 one (VPO_4O) were known and we confirmed them. The most interesting phase was however the fully lithiated one, i.e. Li_2VPO_4O, which had never been published before. Our study on D2B allowed us to figure out the crystal structure and to refine it. The result appears together with an electrochemical study of Li_xVPO_4O on a paper we just submitted to Energy and Environmental sciences. The Rietveld refinement and an image of the structure are reported below.

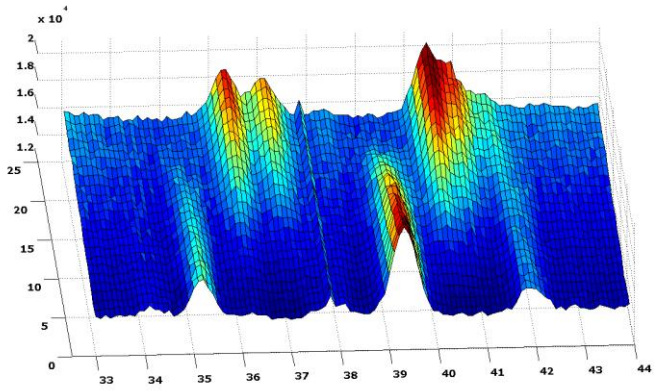




Concerning the intermediate phases of compositions x = 1.5 and 1.75, they were measured but unfortunately they revealed not to be pure phases. For this reason they gave useful indications on their cell parameters but they did not allow a full structural determination.

As stated above, the second goal of the proposal regarded the testing of the developed electrochemical cell for in-situ studies on Li-ion batteries. The initial idea was to validate such cell on the D20 diffractometer using the same $LiVPO_4O$ material, to complement this way the ex-situ studies as well. However, due to the triclinic nature of the material and to the Bragg peaks being quite large, we decided to use other simpler material for our tests. In particular, two materials were chosen since they are well known cathodes for Li-ion batteries: the olivine $LiFePO_4$ and the spinel $Li_{1.1}Mn_{1.9}O_4$. They were both measured in a full battery configuration and the obtained patterns were Rietveld refined. The results were compared to standard powder diffraction patterns of high resolution obtained on D2B on these same materials. The compared results showed a very good agreement in all the structural parameters. A full operando experiment was also conducted on $LiFePO_4$; the material was charged at constant current rate until the final composition $FePO_4$ was reached. The current was chosen to do a complete charge in 24 hours, during which we recorded ND patterns every hour. The figure below shows on the left the in-situ cell and on the right a 3D view of the time-composition dependence of the diffraction patterns of the cathode material $LiFePO_4$ upon cycling. In particular, a two-phase reaction is involved for such material and thus the initial phase can be observed to linearly disappear while the end phase $FePO_4$ linearly appears. More details on this experiment can be found on our recently published paper (1).





Since we have now validated the in-situ cell, our goal will be to use it to study new interesting materials for Li and Na –ion batteries in the forthcoming experimental rounds of ILL.

1. M. Bianchini, J. B. Leriche, J.-L. Laborier, L. Gendrin, E. Suard, L. Croguennec and C. Masquelier, *Journal of The Electrochemical Society*, **160**, A2176 (2013).