Experimental report

27/09/2017

Proposal: 6-06-473 **Council:** 10/2016

Title: Local structure of the new high capacity cathode material Li4-xMn2O5 by neutron PDF analysis

Research area: Materials

This proposal is a new proposal

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Local contacts: Henry FISCHER

Samples: Li4-xMn2O5
SiO2/Al2O3/Na2O/K2O,C3H8O,C3D8O

Instrument	Requested days	Allocated days	From	To
D4	4	3	10/02/2017	13/02/2017

Abstract:

We have elaborated the new nano-crystallized high capacity cathode material in the Li-Mn-O system, exhibiting record capacities larger than 430 mAh/g and good cyclabilities. Besides electrochemical characterization, we have investigated this material using chemical analysis, TEM, magnetic measurements, neutron powder diffraction at D1B, and laboratory x-ray diffraction and PDF analysis. Li ions are exchanged from a starting material of formula Li4Mn2O5. This compound can be described as a disordered MnO type cubic average structure, with Li/Mn substitutional disorder and a coherence length of about 5nm or less. The electrochemical extraction of Li leads to a Li stoichiometry below 1 and a unusually high Mn valence confirmed by magnetic measurements. The averaged structure seems to be globally preserved but x-ray PDF data are insensitive to Li which hinders an accurate description of the local structure. Therefore, we propose to measure neutron PDF data on the D4c instrument for a better characterization of the structure of the pristine and Li depleted materials, in order to understand the Li-insertion/de-insertion in this system.

Experiment Report

Experiment title: Local structure of the new high capacity cathode material $Li_{4-x}Mn_2O_5$ by neutron PDF analysis
Experiment number: 6-06-473
Beamline: D4
Local contact: Henry Fischer
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Experimental section:

Neutron powder diffraction patterns of $Li_{4-x}Mn_2O_5$ compositions were acquired at the D4c diffractometer using λ = 0.5 Å for subsequent Pair Distribution Function (PDF) analysis performed with RMCProfile [1]. The samples were mounted under inert conditions in vanadium cans with an outside diameter of 6 mm with Helicoflex sealing. The data were collected at room temperature in the 1.0-125.0º 2θº range with 3 h of data collection time per sample. The data were corrected and normalized with the Correct software [2] and Fourier Transformed with the Correct software.

Preliminary results:

Ex situ XAS, neutron and X-ray diffraction and PDF experiments on $Li_4Mn_2O_5$ and $Li_{0.5}Mn_2O_5$ revealed that this material shows on average a rock salt structure where the structural correlation length is not markedly modified upon the removal of Li [3]. Mn is octahedrally coordinated and the Mn framework is able to breath while remaining cubic [3]. The local structure of the pristine $Li_4Mn_2O_5$ has been well characterized (see Figure 1.a) by RMC modelling of n-PDF and x-PDF data. In the refined model both Li and O are displaced from their original positions within the rock-salt structure. 5-coordinated Li, clustered around the O vacancies, is able to migrate along the faces of the vacancy-Li_6 octahedra as observed in the BVS isosurface maps calculated for the refined model [2].

The detailed investigation of the local structure of chemically delithiated $Li_{0.5}Mn_2O_5$ was hampered by the presence of amorphous impurities originated by the decomposition of the oxidizing agent used to synthesize $Li_{0.5}Mn_2O_5$ from $Li_4Mn_2O_5$ observed in the n-PDF data. Alternatively, the local structure of $Li_{0.5}Mn_2O_5$ could be decrypted by magnetic PDF studies sensitive only to the magnetic ion i.e. to Mn.

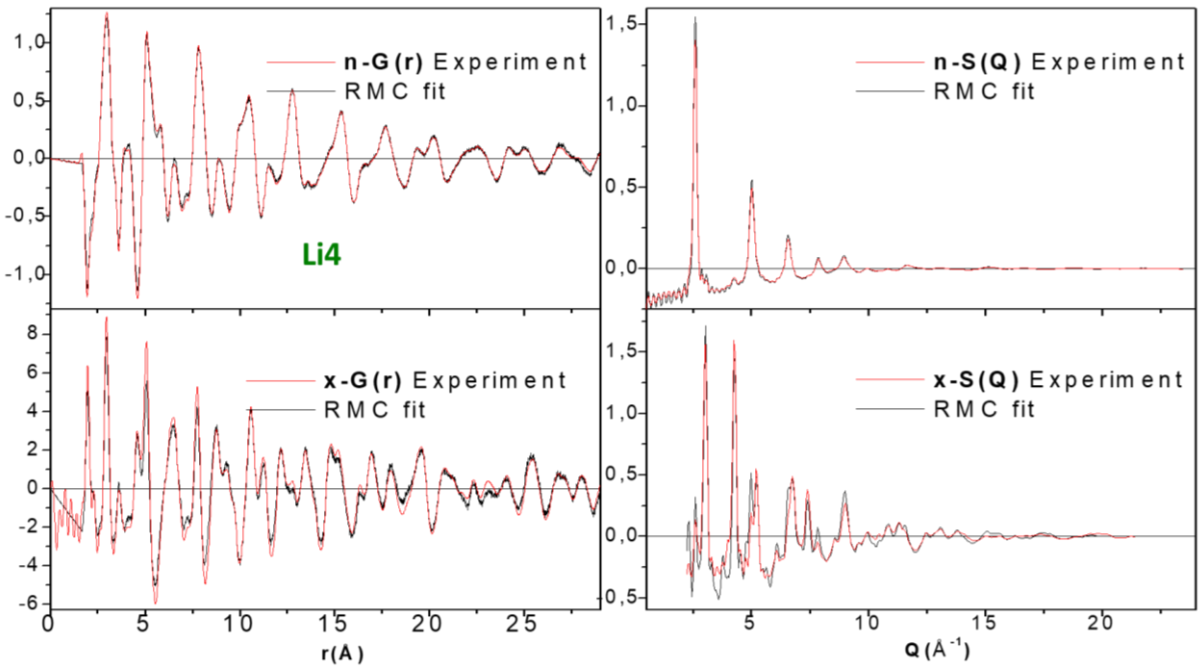

Figure 1. RMC fits of Li_4Mn_2O neutron (top) and X-ray (bottom) G(r) (left) and S(Q) (right).

References:

[1] *Tucker, M.G. et al. J. Phys.: Condens. Matter 19 (2007) 335218.*

[2] *M.A. Howe et al. NFL Studsvik internal report (1996).*

[3] *Diaz, M. et al. Manuscript in preparation.*