

Local structure of  $\text{Li}_{4-x}\text{Mn}_2\text{O}_5$  high capacity cathode probed by PDFMaria Diaz-Lopez<sup>1</sup>, Pierre Bordet<sup>1</sup>, Claire V. Colin<sup>1</sup>, Melanie Freire<sup>2</sup>, Valerie Pralong<sup>2</sup><sup>1</sup>Institut Néel, CNRS & Univ. Grenoble Alpes, Grenoble, France, <sup>2</sup>CRISMAT, CNRS ENSICAEN, CAEN, France  
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For many applications requiring energy storage, the need to increase the energy density of storage devices is of most importance, e.g. in computers, cell phones, electric vehicles, aeronautics, space, etc. The battery scientific community worldwide is intensively studying new high capacity cathodes. Extensive research has focused on the study of lamellar Li-rich  $\text{Li}_{1+x}(\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z)\text{O}_2$  [1] since they can deliver up to 330 mAh/g, which represents a gap in capacity compared to  $\text{LiCoO}_2$  or  $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Al}_y)\text{O}_2$  [2] even when the latter are stabilized by coating or doping for a charge at higher voltage. We have recently discovered a new  $\text{Li}_4\text{Mn}_2\text{O}_5$  nano-crystallized high capacity cathode synthesized by mechanical alloying, which exhibits record capacities of 483 mAh/g and good cyclabilities. This material was investigated by chemical analysis, PXRD, TEM and magnetic measurements [3], showing that  $\text{Li}_4\text{Mn}_2\text{O}_5$  is an original non lamellar oxide. Its average structure could be indexed in an MnO rock-salt type unit cell, albeit the high Li/Mn substitutional disorder in the cation site and the presence of 1/6 of oxygen vacancies (see figure 1.a.). Electrochemical characterizations indicated that almost all Lithium can be reversibly exchanged leading to the proposed chemical formula of  $\text{Li}_{4-x}\text{Mn}_2\text{O}_{6-y}$  where  $0 \leq x \leq 4$  and  $y=1$ . Due to the strong level of cationic disorder in the starting as well as de-lithiated materials, we have used a combination of synchrotron (CRG-D2AM at ESRF) and neutron (CRG-D1B and D4 at ILL) powder diffraction and PDF analysis to characterize their local structures in order to better understand the mechanism of lithium exchange.

This study investigates the local structure of  $\text{Li}_{4-x}\text{Mn}_2\text{O}_5$  with  $x = 0$  and 3.5, with a corresponding change in Mn valence from 3+ to 4.5+.  $\text{Li}_4\text{Mn}_2\text{O}_5$  was chemically oxidized in  $\text{NO}_2\text{BF}_4$  rendering a large amount of  $x = 3.5$  powder required for NPD. Our results confirm that both  $x = 0$  and 3.5 possess a rock-salt type average structure with local distortions affecting mainly the anionic network. Upon Li removal, a 'breathing' of the average structure is observed. The decrease in the cell parameter from 4.170 to 4.069 Å for  $x = 0$  and 3.5 respectively, is induced by the increase of Mn valence and the presence of almost 2/3 vacancies on the cation site. This breathing process is accompanied by clear modifications of the local structure concerning mainly oxygen anions, while the cation network seems to preserve its cubic arrangement. The structural coherence length of about 60 Å is not markedly modified by Li removal. Thus, despite the 3D nature of the average structure, our results indicate that the Li exchange can proceed without major structural rearrangements, as required for good cyclability properties of cathode materials.

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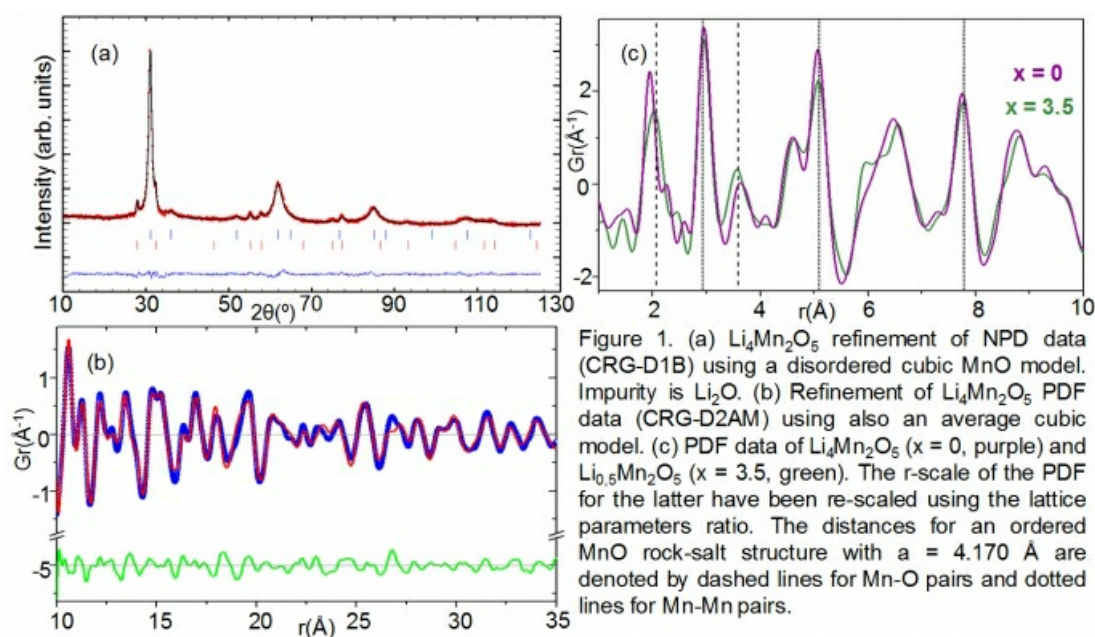


Figure 1. (a)  $\text{Li}_4\text{Mn}_2\text{O}_5$  refinement of NPD data (CRG-D1B) using a disordered cubic MnO model. Impurity is  $\text{Li}_2\text{O}$ . (b) Refinement of  $\text{Li}_4\text{Mn}_2\text{O}_5$  PDF data (CRG-D2AM) using also an average cubic model. (c) PDF data of  $\text{Li}_4\text{Mn}_2\text{O}_5$  ( $x = 0$ , purple) and  $\text{Li}_{0.5}\text{Mn}_2\text{O}_5$  ( $x = 3.5$ , green). The  $r$ -scale of the PDF for the latter have been re-scaled using the lattice parameters ratio. The distances for an ordered MnO rock-salt structure with  $a = 4.170$  Å are denoted by dashed lines for Mn-O pairs and dotted lines for Mn-Mn pairs.

**Keywords:** Cathode Materials, Pair Distribution Function