

Time-Resolved X-Ray and Neutron Pair Distribution Function Analysis of the Positive Electrode Material $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$

by Julien Bréger

Layered lithium nickel manganese oxides are promising, inexpensive and non-toxic alternative positive electrodes materials to the commercial LiCoO_2 electrode used in Li-ion batteries. Among these materials, $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ is particularly attractive due to its high theoretical capacity (280 mAh/g). Its electrochemical and structural properties have, therefore, been thoroughly investigated over the past few years.^{1,2} $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ adopts the layered LiCoO_2 structure (space group $R\bar{3}m$), with Li, transition metal (T.M.) and O layers.

In our previous work,³ Pair Distribution Function (PDF) analysis, in combination with the Reverse Monte Carlo (RMC) technique and ^6Li MAS NMR spectroscopy, was applied for the first time to the study of battery materials, in order to investigate the nature of cation ordering in the T.M. layers in the $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ pristine material obtained from solid-state (SS) routes. In this SS compound, a considerable amount of Li and Ni is exchanged between the Li and T.M. layers due to the similar size of Li^+ and Ni^{2+} cations. The Ni/Ni and Mn/Mn repulsion seen by PDF and the Li/Mn proximity seen by NMR were consistent with an ordering scheme intermediate between the ideal structures proposed so far (“honeycomb” structure and “flower” structure) from first-principle calculations by Van der Ven and Ceder.⁴

Recently, it was further shown that a more layered version of $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$, obtained from an ion-exchange (IE) process using $\text{Na}(\text{NiMn})_{0.5}\text{O}_2$ as a precursor (IE- $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$), can rival the rate capability of the Co-substituted materials.⁵ This excellent rate performance is due to a reduction of the Li/Ni exchange, as seen by Li NMR spectroscopy and XRD.⁵ The objective of the work performed this summer was to investigate the Ni/Mn cation ordering in the T.M. layers of the IE- $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ sample, using neutron PDF analysis associated with RMC calculations. We also commenced an *in-situ* X-ray PDF study to investigate the delithiation process of $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ and characterize any changes in the transition metal configuration that take place upon cycling.

Traditional X-ray or neutron

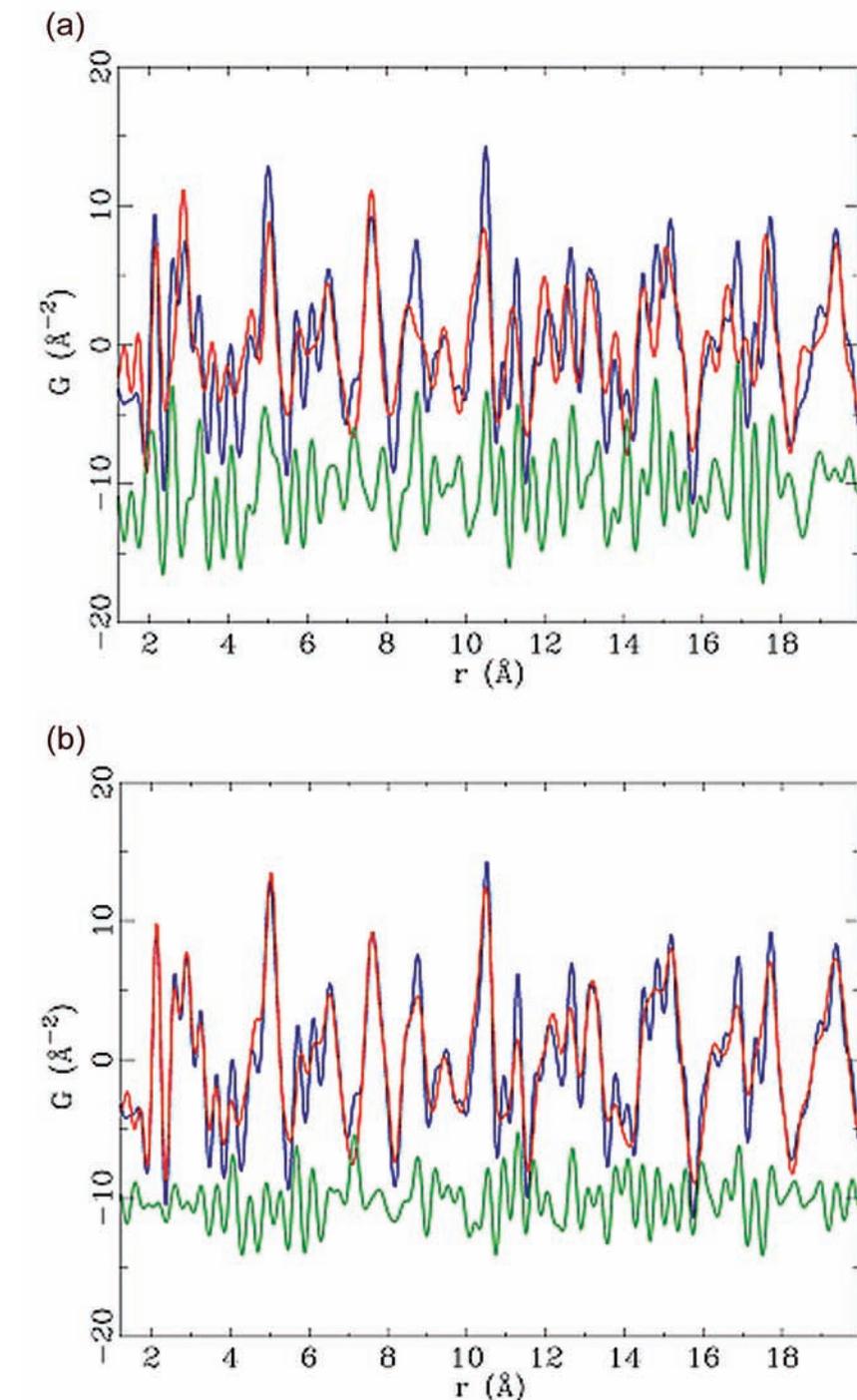


Fig. 1. Reverse Monte Carlo (RMC) results for IE- $\text{Li}(\text{NiMn})_{0.5}\text{O}_2$ pristine material: (a) is the fit before the RMC calculations with the initial random cluster model and (b) is after. The blue and red lines represent the experimental and calculated PDF, respectively. The difference between the calculated and experimental patterns is shown in green. This data was collected at the Intense Pulsed Neutron Source (GPPD).

diffraction analysis considers only the Bragg scattering, which contains information about the long range average structure, whereas the PDF technique uses the total scattering

(Bragg and diffuse scatterings) and is therefore sensitive to local cation environments. The PDF $G(r)$ gives the probability of finding an atom at a given distance r from another atom

TABLE I.

Number of cation pairs in the Ni/Mn layers (*ab* plane) in the two different ordering schemes and comparison with the RMC calculations.

	1 st coordination shell				2 nd coordination shell			
	Ordering schemes		RMC results		Ordering schemes		RMC results	
	Zigzag	Chain	Before	After	Zigzag	Chain	Before	After
			(Random)				(Random)	
%Ni-Ni pairs	16.7%	16.7%	25.0%	19.8%	33.3%	16.7%	24.8%	34.5%
%Ni-Mn pairs	66.7%	66.7%	49.5%	59.9%	33.3%	66.7%	50.0%	30.6%
%Mn-Mn pairs	16.7%	16.7%	25.5%	20.3%	33.3%	16.7%	25.2%	34.9%
Total	100%	100%	100%	100%	100%	100%	100%	100%

and can be considered as a bond length distribution. Like EXAFS, it can be used to determine oxidation states of cations. The main advantage of the PDF technique over EXAFS is that it is sensitive to longer range correlations, and can give additional information about the local ordering and structural parameters. The use of neutron diffraction makes the distinction between Ni/Mn atoms possible, as well as the experimental detection of Li atoms.

In order to model the neutron PDF of IE-Li(NiMn)_{0.5}O₂ taking into account a possible ordering of the Ni/Mn atoms, the Reverse Monte Carlo (RMC) technique was used with the Diffuse program.⁶ A 12×12×2 cluster was built, containing 0% of Li/Ni site exchange as seen by Rietveld refinement and Li NMR data of the same sample and with Ni and Mn atoms randomly distributed in the T.M. layers. During the calculations, Ni and Mn atoms were swapped randomly and all the atoms were

allowed to relax in the *ab* plane. If a generated move improved the fit, the move was accepted. The final calculated PDF is shown in Fig. 1b, and a clear improvement to the fit of the experimental data over that calculated from the ideal LiCoO₂ model (where a random distribution of Ni and Mn atoms in the TM layers is assumed) was obtained (Fig. 1a).

The values for the number of Ni/Ni, Ni/Mn and Mn/Mn pairs were compared to three possible schemes of Ni/Mn cations arrangements in the layer: chain, zig zag and random (Table I).⁷ For the first coordination shell, the numbers of pairs after the RMC are closer to the ones from the ordered models, but we cannot distinguish between these two ordered models. In contrast, the results for the second coordination shell clearly show that the structural model obtained after the RMC calculations is consistent with the zigzag model, as previously predicted by first principles computations.⁷

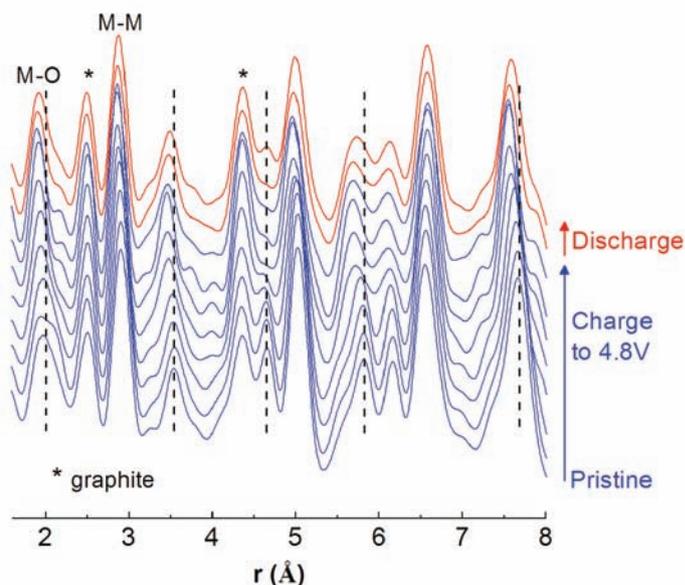


Fig. 2. Time-resolved high-energy X-ray PDF data collected at the Advanced Photon Source (11-ID-C) on SS-Li(NiMn)_{0.5}O₂ charged to 4.8V and discharged at a C/20 current rate. M is Li, Ni or Mn.

Time-resolved high-resolution XRD PDF data for the SS-Li(NiMn)_{0.5}O₂ were obtained for the first time on battery systems, using a cell specifically designed for this experiment. This data displayed in Fig. 2 clearly shows evidence for Ni oxidation and cell parameters changes upon cycling. RMC calculations using this data, jointly with *ex-situ* neutron PDF data, are currently in progress, in order to investigate the evolution of this cation ordering during cycling.

To conclude, ordering of Ni and Mn atoms in the transition metal layers was detected in IE-Li(NiMn)_{0.5}O₂: Ni atoms tend to be surrounded by more Mn atoms in the first coordination shell, while the second coordination shell shows that zigzag ordering scheme is preferred over the chain. The application of this PDF - RMC analysis approach to many battery systems, using structural constraints from other techniques such as NMR to develop even more detailed and accurate models of structure, may be readily envisaged. ■

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