PDF and NMR Study of Ordering in the Positive Electrode Material $Li(NiMn)_{0.5}O_2$

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The local environments and short-range ordering of $Li(NiMn)_{0.5}O_2$, a potential Li-ion battery positive electrode material[1,2], were investigated by using a combination of X-ray and neutron diffraction and isotopic substitution, Li MAS NMR spectroscopy and, for the first time, X-ray and neutron Pair Distribution Function (PDF) analysis, associated with Reverse Monte Carlo (RMC) calculations. $Li(NiMn)_{0.5}O_2$ adopts the $LiCoO_2$ structure and comprises separate Li layers, transition metal (Ni,Mn) layers and O layers.

NMR experiments and Rietveld refinements showed that there is 10% of Li/Ni site exchange. Neutron PDF analysis revealed considerable local distortions in the layers that are not captured in the $LiCoO_2$ model. Large clusters were built to investigate cation ordering, by performing RMC calculations. Both NMR and RMC were consistent with a non-random distribution of Ni, Mn and Li cations in the transition metal layers. Constraints from both methods showed the presence of short-range order in the transition metal layers comprising $LiMn_6$ and $LiMn_5Ni$ clusters combined with Ni and Mn contacts that are consistent with those found in some of the proposed structures based on Li_2MnO_3-like ordering of the cations.

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Keywords: lithium batteries, pair distribution function, NMR