Investigation of Possible Superstructure and Cation Disorder in $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ using Neutron and Anomalous Dispersion Powder Diffraction.

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$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ has been the subject of much interest recently as a proposed cathode material for lithium ion batteries which exhibits high reversible capacities[1] and good thermal stability.[2] Although the crystal symmetry of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ has been assumed to be R-3m, a recent paper explored the likely form for a superstructure if it were to exist.[3]

It was suggested that a [√3 x √3]R30º type superlattice would be a more likely candidate than a layered supercell with alternating Mn-O, Ni-O and Co-O slabs. Either of these superlattice structures would yield diffraction patterns indistinguishable from that of a random distribution of transition metal cations on the 3a site of the R-3m structure when characterized by powder diffraction on a conventional diffractometer using Cu Kα radiation, but radically different patterns would be observed with neutron diffraction measurements (figure 1). It was found that a complete [√3 x √3]R30º type unit cell could not be constructed using the $P3_112$ space group proposed by Koyama *et al*,[3] but $P3_121$ could produce a complete cell. As well as tripling the *a* axis, this supercell also triples the *c* axis, leading to a potential unit cell with $a = 8.59$Å and $c = 43.28$Å. Neutrons of wavelength longer than that of Cu Kα X-rays may be even more likely to detect supercell reflections from such a large unit cell.

In addition to the presence, or not, of a supercell, there is also uncertainty as to the role of the individual cations in site mixing. Although the similar ionic radii of Li^+ and Ni^{2+} make it most likely that Ni^{2+} will migrate to the Li^+ site, it is difficult to preclude the presence of Mn or Co. Although the neutron scattering lengths of Mn, Co and Ni are significantly different, the complexity of the system requires more information, much in the same way as do increasingly complex simultaneous equations.

An alterative method for increasing the contrast between elements is to use anomalous dispersion (or resonant diffraction) techniques. The incident radiation is tuned to the absorption edge of one of the elements, but instead of obtaining purely absorption data, a powder diffraction pattern may be obtained. The effect of the absorption edge is to make an element a weaker X-ray scatterer, so changing the contrast between the elements present. In this way, the locations of the individual elements may be determined.

Samples of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ were produced using a sucrose-based dispersion/combustion method. The transition-metal ratios were determined using wavelength-dispersive X-ray fluorescence. Laboratory X-ray data were obtained from a twin-mirror parallel beam diffractometer using CuKα radiation. Synchrotron data were collected on the X3B1 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory, at 0.6999Å (approx MoKα), and 1.869Å (Mn edge). Neutron data at 1.33 and 2.37Å were collected on the NRC DUALSPEC C2 high-resolution neutron powder diffractometer at the Chalk River Laboratories, Ontario, Canada. The distribution of cations was determined with simultaneous Rietveld refinement of the three X-ray datasets and the 1.33Å neutron dataset.

1. T. Ohzuku, & Y. Makimura, *Chemistry Letters* 642-643 (2001)
2. N. Yabuuchi & T. Ohzuku, *J.Power Sources* **119-121**, 171-174 (2003)
3. Y. Koyama *et al*, *J.Power Sources* **119-121**, 644-648 (2003)

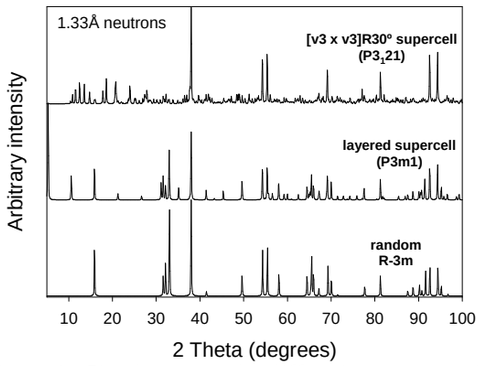

Figure 1. Simulated powder diffraction patterns of the different structural models with 1.33Å neutrons.

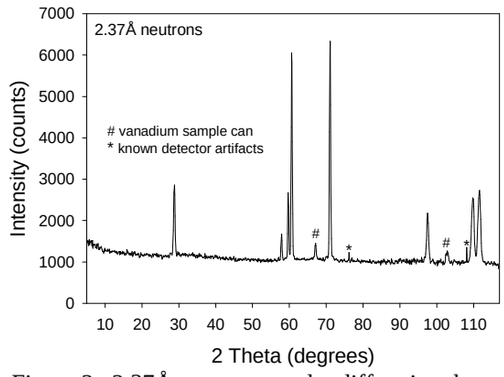

Figure 2. 2.37Å neutron powder diffraction data of $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$

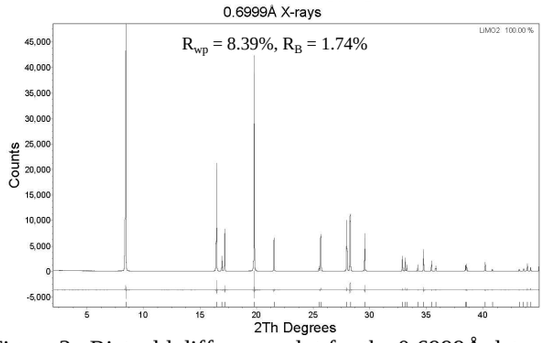

Figure 3. Rietveld difference plot for the 0.6999Å data from the simultaneous refinement.