The role of metal site vacancies in layered Li-Mn-Ni-O solid solutions

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The lithium-rich layered structures joining Li_2MnO_3 to $LiNi_{0.5}Mn_{0.5}O_2$ showing specific capacities above 200 mAh/g have received much attention as potential positive electrode materials. Recent combinatorial work[1,2] showed that the solid solution region extends both above and below the lithium-rich line. Figure 1 shows the phase diagram produced for samples made in oxygen when quenched from 800°C. The focus of the current study is the region inside the black circle, where a solid solution "bump" exists. The right boundary of the bump corresponds to the solid solution series $Li[Li_{1/3-x}Ni_{x/2}\square_{x/2}Mn_{2/3})O_2$, where $\square$ represents a vacancy.

Bulk samples synthesized in air in this region were studied by XRD, helium pycnometry, redox titration and ICP elemental analysis in order to determine the metal site vacancy content of these materials. Table I shows the results for a bulk sample near the upper boundary of this layered region. All three experimental methods show that approximately 6.9% of the metal sites are vacant. This large value results in 66.8 % of the transition metal layers being occupied by manganese.

A Monte Carlo simulation was performed to illustrate the possible local ordering in these structures. For simplicity, all vacancies were assumed to be on the transition metal layer. Figure 2 shows that manganese atoms order on two $\sqrt{3}$ x $\sqrt{3}$ lattices with the third being occupied randomly by lithium, nickel and vacancies. The simulation shows that the resulting low internal energy structure does not phase separate into layered-layered composites during cooling.

This study also includes results for structures in the bump with more lithium, where the vacancy content decreases but does not reach zero, even for the sample lying on the stoichiometric lithium-rich line. Clearly, a better understanding of the starting material in this region of the triangle is essential to understanding the electrochemical performance. As such, electrochemical data on a sample at the top of the boundary will be discussed. Also of interest is the material $Li[Ni_{1/6}Mn_{2/3}\square_{1/6}]O_2$ which represents the layered material with the highest vacancy content possible while maintaining 2/3 manganese occupancy on the transition metal layer. Preliminary XRD and electrochemical data obtained for this material will also be presented.

Table I: Results for vacancy content for a sample near the top of the "bump".

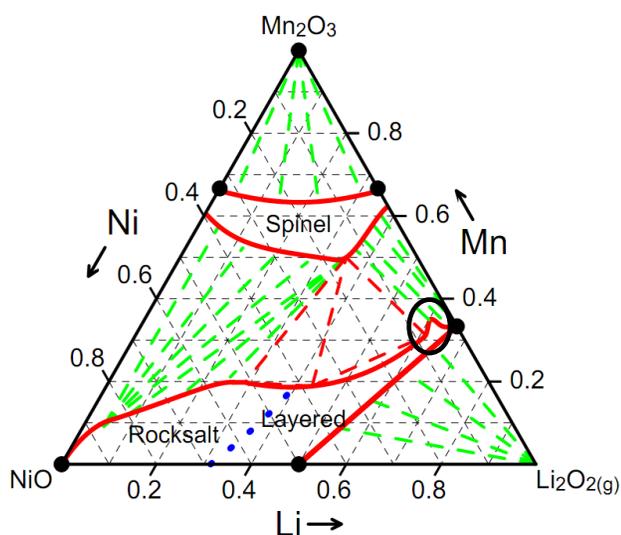| Composition (Li, Mn, Ni)	(0.568,0.359,0.073)
XRD	
a (Å)	2.8582(1)
c (Å)	14.298(1)
Ni on Li layer	3.1(3)%
Vacancies from Rietveld	**6.9(1.8)%**
Pycnometer density (g/mL)	4.138(14)
Vacancies from pycnometer	**6.97(51)%**
Redox titration	
Mn	3.99(1)
Ni	2.00
Vacancies from oxidation state	**6.82(16)%**

Figure 1: The pseudo-ternary phase diagrams obtained by heating combinatorial samples to 800°C in oxygen and quenching back to room temperature. Red lines represent boundaries of single phase regions, green dashed lines are tie-lines, red dashed lines are tie-lines bounding three-phase regions and the blue dotted line is a phase transition between the cubic and layered rocksalt structures.
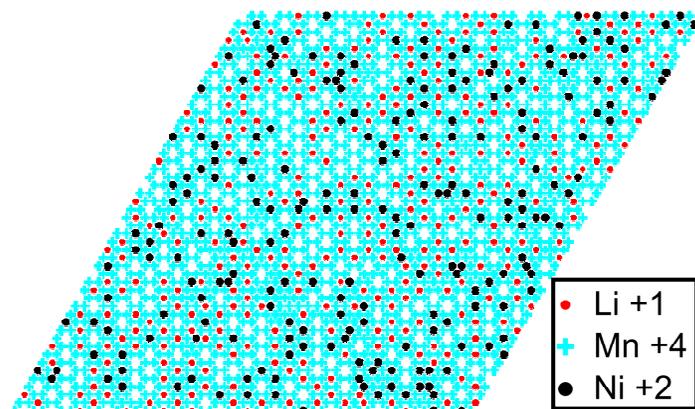

Figure 2: Monte Carlo simulation result obtained for (Li,Mn,Ni) = (0.6,0.35,0.05), which is the top of the "bump" from Fig. 1.

[1] E. McCalla and J. R. Dahn, *Solid State Ionics* (2013) doi: 10.1016/j.ssi.2013.04.003

[2] E. McCalla, A. W. Rowe, R. Shunmugasundaram and J. R. Dahn, *Chem. Mater.* **25**, 989 (2013).