

## Consequences of the Li-Mn-Ni-O phase diagram on the synthesis of positive electrode materials

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In the search for new positive electrode materials for lithium ion batteries, two main solid solutions in the Li-Mn-Ni-O system have received much attention: spinel structures along the composition line joining  $\text{LiMn}_2\text{O}_4$  to  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (point S in Fig. 1) showing high rate capabilities and the lithium-rich layered structures joining  $\text{Li}_2\text{MnO}_3$  to  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  that show specific capacities above 200 mAh/g. Efforts made to design composite electrodes combining these two structures have been difficult; in part due to the fact that no phase diagram for the system existed until now. We report here on combinatorial work<sup>1,2</sup> which involved synthesizing and characterizing with XRD milligram-scale samples at over 300 different compositions. Figure 1 shows the phase diagrams produced for samples made in oxygen. Although evidence will be presented to support the rather complex phase diagrams, the main objective here is to discuss the impact of these phase diagrams on the design of positive electrodes, particularly on spinel-layered composites<sup>3</sup> and so-called layered-layered nanocomposites<sup>4</sup> which have received much attention in the literature.

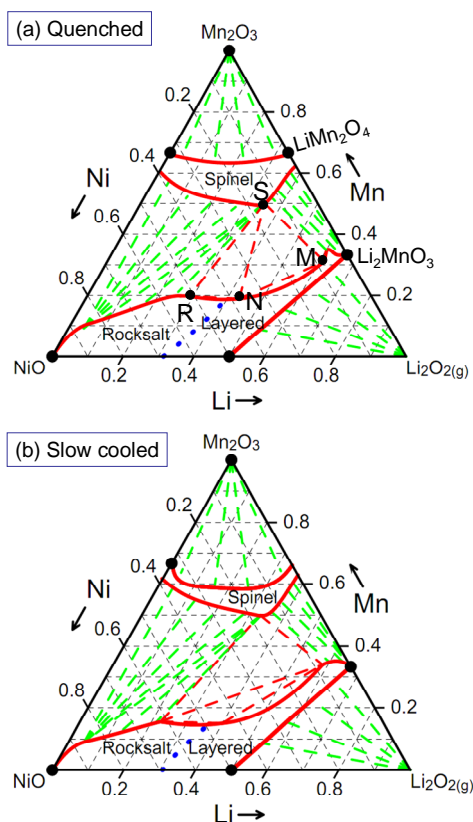


Figure 1: The pseudo-ternary phase diagrams obtained by heating combinatorial samples to 800°C in oxygen and either quenching (a) or slow cooling (b) back to room temperature. Red lines represent boundaries of single phase regions, green dashed lines are tie-lines, red dashed lines are tie-lines bounding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

Figure 2(a) shows a partial phase diagram with the co-existence regions labeled. The layered-layered composites form near the composition of  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  (which lies on the N-M composition line) when slow cooled in oxygen. Figures 2 (b) and (c) show the electrochemistry of these two materials. N shows low capacities which fade rapidly; as expected since it is a layered material with about 33% nickel occupancy on the lithium layer<sup>2</sup>. The M material shows higher capacity comparable to that obtained for Li-rich materials though it shows the typical problems associated with such structures (voltage fade due to conversion to spinel, poor rate capability and high irreversible capacity). **We conclude that layered-layered composites are not favorable to good electrochemical performance in this system. The fact that excess lithium is commonly used to improve performance<sup>5</sup> can be attributed to the fact that a higher lithium content maintains the solid solution.**

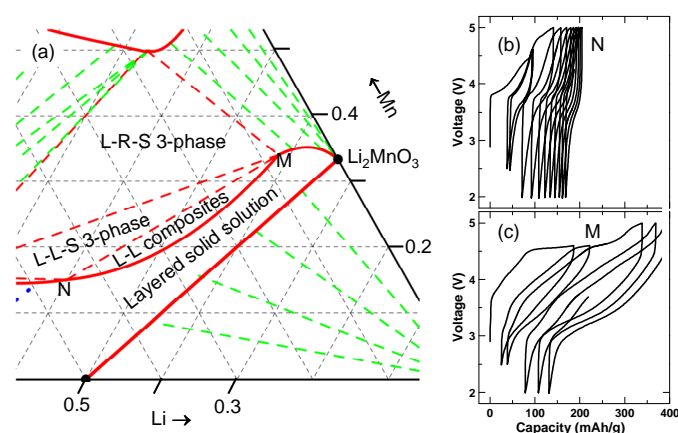


Figure 2: (a) A section of the slow cooled phase diagram showing where layered-layered (L-L) composites form immediately below the line joining the M and N phases. The 3-phase regions are also labeled with R denoting a rocksalt phase and S a spinel. (b) Electrochemical data for the N phase (c) and M phase (c) made in oxygen at 800°C cycled at 10 mA/g at 30°C.

The primary importance of this work is a better understanding of how the phase boundaries and co-existence regions transform when samples are cooled at rates typically used commercially. Anyone attempting to make these materials for commercial use must be mindful of the transformations taking place at lower temperatures such that issues such as temperature gradients within batches must be minimized. Understanding the effects of these transformations on the electrochemical performance of the materials should have a significant impact on research in composite electrodes, limiting the region of interest considerably. The consequences of the unwanted formation of layered-layered composites near the  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  composition also warrants further study.

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