Bulk Sample Phase Diagrams of Li-Mn-Ni-O Positive Electrode Materials

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Complete phase diagrams of the Li-Mn-Ni-O system based on mg-scale combinatorial samples synthesized at 800°C in an oxygen atmosphere have been determined [1,2]. These diagrams, shown in Figure 1, contain several cubic and hexagonal single-phase and multi-phase co-existence regions. The type and quantity of phases that form within these regions depend heavily on sample composition, synthesis temperature, and most importantly, on the cooling rate of the final products. This effect is most pronounced in the region of interest for positive electrode Li-ion battery materials; two very different phase diagrams, with distinctly different co-existence regions, have been produced for samples that are quenched (equilibrium conditions) versus those which are slow-cooled (non-equilibrium conditions) [3]. Analysis of this region based on bulk samples is important to both complement and confirm the results of the combinatorial study. Such an analysis is also highly relevant to Li-ion battery positive electrode researchers, as it encompasses commonly studied materials including layered metal oxides, the lithium-rich oxides, and spinels.

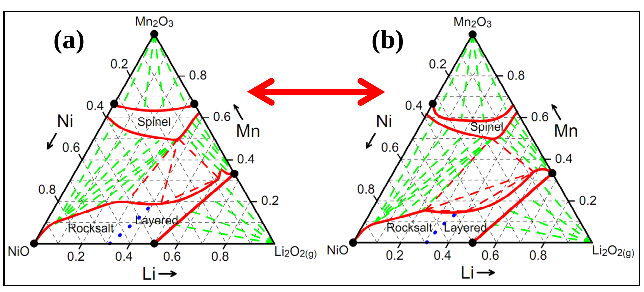

Figure 1. Phase diagrams of the Li-Mn-Ni-O system at 800°C for (a) quenched samples and (b) slow-cooled samples, adapted from Ref. 2.

This work contains a thorough examination of bulk samples within the positive electrode materials region, and the resultant Li-Mn-Ni-O phase diagrams mapped under each reaction condition studied. Bulk samples were synthesized at both 800°C and 900°C in air, and were cooled either by quenching between copper plates or by turning off the oven (in a process we've termed slow or "natural" cooling). Li, Mn, and Ni contents were determined by ICP-OES in order to accurately plot the final compositions on the phase diagram. The phases present in each sample were determined by XRD, and their lattice constants extracted via in-house refinement software.

Figure 2 shows the mapped portion of the phase diagram containing positive electrode materials at 900 °C using quenched samples. The phase diagram contains numerous single- and multi-phase samples, including the M, N, R, and S compositions discovered previously [2]. The resulting phase boundaries, tie-lines, and co-existence regions confirm the results of the combinatorial study. Figure 3 shows XRD patterns of samples A-E in Figure 2. The results clearly show how materials that are single-phase when quenched can become multi-phase when slow cooled, often containing undesired phases such as rocksalt. Given these results, phase diagrams under various reaction conditions would be of great value to positive electrode researchers. Phase-mapped portions of the Li-Mn-Ni-O system under different synthesis conditions will be presented and discussed at the meeting.

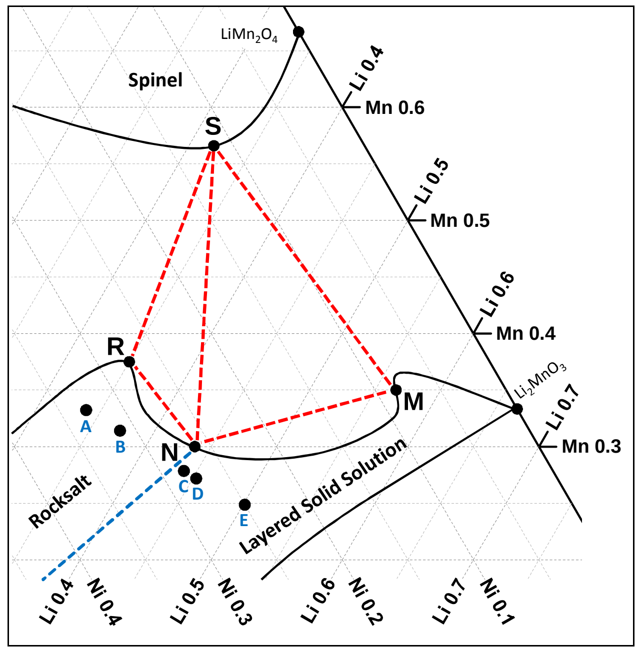

Figure 2. Phase diagram of Li-Mn-Ni-O samples quenched from 900°C. Red dashed lines represent tie-lines between cubic and/or layered end-members, while single-phase boundaries are shown in black.

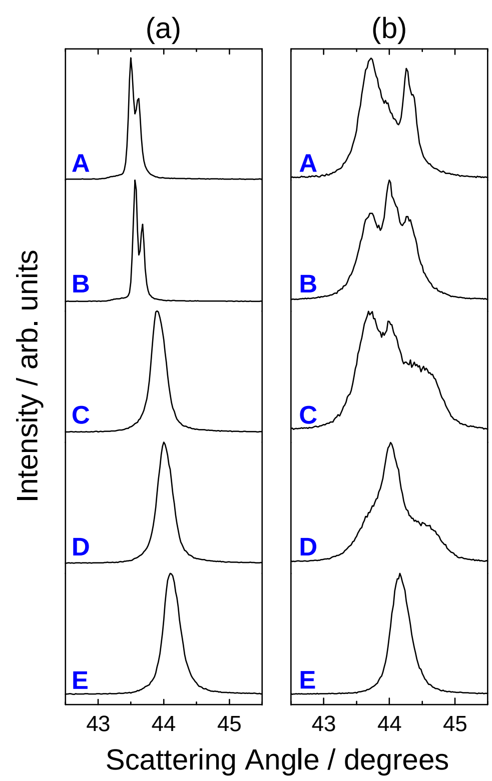

Figure 3. XRD patterns of compositions on the phase diagram in Figure 2 that were (a) quenched and (b) slow cooled from 900°C.

[1] E. McCalla and J. R. Dahn, *Solid State Ionics*, **242**, 1 (2013).
[2] E. McCalla, A. W. Rowe, R. Shunmugasundaram and J. R. Dahn, *Chem. Mater.*, **25**, 989 (2013).
[3] E. McCalla, A. W. Rowe, C.R. Brown, L. R. P. Hacquebard and J.R. Dahn, *J. Electrochem. Soc.*, **160**, A1134 (2013).