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Characterization Techniques for Nickel, Manganese and Cobalt containing Gradient Composition Materials

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A logical step forward in cathode development is gradient and core-shell particle compositions. Gradient and core-shell materials can provide improved performance by protecting compositions that have undesired surface interactions with a coating of a material that has superior stability at its surface **[1]**. It is important to verify that the desired gradients and/or core-shell particles have been properly synthesized, and to determine how the gradients change during lithiation and heat treatment.

Verification of gradient compositions is often accomplished by energy dispersive x-ray spectroscopy (EDS) or similar techniques that sample a cross section of a particle **[2]**, this process samples only a single particle at a time. Although X-Ray Diffraction (XRD) is commonly used to determine compositions in homogeneous samples, little effort has been done in analyzing XRD patterns obtained for gradient materials. Here, we use a simple model assuming spherical particles with a constant growth rate to fit XRD patterns of $Ni_{(1-x)}Mn_x(OH)_2$ with a continuous composition gradient.

This study explores various gradients of Ni, Mn and/or Co hydroxide precursors and their respective lithiated oxides. The hydroxide precursors were developed using a constantly stirring tank reactor (CSTR) **[3]** with a computer controller adjusting the flow rate of inputted metal sulfate solutions to develop the gradient compositions. Figure 1B shows that the solution added to the tank was initially entirely manganese sulfate, while at the end it was entirely nickel sulfate.

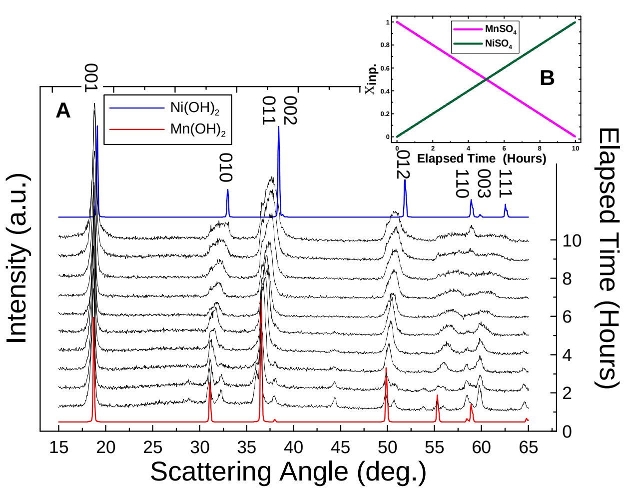

Figure 1A. XRD patterns of samples removed at various times (shown on right axis) during the synthesis of precursor with a Ni and Mn concentration gradient. Figure 1B. Plot of inputted Ni^{2+} and Mn^{2+} mol fraction as a function of elapsed reaction time.

Figure 1A shows that the XRD pattern changes dramatically as reaction proceeds. This is caused by the presence of primary particles with a wide range of lattice constant values over the entire $Ni_{(1-x)}Mn_x(OH)_2$ solid solution. The wide range of the lattice constants is particularly evident in the 55-65° range where two peaks, the 110 and 111 broaden to the point that they overlap to give a small apparent peak at 58° (Figure 1A, 9-10 h).

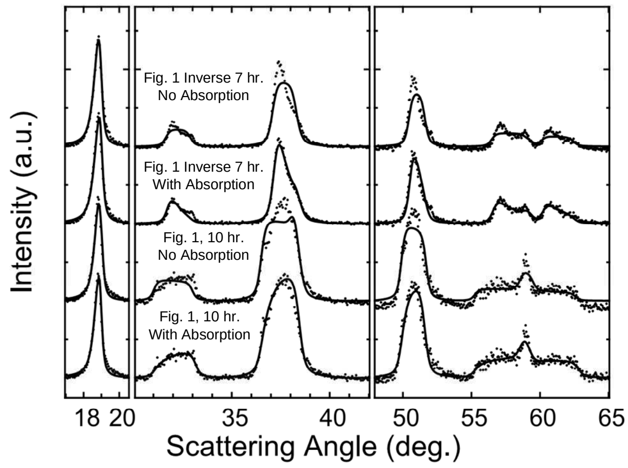

Figure 2. Plots of fitted XRD data of selected samples of Ni/Mn gradient hydroxides.

Figure 2 shows fitted XRD data of the 10 hour sample from figure 1, and the sample obtained after 7 hours with a Ni rich core with a constant gradient towards a Mn rich surface, the inverse of the pumping scheme in figure 1B. The fits in figure 2 improve greatly when the absorption of x-rays by the outer layers is included in the fit, confirming that the composition gradient does exist.

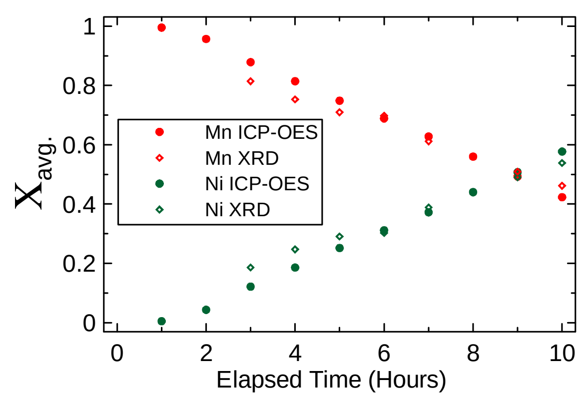

Figure 3. Plot of elemental analysis for both XRD fits and ICP-OES for gradient shown in fig. 1B.

Figure 3 shows that the average composition obtained from fitting the XRD data is in agreement with the data collected from optical emission spectroscopy (ICP-OES); illustrating how XRD can be used to confirm gradient compositions. The linear fit shows that the gradient of the sample is in close agreement with the pumping scheme shown in figure 1B.

Data will be presented on gradient hydroxide precursors and their respective lithiated oxides. SEM, particle size distribution and elemental analysis will be discussed.

References

[1] Y.K. Sun, D.G. Kim, C.S Yoon, S.T. Myung, J. Prakash, K. Amine. Adv. Funct. Mater. 20 (2010) 485.

[2] G. M Koening, I. Belharouak, H. Deng, Y.K. Sun, K. Amine. Chem. Mater. 23 (2011) 1954.

[3] F. Zhou, A. VanBommel, A.W. Rowe, J. R. Dahn. Chem. Mater. 22 (2010) 1015.