Structural Evolution of Lithium Deficient $Li_xNi_yMn_zCo_{1-y-z}O_2$ (x <1) Cathode Materials by *in situ* XRD

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While the conventional approach to developing high energy density cathode relies on the lithium-excess materials such as $xLi_2MnO_3.(1-x)Li(Ni_yMn_zCo_{1-y-z})O_2$, they still lack to satisfy the requirements because of their unsolved issues upon cycling, such as voltage fading and structural transition. A recent work on $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (x<1) with lithium deficient ratio has shown promising result of high cycling stability at high voltage (up to 4.5V vs. Li^+) and high temperature (60°C) [1,2]. Whereas the improved performance is attributed to the stable multiphase structure of the lithium deficient cathode material and the robust SEI formed during cycling, a more comprehensive study on the structural transition of the lithium deficient nickel-based $Li_xNi_yMn_zCo_{1-y-z}O_2$ (x <1) (NMC) is yet to be done. Moreover, the lithium deficient ratio holds the promise to obtain improved cycling performance of high nickel $Li_xNi_yMn_zCo_{1-y-z}O_2$ (y>0.5) cathode material. In addition to all that, use of excess lithium can substantially impact the environmental sustainability.

In this work, we have investigated the structural evolution of three different lithium deficient $Li_xNi_yMn_zCo_{1-y-z}O_2$ (x <1) cathode materials by *in situ* XRD such as $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, $Li_xNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, and $Li_xNi_{0.8}Mn_{0.1}Co_{0.1}O_2$. Specifically, we have studied the phase transition of the metal hydroxide precursor to the cathode material in presence of a lithium source (in a deficient ratio, x<1) during the calcination. Additional study to understand the cathode material structure and composition by time-of-flight secondary ion mass spectrometry are in progress. Preliminary results have shown a multiphase structure in $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ and a positive 2θ shift in the observed XRD which was due to a possible migration of nickel or cobalt.

References:

[1] S.-J. Cho, PCT/US2015/051426, 2016 http://www.google.com/patents/WO2016049014A1
[2] S.-J. Cho, M.-J. Uddin, P.K. Alaboina, S.S. Han, M.I. Nandasiri, Y.S. Choi, E. Hu, K.-W. Nam, A.M. Schwarz, S.K. Nune, J.S. Cho, K.H. Oh, D. Choi, Adv. Sustain. Syst. (2017) 1700026