Florida Energy Systems Consortium

Stress Evolution in Solid State Li Ion Battery Materials

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Industry Partner: Planar Energy

The goal of this work is to understand the structure property relationship of cathodes being developed for solid state Li ion batteries. In conjunction with Planar Energy, various cathodes were supplied with the compositions of $LiMn_{1-x-y-z}Co_xNi_yAl_zO_2$ ($x+y+z \leq 0.30$) using the streaming protocol for electroless electrochemical deposition (SPEED). SPEED is a non-vacuum fabrication technique that enables the development of nano-particle based materials at low cost.

All cathodes received have a crystal structure based off the $R\bar{3}m$ space group. The space group is shared by $LiCoO_2$ and is described as alternating layers of Li and transition metals (Mn, Ni, Co, and Al) separated by oxygen layers in a close packed lattice. The crystal structure was revealed by x-ray diffraction using a Philips Xpert MRD and selected area diffraction (SAD) using JOEL 2010F TEM with the results shown in figure 1. Energy dispersive x-ray spectroscopy (EDS) confirmed the elemental composition of the cathodes with respect to the transition metals. Each cathode of the type $LiMn_{1-x-y-z}Co_xNi_yAl_zO_2$ varied by less than 10% in Mn, Co, Ni, and Al from the theoretical composition.

The result of spraying the cathode onto a steel surface leaves a film that is 2 - 5 µm in thickness with occasional mounds reaching heights of 30 µm. The film and mounds are porous, allowing the electrolyte to reach a larger surface area of the cathode. A cross sectional secondary electron (SED) image reveals three phases. The phase with the darkest contrast relates to the porosity, which was back-filled with an epoxy in order to isolate a single plane. The remaining phases relate to the cathode. The evolution of the cathode from the steel surface to the height of the film is shown in figure 2. The porosity of the sample, $LiMn_{0.7}Al_{0.3}O_2$, is approximately 50% throughout the film. Using transmission electron microscopy (TEM), the structure of the cathode includes both nanoparticles on the order of 5 - 10 nm in size and larger crystalline grains greater than 250 nm in size from figure 3. These different particle sizes are thought to make up the regions of varying contrast in the cathode which are otherwise chemically identical.

The electrochemical properties of the $LiMn_{1-x-y-z}Co_xNi_yAl_zO_2$ cathodes were tested in half-cell configurations. Figure 4 shows the efficiency of the half-cell batteries along with the capacity fade over 50 cycles between 3 – 5 V at 75 µA/cm^2. This sample is $LiMn_{0.7}Ni_{0.1}Co_{0.2}O_2$ and was sintered under O_2 at 923 K for 10 minutes. While the efficiency of the charge/discharge times of the cells vary between 80-100%, the capacity fade follows a more consistent pattern. After 50 cycles, 70-75% of the total capacity is accessible at a charge rate that varies between 1.5C and 2C. Improvements in the capacity fade are being sought through varying the composition of the film and alternate annealing cycles.

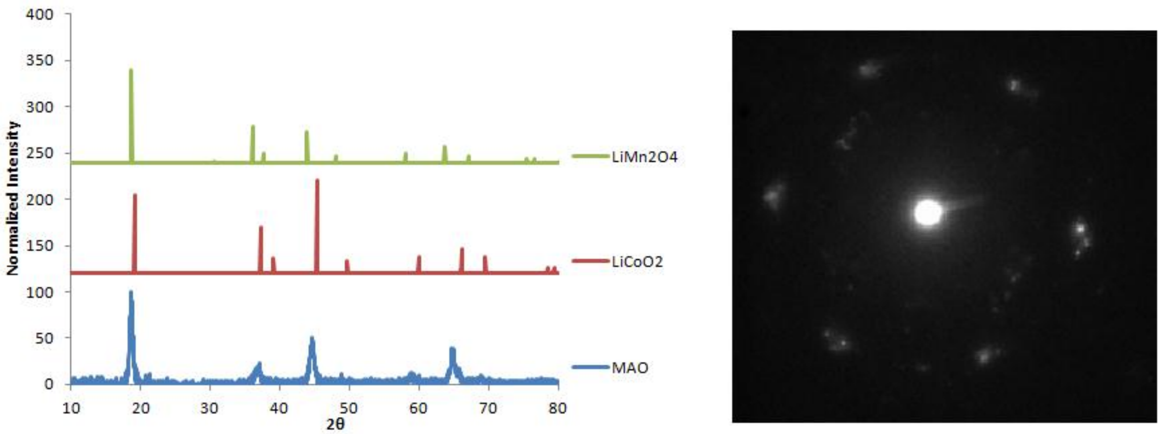

Figure 1. (Left) XRD pattern of $LiMn_{0.7}Al_{0.3}O_2$ (MAO) compared to $LiCoO_2$ and $LiMn_2O_4$, (Right) SAD pattern of a MAO crystal showing hexagonal symmetry

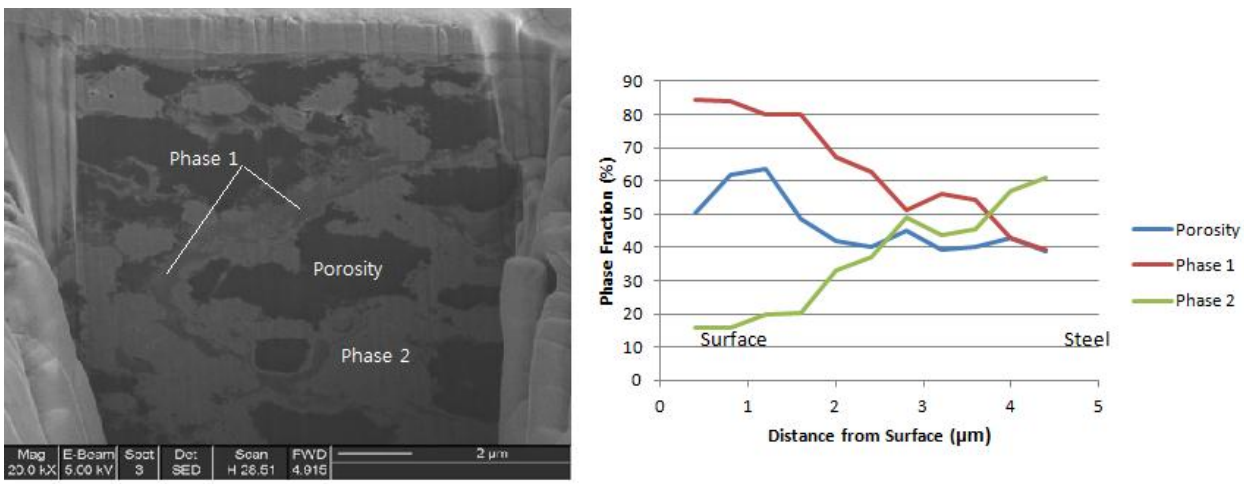

Figure 2. (Left) Cross-sectional SEM image depicting three phases in $LiMn_{0.7}Al_{0.3}O_2$, (Right) Phase fractions mapped from surface to steel substrate interface

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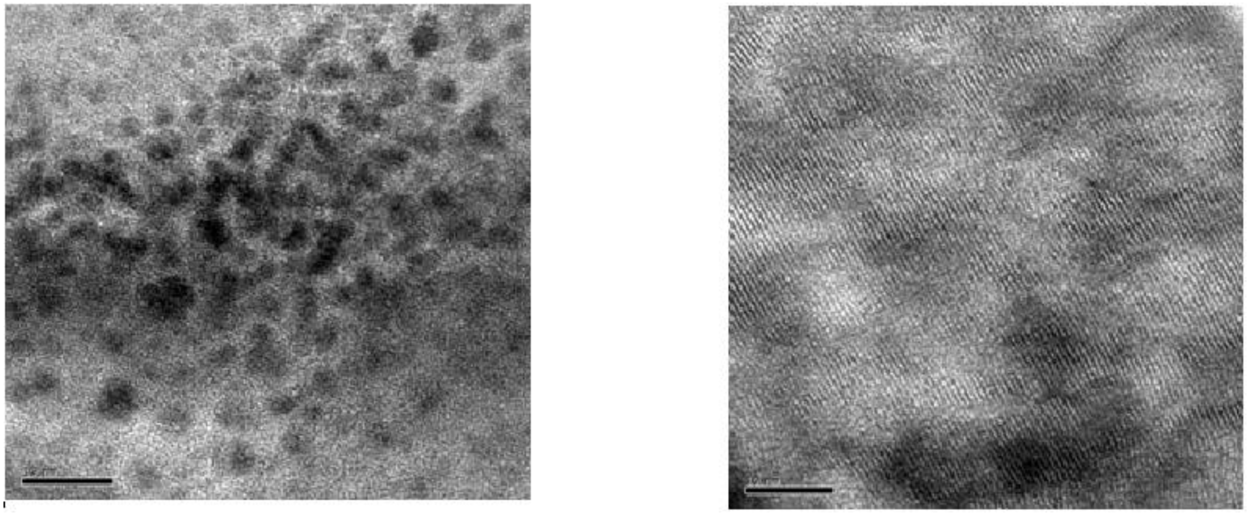

Figure 3. TEM images showing nanoparticles (left) and larger single crystal regions (right)

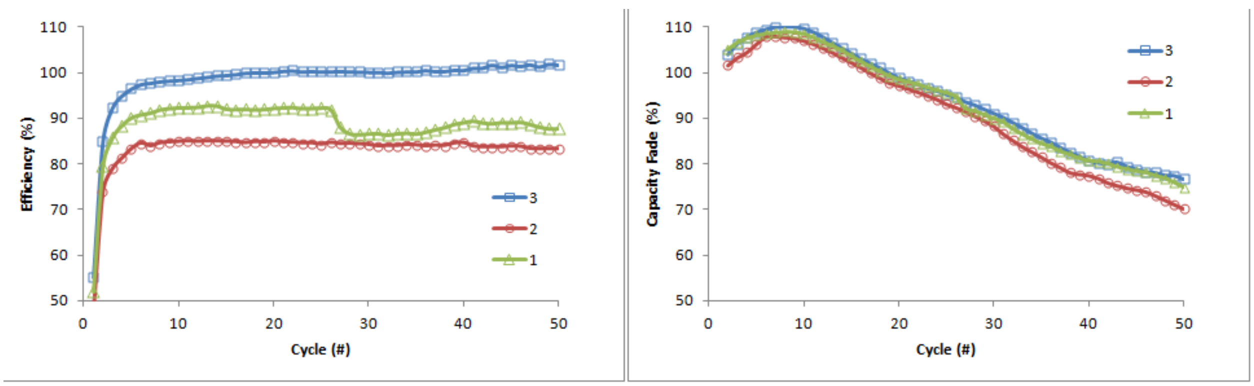

Figure 4. Plots showing discharge/charge efficiency (left) and capacity fade (right) over 50 cycles for 3 samples of $LiMn_{0.7}Ni_{0.1}Co_{0.2}O_2$

Nick Vito constructing a battery in the Glove Box at UF