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Author

Doeff, Marca M

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The Origins of the Rate Enhancement in $\text{LiNi}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}\text{O}_2$ ($0 < y \leq 0.2$) Cathode Materials

James Wilcox*[†] and Marca M. Doeff*

*Materials Sciences Division

Lawrence Berkeley National Laboratory

[†]Department of Material Science and Engineering

University of California

Berkeley, CA 94720 USA

Recently, much research has been directed towards finding a replacement cathode material for LiCoO_2 combining high performance with lower cost and toxicity. One promising candidate material is the mixed transition metal oxide $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$, which delivers 180 mAh/g below 4.4 V versus Li/Li^+ (1, 2). However, in this material, there is 4% anti-site cation mixing, which hinders the mobility of lithium within the lattice, adversely affecting its rate performance in lithium batteries. Ongoing work in our lab has shown that partial or full substitution of cobalt with aluminum, $\text{LiNi}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}\text{O}_2$ ($0 < y \leq 0.2$), can lead to significant improvements in rate performance (3). In particular, $\text{LiNi}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}\text{O}_2$ shows greatly improved rate capability with almost no sacrifice in the overall capacity delivered at low rates between 2.0 and 4.3V (Figure 1). The smaller ionic radius of Al^{3+} in octahedral coordination (0.535 Å) compared to Li^+ (0.76 Å) creates a strong driving force for the formation of a more lamellar structure in the aluminum containing materials (4, 5). XRD experiments and subsequent Rietveld refinement (Figure 2) reveal a significant decrease in anti-site defect

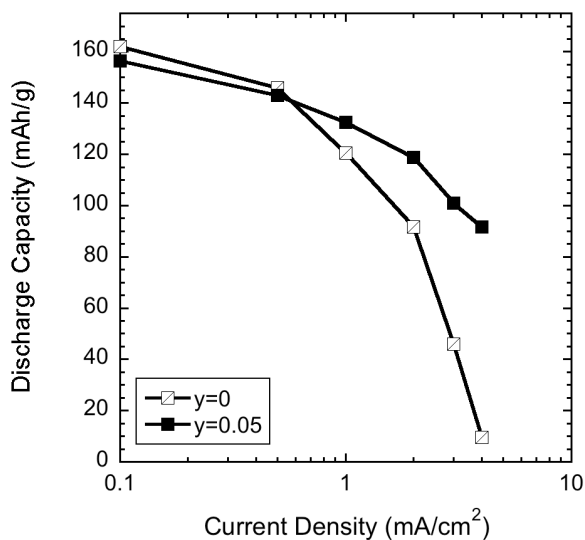


Figure 1: Rate performance of cells containing $\text{LiNi}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}\text{O}_2$ ($y=0, 0.05$) cathodes. Partial Al substitution results in improved rate performance at high current densities.

concentration upon aluminum substitution, dropping from ~4% at $y=0$ to ~2.5% at $y=0.2$. Concurrently, there is an increase in the lithium slab dimension from 2.6 Å to 2.63 Å. This expansion allows for a reduced activation energy and improved lithium diffusivity through the crystal lattice (6). Interestingly, the pressed pellet conductivities of Al-substituted compounds are lower than that of the parent as determined by AC impedance measurements. This lends further credence to the hypothesis that structural effects resulting in improved lithium diffusivity are responsible for the rate enhancement, rather than changes in the electronic structure.

Further experiments to understand the effect of

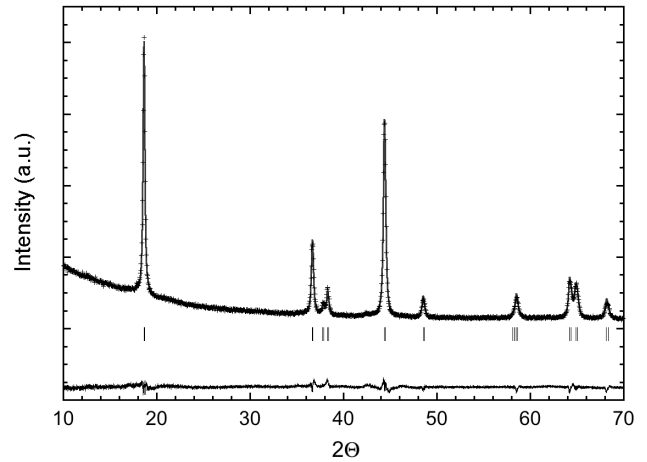


Figure 2: Powder XRD and Rietveld refinement of $\text{LiNi}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}\text{O}_2$ (space group R-3M).

structural changes induced by Al substitution on the transport properties are underway in this laboratory. The changes in electronic conductivity and the chemical diffusion coefficient of lithium as determined by pressed pellet conductivities and GITT experiments will be discussed. Further refinement of cation ordering and crystal structure parameters as determined from neutron diffraction and XANES experiments will also be presented.

Acknowledgment

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