Lithium Rich Layered NMC Cathode Active Materials with Improved Performance for Li-ion Batteries

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Lithium rich layered metal oxide cathode materials, which can be represented as the composite, $xLi_2MnO_3.(1-x)LiMO_2$ (M= Mn, Ni, Co), have been aggressively investigated due to their ability to deliver nearly one electron/metal transfer involving reversible charge and discharge capacities of 230-250 mAh/gram. These materials, however, possess a few drawbacks: i-) first cycle activation of Li_2MnO_3 at high potentials of ~4.6V, accompanied by oxygen evolution, and low columbic efficiency, ii-) low conductivities[(1)] and iii-) low rate capabilities [(2, 3)].

Here, we report the effect of a judiciously selected metal dopant on the electrical, structural and electrochemical properties of $0.3Li_2MnO_3.0.7LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. The metal doped material was prepared as nano-sized particles of about 300 nm (figure 1). It exhibited better capacities during repeated charge/discharge cycles as displayed in figure 2. The higher capacity and improved cycling behavior of the cathode material is attributed in part to 3-4 orders of increased electronic conductivity (measured from DC resistances of pressed pellets) which led to electrodes with lower impedances as demonstrated by the Nyquist plots in figure 3.

Structural characterization using XRD and XAS techniques revealed that the metal dopant facilitates better capacity utilization of the Ni redox couple during the course of cycling. This was further supported by detailed analysis of the current-potential curves from cyclic voltammetry experiments. These results will be reported.

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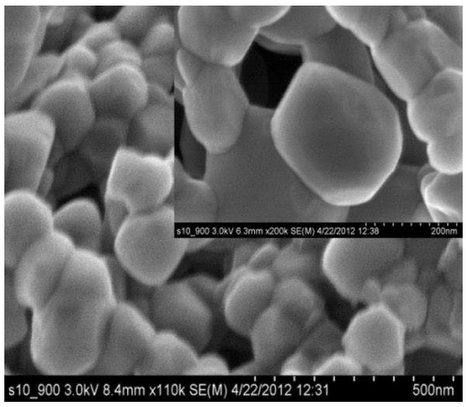

Figure 1: SEM images of $0.3Li_2MnO_3.0.7LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. (Inset shows magnified segment of the sample).

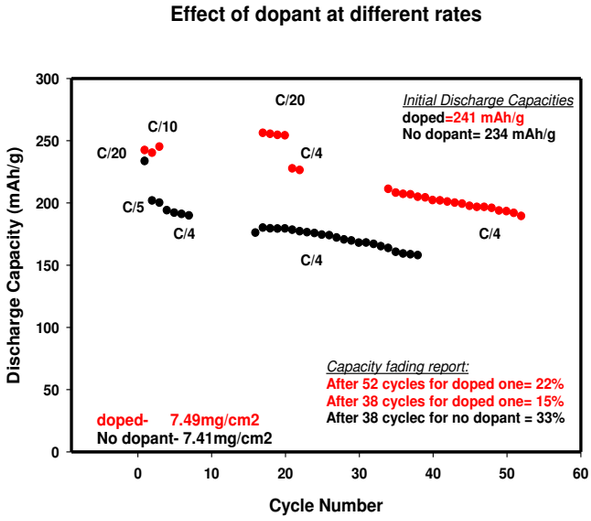

Figure 2: Cycling behavior of $0.3Li_2MnO_3.0.7LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ with and without a a metal dopant between 2-4.9V at room temperature.

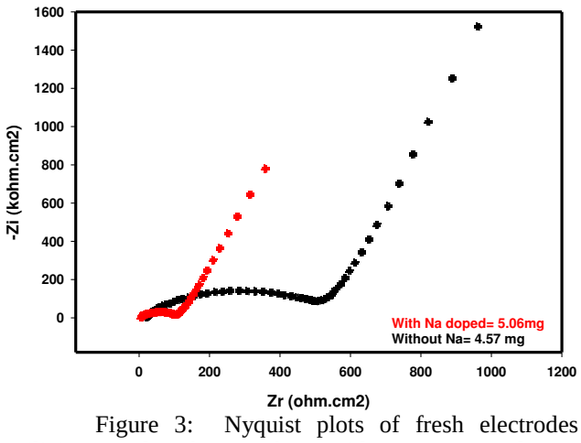

Figure 3: Nyquist plots of fresh electrodes utilizing doped and without a dopant $0.3Li_2MnO_3.0.7LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. The electrodes had similar loadings, noted in the figure.

References:

1. S. K. Martha, J. Nanda, Y. Kim, R. R. Unocic, S. Pannala and N. J. Dudney, Journal of Materials Chemistry A, **1**, 5587 (2013).
2. Z. Lu and J. R. Dahn, Journal of The Electrochemical Society, **149**, A815 (2002).
3. M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li and S. A. Hackney, Journal of Materials Chemistry, **15**, 2257 (2005).