Tailoring the Spinel Component of Composite 'Layered-Layered-Spinel' Electrodes

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Lithium- and manganese-rich composite cathode structures have attracted a great deal of interest as promising cathode materials for advanced Li-ion batteries [1]. These composite structures can be tailored, and their composition tuned, by precise control of the Li to transition metal ratio. For example, reducing the lithium content in 'layered-layered' $xLi_2MnO_3 \bullet (1\text{-}x)LiMO_2$ materials (M=M, Mn, Co) introduces a spinel component [2], thereby generating a 'layered-layered-spinel' structure with formula $y[xLi_2MnO_3 \bullet (1\text{-}x)LiMO_2] \bullet (1\text{-}y)LiM_2O_4$).

We have recently shown that 'layered-layered-spinel' cathodes containing 5-10% spinel can deliver a high-capacity (~250 mAh/g) with a high, first-cycle efficiency [2]; in this previous study, particular attention was paid to the system with end members $xLi_2MnO_3 \bullet (1\text{-}x)LiMn_{0.5}Ni_{0.5}O_2$ and $LiMn_{1.5}Ni_{0.5}O_4$ because both 'layered-layered' and spinel end members have a Mn:Ni ratio of 3:1. We have extended this approach by investigating substituted electrode materials in which Ni is partially replaced by Co, while maintaining a Mn:(Ni+Co) ratio of 3:1.

Figures 1a and 1b highlight how substitution of Ni by Co in the spinel framework dramatically alters the charge and discharge voltage profiles, respectively, when lithium cells are cycled between 5.0 – 2.0 V. Included in the data are the voltage profiles of a $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.25}Co_{0.25}O_2$ electrode after Li had been chemically removed to the spinel stoichiometry, and then annealed at 750°C, prior to cell assembly; the voltage response of this electrode strongly mimics that of the standard $LiMn_{1.5}Ni_{0.25}Co_{0.25}O_4$ spinel sample.

In this presentation, the effects of spinel inclusion in layered-layered composite structures on electrochemical performance and structural stability on cycling (e.g., voltage fade) will be discussed.

References

1. J-S. Kim, C. S. Johnson, J. T. Vaughey, M. M. Thackeray, S. A. Hackney, W. Yoon and C. P. Grey, *Chem Mater.*, **16**, 1996 (2004).
2. D. Kim, G. Sandi, J. R. Croy, K. G. Gallagher, S.-H. Kang, E. Lee, M. D. Slater, C. S. Johnson, M. Thackeray, *J. Electrochem. Soc.*, **160**, A31 (2013).

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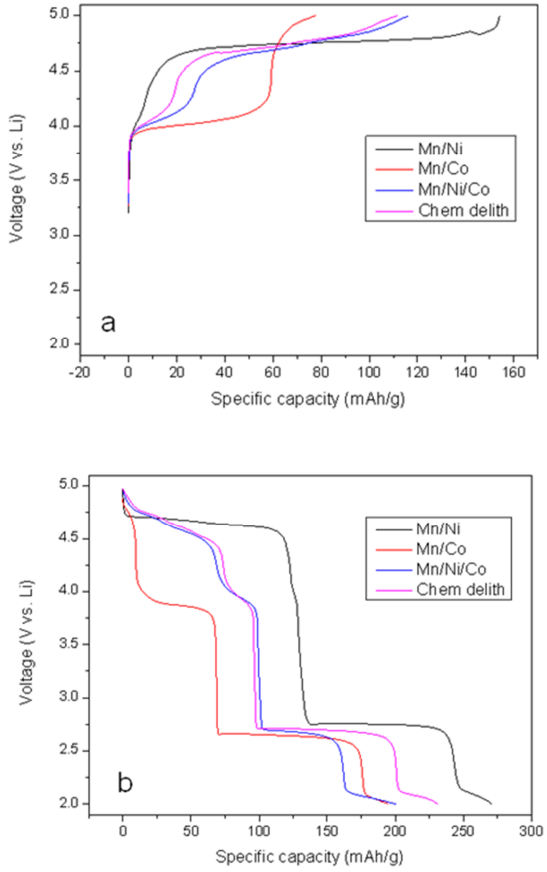

Figure 1. First charge (a) and discharge (b) cycle of $LiMn_{1.5}Ni_{0.5}O_4$ (black), $LiMn_{1.5}Co_{0.5}O_4$ (red), and $LiMn_{1.5}Ni_{0.25}Co_{0.25}O_4$ (blue) spinel electrodes. Pink lines show profiles of a lithium cell with a 'layered-layered' $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.25}Co_{0.25}O_2$ electrode after Li was chemically removed to the spinel stoichiometry, and then annealed at 750°C, prior to cell assembly.