Transformation Mechanisms in Composite $xLi_2M'O_3 \cdot (1-x)LiMO_2$ Electrode Structures

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$xLi_2M'O_3 \cdot (1-x)LiMO_2$ electrode materials, where M' = Mn, Ti, Zr, etc. and M = Mn, Co, Ni, etc., are currently the most promising option for realizing significant advancements in lithium-ion technology in the near-term. Although our current understanding of these materials has increased dramatically in recent years, a mechanistic model for the structural transformations associated with cycling has yet to be verified. As such, much of the work aimed at improving performance is driven by conflicting reports and carried out in an 'Edisonian' fashion without real insight into the atomic-level processes taking place.

This presentation will explore a series of $xLi_2M'O_3 \cdot (1-x)LiMO_2$ electrode materials and their electrochemical behavior under a wide variety of cycling conditions. Both ex-situ and in-situ structural and electrochemical data will be presented and discussed.

As an example, Figure 1 shows selected ex-situ X-ray absorption spectroscopy data from the nickel K-edge of 'activated' $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$ electrodes (Toda HE5050) charged or discharged to various states of charge (SOCs) [1]. From the figure, it is clear that the electrode charged to 3.6 V (red) is different, in both the average oxidation state of the nickel ions and the local structure, to the electrode discharged to this same voltage (orange). Furthermore, these electrodes are at distinctly different SOCs (i.e., they have a different lithium content). Perhaps more interesting are the data from electrodes charged to 4.2 V (blue) and discharged to 3.9 V (purple), i.e., at similar SOCs. Even though these electrodes contain the same amount of lithium, the average transition-metal oxidation states and local nickel environments are clearly different. These data, therefore, represent a spectroscopic manifestation of the hysteresis which is inherent to this class of electrode materials.

A structural model will be used to explain the electrochemical processes in composite electrode structures, including hysteresis and voltage fade [2]. Justification for the model will be given in terms of both experimental data and theory; limitations of the model and future directions will also be discussed.
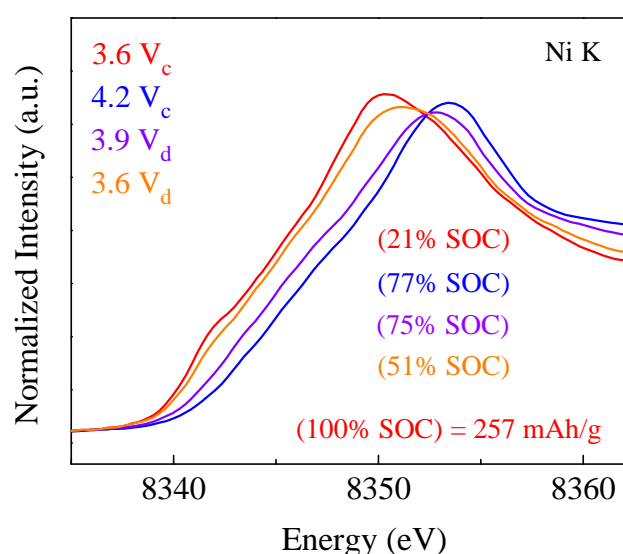
Figure 1. Ni K-edge (XANES) data of Toda HE5050 electrodes charged or discharged to various SOCs. V_c represents the charge voltage while V_d represents the discharge voltage. Percentages, given in parenthesis, are the calculated SOCs based on a practical capacity of 257 mAh/g when cycled between 4.7 – 2.0 V.

References
1. J.R. Croy, K.G. Gallagher, M. Balasubramanian, Z. Chen, Y. Ren, D. Kim, S.-H. Kang, D.W. Dees, and M. M. Thackeray *J. Phys. Chem. C* **117** 6625 (2013).
2. K.G. Gallagher, J.R. Croy, M. Balasubramanian, M. Bettge, D. P. Abraham, A. K. Burrell, M. M. Thackeray, *Electrochem. Comm.* (2013). DOI:10.1016/j.elecom.2013.04.022