

Solid state NMR studies of Li-rich NMC cathodes: Investigating structure change and its effect on voltage fade phenomenon

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The need for low cost, higher energy density cathode materials for wide scale PHEV and EV applications in transportation industry requires the use of advanced materials high voltage spinels or high energy density Li and Mn rich layered materials. The high energy density potential of the Li-rich NMC (Ni, Mn and Co containing) type cathodes is yet to be realized fully due to a number of issues; transition metal dissolution, capacity fade and average voltage fade upon extensive cycling.

In this study, the structure-electrochemistry performance relationship for the Li-rich NMC type composite cathodes are revisited^{1,2} with the voltage fade phenomenon being the primary motivator^{3,4}. Particularly, the local structure(s) of the pristine materials and its evolution upon activation (1st charge above 4.5V vs. Li) and subsequent discharge cycles are investigated with ²H and ⁶Li Magic Angle Spinning (MAS) Solid State NMR and complimentary synchrotron techniques such as Mn-edge XAS and powder diffraction. Several NMC compositions in the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 \leq x < 1$, M=Mn, Ni, Co) phase diagram are studied (Figure 1). Electrochemical activity of disordered Li_2MnO_3 (via a low temperature synthesis) and its analogy to the Li_2MnO_3 component of the composite cathodes are highlighted. A profound loss of the initial local structure and domain arrangement (measured via ⁶Li MAS NMR) is found to accompany to the voltage fade phenomenon whereas no significant insertion of protons (measured via ²H MAS NMR, Figure 2) into the host layered structures is detected. An interpretation of the local structure evolution upon delithiation and relithiation and a proposed voltage fade mechanism based on the experimental results will be presented.

References:

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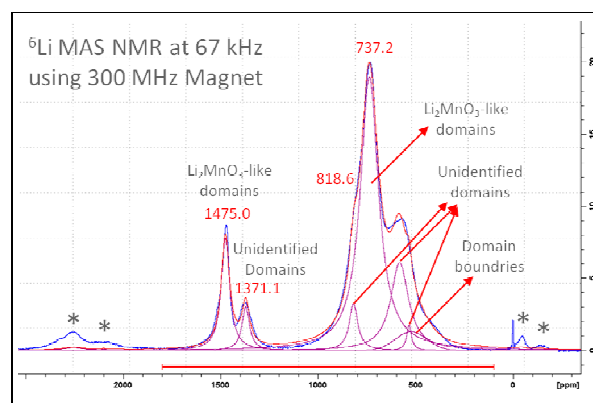


Figure 1. ⁶Li MAS NMR of pristine TODA HE5050 composite ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.375}\text{Mn}_{0.375}\text{Co}_{0.25}\text{O}_2$ or $\text{Li}_{1.0}[\text{Li}_{0.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.10}]\text{O}_2$). * indicates spinning sidebands.

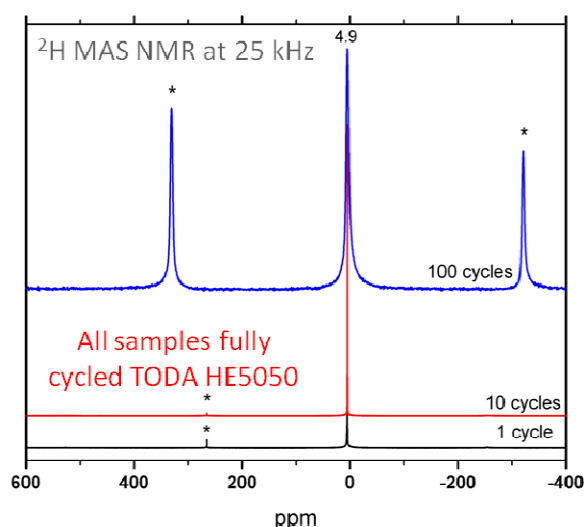


Figure 2. ²H MAS NMR of cycled TODA HE5050 composite electrodes. * indicates spinning sidebands.