

Evidence of Slow Layered-to-Spinel Phase Transformation in High Energy  $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2 - (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  Cathodes Accompanied by a Drastic Rise of Serial Resistance

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$x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2 - (1-x)\text{LiMO}_2$  (M=Mn, Ni, Co) (HE-NMC) material has been an attractive cathode due to its high capacity of about 250 mAh/g, which is promising in enabling high energy density Li-ion batteries. The high capacities of this class of materials are due to an activation process with charging at  $\sim 4.5$  V vs. Li, which involves loss of oxygen ions from the lattice. Thus, during the following discharge, Mn ions can be reduced to lower valence state than possessed in the initial material, resulting in high capacity which is retained in subsequent cycles.<sup>1,2</sup>

Unfortunately, this activation process induces a layered-to-spinel phase transition accompanied by progressive increase of portion of the cell capacity below 3.5 V during cycling.<sup>3</sup> This is illustrated in Figure 1 for the  $0.6\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2 - 0.4\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  material cycled only up to 4.4 V (A), activated once at 4.8 V and subsequently cycled either up to 4.4 V (B) or 4.6 V (C). This HE-NMC material was obtained by the self-combustion method and further annealed as reported previously.<sup>4</sup> It is seen that the increase of discharge capacity proportion below 3.5 V (labeled by dashed arrows) after 50 cycles is more severe for samples that went through activation and were cycled in a wider voltage window, 4.6 to 2.0 V. HRTEM study has shown that spinel-type structure is formed during cycling of the HE-NMC material. The amount of spinel phase progressively increases with the anodic cut-off potential and the number of cycles.

In recent studies, the poor rate performance of HE-NMC has been attributed to the fact that spinel phase, by destroying the layered characteristics of the initial phase, blocks simultaneously the  $\text{Li}^+$  fast diffusion channels.<sup>3</sup> Our highly resolved PITT studies show that the minimum of the chemical diffusion coefficient of Li-ions falls in the potential region between 3.25-3.30 V. The highest total serial resistance of the electrode obtained by refined PITT method also relates to 3.25-3.30 V in the beginning and then slips further towards 3.0 V during cycling. This suggests that the rise of resistance in the 3.25-3.30 V domain relates to the kinetic limitations in spinel phase with high lithiation.

In conclusion, long-term cycling of HE-NMC to potentials higher than 4.5 V results in accumulation of spinel-type phase and leads to development of a greater proportion of lithiation below 3.5 V. The kinetic limitations typical for lithiation/delithiation of more than one lithium per formula in  $\text{LiMn}_2\text{O}_4$  spinel may also relate to the activated HE-NMC cathode. In addition, cycling performance of HE-NMC may be limited by decomposition of pristine particles into much smaller particles (revealed by HRTEM), which promotes surface reactions of electrolyte solution species and a resulting increase of electrode impedance.

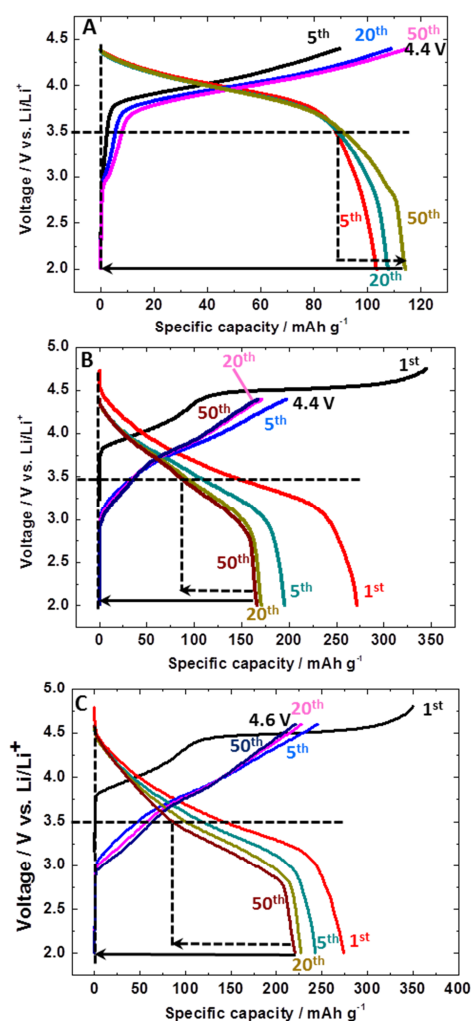


Figure 1. Voltage profiles of  $x\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2 - (1-x)\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$  ( $x=0.6$ ) in half cells in 1 M  $\text{LiPF}_6/\text{EC}+\text{DMC}$  (1:1) solution at C/10 rate up to 4.4 V (A), first cycle activation at 4.8 V and subsequent cycling up to 4.4 V (B), first cycle activation at 4.8 V but the subsequent cycling up to 4.6 V (C). Cycle numbers are indicated.

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