

## <sup>6</sup>Li MAS NMR Studies of the Lithium Nickel Manganese Oxide Cathode Materials Before and After Electrochemical Cycling

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<sup>6</sup>Li MAS NMR spectroscopy has been used to examine the lithium local structures in the nickel manganese oxide  $\text{Li}[\text{Ni}_x\text{Mn}_{(2-x)/2}\text{Li}_{(1-2x)/3}]\text{O}_2$  electrode systems.<sup>1,2</sup> For example, Figure 1 shows the <sup>6</sup>Li MAS NMR spectra of  $\text{Li}_{1-x}[\text{Li}_{1/9}\text{Ni}_{3/9}\text{Mn}_{5/9}]\text{O}_2$  as a function of state of charge. Two groups of resonances are clearly observed, one at approximately 733 - 590 ppm and the other at 1498 - 1324 ppm. On the basis of our earlier <sup>6</sup>Li NMR studies of  $\text{Li}_2\text{MnO}_3$  and  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.4}\text{Cr}_{0.4}]\text{O}_2$ ,<sup>3</sup> both the shifts and the size and shapes of the spinning sideband manifold of the resonances are consistent with the assignment of these groups of resonances to Li in the predominantly Li layers (711 - 594 ppm), and Li in the transition metal ( $\text{Ni}^{2+}/\text{Mn}^{4+}$ ) layers (1486 - 1370 ppm).<sup>3,4</sup>

On charging, Li ions in the octahedral sites of both the  $\text{Mn}^{4+}/\text{Ni}^{2+}$  and lithium layers are removed and no new resonances are observed. Only the resonance due to Li in the lithium layers at ~ 590 ppm is observed for the 231 mAh/g charged sample. Thus, sites such the one found in the transition metal layers,  $\text{Li}(\text{OMn})_6$  (which gives rise to the resonance at approx. 1500 ppm) is removed, even though this process must involve the oxidation of a more distant transition metal ion.

Figure 2 shows the <sup>6</sup>Li spectrum of the same material at the end of the first cycle. Li has returned to sites in both the Li and transition metal layers. Small changes in the relative concentrations of the different local environments are, however, observed consistent with small changes in the local structure.

In related experiments, we have investigated the role that the synthesis conditions and metal doping (with ions such as  $\text{Co}^{3+}$ ) play in determining the concentration of Li in the transition metal layers and the subsequent electrochemical performance of the materials. A more detailed discussion of the effect of extended cycling and charging at high voltages (>4.5V) on the local environments in all these materials will be presented.

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Figure 1. <sup>6</sup>Li MAS NMR spectra of  $\text{Li}_{1-x}[\text{Li}_{1/9}\text{Ni}_{3/9}\text{Mn}_{5/9}]\text{O}_2$  as a function of state of charge. All spectra were acquired with spinning speeds of 38 kHz.

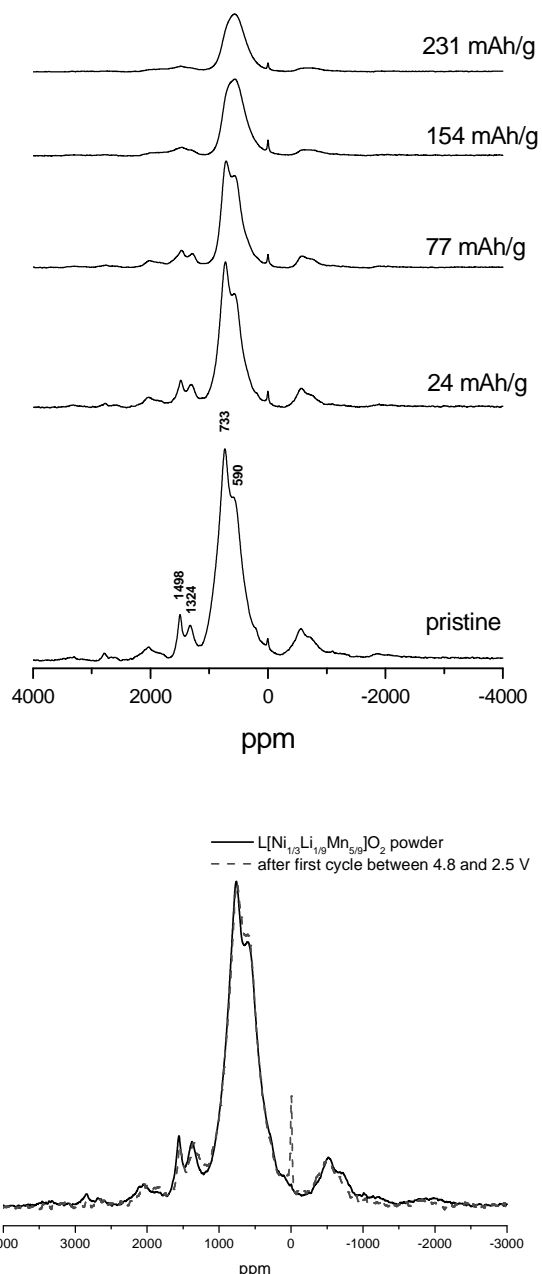


Figure 2. <sup>6</sup>Li MAS NMR spectra of  $\text{Li}_{1-x}[\text{Li}_{1/9}\text{Ni}_{3/9}\text{Mn}_{5/9}]\text{O}_2$  before and following the first cycle. The spectra have been scaled to the intensity of the most intense resonance.