# The 2008 Joseph W. Richards Summer Research Fellowship — Summary Report

## High Voltage Study of Li-Excess Material as a Cathode Material for Li-Ion Batteries

### by Meng Jiang

A series of potential cathode materials for Li ion batteries, $Li[Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}]O_2$, was first reported by Dahn, *et al.* and Ohzuku, *et al.* in 2001.[1,2] These materials all adopt the $R\bar{3}m$ space group and have an ideal layered structure, like $LiCoO_2$, with predominantly lithium layers, transition metal layers and oxygen layers (Fig. 1). $Ni^{2+}/Ni^{4+}$ acts as the active redox couple and compensates the deintercalation (intercalation) of Li ions from (into) the layers.[7] The phases with $x < 1/2$, in which the amount of lithium ions is higher than the amount of electrons that can theoretically be produced through the $Ni^{2+}/Ni^{4+}$ oxidation, are called Li-excess compounds.[2-5] In this type of compound, some of the lithium ions are present in the transition metal layers in the pristine materials. During cycling, capacity values that are higher than those expected theoretically from the $Ni^{2+}/Ni^{4+}$ redox reaction are obtained when the battery is charged for the first time. However, this extra capacity is neither recovered in the subsequent discharge nor generated again in the following cycles. Much scientific effort has been devoted to understand where the overcapacity comes from.[3-6] However, many questions still remain. $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ is chosen as a model compound for the class of Li-excess materials in this work to investigate what happens to the structure during the charge-discharge cycle.

$Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ shows very good electrochemical performance. A stable capacity of 200mAh/g, which corresponds to the theoretical capacity based on the $Ni^{2+}/Ni^{4+}$ reaction, could be achieved by cycling the battery between 5.3-2.5 V up to 10 cycles using a C/20 rate (C is the specific theoretical capacity of the active electrode material). However, only 160 mAh/g could be obtained when the battery is cycled between 4.6-2.5 V (Fig. 2). There is an "activation process" in the first cycle which needs to be performed by charging the material to a higher voltage than 4.6V. Several techniques are combined to address the following questions: What does this "activation process" do to the structure? What is the structure of the activated material? Previous studies on this type of layered materials for Li-ion batteries have underscored the strong correlation between the electrochemical performance of a compound and its structure.[8-10] Since Li ions are directly involved in the electrochemical process, $^6Li$ solid state Magic Angle Spinning (MAS) NMR is used in our work to probe the local environment both in pristine and electrochemically cycled samples, which were stopped at different charging and discharging voltages. As valuable complement to these results, high resolution XRD and neutron diffraction experiments are performed on the same samples in order to obtain long range structural information.

The $^6Li$ NMR spectrum of pristine $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ is displayed in Fig. 3. Two groups of resonances are clearly observed: one at 737-587 ppm, and another at 1511-1341 ppm. Based on previous studies,[7, 8, 11, 12] they can be assigned to the Li ions in lithium layers, and to the Li ions in transition metal layers, respectively. The large width of the peaks at 737-587 ppm is due to the range of different local environments for Li ions in the Li layers that results from the presence of $Ni^{2+}$, $Mn^{4+}$, and $Li^+$ in the first and second coordination shells (in the transition metal layer) surrounding the lithium ions. Since the resonance at 1511 ppm appears at a similar shift to that of Li in the manganese layers in $Li_2MnO_3$, it is assigned to $Li^+$ surrounded by 6 $Mn^{4+}$ in the transition metal layers, indicating that there are $Li_2MnO_3$-like local environments in the pristine compound. Likewise, the resonance at 1341 ppm is assigned to a $Li^+$ surrounded by 5 $Mn^{4+}$ and 1 $Ni^{2+}$ ion.

Figure 4 shows the $^6Li$ NMR spectra of $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ as a function of the state of charge (expressed as the cutoff voltage). The spectra have been



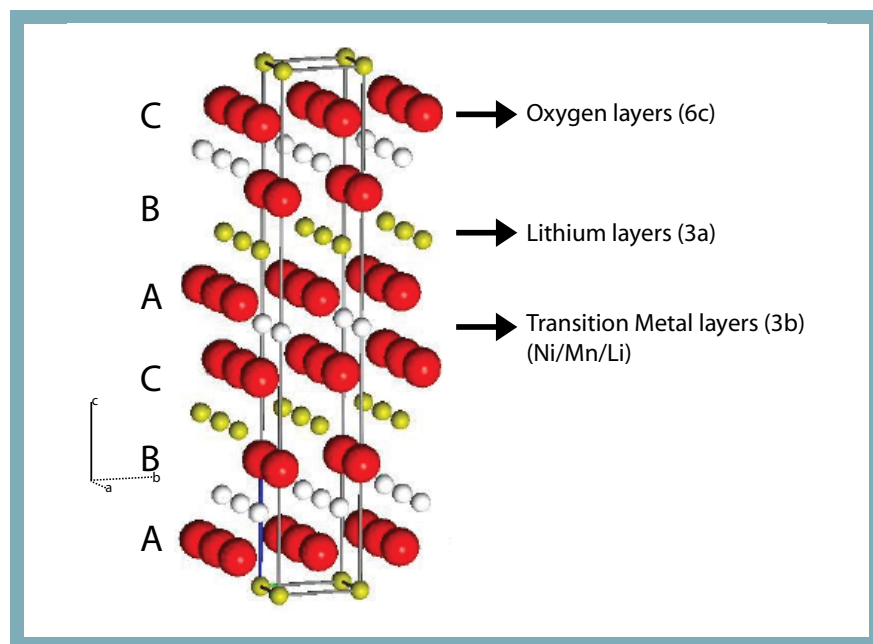**Fig. 1.** *Structure model of $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$. Crystallography site of each atoms are labeled in the bracket. The Li, M, and O atoms are in yellow, white, and red, respectively.*
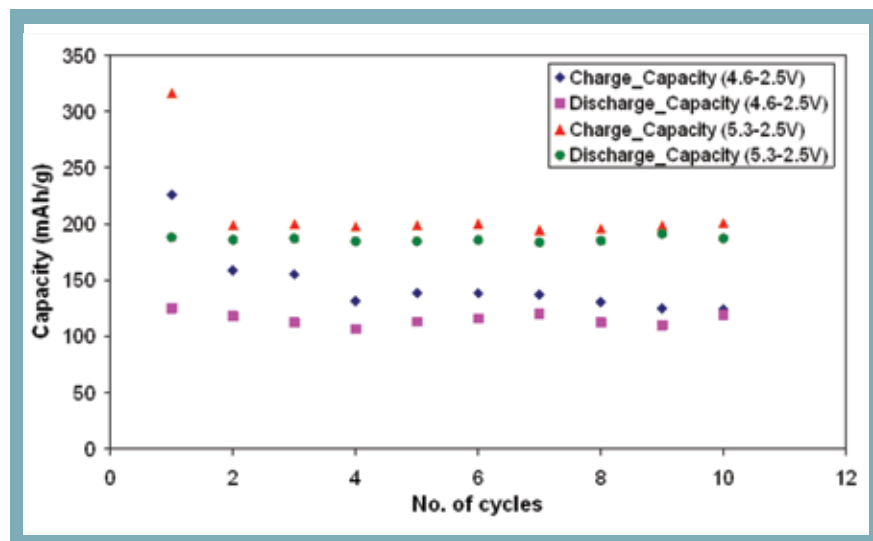


**Fig. 2.** *The comparison of cyclability of $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ with different voltage windows (4.6-2.5 V and 5.3-2.5 V). The cycling rate for both voltage windows is C/20.*

normalized by the data acquisition number and the weight of active material packed in the sample rotors, so that the amount of Li ions in each sample can be related to the intensity of each resonance. When the compound is charged to 4.4 V, the intensity of the peaks ascribed both to Li in the lithium layers and Li in the transition metal layers decreases compared to that of pristine material, which means that lithium is removed from both the Li layers and the transition metal layers upon charging. From 4.6 to 5.3 V, the intensity of the peaks around 600 ppm gradually decreases, consistent with the removal of lithium from the structure, and with the compound still being electrochemically active at these voltages. At 5.3 V, no peaks around 1500 ppm are observed and only one broad symmetric peak is seen around 600 ppm, which indicates that the Li ions in the transition metal layers are totally removed at the end of charge, and that there are still some Li ions left in the lithium layers. No extra peaks are observed in the charged materials except for one at 0 ppm, which arises from the Li ions in the electrolyte salt ($LiPF_6$) or from a passivation layer on the surface of the electrode. Discharged samples of different cut-off voltages (*e.g.* 4.6-2.5 V, 4.8-2.5 V, and 5.3-2.5 V) were also studied by solid-state NMR. Lithium absence in the transition metal layers and cations rearrangement are observed in the samples that have been charged to 5.3 V. The high-resolution XRD data of the series of cycled samples show consistent results with solid state NMR. The superstructure peaks which represent the $Li_2MnO_3$-like cation ordering have disappeared in the high voltage sample.

In conclusion, the cathode material $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ shows good electrochemical performance especially when it is cycled between 5.3-2.5 V. Higher charge/discharge capacity and better cyclability could be achieved between 5.3-2.5 V compared to 4.6-2.5 V. Solid state NMR and high resolution XRD were combined to study the structural change of this compound that occurs during the high voltage process. Li ions are removed from both Li layers and transition metal layers during charge, and they no longer return to the transition metal layers during discharge. In subsequent cycles, Li deintercalation and intercalation involves the Li layers only.
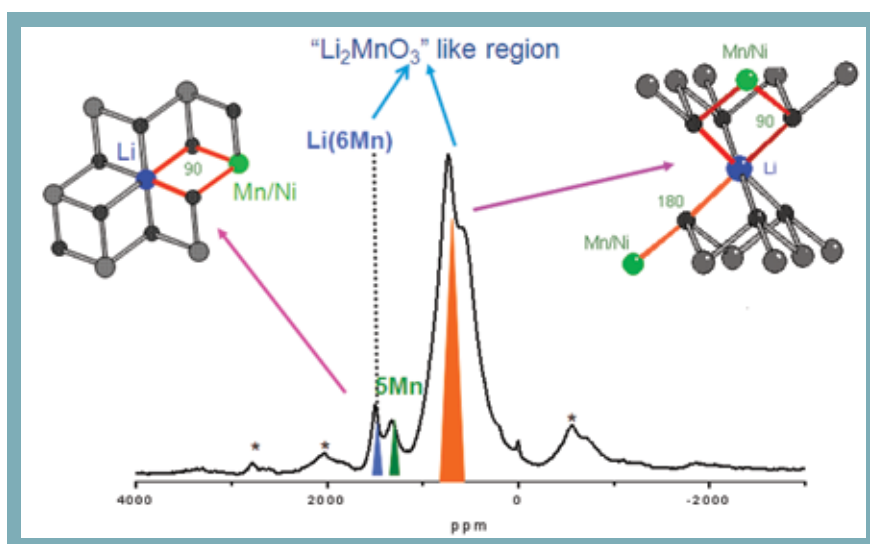
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**FIG. 3.** *$^6$Li MAS NMR of pristine $Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$ acquired at spinning speed 38 kHz at room temperature. The spinning sidebands due to Magic Angle Spinning are labeled with asterisks.*
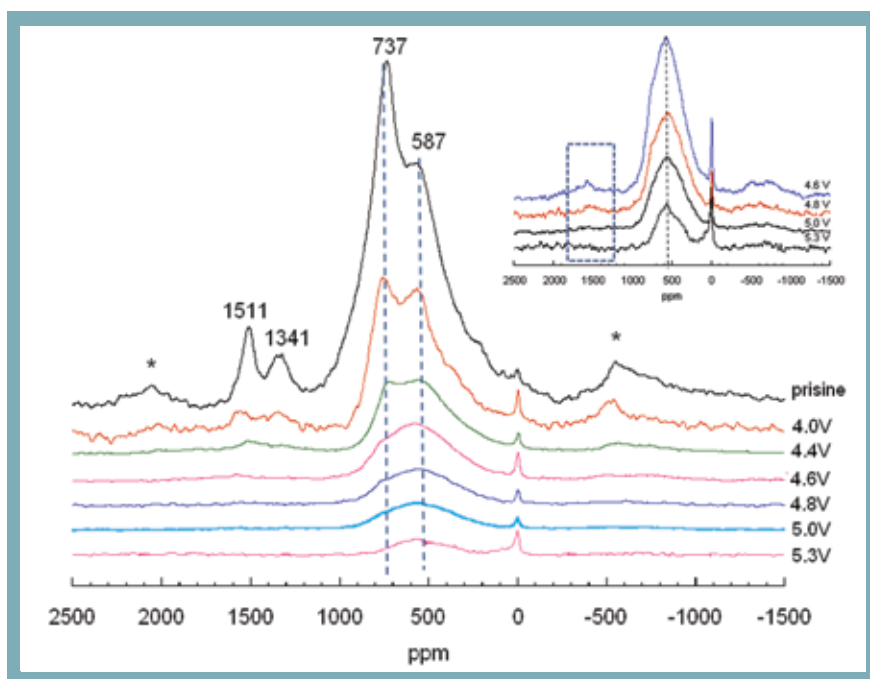


**FIG. 4.** *$^6$Li MAS NMR spectra of charged samples. The voltages where the samples were stopped are marked in the spectra. Sidebands are marked with asterisks. The inset shows the enlargement of the high voltage samples.*

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