



## Solid NMR Studies of Cathode Materials for Rechargeable Li Battery

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**Abstracts:**  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  electrode has been studied by  $^7\text{Li}$  MAS NMR. A sharp resonance at  $-1$  ppm and a very broad resonance at approximately 400 ppm are assigned to the Li ions in Co-only environment and Ni/Mn(Co) environment, respectively, indicating a segregation of Co ions and Ni/ Mn ions. Different temperature behavior of the peak position is observed for Co-only environment and Ni/Mn(Co) environment. Oxidation of Ni ions is involved during the entire charging process. At high temperature, a peak narrowing caused by the electron hopping is observed.

### INTRODUCTION

The development of the portable technology and the hybrid vehicle has created a high demand for the batteries, which have high energy density and long cycle life. Currently the material of choice for the cathode is  $\text{LiCoO}_2$ . However, the high cost and the toxicity of the Co leads to a search for the new materials. Recently, the layered  $\text{Li}[\text{Ni},\text{Co}]\text{O}_2$  and  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  system have drawn interest as cathode materials substituting  $\text{LiCoO}_2$ .<sup>1,2,3</sup> These materials exhibit a layered structure, which is composed of alternating layers of Li and transition metal octahedral. The clustering of Co and electron mobility for  $\text{Li}[\text{Ni},\text{Co}]\text{O}_2$  system was previously studied.<sup>1,2</sup> In this work, we will present the effect of the addition of Mn in this layered structure by using Li NMR spectroscopy.

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## EXPERIMENTALS

### Sample Preparation

Composite cathodes were prepared by mixing  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$ , carbon black, PVDF in a 93:3:4 ratio by mass. The mixture was dispersed in 1-methyl-2 pyrrolidinone, spread on Al foil and dried under vacuum at 110 °C. The cell was assembled in Ar-filled glove box with Li foil anode and  $\text{LiPF}_6$  electrolyte in EC/EMC(1/2, v/v) solvent mixture. The charge/discharge experiment was carried out at a current rate of C/10 between cut-off potentials of 4.2 and 3.0 V. For the NMR experiments, the cell was charged to a certain level and the cathode was extracted. The status of charging (SOC) was calculated from the total number of coulombs passed and the weight of the active material. The SOC100% corresponds to the capacity measured during the 1<sup>st</sup> charging cycle.

### Solid State NMR Spectroscopy

$^7\text{Li}$  MAS NMR experiments were performed at 77.75 MHz on an INFINITY Plus-200 spectrometer with a Varian probe equipped with 4 mm rotors for MAS. All spectra were collected with a rotor-synchronized Hahn-echo pulse sequence (evolution periods  $\tau = 1/\text{spinning frequency}$ ). The  $^7\text{Li}$  90° pulse length was 2.1  $\mu\text{s}$ , the recycle delay 1 s, and the dwell time 2.5  $\mu\text{s}$ . The MAS speeds were varied from 12 to 16 kHz. All spectra were referenced to 1M  $\text{LiAsF}_6$  solution, at 0 pp

## RESULTS

Fig. 1 show the  $^7\text{Li}$  MAS NMR spectra acquired at room temperature for the  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  electrodes charged to various status of charging. Two distinct components are seen for all the samples: a broad resonance exhibiting a center of gravity at approximately 400 ppm and a sharp resonance at -1 ppm with the spinning sidebands manifold. As the extent of charging increases, the Li NMR signal intensity decreases. However, the variation in the signal intensity is not consistent with the amount of Li remaining in the sample; Compared to the fresh electrode, the intensity of the broad component decreases drastically in the spectrum of the SOC30% sample and is slightly reduced as the charging proceeds further. The  $^7\text{Li}$  MAS NMR spectra of  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  electrodes obtained at 220°C are shown in Fig. 2. No significant change is seen for the fresh electrode in the temperature range studied. On the contrary, a new resonance is observed for the electrodes following 30 to 100 % charging. In addition to the original resonance at 0 ppm, a second resonance appears at 315 ppm for SOC30% and shifts to lower frequency as the charging proceeds. At 100% charging, very weak resonances at 73 and 138 ppm are seen. At overcharged state, very weak broad component and a sharp

resonance at  $-1$  ppm remain.

## DISCUSSION

Hyperfine coupling is the major interaction that governs the NMR spectra of paramagnetic compounds.<sup>4,5</sup> The interaction between the nuclear magnetic moment and the electron magnetic moment (unpaired electron) gives rise to a large NMR shift and spinning sideband manifolds. It was shown that Li NMR shifts of  $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$  is dominated by Fermi contact interaction.<sup>1,2</sup>

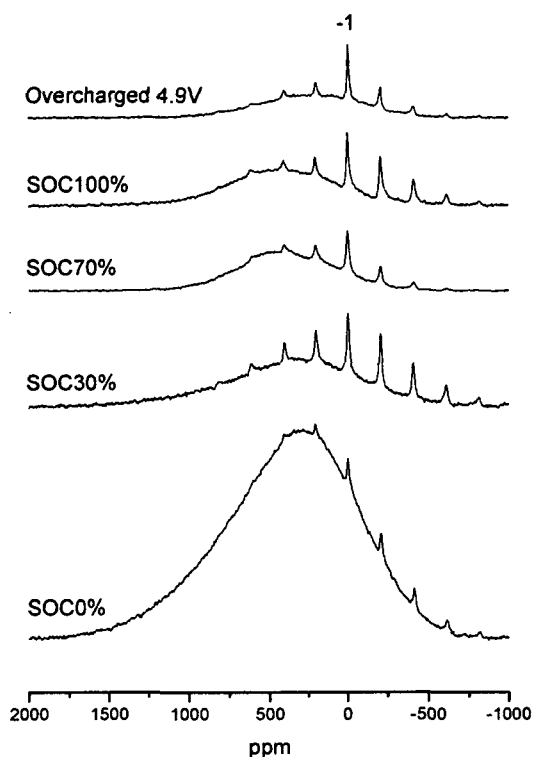


Fig. 1. *Ex situ*  $^7\text{Li}$  MAS NMR spectra of  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  electrode during the 1<sup>st</sup> charging cycle. The spectra were acquired at room temperature with spinning speeds of 16 kHz. Spectra are plotted in an absolute intensity scale, taking into account the sample mass and the number of transients. The status of charging and the isotropic resonances are denoted on the spectra.

Thus, it is proposed that the NMR spectra of  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  can be rationalized by Fermi contact interaction. The sharp peak at -1 ppm can be assigned to Li cations coordinated only to  $\text{Co}^{3+}$  ( $e_g^6 t_{2g}^0$ ) ions, i.e., Li in the diamagnetic  $\text{LiCoO}_2$  environment. The temperature behavior of this resonance agrees well with the diamagnetic environment. No significant change in the peak position for this resonance is observed for the temperature range studied. This is contrary to the temperature behavior of the paramagnetic compounds; The NMR peak position for the paramagnetic compounds shifts to the lower frequency as the temperature is raised. In Fig. 1, the broad resonance is assigned to Li interacting with  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  (and/or  $\text{Co}^{3+}$ ) in the 1<sup>st</sup> and 2<sup>nd</sup> nearest coordination environment. Therefore, this suggests that the transition metals are not randomly distributed in the structure, i.e., clustering of Co is present as shown in Fig. 3.

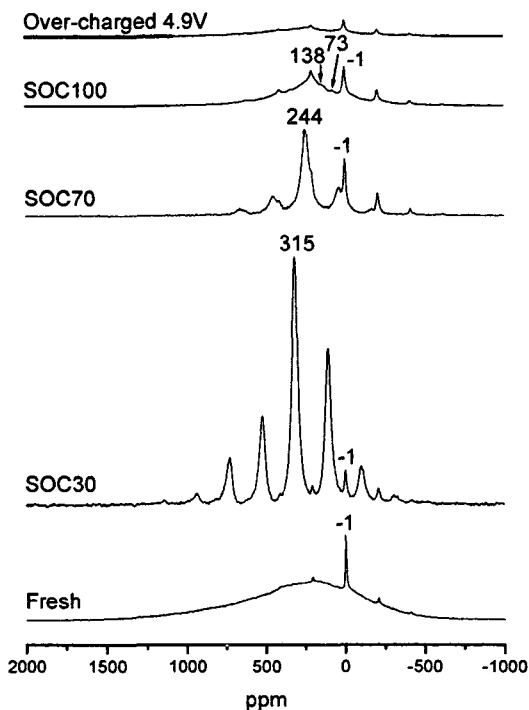


Fig. 2. *Ex situ*  $^7\text{Li}$  MAS NMR spectra of  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  electrode during the 1<sup>st</sup> charging cycle. The spectra were obtained at 220 °C with spinning speeds of 16 kHz. The other conditions are the same with those described in Fig. 1.

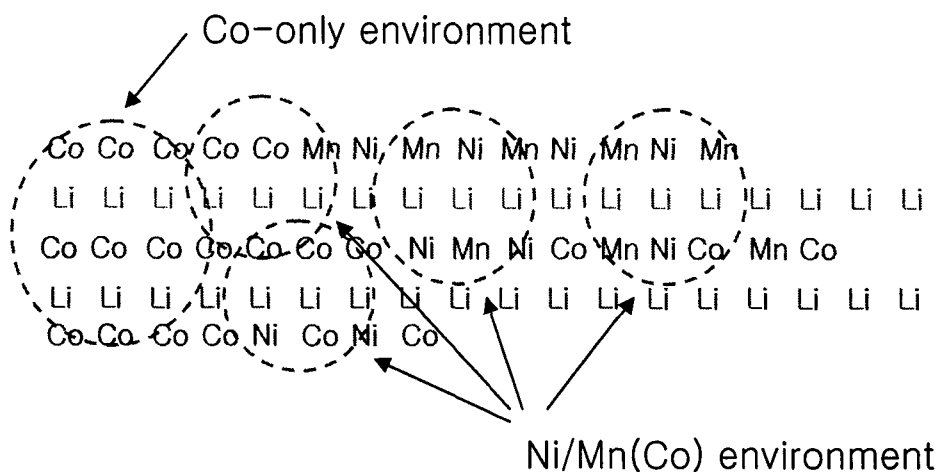


Fig. 3. The distribution of the transition metals in  $\text{Li}[\text{Ni,Mn,Co}]\text{O}_2$ . Various environments for the Li are possible; Co-only, Ni-only, Mn-only, [Ni, Mn], [Ni, Co], [Co, Ni] and [Ni, Mn, Co] environments. The Li ions containing either Ni or Mn ions in the coordination sphere cannot be distinguished in the spectra. Thus, the environment for the Li are denoted as Co-only environment (diamagnetic environment) and Ni/Mn(Co) environment (paramagnetic environment) in this paper.

At high temperature, the broad component disappears and a new resonance at 315 ppm starts to appear for the charged electrode. This phenomenon can be explained by at least two mechanisms.

(1) The dipolar coupling between a nucleus and an electron can be represented by:<sup>6</sup>

$$H_{en} = \frac{\mu_0 \mu_B^2 S(S+1)}{4\pi 3k_B T} \tilde{g} \cdot \tilde{g} \cdot \tilde{B}_0 \cdot \tilde{D}_{en} \cdot \tilde{\mu}_N$$

where  $\mu_B$  is the Bohr magneton,  $g$  the electron  $g$  tensor,  $B_0$  the magnetic field and  $D_{en}$  the dipolar coupling tensor. The dipolar interaction is reduced at elevated temperature, resulting in a spectrum with a higher resolution.

(2) As the extent of charging is increased, the electronic hopping between  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$  and  $\text{Ni}^{4+}$  ions may occur. The signal involved in the mobility may not be refocused by the rotor-synchronized echo sequence, leading to a loss of the signal. The decrease in the signal intensity due to the electron motion<sup>2</sup> and ionic motion<sup>7</sup> was previously reported. As the temperature is raised, however, the motion increases further and thus averages the dipolar interaction, resulting in the emergence of the sharp resonance.

The lower resolution of the NMR spectrum for the fresh electrode can be ascribed to the large magnetic moment and the slow motion of this compound. The fresh electrode

contains  $\text{Ni}^{2+}$  ( $S=1$ ) cations and  $\text{Ni}^{2+}$  ions are gradually oxidized to  $\text{Ni}^{3+}$  ( $S=1/2$ ) and further to  $\text{Ni}^{4+}$  ( $S=0$ ) as the extent of charging increases. Thus, as Li ions are deintercalated, the average magnetic moment gradually decreases and the electronic hopping increases, giving rise to a highly resolved signal with recovered signal intensity at elevated temperature. Now, the Li ions in Ni/Mn(Co) environments see an average value of  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$  and  $\text{Ni}^{4+}$ , resulting in a resonance at 315 ppm for SOC30. This resonance shifts to the lower frequency as the temperature increases, consistent with the Curie-Weiss behavior of the paramagnetic compounds.

At overcharged state, the sharp resonance disappears and a weak broad signal in addition to a sharp resonance at  $-1$  ppm remains. The broad component can be attributed to the Li cations interacting with higher number of  $\text{Mn}^{4+}$  or with only  $\text{Mn}^{4+}$  and  $\text{Co}^{3+}$ . The existence of the resonance at  $-1$  ppm indicates that the oxidation of  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$  may occur, however, is not complete.

## CONCLUSION

The Li NMR spectra show that  $\text{Li}[\text{Ni},\text{Mn},\text{Co}]\text{O}_2$  has a tendency to segregate, forming the Co-only environment and the Ni/Mn-rich environment. The oxidation of Ni ions occurs in the beginning of the charging and through the entire charging range. Thus, the capacity of this compound is mainly contributed from the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$ . As the charging proceeds, the electron hopping occurs between  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$  and  $\text{Ni}^{4+}$  ions, resulting in the signal loss at room temperature and sharpened signal at high temperature. Further study is ongoing to investigate the oxidation of  $\text{Co}^{3+}$  ions and mobility of the Li cations.

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