***In Situ* NMR Studies of Sites Dynamics for Rechargeable Batteries**

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**Introduction**

The fast growing demand for safe and low-cost energy storage technologies with high power and energy densities drives the continuous improvement of rechargeable Li-ion batteries (LIBs). Nuclear Magnetic Resonance (NMR) has been shown to be a powerful tool for determining Li local environments and their evolution during electrochemical operation.1,2 *In situ* NMR can follow the Li evolution during battery cycling to offer insights that cannot be obtained from *ex situ* studies, especially real time Li extraction and reinsertion dynamics. Even though the resolution of static *operando* NMR is poor for the paramagnetic cathode systems such as Li2MnO3, it is sufficient to resolve Li in Li layers (LiLi) and Li in transition metal layers (LiTM), making it possible to follow their individual evolution in real time.3

**Experimental**

7Li NMR spectra were collected while the batteries were cycled at a rate of C/30, with the theoretical capacity C=458 mAh·g-1 (assuming all Li ions are completely extracted) used for Li2MnO3. All *in situ* 7Li NMR acquisitions were carried out on a Bruker Avance I spectrometer in a 9.4 T magnetic field with a 7Li Larmor frequency of 155.4 MHz. The 7Li spectra were obtained using a spin echo sequence with a 90° pulse length of 2.6 µs. 3584 scans were acquired for each spectrum with a recycle delay of 0.5 s. The transmission frequency (SFO1) is placed at 600 ppm.

**Results and Discussion**

Selective *operando* 7Li NMR spectra are shown in Fig. 1 for the first charge-discharge process. The three spectra plotted in thick black, red, and green lines correspond to the pristine cell, top of charge, and end of 1st discharge, respectively. The broad signals from the Li2MnO3 cathode decrease upon charge due to Li extraction. Meanwhile, the intensity of the sharp peak at 250 ppm increases due to Li deposition onto Li metal surface. The broad signal partially recovers upon discharge as Li is re-intercalated into the Li2MnO3 cathode. On the other hand, Li anode NMR signal shows a decrease due to Li stripping upon discharge. It is worth noting that upon charge, the phase of Li metal peak is significantly distorted because of the magnetic susceptibility

effects on the newly-formed Li microstructure (moss and dendrite). The phase comes back to normal upon discharge as the Li microstructure on the anode is removed.

**Conclusions**

Optimized *in situ* NMR is implemented for high temporal resolution in order to monitor lithiation and delithiation

**Fig. 1.** a) 7Li spectra of a pristine Li2MnO3//Li half-cell battery. b) Selective *operando* 7Li NMR spectra. c) Electrochemical profile of a Li2MnO3//Li half-cell battery. d) and e) Normalized area integrals of NMR resonances of Li in Li layers and TM layers in *operando* 7Li NMR spectra.

dynamics of various Li sites in real time. *In situ* NMR investigations consistently show that Li extraction starts preferably from transition-metal (TM) layers and this preference lasts until approximately 20% of the practical capacity is reached. After this initial conditioning, a similar extraction and reinsertion rate of Li from both TM and Li layers is observed in Li2MnO3. Significant residual Li in both TM and Li layers are seen in Li2MnO3 cathodes.

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**References**

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