***In Situ* Studies of Rechargeable Battery Electrodes**

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**Introduction**

Secondary batteries are highly utilized as a major energy storage technology. In order to further optimize the performance of these batteries, the mechanisms of fundamental reactions and structural changes, which occur within the batteries, are studied in real-time. Lithium titanium oxide (Li4Ti5O12, or LTO) is a common anode used in Lithium ion batteries, which shows stable electrochemical performance. One of the challenges with studying this material using *in situ* NMR is that the 7Li signal from LTO is very broad and difficult to distinguish from the sharp, dominating signal from the LiPF6 electrolyte. In order to further continue with the characterization of Lithium ions in the material, a reliable way to separate the LTO peak from the electrolyte peak is crucial.

**Experimental**

7Li *in situ* NMR spectra were acquired on a Bruker DRX-400 spectrometer at a Larmor frequency of 155.5 MHz using

a Bruker static low-gamma probe modified for in situ NMR of rechargeable batteries (Fig. 1). A spin-echo pulse sequence was employed for all experiments. All r.f. pulse lengths were optimized using a saturated LiCl solution. The recycle delay was 5 s and a total of 1536 scans were acquired for each spectrum. The orientation for the bag cell batteries was 90 degrees using a vertically oriented coil. The experimental sequence consisted of two alternating NMR experiments,

each with a different d6 value (30 s, 100 s), while the

battery was discharged to a set voltage.

**Fig.1** *In situ* sum 7Li NMR spectra of electrolyte and electrode for the LTO Bag Cell battery. Inset: *in situ* probehead.

**Results and Discussion**

A series of experiments were done on both the LTO powder and the electrolyte measuring the effects of d6 variation and recycle delay variation. The initial d6 value

used was 30s. There was no signal left from the LTO Powder once the d6 was increased to 100s. However, no changes were distinguishable from the electrolyte peak when the d6 was increased from 30s to 100s. Due to this data, two spectra were run for portion of the discharge process. One spectrum was run with a d6 of 30 s and a second spectrum was run immediately after with a d6 of 100s. While processing the data, the difference was taken between these two spectra in order to observe only the LTO peak. The recycle delay variation experiments showed that the optimal value is 5 s for both the electrolyte and LTO electrode.

**Conclusions**

The difference in T2 relaxation between NMR signals of LTO and the electrolyte was used to separate them in 7Li static NMR. Ways to separate these overlapping peaks with better signal-to-noise ratio are currently being explored, such as multiple quantum coherence filtering. Once clean and good-quality spectra are obtained without interference from the electrolyte, it will be possible to track the changes in the 7Li local environments during battery charge and discharge.

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**References**

[1] Trease, N.M., *et al*., Interface-Electrochemical Society, **20.3**, 69-73 (2011).