In-Situ ^{7}Li Solid-State NMR Study of Li-Ion Capacitor

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Introduction

^{7}Li Nuclear magnetic resonance (NMR) has been used to identify Li-ions intercalated in graphite and other carbons.[1] Performing NMR studies *in-situ* has the advantage of completely preserving the integrity of energy storage devices without destruction of the sample, while allowing quantitative measurements on the same sample over multiple cycles. We have developed a new type of Li-ion capacitor,[2] which is different from conventional double-layer capacitors. A high specific energy (82 Wh Kg^{-1}) can be achieved since the electrolyte is not consumed during discharge/charge cycling. We report here *in-situ* ^{7}Li NMR study of the Li-ion capacitor during charge-discharge cycling to understand the involved electrochemical processes.

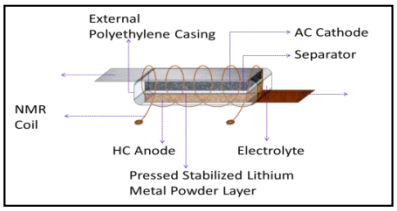

Figure 1. Polyethylene-bag capacitor.

Experimental

A polyethylene-bag Li-ion capacitor (15 x 4 x 2 mm) was assembled for the NMR measurement. The anode consists of Li-intercalated graphite (hard carbon) with stabilized lithium metal powder (SLMP) applied on the surface. A double-layer capacitor type activated carbon was used for the cathode. A solenoid coil wound around the capacitor (**Figure 1**) was mounted on a home-built probe platform for the NMR measurement. *In-situ* ^{7}Li NMR was performed using a 14.1 T (600 MHz) wide bore magnet at the NHMFL.

Results and Discussion

Figure 2 shows ^{7}Li NMR spectra of the bag capacitor acquired *in-situ* after various stages of charge/discharge cycling. The signals near 0 ppm correspond to Li in diamagnetic environments, such as the electrolyte and the Li^{+} trapped irreversibly in the passivation layer of the solid electrolyte interface (SEI). Bulk Li metal and metallic Li layer adhering to the anodic carbon appear around 250 ppm due to Knight shift. These two resonances are a permanent feature over the various stages of cycling. We assign the signal intensity between 20 and 70 ppm to Li^{+} intercalated into the graphitic anode. The shift of this signal follows the movement of Li^{+} into and out of the hard carbon anode.

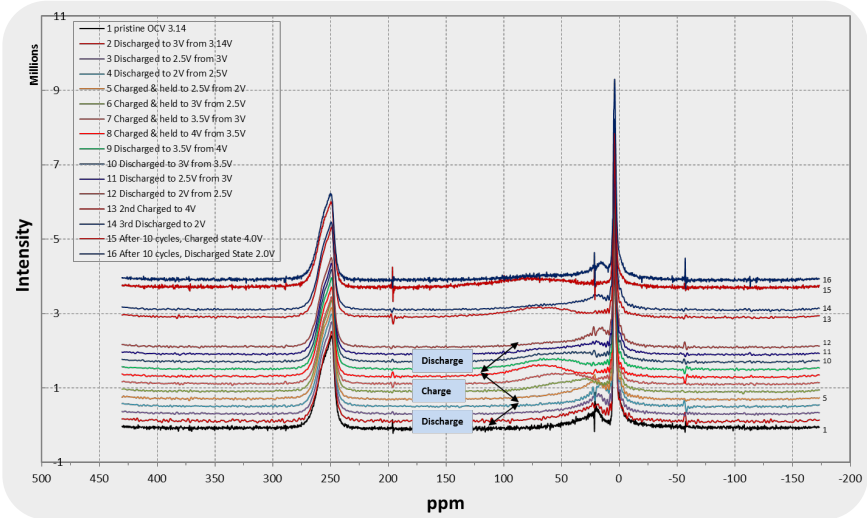

Figure 2 ^{7}Li NMR spectra for the Li-Ion capacitor held at different voltages during discharge and charge (1st, 2nd & 10th cycles are shown here).

Conclusions

The robust bag-capacitor design and *in-situ* ^{7}Li NMR enables monitoring of ion migration in a working energy storage device while completely preserving the cell integrity over multiple cycles. This technique will help improve capacitor/battery design by aiding the investigation of the structure and dynamics of the processes occurring in electrodes. Further study can be performed to improve our understanding of processes like SEI formation, electrolyte changes and capacitive double layer phenomenon.

Acknowledgements

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References

[1] Greenbaum, S.G., *et al*., J. Electrochem. Soc., **145(4),** (1998).
[2] Cao, W. J., *et al.,* 221st ECS Meeting, Seattle, WA**,** #190 (2012).