In-Situ Solid State NMR Study of Li-Ion Capacitor

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Introduction

Advanced energy storage devices with high gravimetric energy and long cycling life have become a socio-economic priority. In-keeping with this, a novel energy storage device 'lithium-ion capacitor' has been developed[1] which can achieve a high specific energy (82 Wh Kg^{-1}) making it an ideal candidate for electric vehicle (EV) applications. The performance of an energy storage device is intimately tied to the electrode materials in an electrode sandwich structure. And hence there is a need to understand various electrochemical processes materializing inside the capacitor at various stages of cycling and delineating the contribution of each of the electrodes. In-Situ NMR technique has become an effective tool in studying energy storage devices[2,3] due to its non-destructive nature, enabling study over multiple cycles on a same sample.

Experimental

In-situ ^{7}Li NMR experiments were conducted on the li-ion capacitor comprising of li-intercalation hard carbon (HC) with stabilized lithium metal powder (SLMP) applied on surface of anode and a double-layer capacitor type activated carbon cathode. A polyethylene-bag li-ion capacitor, developed for this purpose, was inserted in the NMR probe coil (inset of figure 1a). The NMR measurements were made using the 600 MHz (14.1 Tesla) High Resolution Wide Bore NMR Magnet #2 facility at NHMFL and a Gamry instrument was used for cycling purpose.

Results and Discussion

The NMR spectra were recorded simultaneously at regular intervals while the capacitor was cycled galvanostatically. A part of spectra recorded during the start and end of 11th discharge process is shown in figure 1a. A broad li-metal peak appearing around 270ppm (not shown here) always exits, pointing to the SLMP layer. A sharp narrower peak around 0ppm is attributed to the electrolyte ions and the ions trapped in the SEI layer. In the fully charged state, intercalation in HC electrode appears as a separate broad peak around 12 ppm. During the discharge process, the intercalation peak continuously reduces in its intensity while slightly moving downfield, with fully discharged state shown in figure 1a, consistent with the de-lithiation process.

Figure 1b shows the contribution of each electrode, obtained from the assembled 4mm-gap capacitor (inset). As expected, the SLMP lithium-metal peak appears only on anode side. The presence of electrolyte everywhere in the capacitor is shown by the appearance of the electrolyte peak (around 0ppm) in both the spectra while the intercalation peak expectedly appears on the anode side pointing towards the lithium intercalated in HC electrode.

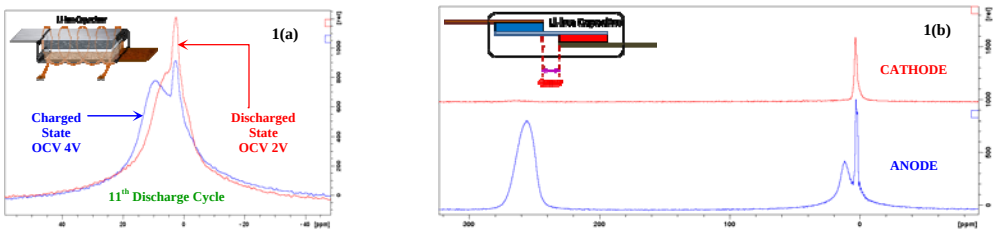

Fig.1. NMR spectra from **(a)** Cycled Polyethylene-bag Capacitor, **(b)** Pristine 4-mm gap capacitor

Conclusions

The application of in-situ NMR technique enables the monitoring of the electrochemical activity in an energy storage device in real time. This has permitted us to not only identify various electrochemical processes in the li-ion capacitor but also delineate the contribution of each individual electrodes. This will certainly help improve the capacitor design by aiding in the investigation of the structure and dynamics of the processes in the electrodes.

Acknowledgements

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References

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