In-Situ Mapping of the Li Concentration in Graphite Electrodes by Magnetic Resonance Techniques

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Thicker electrode layers for lithium ion cells are presently getting increased attention because they can provide higher energy density at lower production cost, due to a favourable electrode-to-current collector ratio per stack volume. It appears, however, that the transport of ions in such electrodes becomes the limiting step during high-rate charging and discharging, leading to significant cell polarization and the under-utilization of cell capacity. Both the design and fabrication techniques for thick electrodes must be optimized in order to enhance Li^+ transport through the electrolyte-filled pores network. It would be beneficial to establish an *in situ* method capable of directly providing spatially resolved details about lithiation/delithiation of active material during battery operation.

We show herein that the optimized single-point magnetic resonance imaging technique enables the mapping of lithium concentration profiles in a 300 μm thick graphite electrode with a spatial resolution of 50 μm during the cycling of a Li // graphite cell, including the spatial distribution of dilute and concentrated stages. We demonstrate that the thick electrode lithiation is non-uniform process both in space, with significant Li concentration gradient appearance, and in time, with reduction of the intercalation rate due to parasitic reactions, even at low currents (C/40). We show that a higher overall state of charge can be achieved if charging will be interspersed with a brief discharging step. In addition, we extract diffusion coefficients and exchanged current densities by fitting the lithium concentration profiles derived with a porous electrode model to the concentration profiles obtained from the experimental data.

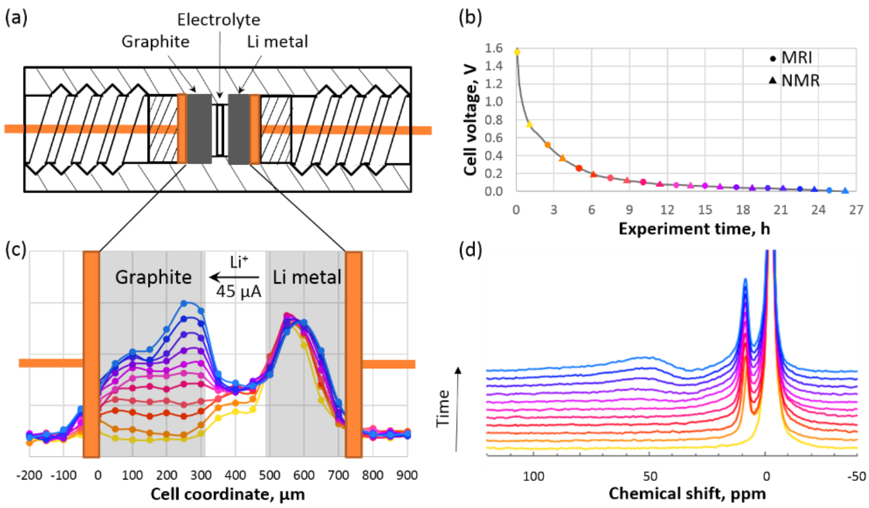

Figure 1. *(a) Schematic representation of the in situ cell; (b) voltage profile of the first charging of the cell at a C/44 Li intercalation rate; (c) axial ^{7}Li MR images and (d) ^{7}Li NMR spectra collected during the charging. The circles of a given color in panel (b) correspond to the curves with same color from panel (c), while the triangles correspond to the curves with the same colors from panel (d).*