Electronic Supplementary Information

Mechanisms for overcharging of carbon electrodes in lithium-ion/sodium-ion batteries analysed by *operando* solid-state NMR

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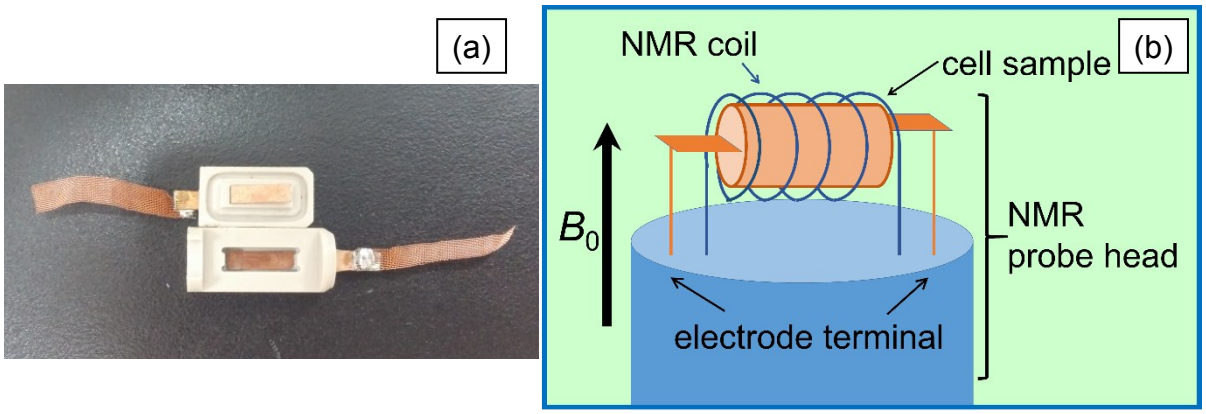

Fig. S1 Photograph of cylindrical sample cell for *operando* NMR measurement (a) and schematic illustration showing the orientation of the cell in a NMR probe (b).

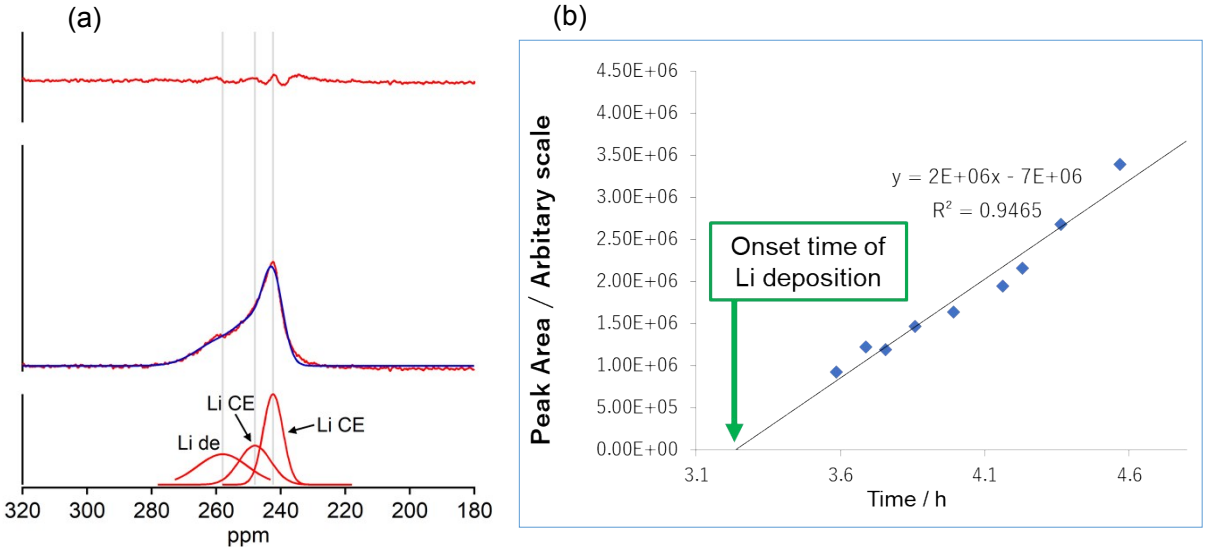

Fig. S2 Fitting of Li metal signal in a ^{7}Li NMR spectrum taken at 4.0 h by three Gaussian curves (a), and estimation of onset time of Li dendrite deposition for a graphite cell with lithiation at 0.35C (b).

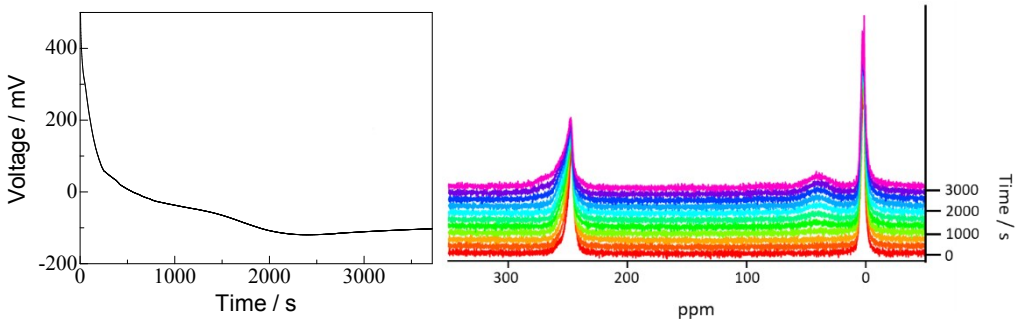

Fig. S3 Discharge (lithiation) profile of graphite electrode at 1C without pre-cycling treatment and corresponding *operando* ^{7}Li NMR spectra.

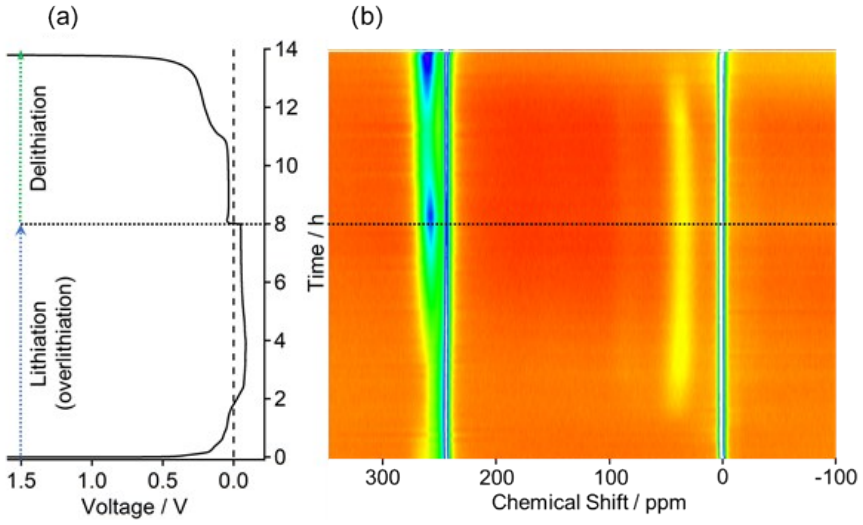

Fig. S4 Discharge (overlithiation) and subsequent charge (delithiation) profiles of a graphite cell at 0.3C in the second cycle and corresponding *operando* ^{7}Li NMR spectra. The cell was pre-cycled at 0.1C between 2.0 and 0.0 V.

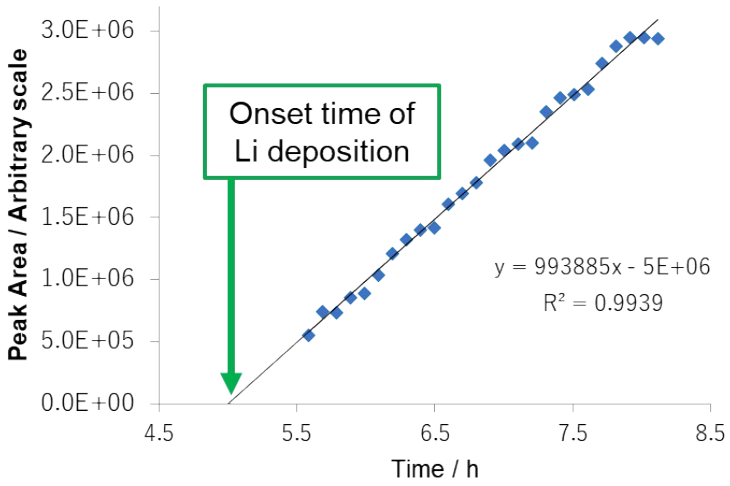

Fig. S5 Estimation of onset time of Li dendrite deposition for a hard carbon cell with lithiation at 0.4C.

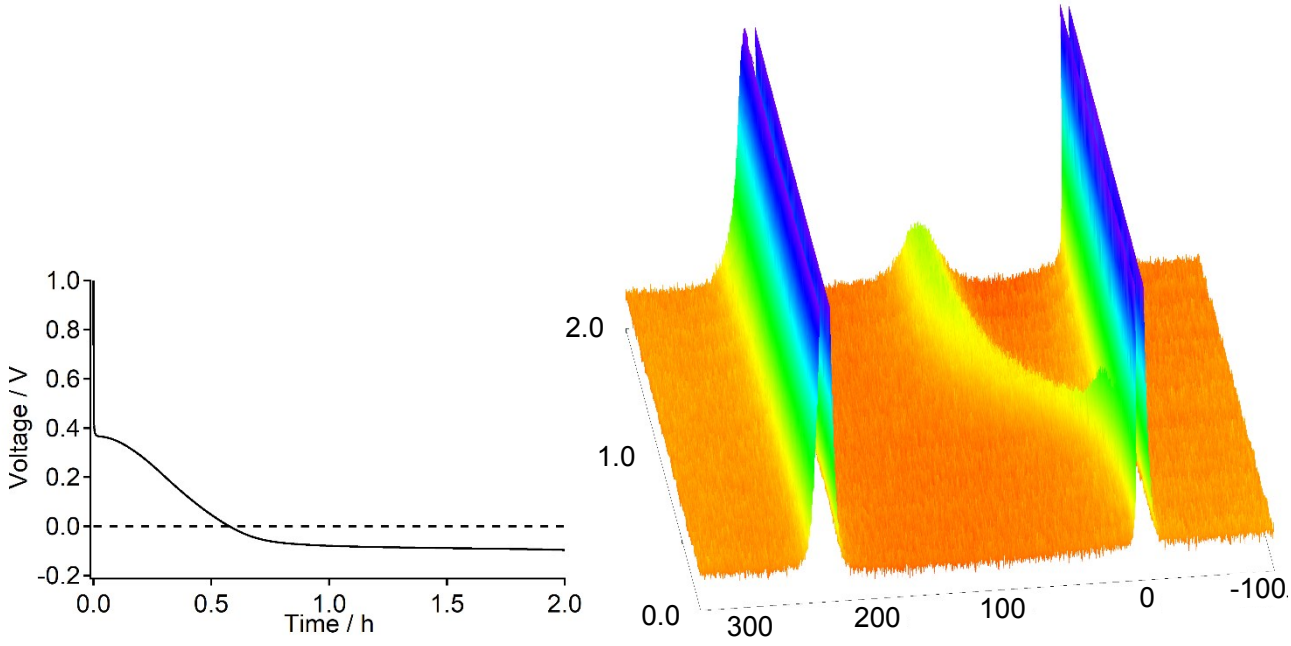

Fig. S6 Discharge (lithiation) profile of hard carbon electrode at 1.5C without pre-cycling treatment and corresponding *operando* ^{7}Li NMR spectra. Some carbon samples did not show clear minima of the electric potential. The dendrite deposition was not observed before the end of quasimetallic Li cluster formation (2.0 h) in the NMR spectra.