In-situ ^{7}Li NMR of Lithium Plating in Graphite Electrodes at Low Temperature

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Lithium intercalation into graphite, which is one of the most widely used materials for the negative electrode in lithium-ion batteries, occurs by charging. In addition to the intercalation, when the amount of reduced lithium exceeds the limit of LiC_6, metallic lithium deposition (plating) does occur in a non-equilibrium manner when there is reaction distribution in the graphite electrode. In this study, lithium plating in $LiCoO_2$/graphite cells is studied at 0 ˚C by direct *in situ* observation of ^{7}Li NMR, which is well suited for examination of metal plating as the metallic ^{7}Li NMR signal at ca. 265 ppm is well isolated from the other ^{7}Li signals of electrodes/electrolytes. By examination of the ^{7}Li NMR signals of metallic lithium, the graphite intercalation compounds (LiC_x, x = 6 and 12), the electrolyte ($LiPF_6$), and $LiCoO_2$, we show that, at high charging rates over 0.5 C, the amount of the lithium metal signal increases with the charging rate. Further, lithium metal deposition slows down or almost ceases at the last stage of the constant-voltage charging with slow relaxation of lithium inhomogeneous distribution among different stages. During the rest period, the observed ^{7}Li NMR spectral change suggests that the deposited metallic lithium is used for lithiation of the low-stage compounds. At the end of discharging, a small metallic signal still remains. Results of *ex situ* examination of the Li re-distribution among the LiC_x structures by using 2D NMR is also presented.

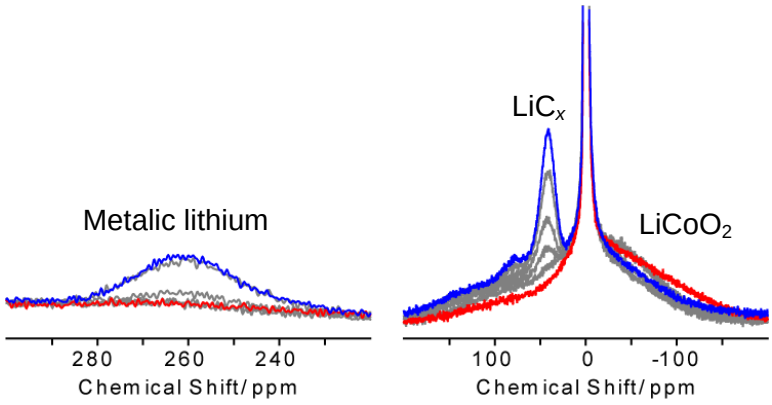

Fig. 1. *In situ* ^{7}Li NMR spectra observed at 0 ˚C with the charging rate of 1 C during the charging process. Red and blue lines correspond to the first and the last spectrum, respectively.

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