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OPERANDO NMR ANALYSIS OF LI PLATING ON GRAPHITE AND HARD CARBON ELECTRODES

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Introduction

Carbon materials such as graphite or hard carbon have been used as active materials on negative electrode in lithium ion batteries (LIBs). While the batteries are overcharged (over-lithiated), Li metal is deposited on the surface of carbon electrode as dendrite, which is the cause of short circuit of the battery. Therefore, precise analysis of the nucleation and the growth of lithium dendrites during lithiation/over-lithiation is important to improve the safety. We have reported a relaxation effect of deposited Li-metal in practical lithium ion batteries after overcharging using *in situ* solid state nuclear magnetic resonance (SSNMR).[1] In the present research, we apply *operando* NMR analysis to observe the Li plating behavior on graphite electrode and hard carbon electrode during the lithiation at overcharged state.

Materials and Methods

Cylindrical plastic half-cells (Li/G and Li/HC) were assembled for NMR measurement using carbon (graphite and hard carbon, respectively) electrode, separator, Li metal (counter electrode), and electrolyte solution (1M $LiPF_6$ EC/DEC). *Operando* ^{7}Li NMR measurement was performed by a spectrometer using a 11.7 T magnet with a customized probe for *in situ* measurement. Each cell was lithiated (discharged) by constant current (1/3 C) and over-discharged until 500 $mAhg^{-1}$ (for Li/G) or 900 $mAhg^{-1}$ (for Li/HC) during the acquisition of NMR data. NMR spectra were taken every two minutes.

Results and Discussion

Discharge curves of Li/G cell and Li/HC cell showed a minimum of electric potential at -0.08 V and -0.05 V, respectively, and then flattened. Both NMR spectra of Li/G cell and Li/HC cell demonstrate Li plating at the overcharged state, however, the behavior of the plating is different. Li plating on the graphite electrode starts at almost the same time with the minimum of electric potential during over lithiation. In the case of hard carbon, start of Li deposition is 50 minutes later than the appearance of the minimum of electric potential. We conclude that Li plating on the surface of the electrode starts after a formation of Li clusters in the closed pore of hard carbon.

References

1. K. Gotoh, M. Izuka, J. Arai, Y. Okada, T. Sugiyama, K. Takeda, and H. Ishida, *In situ* ^{7}Li nuclear magnetic resonance study of the relaxation effect in practical lithium ion batteries, *Carbon* (2014) 79, 380-387.