HIGH RESOLUTION SOLID-STATE NMR STUDY OF LITHIUM RECHARGEABLE BATTERY MATERIALS

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Introduction

Energy capacity and charge/discharge cycle (i.e. the inter-conversion between electrical and chemical energy) are important characteristics of Li-rechargeable batteries. During the charge/discharge cycling, many inter-exchangeable structural phases are developed in the anode and cathode electrodes as well as in the electrolyte of the batteries. Some of the structural phases become irreversible, leading to capacity decay, low energy efficiency, and a short cycle life. One of the important aspects in high-resolution solid-state NMR study of battery materials is to resolve and identify lithium chemical formations during the charge/discharge cycling. Thus, there is an everlasting quest for enhanced spectral resolution, since the Li chemical formations of the battery materials seem to involve minute changes in the lithium local environments. In this work, we demonstrate that $^6$Li NMR provides much higher spectral resolution than $^7$Li, which enable us to study the changes of the Li chemical formations in the Li rechargeable battery materials at various charge potentials, thus to understand the degradation mechanism of the battery.

Experimental

After a Li-polymer rechargeable battery cell was fully discharged by the battery cycling system, the cell was opened under an argon atmosphere in a glove box where the cathode and anode materials, as well as the polymer electrolytes (or liquid electrolytes soaked by membranes) of the cell were removed from the current collectors and packed and sealed separately in different MAS rotors for the high-resolution solid-state Li NMR measurements.

Results and Discussion

Fig. 1 shows the Li MAS NMR spectra of the Li$_x$C$_6$ anode materials extracted from a fully discharged battery cell. In the $^7$Li NMR spectrum, there exist a significant line-broadening as well as many spinning sidebands due to the large dipolar couplings between $^7$Li and the electrons. As a result, not much spectral resolution is revealed in the $^7$Li NMR spectrum. In contrast, no spinning sidebands are visible and the resonance signals appear to show some structure in the $^6$Li NMR spectrum. Thus, with low $\gamma_{6Li}$ in $^6$Li NMR, the dipolar interactions are largely reduced, resulting in high resolution $^6$Li NMR spectra. However, such an improvement in spectral resolution in $^6$Li NMR is at the expense of sensitivity, as shown in Fig. 1b. It is known that $^6$Li NMR has low sensitivity because of a low $\gamma_{6Li}$ and 7.4% natural abundance, compared to $^7$Li NMR with a high $\gamma_{7Li}$ and 92.6% natural abundance. Thus, by going to high fields, $^6$Li NMR sensitivity can be significantly enhanced, while $^6$Li NMR spectral resolution may be further improved through expanded chemical shift dispersion, despite the increased dipolar couplings between $^6$Li and the electrons. In addition, the relaxation-based NMR technique may also be applicable for resolving the $^6$Li resonances if their relaxation times have a large variation.

References


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