The occupied/emptied sites analysis of Lithium Titanium Oxide anodes: How can we obtain high resolution solid state Lithium NMR spectra?

Product used: Nuclear Magnetic Resonance

Lithium ion secondary batteries using spinel-type lithium titanium oxide (LTO) as the negative electrode material are excellent in safety and cycle characteristics due to their chemical stability, and have already been put into practical use. The reaction mechanism of LTO in LIBs well known as the two-phase transition is described as follows.

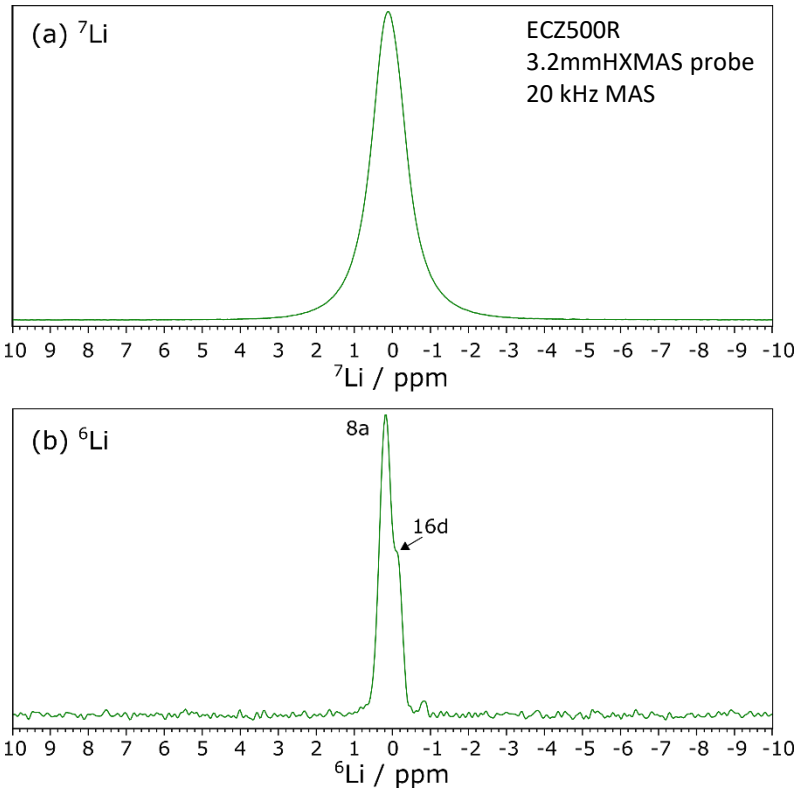
$(Li_3)^{8a}(LiTi_5)^{16d}O_{12} + 3Li^+ + 3e^- \Leftrightarrow (Li_6)^{16c}(LiTi_5)^{16d}O_{12}$

In order to analyze the sites that are occupied / emptied during Li insertion/removal, it is desirable to distinguish three sites, 8a, 16d and 16c. However, the chemical shifts difference between 8a and 16d sites are very small, and only single signals can be confirmed with a wide line width in the highly sensitive and commonly used ^{7}Li solid-state NMR spectrum as shown in Figure 1a.

^{6}Li MAS NMR

There are also ^{6}Li atoms that can be observed by NMR. Although the sensitivity is about 1/30 of ^{7}Li due to its smaller natural abundance and magnetic ratio, the smaller quadrupole moment and homonuclear dipolar coupling result in a narrower line width than ^{7}Li. As shown in Figure 1b, the 8a and 16d sites can be distinguished in ^{6}Li solid state NMR spectrum Although the measurement takes time, a typical solid-state NMR sample tube, such as 3.2mm in diameter, can acquire spectra.

	^{6}Li	^{7}Li
Natural abundance / %	7	93
Spin	1	3/2
Magnetic ratio / rad s^{-1} T^{-1}	3.94×10^7	10.4×10^7
Quadrupole moment	-8×10^{-4}	-4×10^{-2}



The sample is kindly provided by Dr. M. Kitta (AIST)

A part of the spectra in this application note is from a paper in the following.

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