Operando Battery Probe

Product used : Nuclear Magnetic Resonance (NMR)

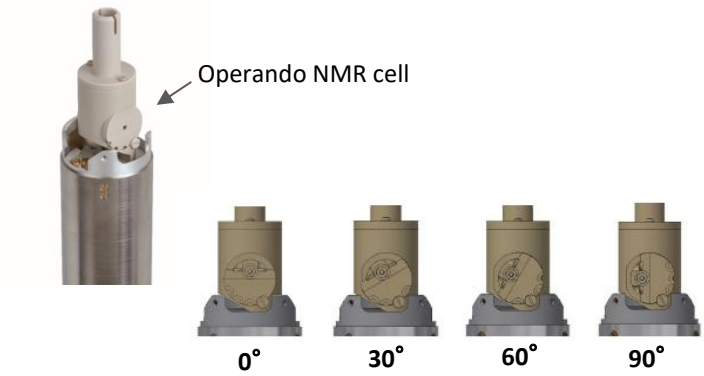
In the field of battery material development, NMR spectroscopy is a vital tool for the direct observation of Li and Na nuclei, providing detailed information on local structures and reaction processes. Our operando battery NMR probes allow for the real-time monitoring of structural changes during charge-discharge cycles, offering valuable insights into the electrochemical behavior of materials under actual operating conditions.

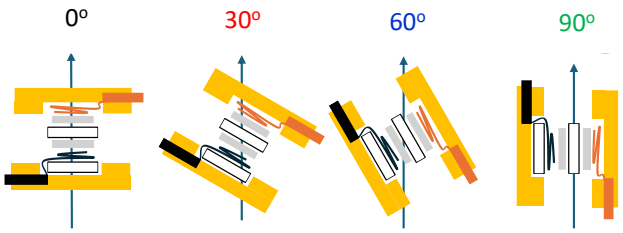
Operando Battery Probe

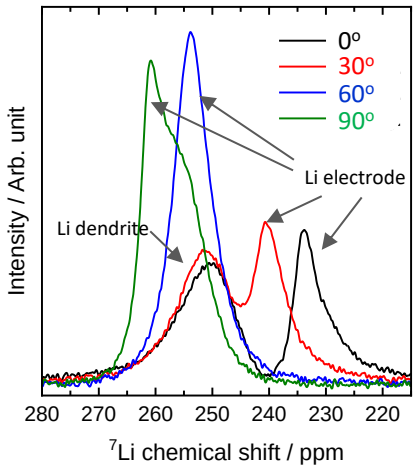
Operando NMR Cell

	Specification
Cell size	15mm O.D.
Cell compatibility	Only dedicated designed cells
Observable nucleus	^{31}P, ^{7}Li, ^{23}Na, ^{27}Al, ^{13}C, ^{6}Li, ^{17}O
High VT range	Up to100 °C with probe heater
Low VT range	Down to -100 °C with Liquid N2 dewar
Electric current	Up to 1.5A
DC range	Up to 5V
Low frequency unit	compatible

Pseudo Goniometer







The Operando NMR cell allows angle adjustment in four steps: 0° , 30° , 60° , and 90° . Changing the sample's angle relative to the magnetic field is useful for obtaining orientation information and identifying signals. The figure on the right shows the angle dependence of the signals from the Li electrode and Li dendrites. Since both signals originate from Li metal, they appear close to each other; however, Li dendrites consist of needle-like metallic Li structures several micrometers in size that grow in various directions relative to the magnetic field, whereas the electrode exhibits a strong angle dependence because only surface signals are detected due to the skin effect. As a result, the electrode signal shows a larger angular dependence.

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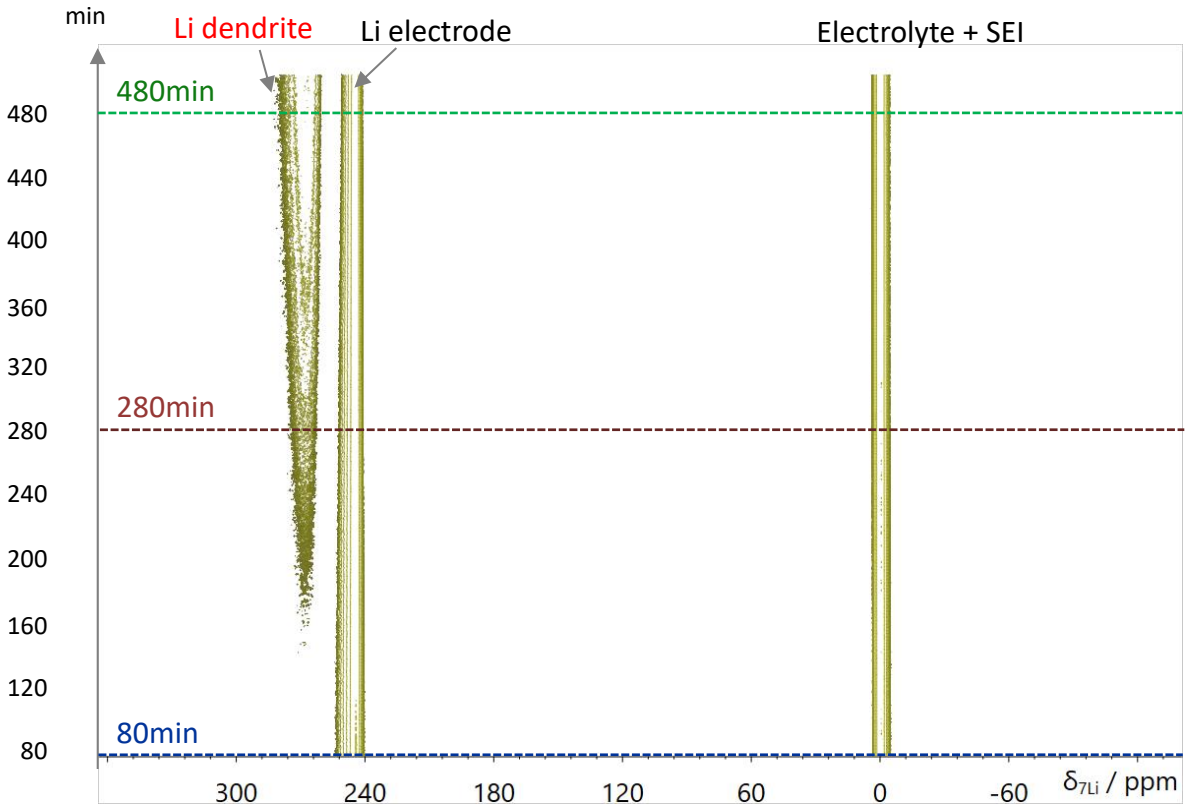
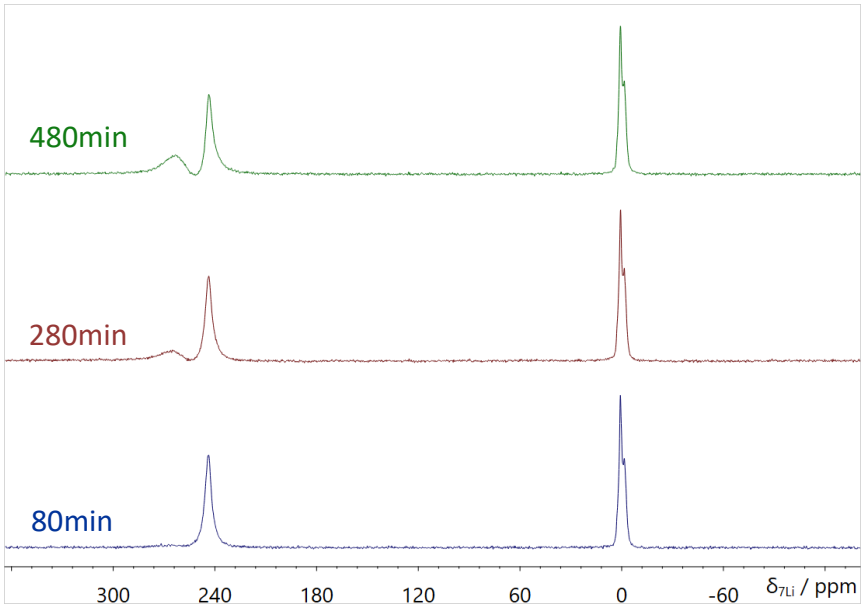
Example 1: Operando Observation of Lithium Dendrites

NMR is the only analytical technique capable of distinguishing Li dendrites from Li species in electrolytes or active materials. By using the operando battery probe, the formation and disappearance of dendrites inside a battery can be monitored in real time. Here, the generation of dendrites caused by overcharging is observed by ^{7}Li operando NMR measurements. The dendrite signal appears at around 270 ppm due to the Knight shift. The cell used in this experiment is a Li symmetric cell in which both electrodes are composed of Li metal. Although the Li electrode signal also appears near this region because of the Knight shift, the signals originating from the dendrites and the electrode can be distinguished, as they appear at different positions owing to their different orientations relative to the magnetic field.

Sample: Li symmetric cell
Li / glass filter / Li
Current collector: Cu
electrolyte: 1 M $LiPF_6$/ EC+ DMC (3:7 v/v) 60µL

Measurement condition
ECZL-500G
^{7}Li 90 pulse width = 12us
Frip angle =45 deg
Relaxation delay =5s
Scans =8 / 1 spectrum





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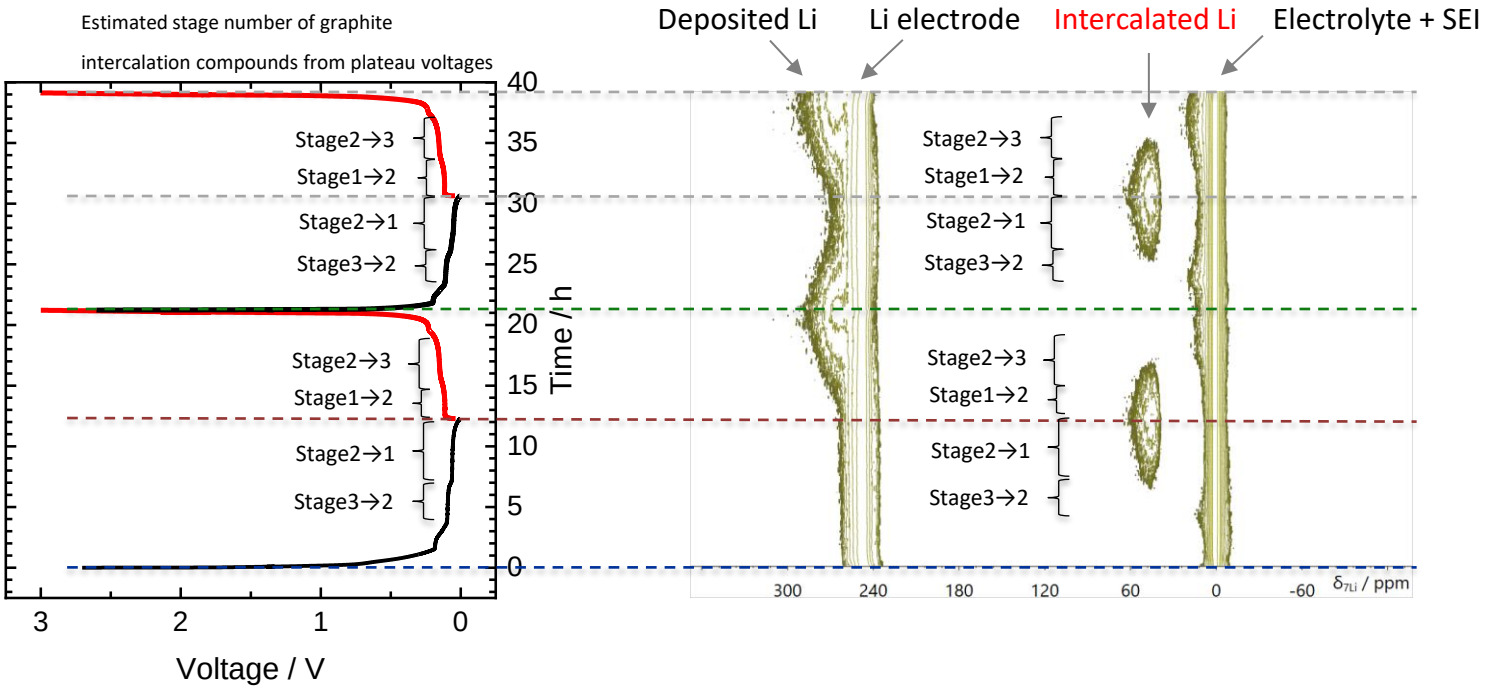
Example 2 : Operando Observation of Li ion Intercalation/Extraction in Graphite

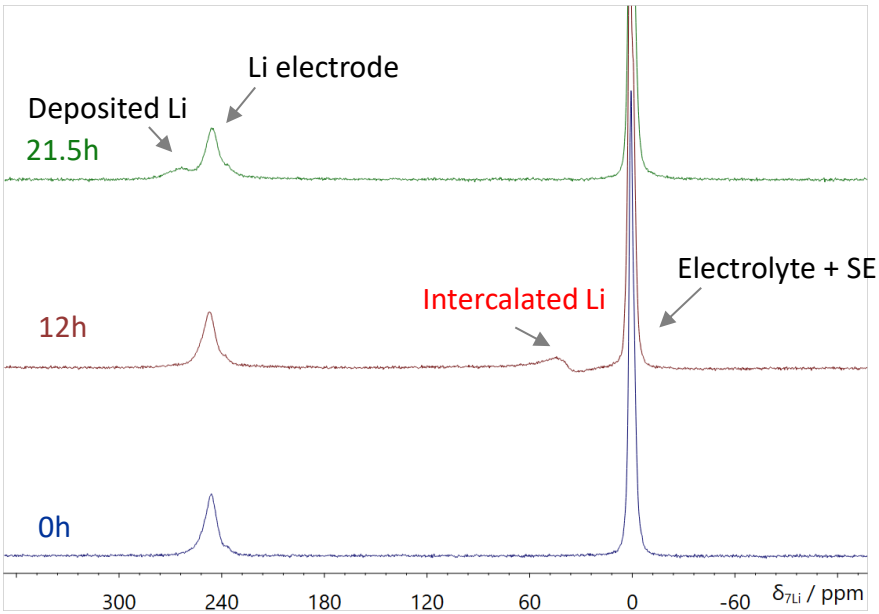
Graphite is the most commonly used layered compound for the anode material in lithium-ion batteries due to its low potential and high stability. During charging, Li is inserted into the interlayer spaces, while during discharging, it is deintercalated. Operando measurements make it possible to observe, in real time, the insertion and extraction of Li in graphite during charge–discharge processes.

Here, ^{7}Li operando NMR spectra of a half-cell using a Li metal counter electrode are shown. In the half-cell configuration, the Li electrode serves as the anode and graphite as the cathode, because lithium has a lower potential. During discharge, a signal originating from Li inserted into graphite appears at around 40 ppm. During charging, this signal disappears and a new signal emerges at approximately 250 ppm. These observations indicate that Li is deintercalated from the graphite and deposited onto the Li electrode during charging.

Sample: Li graphite half cell
Li-Graphite half cell
Li / glass filter / Graphite:PVdF=90:10 (w/w)
Current collector: Cu
electrolyte: 1 M $LiPF_6$ / EC+ DMC (3:7 v/v) 120µL

Measurement condition
ECZL-500G
^{7}Li 90 pulse width = 12us
Frip angle =45 deg
Relaxation delay =5s
Scans =256 / 1 spectrum





Courtesy of Dr. Yuta Ito (AIST) for sample preparation and measurement support

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