



## MAGNETIC RESONANCE FOR BATTERY RESEARCH AND BEYOND

# Advancements in Solid-State NMR Spectroscopy for Paramagnetic Materials

## Introducing the Avance Neo-X 200 MHz pNMR

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Innovation with Integrity

### Introduction

Linking structure and function of energy materials is an essential step in improving their performance. Characterizing these materials, in both crystalline and amorphous phases, requires advanced techniques capable of probing atomic-level structure and also dynamics. Solid-state Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool for this purpose, providing local chemical and structural information that complements data from techniques like XRD, XPS, and EPR. Yet, many energy materials contain paramagnetic species, which makes NMR studies more demanding due to paramagnetic broadening of signals.

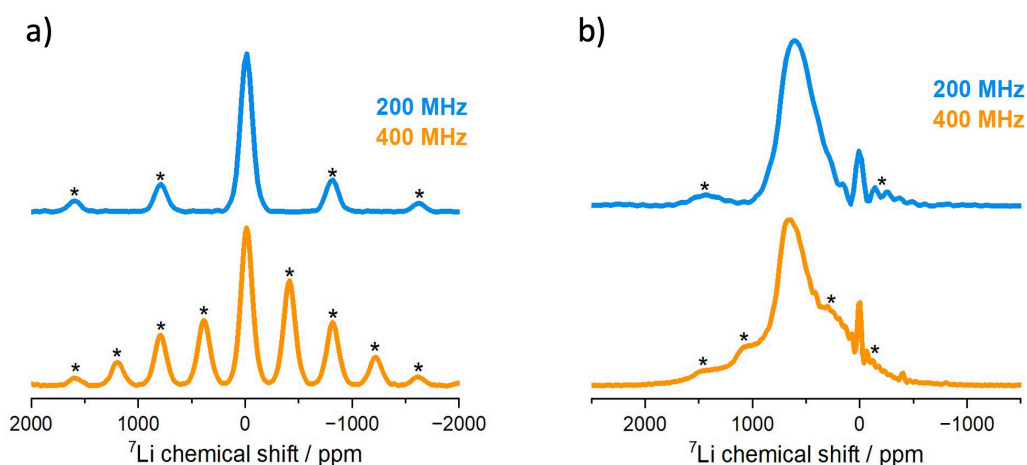
To address these challenges, we present the Avance Neo-X 200 MHz pNMR, our lowest-field solid-state NMR system, for the analysis of paramagnetic materials. By combining 200 MHz (4.7 T) magnetic field strength with fast Magic Angle Spinning (MAS), this system enhances the resolution in spectra of paramagnetic solids. It offers unique insights into local order/disorder, and ion dynamics, opening new possibilities for characterizing complex energy materials.

## Field Strength Matters: Optimizing NMR for Paramagnetic Materials

Analyzing paramagnetic materials by solid-state NMR is challenging due to the presence of unpaired electrons, that introduce strong hyperfine interactions with surrounding nuclei. These interactions, through-bond (Fermi contact) and through-space (dipolar), result in broadened signals, large frequency shifts, rapid relaxation, baseline roll and phase distortion, complicating spectral interpretation.<sup>1,2</sup> Contrary to common expectations in NMR spectroscopy, where higher magnetic fields generally improve resolution, the opposite is true for paramagnetic systems. As shown by Y. Shin et al.,<sup>2</sup> paramagnetic interactions scale with the strength of the external magnetic field, leading to broader isotropic signals and therefore broader spinning sideband patterns at high fields. Lowering the magnetic field can significantly reduce these effects. As an example, Figure 1 compares the  $^7\text{Li}$  MAS NMR spectra of  $\text{LiFePO}_4$  (LFP) and  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC), commonly used cathode materials for lithium-ion batteries, acquired at 200 MHz (4.7 T) and 400 MHz (9.4 T). The data acquired at 200 MHz have narrower isotropic signals and a cleaner sideband pattern, resulting in improved spectral resolution which simplifies the interpretation.

This field dependence makes the Avance Neo-X 200 MHz an excellent instrument to study paramagnetic materials. A key practical advantage of operating at lower magnetic fields is the reduced generation of eddy currents in conductive samples, which facilitates more stable and higher-speed sample rotation. As a result, achieving fast MAS becomes less technically demanding at 200 MHz, enabling more reliable data acquisition.

The combination of 200 MHz field strength with 1.3 mm probes is already widely adopted in academic laboratories as a setup for paramagnetic solid-state NMR.<sup>3-6</sup> In the following sections, we present examples from recent studies that illustrate how this configuration has advanced the understanding of complex energy materials.



**Figure 1:**  $^7\text{Li}$  MAS NMR spectra of a) LFP and b) NMC811 cathodes acquired at 200 MHz and 400 MHz with a spinning frequency of 62.5 kHz.

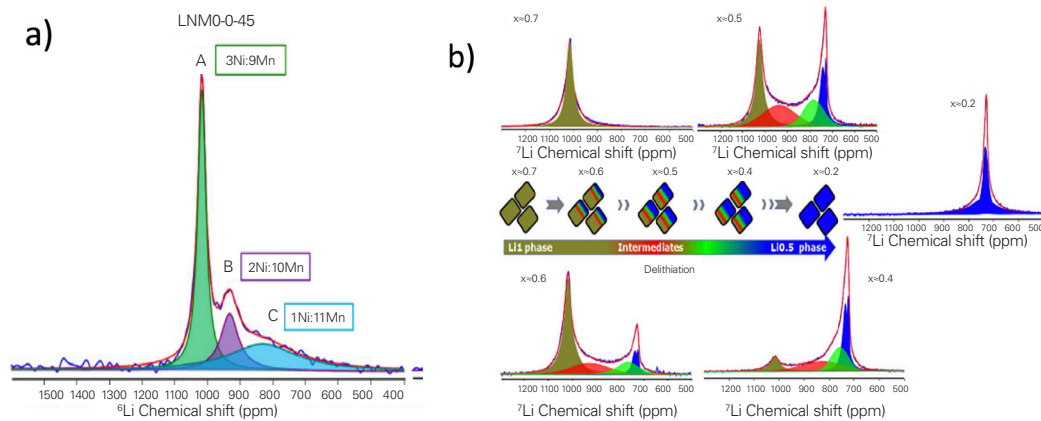
## Expanding Horizons in Battery Research

### Cathodes

Many lithium-ion cathodes contain transition metals in mixed oxidation states. These elements are often paramagnetic in their initial state or become paramagnetic during cycling, making 200 MHz NMR especially useful for their investigations. For example, N. Asres et al.<sup>3</sup> studied the effect of transition metal disorder in LNMO ( $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ) spinel cathodes using both  $^6\text{Li}$  and  $^7\text{Li}$  solid-state NMR.

$^6\text{Li}$  NMR at 200 MHz was used to identify and quantify the degree of transition metal disorder in Ni-deficient LNMO. The improved resolution allowed differentiation between lithium environments: one peak corresponding to ordered lithium sites (surrounded by three Ni and nine Mn atoms), and other for disordered lithium sites (Figure 2a).

Following the characterization,  $^7\text{Li}$  NMR was employed to study the structural evolution of the cathode at various states of charge. While operando XRD suggested a biphasic mechanism between  $\text{Li}_1$  and  $\text{Li}_{0.5}$  phases, the NMR data revealed the presence of intermediate phases that are not visible to XRD (Figure 2b), due to their non-crystallinity. These intermediates suggest a more continuous transition, which may facilitate lithium mobility during cycling.

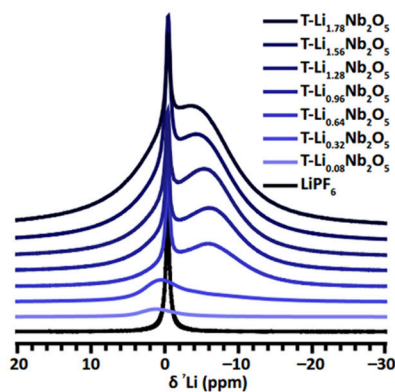


**Figure 2:** a)  $^6\text{Li}$  MAS NMR of pristine  $\text{LiNi}_{0.45}\text{Mn}_{1.55}\text{O}_4$  (LNMO-O-45) b)  $^7\text{Li}$  MAS NMR of LNMO-O-45 at different states of charge. All NMR spectra are collected at 4.7 T and 50 kHz. Adapted from reference<sup>3</sup> in accordance with CC BY 3.0 License.

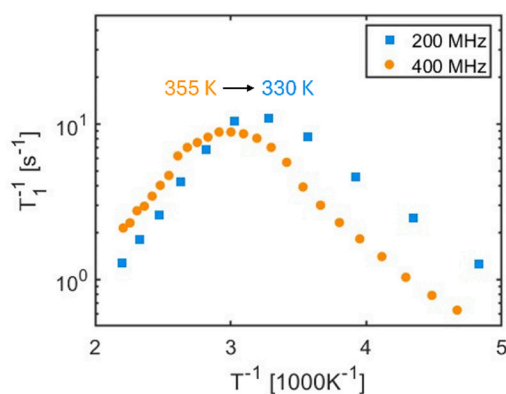
## Anodes

Similarly to cathodes, some anode materials are paramagnetic or become paramagnetic during cycling. An illustrative example was published by K. Griffith et al.,<sup>4</sup> who used  $^7\text{Li}$  solid-state NMR at 4.7 T to investigate the structure and lithium dynamics of  $\text{T-Nb}_2\text{O}_5$ , a promising anode material for lithium-ion batteries. 1D  $^7\text{Li}$  NMR spectra revealed two distinct lithium environments: a rigid population present in the initial stages of lithiation and a larger, more mobile lithium distribution that emerges with increasing lithium content (Figure 3). In addition, the authors used variable temperature NMR measurements to study lithium dynamics during lithiation. These measurements showed very low activation energy for the mobile lithium attributed to the delocalization of electrons in the Nb–O–Nb network.

Beyond lithium-ion batteries, 200 MHz solid-state NMR has also been applied to investigate anode materials for sodium-ion batteries. An example is the study of the sodium intercalation in tin anodes by J. Stratford et al.<sup>7</sup> Here,  $^{23}\text{Na}$  and  $^{119}\text{Sn}$  MAS NMR measurements were performed to monitor the structural evolution of tin anodes during sodium intercalation. The study showed the formation of  $\text{NaSn}_2$  and  $\text{NaSn}_3$  phases, which were not detected by XRD, highlighting the value of solid-state NMR in tracking subtle structural changes during and after battery operation.



**Figure 3:**  $^7\text{Li}$  MAS NMR spectra of  $\text{Li}_x\text{Nb}_2\text{O}_5$  collected at 4.7 T and 9 kHz. Reproduced from reference<sup>4</sup> in accordance with CC BY 4.0 License.



**Figure 4:**  $^7\text{Li}$   $T_1$  relaxation measurements of  $\text{LiPS}_5\text{Cl}_6$  solid electrolyte at 4.7 T (blue)<sup>8</sup> and 9.4 T (orange).

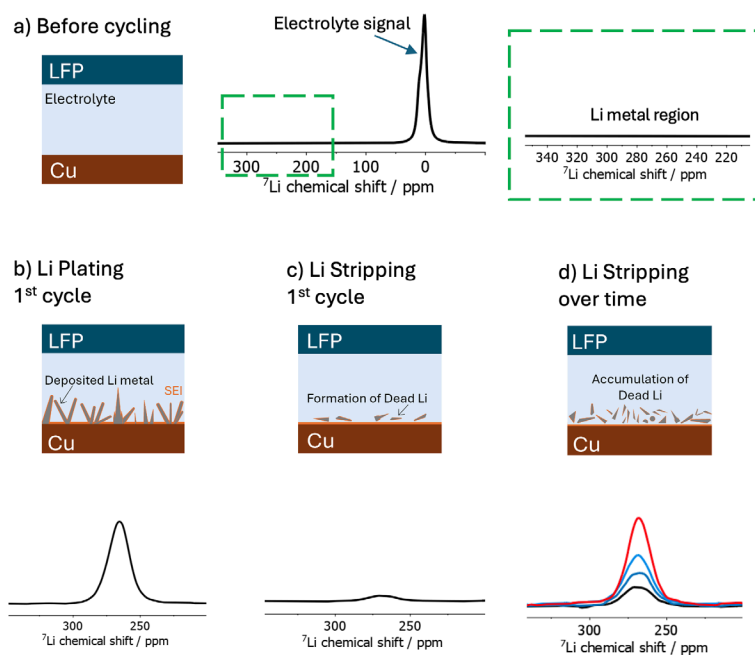
## Solid-State Electrolytes

While structural investigations of non-paramagnetic materials such as solid-state electrolytes generally improve with higher magnetic fields, their dynamic studies can benefit from lower fields. For example, M. Kaus et al.<sup>5</sup> applied NMR relaxometry at 200 MHz to provide insights into bulk conductivity of sodium ions in  $\text{Na}_{3.4}\text{Sc}_2(\text{SiO}_4)_{0.4}(\text{PO}_4)_{2.6}$  (NASICON) electrolyte revealing local hopping rates and determining activation energy for single sodium ion jumps. The main advantage of using low magnetic fields is that the maximum of temperature-dependent relaxation rates, which is used to calculate the local hopping rate of ions and activation energy for single ion jumps, shifts to lower temperatures compared to higher fields (Figure 4).<sup>8</sup> This makes relaxometry measurements more practical and efficient, as they can be performed over a reduced temperature range using conventional probes, eliminating the need for specialized setups such as LaserMAS probes.

## Operando NMR

Operando and in-situ solid-state NMR studies have gained significant attention as an effective technique to investigate plating and stripping processes under battery working conditions. A common application is the monitoring of dead lithium accumulation over time, as illustrated in Figure 5. During plating, operando solid-state NMR enables direct observation of metallic lithium formation. The residual peak that remains after stripping corresponds to dead lithium. By integrating this peak across multiple cycles, it is possible to directly track and quantify dead lithium in a simple and effective manner. This approach was first developed by C. Grey et al.<sup>9</sup> and has since been successfully applied to various battery types.<sup>10-12</sup>

An important factor in quantifying spectra of conductive samples is the skin depth. This effect reflects the fact that the radiofrequency field only penetrates metals to a limited depth, which may cause signal loss and quantification errors. To mitigate this issue, it is essential to ensure that the skin depth exceeds the thickness of the metallic structures under investigation. Since skin depth increases at lower magnetic fields, measurements at 200 MHz are particularly well suited for this purpose. For example, at 200 MHz the skin depth of  $^7\text{Li}$  is 14.7  $\mu\text{m}$  (compared to  $\sim 10 \mu\text{m}$  at 400 MHz),<sup>13</sup> which is greater than the thickness of lithium deposits ( $\approx 12 \mu\text{m}$ ). This ensures complete excitation and accurate quantification of dead lithium, as demonstrated in the work of G. Brunklaus et al.<sup>10</sup>



**Figure 5:**  $^7\text{Li}$  operando NMR spectra of a cell containing  $\text{LiPF}_6$  electrolyte, copper foil and  $\text{LiFePO}_4$  (LFP).

## Magnetic Resonance Imaging

Another useful technique for the investigation of batteries is Magnetic Resonance Imaging (MRI), which enables spatially and temporally resolved insights into materials. The challenge with this technique is that the paramagnetic centers in electrodes introduce magnetic susceptibility artifacts and cause rapid relaxation that diminishes signal. This results in images with signal intensity depending on the distance from the paramagnetic centers.

Operating at 200 MHz mitigates both issues: it reduces susceptibility and increases relaxation times, resulting in images with minimal distortions. This improvement is well demonstrated by R. Balbierer et al.,<sup>14</sup> who used  $^7\text{Li}$  and  $^1\text{H}$  MRI to follow the electrolyte distribution and the accumulation of lithium at the anode surface in lithium-ion batteries. The images indicated homogeneous electrolyte filling, the layered structure of the separator stack, and spatially resolved changes in ion concentration and relaxation near the electrodes, allowing defective passivation and material detachment to be directly visualized. Furthermore, it is shown that information about the concentration of paramagnetic species can be obtained by measuring the  $^7\text{Li}$  and  $^1\text{H}$  MRI relaxation rates near the anode surface.

## Beyond Batteries – 200 MHz in Energy Research

### Solar Cells: Perovskites

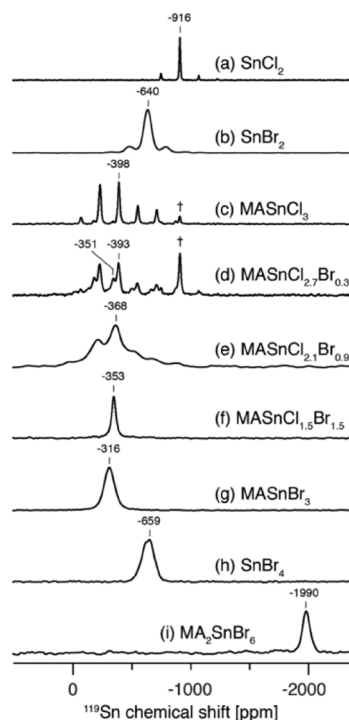
Perovskites are considered highly promising materials for energy applications due to their exceptional optoelectronic properties. Some perovskites incorporate transition metals or rare-earth elements into their crystal structure, which can induce paramagnetic behavior. Such systems naturally benefit from measurements at 200 MHz, for the reasons outlined in the previous paragraphs. In addition, D. Kubicki et al.<sup>15</sup> demonstrated that  $^{119}\text{Sn}$  solid-state NMR at 200 MHz can also be effectively applied to study the local structure of non-paramagnetic perovskites, thanks to the  $^{119}\text{Sn}$  wide chemical shift range and peak distribution (Figure 6). For example, the  $^{119}\text{Sn}$  resonances corresponding to Sn(II) and Sn(IV) appear at clearly distinct chemical shifts, allowing straightforward identification of compounds in different oxidation states in mixed-halide perovskites. Different tin precursors and degradation products also display characteristic spectral fingerprints, enabling their identification. Particularly important in this paper is the detection of metallic tin and amorphous  $\text{SnO}_2$  using solid-state NMR at 200 MHz, two critical degradation products that are invisible to XRD.

### Solid Oxide Fuel Cells: Mixed Ionic-Electronic Conductors

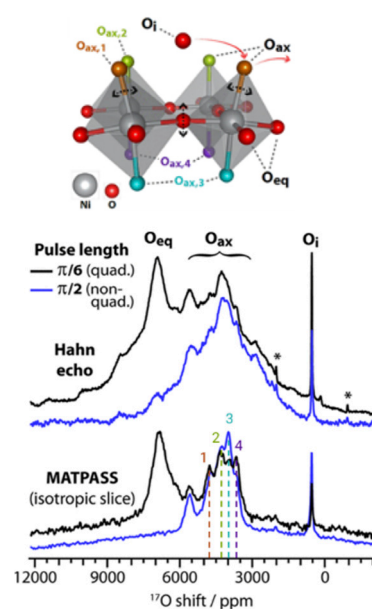
Mixed Ionic-Electronic Conductors (MIECs) show high electronic and ionic conductivity, making them attractive cathode materials for Solid Oxide Fuel Cells (SOFCs). MIECs contain paramagnetic features originating from transition metals, making the 200 MHz pNMR system a valuable tool for the analysis of these compounds. An excellent example was published by D. Halat et al.,<sup>16</sup> where 200 MHz NMR was used to probe  $^{17}\text{O}$  in enriched  $\text{La}_2\text{NiO}_{4+\delta}$  cathodes, as shown in Figure 7. 1D  $^{17}\text{O}$  experiments distinguished equatorial, axial, and interstitial oxygen sites. Highly relevant is that these local environments would be extremely challenging to resolve with higher fields due to overlap of spinning sidebands. In addition, D. Halat et al.<sup>16</sup> applied more advanced techniques such as Magic Angle Turning and Phase-Adjusted Sideband Separation (MATPASS) at 200 MHz combined with quadrupolar filtering to resolve distorted axial oxygen environments. These local displacements, induced by interstitial defects, are linked to oxygen mobility and phase transitions, key factors for the SOFC cathode performance.

### Gas Separation & Storage Applications: Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs) are a class of porous crystalline materials with high specific surface, applied for gas storage and separations, sensing, catalysis, energy research, etc.<sup>17</sup> 200 MHz finds its application even for studies on MOFs. For example, in the work of D. Bryce et al.,<sup>18</sup>  $^{207}\text{Pb}$  solid-state NMR was employed to obtain structural information about lead coordinated to hydrazone-based ligands in MOFs. Here the advantages do not come from the fact that compounds are paramagnetic, rather by the fact that  $^{207}\text{Pb}$  exhibits large chemical shift anisotropy. Lowering the magnetic field strength to 4.7 T (200 MHz) provides remarkable benefits: the broadening of spectral linewidth caused by chemical shift anisotropy diminishes at lower fields, resulting in sharper signals and improved resolution. As a result, the authors distinguished between hemidirected and holodirected lead coordinations.



**Figure 6:**  $^{119}\text{Sn}$  MAS NMR of mixed-anion tin halostannates and their precursors acquired at 4.7 T and 12 kHz.  $^{119}\text{Sn}$  MAS NMR spectrum of  $\text{SnBr}_4$  was collected with a spinning frequency of 0.6 kHz. Reproduced from reference<sup>15</sup> in accordance with CC BY 4.0 License.



**Figure 7:**  $^{17}\text{O}$  MAS NMR spectra of  $\text{La}_2\text{NiO}_{4+\delta}$  at 4.7 T and 40 kHz. Adapted from reference<sup>16</sup> in accordance with CC BY 4.0 License.



## Avance Neo-X 200 MHz pNMR

### System configuration

- Ascend 200 MHz WB Magnet
- AVANCE Neo-X Console
- 1.3 mm H-F/X ( $^{31}\text{P}$ - $^{15}\text{N}$ ) CPMAS probe, MAS up to 67 kHz

### Optional probes

- 4 mm H-F/X CPMAS probe for low-sensitivity nuclei
- Operando/In-situ probes (ePROBE) for electrochemical cells
- Microimaging probes inc. in-operando

### Key advantages

- Enhanced resolution of paramagnetic solids
- Reduced eddy currents: Improved sample spinning
- Relaxometry studies in lower temperature range
- Larger RF skin depth: Full quantification of metallic species
- Ideal for studies of battery, supercapacitor, catalyst, fuel and solar cell materials

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