# NMR as a Key to Unlocking Defect Structure and Dynamics in Emerging Solid Electrolytes

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## 1 NMR in Solid Electrolyte Research

The solid electrolyte, either as a ceramic or a hybrid material composed of ceramic and polymer, is a central component in all-solid-state and quasi-solid-state batteries, ensuring efficient transport of charge carriers between the two electrochemically active compartments. Nuclear magnetic resonance (NMR) spectroscopy [1, 2] is exceptionally well-suited to investigate local structural environments using high-resolution techniques such as fast magic angle spinning (MAS). NMR has been employed not only to identify the structural motifs associated with spin-active charge carriers (*e.g.*, $^{6}$Li, $^{7}$Li, $^{23}$Na, $^{19}$F, $^{17}$O) but also to probe the local coordination geometry of framework elements in solid electrolytes (*e.g.*, $^{31}$P, $^{19}$F, $^{119}$Sn, $^{11}$B, $^{29}$Si, $^{27}$Al). Such site-specific information, derived from chemical shifts, anisotropies, and coupling constants, is essential for elucidating both the average and defect structures of emerging (electrolyte) materials [1]. In addition, NMR can detect structural disorder, polymorphs, and local phase heterogeneity, providing insight into how these variations influence ionic mobility and overall electrolyte performance [3]. When combined with complementary methods such as diffraction and scattering, NMR contributes to a comprehensive understanding of structure-dynamics relationships, which are critical for advancing electrolyte design [4, 5].

To investigate ion dynamics, NMR offers a uniquely versatile set of techniques capable of non-invasively probing ionic motion over an exceptionally broad timescale, spanning, in some cases, more than ten orders of magnitude. Figure 1 provides an overview of the various NMR methods [6-9] available to quantify both microscopic jump rates and macroscopic diffusion coefficients.

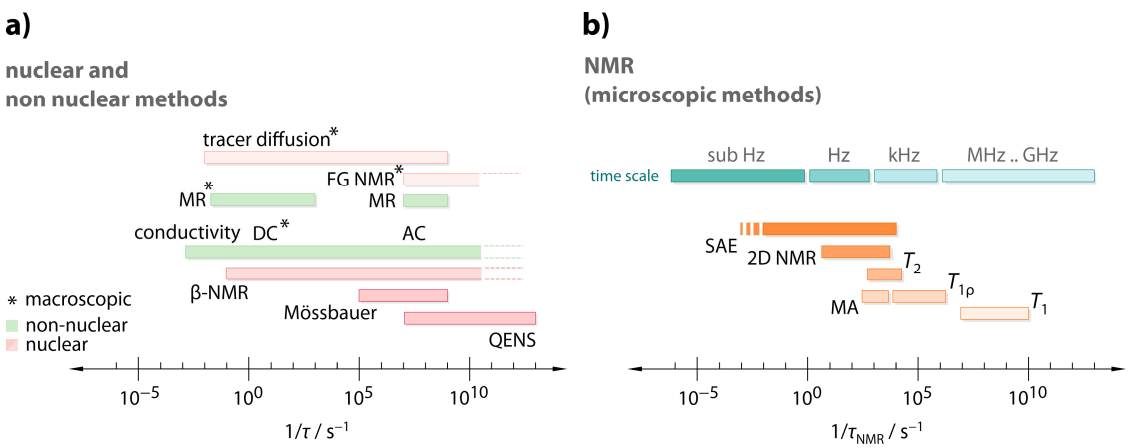


**Figure 1. (a)** Overview of nuclear and non-nuclear methods used to probe diffusion properties, along with the characteristic timescales to which they are sensitive (FG NMR: field-gradient NMR; QENS: quasi-elastic neutron scattering; MR: mechanical relaxation; DC, AC: direct-current and alternating-current measurements). **(b)** Selected NMR techniques (time-domain and high-resolution 2D NMR) and their respective timescales [8], spanning a dynamic window from the sub-Hz to the GHz regime (SAE: spin-alignment echo NMR; MA: motional averaging of NMR lines; $T_{1(\rho),2}$ relaxation NMR methods.)

These results can be directly compared with dynamic parameters obtained from complementary nuclear and non-nuclear techniques, enabling a comprehensive understanding of ion transport processes. Furthermore, NMR-derived jump rates and site occupancies can serve as benchmarks for computational models and molecular dynamics simulations, providing a quantitative link between experiments and theory [10, 11].

In recent years, time-domain and high-resolution $^{7}$Li and $^{23}$Na NMR measurements have been employed to investigate sequentially activated diffusion processes in some of the most prominent solid electrolytes, including, *e.g.*, LGPS-type compounds [11], argyrodite materials [5, 8, 12, 13], and LTPS [14]. The results from the latter are exemplarily shown in Figure 2. Future studies will aim to deepen our understanding of how local defect structures influence both short-range and long-range ionic dynamics, within the bulk and particularly at interfacial regions, *i.e.*, at the contact zones between the solid electrolyte and the electrochemically active materials.

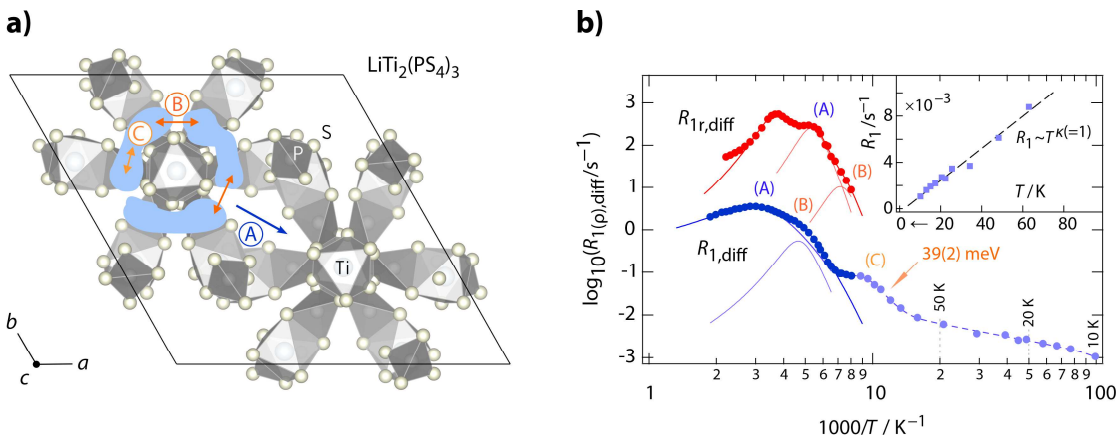


**Figure 2.** **(a)** Crystal structure of $LiTi_2(PS_4)_3$, a fast ionic conductor, showing several $Li^+$ diffusion pathways: strictly localized motions within pocket-like regions (C), interpocket jumps (B), and inter-ring hopping (A). The latter is the rate-determining step that governs long-range ion transport. **(b)** Using $^{7}$Li NMR relaxation rate $R_1 = 1/T_1(1/T)$ measurements, these processes can be studied separately, provided a sufficiently wide temperature range is accessible [14]. For example, fast intra-pocket motions are characterized by an activation energy of only 0.04 eV and give rise to peak C, observed at temperatures as low as $T \approx 100$ K. At even lower temperatures, the relaxation rate enters a regime $R_1 \sim T^{\kappa=1}$, where it is dominated by coupling to conduction electrons.

## 2 Probing Ion Dynamics Beyond the Average

The properties of solid electrolytes are highly sensitive to structural, compositional, and processing factors, which can strongly influence both short- and long-range ion transport [15]. Even slight variations in preparation conditions, such as small changes in composition, annealing, or calcination protocols, can strongly affect the transport parameters of a solid electrolyte. Even if long-range transport remains essentially unchanged, the elementary jump processes that govern ion dynamics on shorter length scales may be significantly altered. NMR, depending on the temperature and frequency window chosen for relaxation-rate measurements, can probe both regimes: short-range motions and long-range transport. This makes it a powerful tool to unravel the impact of defect structures that emerge from different preparation conditions [16]. The next step would be to benchmark such findings against commercially available electrolytes to assess their quality in terms of ionic transport properties [17].

In general, the strength of NMR lies in its ability to provide not only average transport parameters but also site-specific information on dynamic processes [18]. Future studies may therefore apply high-resolution techniques, such as 2D exchange spectroscopy, to identify energetically favored diffusion steps and exchange mechanisms. For very fast ion conductors, such methods must be carried out at sufficiently low temperatures, as 2D NMR is most sensitive to slow exchange processes. At higher temperatures, coalescence effects may obscure the off-diagonal cross-peaks that encode this site-specific information. A limitation arises from the narrow chemical

shift range of $^{6}$Li, the preferred isotope for these experiments since second-order quadrupolar effects are largely suppressed. In diamagnetic materials, this range may be insufficient to resolve the relevant processes. By contrast, in materials containing moderate concentrations of paramagnetic centers [19], hyperfine (Fermi contact) interactions provide enhanced spectral separation, provided that longitudinal relaxation times remain long enough. Such studies require low magnetic fields and fast magic-angle spinning, a combination that has been available for many years. For diamagnetic electrolytes, extending both the frequency and temperature ranges [11] will be crucial to capture the various diffusion steps of charge carriers across different material classes, including oxides, sulfides, thiophosphates, halides, and hydrides [20].

As already noted, understanding degradation processes at macroscopic interfaces in all-solid-state batteries poses a further challenge for NMR spectroscopy. *Operando* and *in situ* studies are often limited by low spin densities in interfacial regions, leading to weak NMR signals. Polarization transfer methods are expected to help overcome this limitation [21]. An early approach is β-NMR, where the polarization of the $^{8}$Li isotope, generated for example after neutron capture, is independent of the Boltzmann factor [22]; other approaches benefit from ion-implanted methods [23, 24]. Similar sensitivity issues arise when studying microscopic interfacial dynamics in hybrid electrolytes [25, 26] that combine polymer and ceramic phases. In these cases, signal-enhanced NMR could provide key insights not only into ion dynamics but also into the local environments of Li ions at interfaces. Nanocrystalline materials, with their high fraction of interfacial regions (thicknesses on the order of ~2 nm), already provide sufficiently high spin densities to be probed by NMR [27-30]. Alternatively, ion dynamics in interfacial regions may be studied by suitable ex situ measurements, provided that larger samples can be prepared to mimic *operando* conditions [31].

Finally, care must be taken when interpreting *in situ* or *operando* NMR experiments carried out under strong external magnetic fields [32], as these fields can influence the formation of metallic Li phases compared with cells cycled in zero-field conditions. In such cases, *ex situ* high-resolution measurements, taking into account and overcoming NMR skin effects, remain an indispensable complement.

## 3. Future Directions

NMR, widely used in medicine, life sciences, and materials research, is also an indispensable tool in battery science due to the excellent NMR receptivity of key charge carriers such as $Li^{+}$ and $Na^{+}$. Their nuclear spin interactions with local magnetic and electric fields enable detailed characterization of atomic-scale structures and dynamic processes. In the study of ion dynamics, future research should move beyond measuring average transport behavior toward probing individual ion hopping events [14]. In particular, the investigation of rotational–translational couplings remains an important research area for fundamentally understanding interrelation effects in electrolytes with polyanion host frameworks [33, 34].

In battery devices, operando and *in situ* NMR [21, 35, 36], even under MAS conditions [37], will be crucial for visualizing local structural changes, particularly those associated with degradation mechanisms, and for tracking the corresponding dynamics at interfaces. Importantly, NMR can directly detect the formation of metallic Li, enabling monitoring of dendrite growth under operating [38-40] conditions. However, because interfacial regions often contain only a small number of NMR-active nuclei, achieving sufficient signal intensity remains a significant challenge. Advanced methods for enhancing spectral resolution and NMR sensitivity [21, 36] will therefore be essential for future studies aiming to understand the diverse interfacial phenomena in all-solid-state batteries. Emerging NMR approaches [1], such as ultra-fast MAS, multi-nuclear correlation experiments, and especially dynamic nuclear polarization (DNP [36, 40]), are not only expected to enable the study of dilute nuclei at interfaces but also in low-abundance phases.

Combined with time-domain relaxation rate measurements across broad frequency and temperature ranges [14], these techniques will allow detailed mapping of ion dynamics over multiple timescales. Together, these advances promise to extend the reach of NMR, providing deeper insight into both bulk and interfacial transport processes in solid electrolytes.

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## Conflict of Interest

The author declares no conflict of interest.

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