

1. Title of Case Study: Solid-State NMR of Fast Ion Conductors

2. Grant Reference Number: EP/N004884/1, EP/M009521/1, EP/K031511/1, EP/H000925/1, EP/L015277/1, EP/S023259/1, Faraday Challenge Project SOLBAT, EU ERC LIBNMR

3. One sentence summary: Understanding of ionic transport in advanced functional materials is enabled by multinuclear ^1H , ^6Li , ^7Li , ^{17}O , ^{23}Na , ^{27}Al , ^{33}S and multidimensional NMR spectra obtained at the UK High-Field Solid-State NMR National Research Facility.

4. One paragraph summary: Solid-state NMR spectroscopy is a powerful tool for the atomic scale structural understanding of functional materials, yet can also be very effectively employed for the direct assessment, in a non-destructive manner, of site-selective ion dynamics and diffusion processes over a very wide range of timescales and temperatures. This case study illustrates the use of experimental solid-state NMR approaches to probe the mobility of Li^+ and O^{2-} ions specifically via ^6Li , ^7Li and ^{17}O that complement other approaches (for example, impedance). Many of the targeted nuclei (^6Li , ^7Li , ^{17}O , ^{23}Na , ^{27}Al , ^{33}S , ^{71}Ga , ^{93}Nb) are quadrupolar, some with poor receptivity, and their spectra benefit greatly from the enhanced resolution and sensitivity achieved at UK High-Field Solid-State NMR National Research Facility. Additionally, structural disorder induced by, for example, vacancies and interstitials play an important role in enabling this mobility and solid-state NMR spectra provide important information about the local structure. The identification of factors limiting ionic mobility coupled to the effects of structural modification provide a framework for the further development of advanced functional materials with enhanced ion transport for the next generation of energy storage and conversion technologies.

5. Key outputs in bullet points:

- *Understanding of ionic transport and disorder in advanced functional materials*
- *Key insights into developing new materials with enhanced properties*
- *Training of several early career researchers from multiple UK institutions in state-of-the-art NMR instrumentation*
- *New collaboration in NMR crystallography for the study of electrochemical devices*
- *Increasing visibility of the UK High-Field Solid-State NMR National Research Facility in flagship research (Faraday Institution, EU ERC) and training (CDT) programmes*

6. Main body text: In a series of three highly collaborative research papers, published in *Chem. Mater.*, that target the discovery of new Li^+ ion solid electrolytes of various compositions (Li_3AlS_3 and $\text{Li}_{4.3}\text{AlS}_{3.3}\text{Cl}_{0.7}$) for the future of all solid-state batteries, ^{27}Al Magic Angle Spinning (MAS) NMR spectra at a magnetic field strength of 20 Tesla, enabled the structural understanding of key Al_2S_6 dimer units consisting of Al tetrahedra. Upon sulphide S^{2-} / chloride Cl^- anion mixing forming $\text{Li}_{4.3}\text{AlS}_{3.3}\text{Cl}_{0.7}$, a large degree of cationic site disorder on the Al tetrahedra is created, as revealed by high resolution multi-quantum MAS (MQMAS) NMR spectra, that is associated with disordered Li^+ vacancies. This results in faster Li^+ mobility and the creation of three-dimensional diffusion pathways which are directly captured by ^6Li and ^7Li NMR. Sulphides are thus important ions and the ^{33}S nucleus offers an exciting avenue to understand its structure in energy materials. However, ^{33}S suffers from very poor receptivity arising from low gyromagnetic ratio, very low natural abundance and large quadrupolar moment, but its detection was successfully overcome in the Li^+ ion battery conversion electrode NbS_3 by combining high field at 20 Tesla too with large sample volume (almost 1 g) and advanced data acquisition strategies which was reported in *Chem. Comm.* The ^{33}S NMR data revealed spectral signatures for both S^{2-} and disulphide units S_2^{2-} , opening up avenues to

provide local insights into the anionic redox behaviours during electrochemical cycling. The formation of a solid-electrolyte interface, which challenges the reversible operation of Li⁺ ion batteries, often occurs during these redox processes. An NMR crystallography approach, published in *Nature Chemistry*, that deployed multinuclear ¹H and ⁷Li MAS NMR at 20 Tesla jointly with first principles calculations contributed to the understanding of the decomposition products. The work notably revealed that the identity of the major organic solid-electrolyte interface on graphite anodes to be lithium ethylene mono-carbonate, rather than lithium ethylene di-carbonate as previously thought, paving the way for further understanding of electrochemical processes. A further NMR crystallography publication in *Magn. Reson. Chem.* this time employing ²³Na (MQ)MAS NMR at the highest field of 23.5 T of the Facility, established the local-range structure of a different type of anode material, namely conjugated alkali metal di-carboxylates which have received significant attention.

While these outcomes largely focused on Li⁺ batteries, the last few years also saw interests in solid oxide fuel cell materials, in particular, those exhibiting fast O₂⁻ transport from the presence of oxygen interstitials for which discoveries were published in two papers in *Chem. Mater* that focus on materials with different compositions (LaNb_{1-x}W_xO_{4+2/x} with x < 0.17 and La₃Ga_{5-y}Ge_{1+y}O_{14+y/2}, y < 1.51). The key here is the possibility for Ga³⁺ and Nb⁵⁺ cations to change their coordination numbers to accommodate extra oxygens which could be captured from ⁷¹Ga and ⁹³Nb NMR spectral features such as the shift and quadrupolar parameters, thanks to known relationships between those and coordination numbers. The high external magnetic field of 20 T enabled highly resolved ⁷¹Ga and ⁹³Nb (MQ)MAS NMR spectra to be collected and which were assigned to niobium and gallium tetrahedra extending their coordination to five in LaNb_{1-x}W_{0.16}O_{4.08} and La₃Ga_{3.5}Ge_{2.5}O_{14.75}, respectively – that is hosting extra oxygens. These oxygen interstitials were then also detected directly in ¹⁷O MAS NMR spectra on ¹⁷O-enriched materials and allow for probing oxide ion diffusion pathways.

References: [B. B. Duff et al. *Chem. Mater.*, 2023, 35, 27.](#) [J. Gamon et al. *Chem. Mater.*, 2021, 33, 8733 & 2019, 31, 9699.](#) [D. M. Halat et al. *Chem. Commun.*, 2019, 55, 12687.](#) [L. Wang et al. *Nature Chemistry*, 2019, 11, 789.](#) [T. Whewell et al., *Magn Reson. Chem.*, 2022, 60, 489.](#) [M. Diaz-Lopez et al. *Chem. Mater.*, 2019, 31, 7183.](#) [C. Li et al. *Chem. Mater.*, 2020, 32, 2292.](#)

7. Names of key academics and any collaborators:

Professor Frédéric Blanc, University of Liverpool
Professor Steven P. Brown, University of Warwick
Professor Dame Clare P. Grey FRS, University of Cambridge
Dr John M. Griffin, Lancaster University

8. Sources of significant sponsorship (if applicable):

EPSRC (and BBSRC) funding for the UK High-Field Solid-State Nuclear Magnetic Resonance Facility

9. Who should we contact for more information?

Professor Frédéric Blanc, University of Liverpool, frederic.blanc@liverpool.ac.uk