1. Title of Case Study: Applications of Solid-state NMR Spectroscopy for the Study of Battery Materials

2. Grant Reference Number: NS/A000061/1 and EP/M009521/1

3. One sentence summary: Solid-state NMR spectroscopy has been applied to uncover structural and mechanistic information about new battery materials.

4. One paragraph summary:

The development of new battery materials requires a detailed understanding of the atomic-level structure, as well as the changes that take place as the device is charged and discharged. Often the structural changes may be highly localised or involve the formation of disordered or multicomponent breakdown products. Solid-state NMR spectroscopy is a powerful tool for studying these systems as it is sensitive to the local structure and can therefore be applied to complex or disordered battery components. However, while battery materials often contain nuclei amenable to NMR, many have strong quadrupolar interactions and low receptivities which makes them very challenging to observe and study. By exploiting the high magnetic field of the UK 850 MHz Solid-State NMR Facility, the second-order quadrupolar interaction is significantly reduced, thereby providing the best opportunity to observe challenging nuclei and extract structural and mechanistic information.

5. Key outputs in bullet points:

- *Structural characterisation of important materials for new battery technologies*
- *Demonstration of solid-state NMR spectroscopy for low receptivity nuclei*
- *Publications in leading international journals*
- *Dissemination at an international conferences (ENC conference, Rocky Mountains Conference on Solid-State NMR)*
- *International collaboration with Prof. Gillian Goward, McMaster University*

6. Main body text

Transition metal sulfides such as NbS_3 have potential applications as electrode materials for lithium-ion batteries. The electrochemical mechanisms of these materials have been attributed to changes of redox state in the sulfur polyanions from S_2^{2-} to S^{2-} during discharge. In order to fully understand the structural and chemical changes that take place, it is desirable to study the anion itself; however, the ^{33}S nucleus is very challenging to study by solid-state NMR spectroscopy on account of its very low receptivity and substantial quadrupole moment.

To determine the feasibility of ^{33}S solid-state NMR for the study of battery materials, measurements were carried out at 20.0 T using dynamic field sweep pulse excitation combined with Carr-Purcell Meilboom-Gill signal acquisition. The high-field available at the Facility was critical to minimise the quadrupolar broadening of the central transition lineshape. In addition, density functional theory (DFT) calculation allowed experiments to be designed to favour observation of the key lineshape features that are important for extracting NMR parameters. By combining the high-field measurements with DFT in this way, it was possible to record high-quality ^{33}S NMR spectra in as little as 6 hours. From this data, it was possible to extract quadrupole coupling and asymmetry

parameters with sufficient accuracy to compare with the DFT calculations. Good agreement was observed, showing that the Peierls distortion predicted by DFT is present at ambient temperature.[1]

Another system of intense interest in the battery research community is the lithium-air battery which functions through the reaction of lithium with oxygen gas. This has the highest gravimetric energy density of any battery chemistry, but the precise reaction mechanism remains a matter of debate. ^{17}O solid-state NMR is the ideal choice to study battery discharge products, but the low natural abundance and large quadrupolar broadening of ^{17}O precludes its observation in most situations.

By cycling a Li-air battery in ^{17}O-enriched gas, it was possible to isotopically enrich the battery discharge products. These were then studied at the 850 MHz solid-state NMR Facility, again taking advantage of the high magnetic field to minimise the ^{17}O quadrupolar broadening. Using a Facility fast MAS probe, it was possible to record and measure ^{17}O central transition lineshapes and compare these with DFT calculations and experimental data for model compounds. The results showed that the main discharge product is lithium peroxide, but minor contributions from lithium carbonate and lithium hydroxide are also present.[2,3]

These studies have enabled a better structural descriptions of new battery materials for lithium-ion batteries and provide a starting point for understanding the structural changes that take place upon charging and discharging. Moreoever, the experimental demonstration of NMR measurements for highly quadrupole-broadened and low-receptivity nuclei such as ^{33}S and ^{17}O open the way for wider application of these techniques to study the chemistry taking place in other battery technologies.

- 1. D. Halat, S. Britto, K. J. Griffith, E. Jónsson, C. P. Grey, *Chem. Commun.*, **2019**, 55, 12687-12690.
- 2. M. Leskes, N. E. Drewett, L. J. Hardwick, P. G. Bruce, G. R. Goward, C. P. Grey, *Angew. Chem. - Int. Ed.*, 2012, **51**, 8560-8563.
- 3. M. Leskes, A. J. Moore, G. R. Goward, C. P. Grey, *J. Phys. Chem. C*, **2013**, 117, 26929.

7. Names of key academics and any collaborators:

Prof. Clare Grey (University of Cambridge)
Prof. Gillian Goward (McMaster University)

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9. Who should we contact for more information?

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