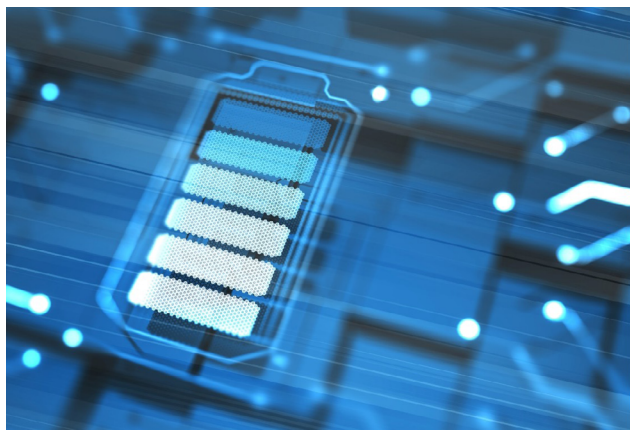


Whitepaper

Optimising battery electrolytes with benchtop NMR



Introduction

The development of higher performance, more sustainable energy storage devices has been widely recognised as a key challenge for the scientific community and industrial manufacturers. The market for Lithium-ion batteries which currently provide the highest energy density levels is projected to grow to \$116 billion by 2030. Improvements in energy and power densities, charge and discharge times, cost, lifetime and safety are all critical to the success of next generation batteries.

Figure 1 shows a schematic of the components within a typical lithium ion-battery. The current carrying electrolyte has a critical role in defining all these performance, safety and cost parameters of commercial battery systems. The mixture of different solvents, additives, and lithium salts contained within complex electrolyte systems needs to be finely tuned to deliver optimal performance and sustainability. Hence, accurate, quantitative, and reliable electrolyte characterisation and analysis methods are needed - right through from incoming raw materials checking to development of new formulations and quality control within high volume manufacturing.

In this white paper, we highlight why broadband benchtop Nuclear Magnetic Resonance (NMR) Spectroscopy is now a key technique to exploit across the complete product lifecycle.

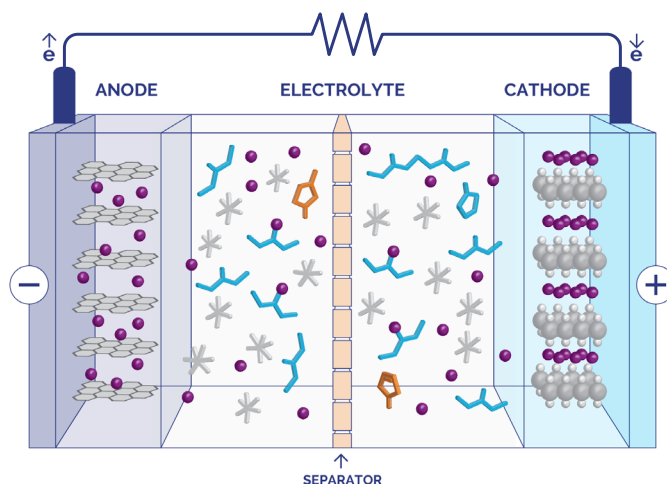


Figure 1: Schematic of a lithium-ion battery

Benchtop NMR Spectroscopy

In NMR (Nuclear Magnetic Resonance) spectroscopy particular isotopes of elements in the sample, mostly in the liquid state, are probed by a radio frequency pulse while exposed to an external magnetic field. This provides information about the chemical structure, concentration and local chemical environment of the probed nuclei. To obtain a detailed structural understanding of your analyte (electrolyte in the case of batteries), the probing of many different nuclei across a broad frequency range is needed. Uniquely, broadband benchtop NMR spectroscopy now enables the qualitative and quantitative analysis of all constituents in a complex electrolyte mixture. Previously, instruments were restricted to just a few nuclei and had blind spots for many compounds.

Portable benchtop NMR instruments operating at room temperatures using permanent magnets now remove the accessibility barriers (cost, maintenance, space requirements and skilled operators) of large cryogenic NMR systems. This ease of use makes them ideal for rapid development, reaction monitoring and quality control, where quick and accurate results are important for instant feedback and optimisation. Oxford Instruments X-Pulse benchtop NMR is the only true broadband spectrometer that gives the freedom to investigate any electrolyte design and composition of choice. While the H/F channel can collect spectra from ^1H and ^{19}F , its broadband channel excites and detects a wide range of nuclei including ^{13}C , ^7Li , ^{31}P , ^{11}B , ^{29}Si , ^{27}Al and ^{23}Na . all those with a Larmor frequency between 25 and 11 MHz in a 1.4 Tesla magnetic field. The capability to perform two-dimensional spectral methods with pulsed field gradients and shaped pulses enables a multitude of advanced experiments to quantify specific chemical and physical properties that define electrolyte performance.

Battery performance, where does NMR fit?

Battery technology is often considered a balancing act between 5 key parameters: charge density, the amount of energy stored in the cell; power density, how quickly that energy can be extracted from the cell; lifetime, sometimes known as charge cycle life time and a measure of how quickly the charge density is reduced; safety, how safe the battery is through its lifetime and cost, how much energy per unit currency. Trying to maximise all of these parameters for a single battery chemistry is at the forefront of today's materials research. An example of how some typical battery chemistries (defined by the cathode material) balance these

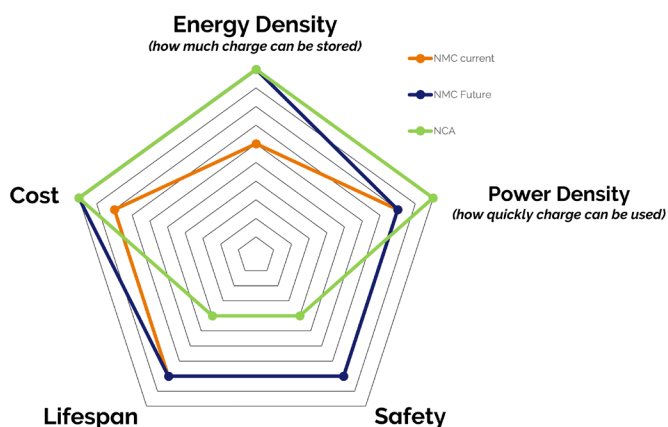


Figure 2: Chart showing the balance of critical parameters for 3 common battery chemistries

parameters is shown in figure 2. Benchtop NMR can assist the development of new electrolyte chemistries by giving rapid understanding of the physical and chemical properties that underpin those critical performance parameters, these will be discussed in detail through this white paper. NMR is inherently quantitative allowing measurement of ion concentration (Li^+ , Na^+ , etc) which underpins energy density, solvent composition or degree of degradation which ensures safety, and these can be performed in seconds minimising cost. Using a quick set of measurements, the diffusion properties of electrolyte components, and therefore the ionic conductivity, can be calculated allowing understanding of potential power density as the chemistry is being developed.

Rapid assessment of electrolyte composition

In case of a non-aqueous electrolyte an organic solvent or a mixture of solvents, the majority compound will be visible in simple ^1H NMR spectra. ^1H nuclei of different species and positions within the molecules result in distinct signals with characteristic chemical shifts. Some signals might be split into doublets, triplets or other multiplets, which gives valuable information about the nature of other NMR active nuclei in the vicinity, such as the isotope (element), distance and quantity.

An easy example for a spectrum like that is given in figure 3, where a simple ^1H spectrum was taken of a mixture of typical solvents contained in lithium-ion batteries: ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC).

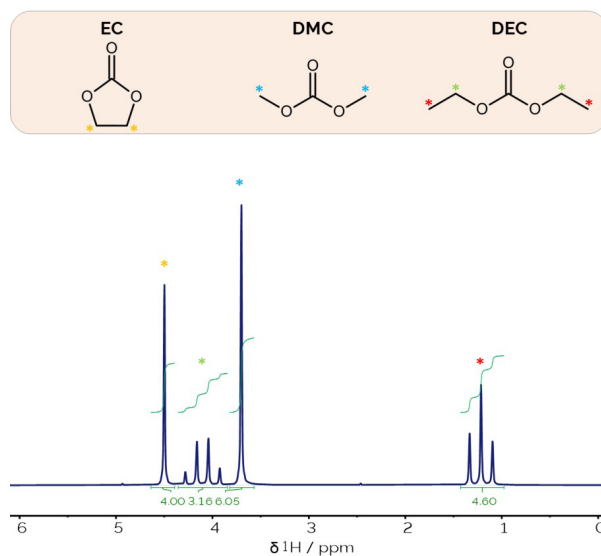


Figure 3: ^1H spectrum of a simple solvent mixture typical for electrolytes

The resulting peaks are distinct from each other, with EC and DMC showing one distinct singlet each typical their chemical composition and structure. As we have two ^1H positions in DEC, we can see two signals in the spectrum, with the signal for the CH_3 group being split into a triplet, while the CH_2 signal is split into a quadruplet. This is explained through the n+1 rule for spin ^1H and similar nuclei, where a peak will split into n+1 signals if n equivalent NMR active nuclei are close enough to cause coupling. This is the case here, as the three protons in CH_3 cause the splitting of the CH_2 signal into n+1 = 4, while the CH_2 group causes the CH_3 position to be split in three. This splitting can be interpreted to gather information about the structure of unknown compounds.

It is further possible to quantify the components against each other or a standard, as the area beneath the peaks is proportional to the amount of nuclei present. Using this integration result, a ratio of 1:1:1 by mass could be determined.

The same principles can be applied to more complex mixtures and to nuclei beyond ^1H

multinuclear NMR spectra taken from a commercial battery electrolyte are shown in figure 4. Again, all signals are distinct and well defined in all spectra. Species with the nuclei ^{13}C , ^{19}F , ^{31}P , ^{11}B and ^7Li could be detected. The n+1 rule holds true again for ^{19}F and ^{31}P even in the case of coupling between different nuclei. The splitting of the ^{31}P signal into seven suggests six coupling nuclei, while the ^{19}F signal at -69 ppm is split into two, which indicates one coupling species. As the distance between the peaks in the doublet and septet are the same (710.1Hz), these nuclei can be assigned to couple to each other. This is characteristic for $[\text{PF}_6]^-$ a common anion used in electrolytes. This is an example of how the structure of even unknown species can be reconstructed through NMR spectroscopy.

This depth to the NMR technique and the ability to locate it in the lab next to where you are developing new electrolyte formulations allows can significantly reduce develop time and cost allowing users to confirm their new formulations .

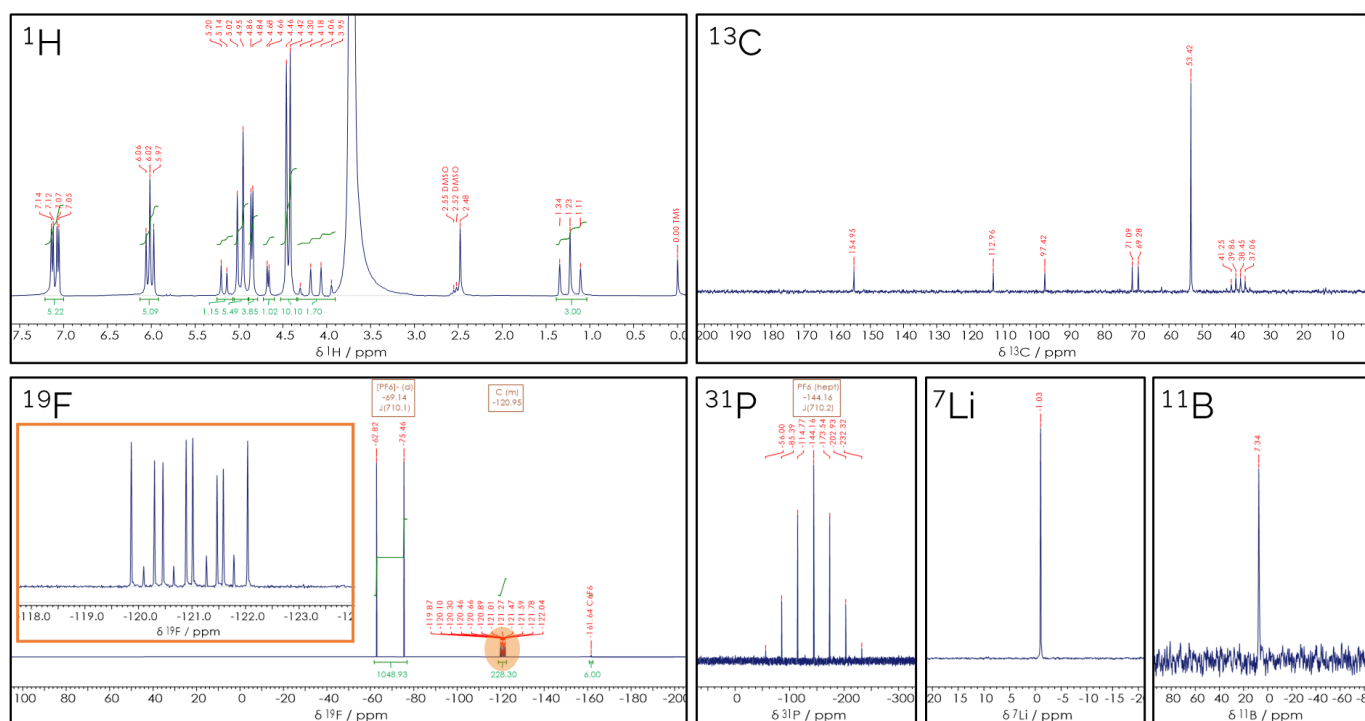


Figure 4: Multinuclear NMR spectra of the same electrolyte taken on a single X-Pulse spectrometer with broadband channel.

Quality control and reaction monitoring to maximise safety and lifespan

Due to its high sensitivity and accessibility, the X-Pulse is uniquely suited for quick reaction monitoring and quality control. Its broadband channel enables the detection of compounds invisible in routine ^1H and ^{13}C spectra. In a case study, two electrolyte solutions of supposedly the same constituents differed significantly in performance when used to build a test cell. There were, however, no visible differences, so the question arose as to whether it is possible to test electrolyte to ensure performance before spending time building a cell. The ^1H spectrum of the samples is identical, giving no clues to what might be wrong with one of the mixtures but suggesting that the organic solvent mixture is not the root cause (figure 5).

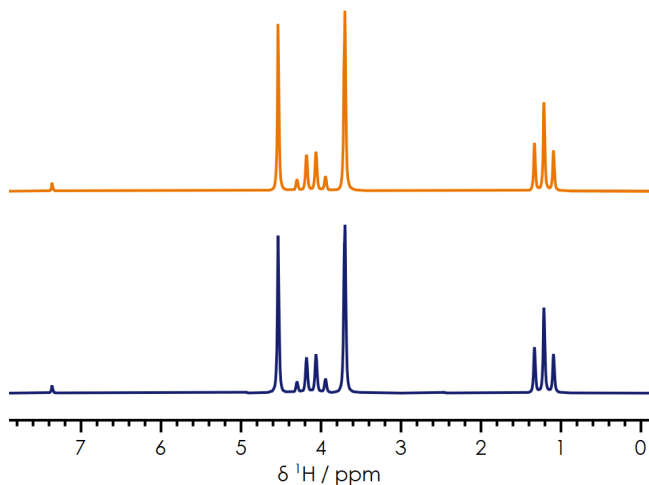


Figure 5: ^1H benchtop NMR spectra of two electrolytes presenting different performance characteristics.

However, in a ^{19}F NMR spectrum we can observe an additional doublet in one of the spectra corresponding to a decomposition product of the $[\text{PF}_6]^-$ (figure 6). From the chemical shift we can attribute this to Difluorophosphoric acid, $\text{OPF}_2(\text{OH})$, a common breakdown product of $[\text{PF}_6]^-$ in the presence of water. Another species seen in the spectrum is LiF which is a biproduct of the hydrolysis reaction of $[\text{PF}_6]^-$ to $\text{OPF}(\text{OH})_2$ and confirms the electrolyte failure has been caused by a hydrolysis reaction in the presence of unwanted water.

The X-Pulse is also well equipped to quantify impurities below a quantity of 1% in your electrolyte. It is possible to easily perform acquisition of spectra with carbon decoupling. This removes the carbon satellites which might overlap or be confused with low concentration impurities or additives, as is shown in figure 7.

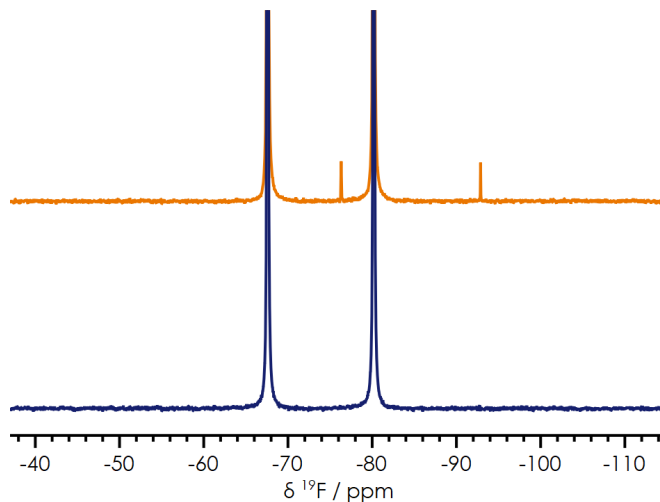


Figure 6: ^{19}F benchtop NMR spectra of two electrolytes presenting different performance characteristics

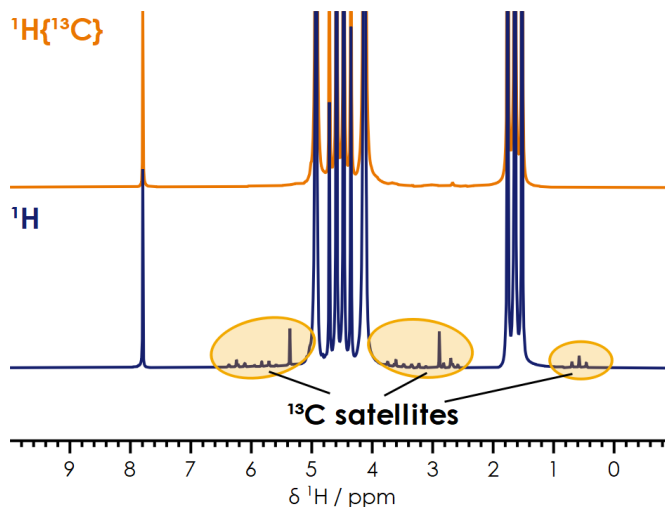


Figure 7: ^1H benchtop NMR spectra of the same sample with (top) and without (bottom) ^{13}C decoupling.

Beyond just identifying and quantifying degradation and impurities the form factor of benchtop NMR means that you can continue to take measurements as your formulations age, are exposed to the typical lab environment or are cycled in test cells. This enables understanding of the processes and kinetics that drive electrolyte degradation, whether through hydrolysis as previously discussed, interaction with electrodes, exposure to high voltages or changes in temperature. Understanding these processes allows the formulation of new electrolyte and additive combinations to minimise parasitic reactions and significantly increase cell life time. Figure 8 demonstrates this, by integrating the peak areas of ^{19}F spectra collect periodically after exposing a combination of LiPF_6 and DMC to a small amount of H_2O the hydrolyses reaction can be followed and the kinetics understood.

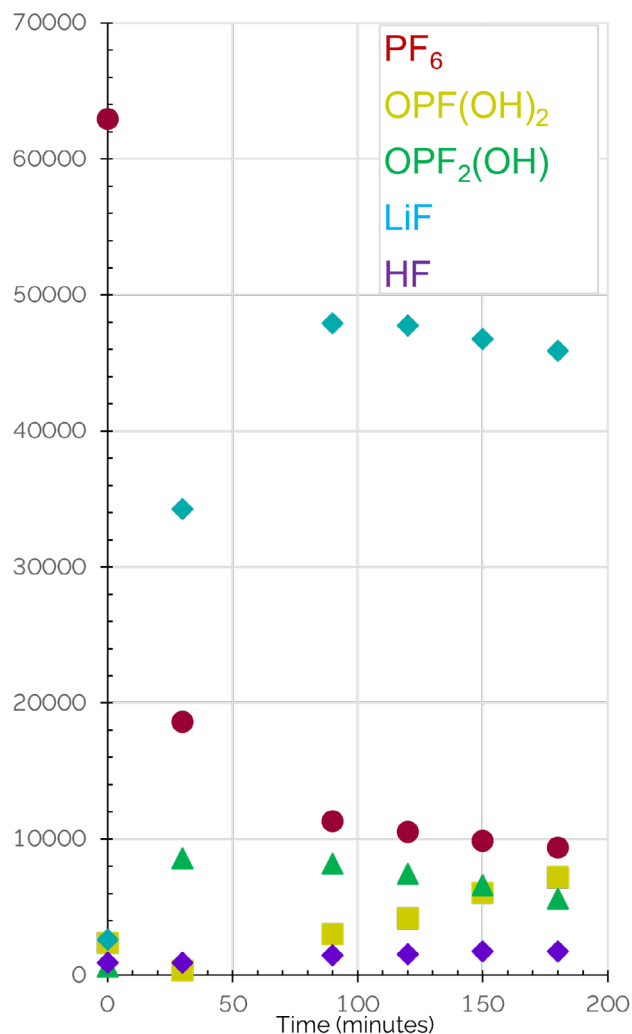


Figure 8: ^{19}F peak integrals for different compounds collected every 30 minutes after exposing $\text{Li}[\text{PF}_6]$ in DMC to H_2O .

Using Diffusion to understand Power density and performance

Equipped with pulsed field gradients, the X-Pulse can perform experiments that go beyond identification and quantification of materials. The Pulsed field Gradient Spin Echo (PGSE) experiment enables the determination of diffusion coefficients for each species in solution. Due to the broadband capabilities, even the inorganic compounds can be investigated. Figure 9 shows such experiments for $\text{Li}[\text{PF}_6]$ in DMC, in which a series of spectra with increasing field gradient strength are collected, which results in a decline of the signal strength related to the diffusion coefficient of the molecules. This value can also be used to obtain some crucial key properties for electrolytes like ionic conductivity or the cation transference number. By this experimental feedback loop, the physical properties of electrolytes can be optimized by specifically targeting the most impactful components one by one. Through the variable temperature options on the X-Pulse, all those parameters can be determined over most of the operation temperature range of the cell.

This allows experiments to confirm predictions based on models before building test cells and can significantly shorten formulation optimisation.

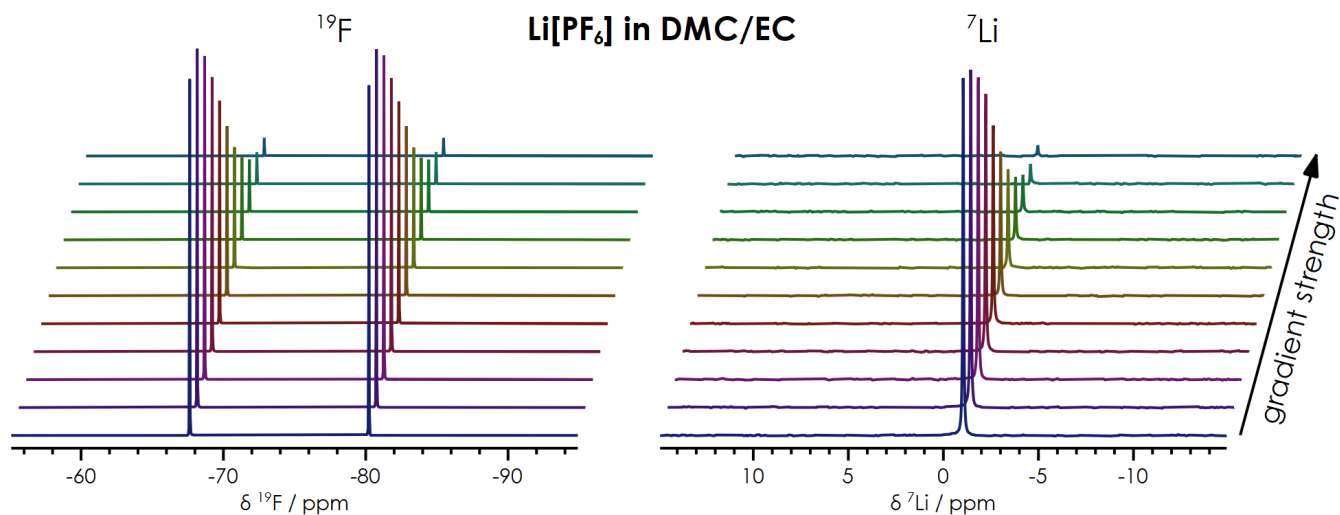


Figure 9: PGSE series for the determination of the diffusion coefficient of $\text{Li}[\text{PF}_6]$ in DMC.

Summary

Through its unique broadband NMR capabilities, the X-Pulse can provide accurate analysis for all compounds commonly used in electrolytes in any workspace. This analysis can also be performed across the range of typical battery operating temperatures. Hence, the performance of your electrolyte can be optimised at realistic conditions. The measurements that can be performed by X-Pulse support all five of those critical performance parameters discussed earlier:

- Energy Density
 - Ion concentration (Li⁺, Na⁺)
- Power Density
 - Ionic Conductivity and Cation transference over a range of temperatures
- Safety
 - Raw material quality
 - Electrolyte quality and consistency
 - Additive development
- Lifespan
 - Understanding of electrolyte degradation
 - Additive development
- Cost
 - Rapid low-cost analysis of new formulations
 - Reduced cost of poor quality

This makes benchtop NMR a perfect fit to support this industry which will be crucial to ensuring the future sustainability of our planet.



If you have any questions about this whitepaper, please contact our experts:
magres@oxinst.com

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