MAGNETIC RESONANCE FOR BATTERIES RESEARCH AND MANUFACTURING

High-Resolution Multi-Nuclear NMR Spectroscopy for Better Lithium-ion Battery Electrolytes

Andrea Steck Ph.D, Principal Scientist, Bruker BioSpin, Ettlingen, Germany

Innovation with Integrity

Introduction

Batteries are indispensable electric power supplies for a multitude of mobile and stationary systems, from small portable devices to electrified vehicles and large-scale energy storage for grid and off-grid applications.

While primary batteries, which have to be discarded after one single use, are becoming increasingly less important, the global demand for secondary ("rechargeable") batteries is persistently growing. Large-scale applications like stationary storage and Battery Electric Vehicles (BEV) are only feasible with re-usable power storage system. This development is also driven by changed consumer preferences towards more sustainability, and by material science innovations improving the batteries' performance [Ref. 1].

Among the other advanced rechargeable batteries, lithium-ion batteries (LiBs) currently are predominantly used due to their many advantages, especially their very high energy densities. It is projected that this will still be the core technology into the next decade.

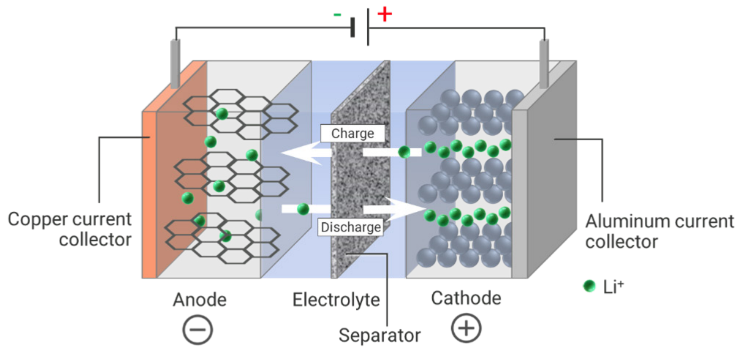

Figure 1 Schematic view of the lithium-ion battery

The LiBs' essential components are the electrodes (anode and cathode), a separator membrane, and the liquid electrolyte as the conductive medium. During charging, lithium ions are extracted from the Li-containing cathode material, move through the electrolyte, penetrate the separator, and intercalate into the anode material, where they recombine with their electrons. This process is reversed during discharging (Figure 1).

However, there are still requirements for improvements in cost-reduction, supply chain safety, battery lifetime, performance, sustainability and operational safety. Extensive battery research is being accomplished to meet these and many more future demands.

Increasing production efficiency will be linked with decreasing raw material demand and basic production cost. Material innovation is leading to improved electrochemical make-up of LiB's which can feature reduced raw material demand or increased energy storage capacity per battery unit.

Therefore, thorough understanding of the batteries' electrochemistry is a prerequisite for developing novel battery materials, and progress further to overcome the shortcomings.

Electrolytes

$LiPF_6$ is the most widely used conducting salt in LiBs. The conducting salt is dissolved in (mixtures of) carbonates, such as ethylene carbonate (EC), dimethyl carbonate (DC), or diethyl carbonate (DEC). Further additives like stabilizers or performance enhancers are usually added. But $LiPF_6$ is by far the most significant cost contributor for the complete electrolyte formulation making the most precious ingredient.

The LiB's electrolytes play a key role in lithium-ion transporting, but are delicate mixtures – they are subject to aging during the charging/discharging cycles and storage, and are sensitive against thermal effects and protic contaminations, like water. The resulting reaction products have negative impact on the battery's performance, lifetime, operational safety, and can become hazardous to health, especially when hydrofluoric acid (HF) comes into play [Ref 2].

Consequently, there is a need for analytical solutions, enabling battery producers and researchers to identify and quantify main components and impurities accurately and precisely, and reaction by-products in aged electrolytes. Such tests must be non-invasive, fast, easy to run, non-targeted, and reliable with a minimum of calibration.

Figure 2 AVANCE 400 MHz NMR spectrometer

About NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy is a non-destructive technique, using the inherent magnetic properties of specific atomic nuclei to characterize the molecular structure of a sample in solid-state or solution.

NMR spectroscopy has several strengths: it is intrinsically quantitative as the area of a certain signal directly corresponds to the number of nuclei contributing to this signal, highly reproducible even from instrument to instrument, and capable to detect and quantify components within mixtures while covering a wide concentration range. LiB electrolyte samples can be measured without any sample preparation in their operational state.

The Multi-Nuclear Avance 400 NMR Solution for Electrolytes

Due to the chemical nature of the electrolytes' components, multi-nuclear NMR spectroscopy is a powerful technique to obtain a comprehensive picture of the range of components in pristine, aged, or recycled electrolytes. For identification and quantification of already known components, for example ^{1}H, ^{7}Li, ^{13}C, ^{19}F, or ^{31}P NMR spectra are easily accessible with the tunable broadband probe. If structure elucidation of unidentified components is required, a broad range of suitable experiments – pre-defined or custom-tailored – provide detailed information on the molecular structures.

The full NMR process can be performed in full automation, including experimental run, compound quantification and analysis report output.

Identification and Quantification of Contaminants and Degradation Products in Electrolytes

Defining contaminant thresholds and additive performance by understanding degradation pathways requires robust and reproducible analytical methods with high throughput capabilities. These technologies must be flexible in terms of target molecules as electrolyte formulations have a broad range of variations.

Testing for solvent composition and water content

Within an instant, the characteristic electrolyte solvent signals appear in the ^{1}H-NMR spectrum, and – if present – also the water signature (Figure 3). The peak areas spanned by the signals are used to determine the components' concentrations.

This determines the baseline for any further studies within R&D environments which involve adjusted formulations or degradation pathways. But these methods can also be used in production affiliated environments for incoming goods, process intermediates, or final product quality control testing.

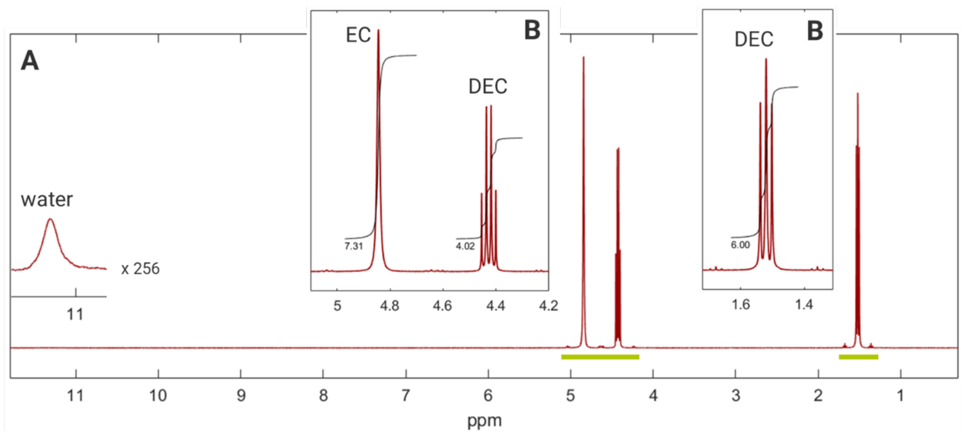

Figure 3 ^{1}H-NMR spectrum at 400MHz of an electrolyte solution: A = full spectrum, B = y-zoomed cutouts of the EC (ethylene carbonate) and DEC (diethyl carbonate) signals.

Catching $LiPF_6$ Decomposition Products with ^{19}F-NMR

Many $LiPF_6$ decomposition products contain fluorine and can be detected – or monitored in a time series – by the highly sensitive ^{19}F-NMR (Figure 4). HF also betrays itself as a characteristic signal.

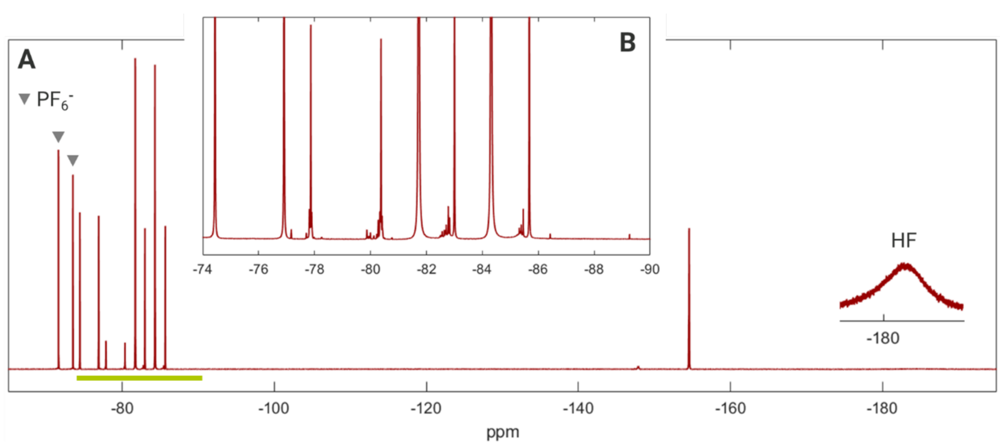

Figure 4 Decomposition products in an aged electrolyte as seen in the ^{19}F-NMR spectrum: A = full spectrum, B = y-zoomed cutout with fingerprint of degradation products.

If a deeper insight into spectral information is required, this technology is fully flexible to set up advanced experiments for answering specific analytical questions. Figure 5 shows an example where a ^{19}F-^{31}P Heteronuclear Single-Quantum Coherence (HSQC) experiment is used to identify degradation products containing a direct chemical bond between phosphorous and fluorine nuclei, and to derive signal assignment from that.

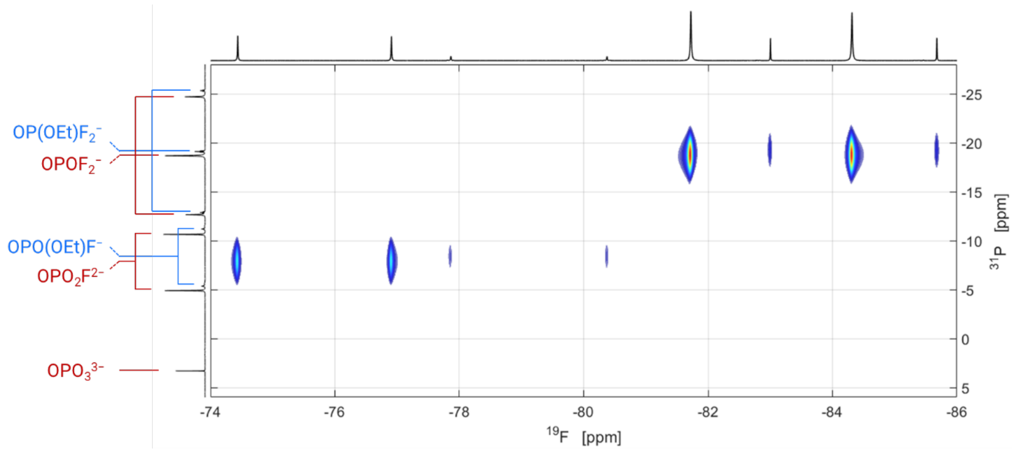

Figure 5 ^{19}F-^{31}P Heteronuclear Single-Quantum Coherence (HSQC) spectrum, showing direct ^{19}F-^{31}P chemical bonds (Et = Ethyl group CH_2CH_3).

Assessing Solvent Degradation Products Using ^{31}P-NMR

As one of many chemical reactions in aged electrolytes, the solvent molecules can be attacked by reactive aging products. In the ^{31}P-NMR spectrum (figure 6) the signals of such products are assigned to the corresponding components by taken advantage of their characteristic signal multiplicity patterns, containing large ^{19}F-^{31}P, and much smaller ^{1}H-^{31}P coupling constants. The latter, verified by recording both a ^{31}P-NMR spectrum with and without ^{1}H decoupling, immediately unveils CH_2-bearing phosphate derivatives.

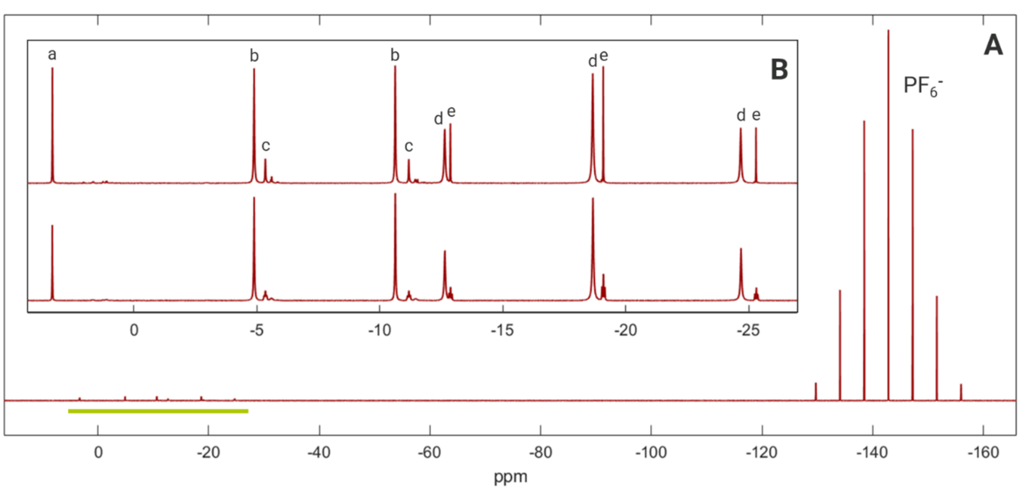

Figure 6 ^{31}P-NMR spectrum of a matured electrolyte (solvent DEC). A = full spectrum, B = y-zoomed cutout without (bottom) and with (top) ^{1}H-decoupling. Signal assignment: a = OPO_3^{3-}, b = OPO_2F^{2-}, c = $OPO(OEt)F^{-}$, d = $OPOF_2^{-}$, e = $OP(OEt)F_2^{-}$.

NMR spectroscopy offers a wide range of electrolyte-related analyses for spectroscopic experts and non-experts.

- Rapid assessment of electrolyte composition, plus water and/or HF quantification using a Fourier 80 Benchtop NMR [Application Note - Ref. 3]
- Optimizing bulk conductivity in electrolytes for higher battery performance – a fast and reliable ^{7}Li-NMR based $LiPF_6$ quantification [Application Note - Ref. 3]
- Understanding transport properties in electrolytes by multi-nuclear NMR diffusion [Application Note - Ref. 4]
- Operando NMR analysis of battery materials during battery cycling [Application Note – Ref. 5]

Conclusion

The electrolyte with its most precious ingredient, the conducting salt, is the center piece of LiBs. Aging of the electrolyte also leads to chemical changes of other key components such as electrodes and their interfaces. Understanding aging and degradation pathways and defining countermeasures within the chemical make-up or within industrial production processes significantly enhances todays and future batteries. NMR spectroscopy is a flexible tool providing robust and reproducible results in electrolyte analysis. Academic researchers and scientists in industrial product innovation environments take advantage of this technology.

Enhanced software solutions for data interpretation and visualization offered by Bruker reduces the workload for the spectroscopic expert. This enables broader statistical investigations in high throughput operation, but also opens the door to non-spectroscopic expert usage.

References:

1. Adv. Energy Mater. 2022, 12, 2102904
2. Electrochimica Acta 2016, 222, 1267-1271
3. AN Available soon
4. Quantifying Ionic Conductivity and Cation Transfer Coefficient in Lithium-ion Battery Electrolytes by Diffusion Ordered NMR Spectroscopy, AN 2023
5. Battery research probes for Li-ion technologies, AN 2023

BRUKER ANALYTICAL EXCELLENCE Battery Research & Manufacturing

Bruker BioSpin
info@bruker.com

bruker.com

Customer Support
https://www.bruker.com/en/services/support.html

Online information
bruker.com/