Application Note 18

Observing and Monitoring Electrolyte Decomposition by Benchtop NMR

Introduction

Lithium-ion (Li-ion) batteries have become ubiquitous in daily life, providing power for a diverse range of applications, ranging from mobile phones, computers, power tools, and medical devices, to the power storage behind emerging green technologies such as electric cars and solar panels, among many others. As our usage of lithium-ion batteries has grown, so has the need to optimise their performance and to ensure reliability over a long lifetime.
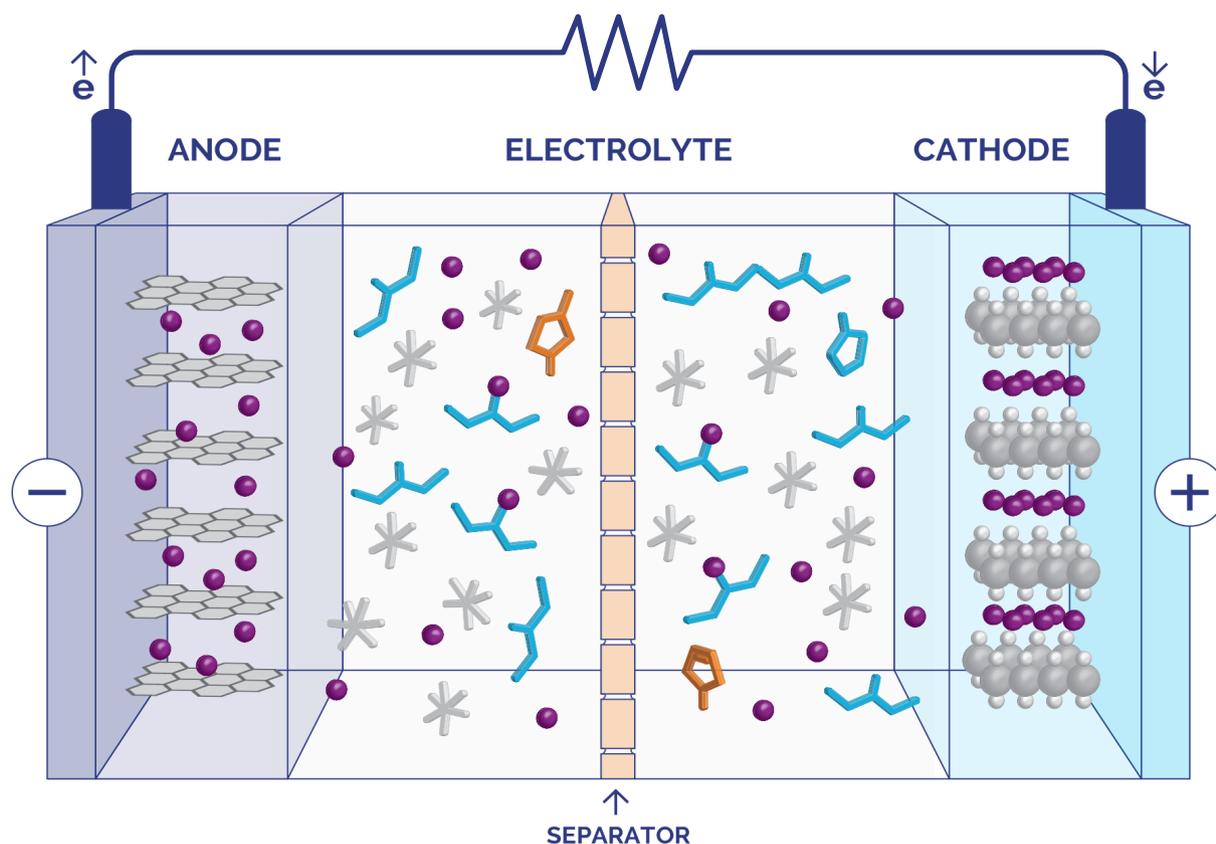

Figure 1: Diagram of a lithium-ion battery, showing major components including the anode, cathode, separator, and electrolyte.

Lithium-ion battery electrolytes play a crucial role in their performance and reliability, providing the medium that allows anions and cations to carry charge between the electrodes, as shown in Figure 1. The electrolyte is typically made up of organic small-molecule liquid solvents, such as ethylene carbonate/dimethyl carbonate, combined with small ionic species, such as Li^+ and hexafluorophosphate, $[PF_6]^-$. The ability of the electrolyte to transfer charge quickly between the anode and cathode, as well as to form effective solid electrolyte interphase (SEIs), can be impaired by contamination, chemical degradation, or a combination of both, compromising battery power density, lifespan, and safety. As a result, strict quality control during product development and manufacturing is imperative.

While lithium-ion batteries have played a major role in transforming our daily lives, benchtop NMR spectroscopy has similarly begun to revolutionise quality assurance and quality control (QA/QC) processes by making a powerful technique easier and more accessible for routine analysis in any laboratory. Benchtop NMR has many potential lithium-ion battery QA/QC applications, as the well-resolved spectra of the small organic molecules and ions are ideally suited for quick, convenient analysis. Compared to more limited benchtop NMR systems, the X-Pulse broadband benchtop NMR spectrometer provides significant advantages for battery electrolytes. A single broadband X-Pulse instrument can analyse typical NMR nuclei such as ^1H, ^{19}F, and ^{13}C, as well as many other nuclei commonly used in electrolytes, such as ^{31}P ($[PF^6]^-$), ^{11}B ($[BF_4]^-$), ^7Li (Li^+) and ^{23}Na (Na^+), making it an extremely valuable tool for both qualitative and quantitative analysis in the battery industry.

Broadband benchtop NMR is particularly suited for the detection, identification, and characterisation of impurities and breakdown products. NMR can analyse mixtures without requiring lengthy separation steps, greatly simplifying accurate measurement of breakdown rates, and determination of effects of impurities on critical electrolyte properties such as diffusion rates. Broadband benchtop NMR offers fast, convenient analysis of many nuclei, providing crucial information when and where it is needed most.

Detecting and Monitoring Breakdown Products

For battery performance optimisation, assuring electrolyte purity is critical. Any breakdown components can cause significant performance issues, ranging from decreased charge/discharge performance, to reduced lifetime, and even safety issues.

Given two supposedly identical electrolyte samples that show different performance characteristics, simple one-dimensional (1D) NMR spectra can both determine the nature of the difference and provide a fast, accurate monitoring method to prevent deviations from specifications.

Figure 2 shows spectra from two such samples of Li $[PF^6]$ in a solvent mixture of ethyl methyl carbonate and ethylene carbonate. Because hydrogen is an extremely common element and has the highest NMR sensitivity, the standard one-dimensional (1D) ^1H NMR spectrum is often the starting point for NMR analysis. As seen in Figure 2A, the spectra of both samples are identical, suggesting that the organic solvent mixture is unlikely to be the cause.
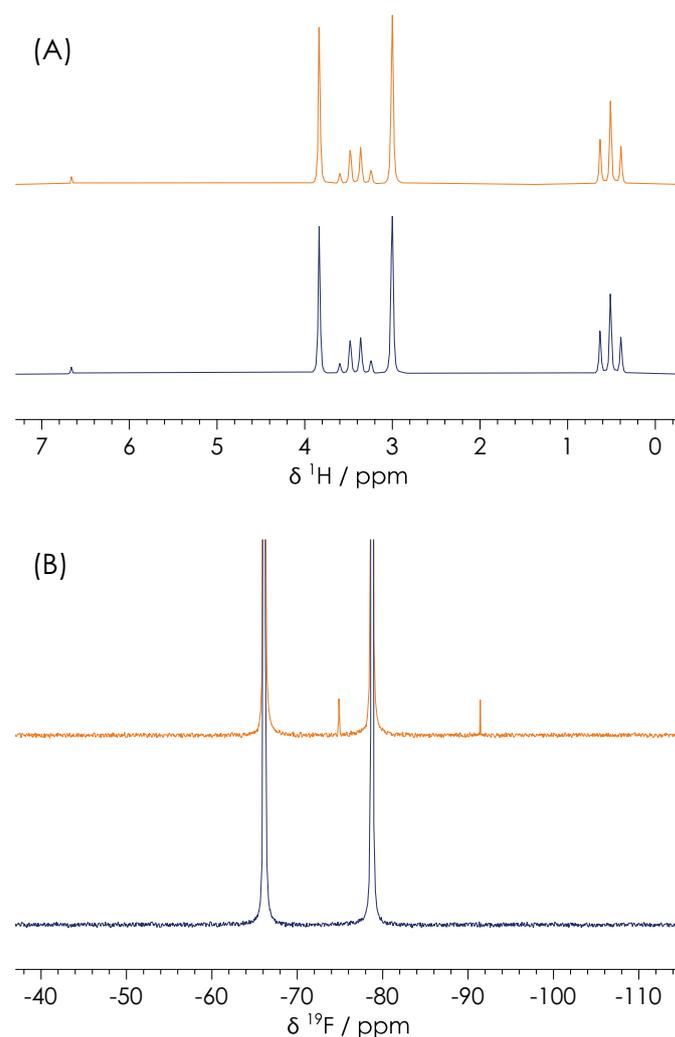

Figure 2: (A) NMR analysis of electrolytes. Standard ^1H 1D NMR spectrum of good sample (orange) and suspect sample (blue) shows no differences. (B) ^{19}F 1D NMR spectrum of good sample (orange) and suspect sample (blue) shows two clear additional peaks in the suspect sample.

In contrast, as Figure 2B shows, the ^{19}F NMR spectra tell a different story about the ionic species. The spectrum of the good sample (red) contains just one doublet, corresponding in both, chemical shift and J-coupling constant, to the expected peaks for fluorine in the $[PF_6]-$ anion. However, the spectrum of the sample with degraded performance (blue) shows both the $[PF_6]-$ doublet and a second, smaller doublet, indicative of the presence of a minor component. This doublet was assigned by chemical shift and J-coupling constant to difluorophosphoric acid, $OPF_2(OH)$, a common breakdown product of $[PF_6]-$ in the presence of water. The spectra in Figure 2B also demonstrate the ability of the NMR technique to detect small amounts of breakdown products; in this case, the molar ratio of $OPF_2(OH)$ to $[PF_6]-$ is 0.6%.

Another product of the hydrolysis reaction of $[PF_6]-$ to $OPF(OH)_2$ is LiF, which is separated by more than 120 ppm from the downfield peak of the $[PF_6]-$ doublet. In some cases, it can be challenging for a high-field NMR spectrometer to provide uniform excitation of peaks that are separated by hundreds of ppm, using standard parameters. However, because of the lower field strength of benchtop NMR, and because the X-Pulse has adjustable tuning and matching, an experiment run with standard parameters can provide uniform, accurate results over a very wide range of chemical shifts in a single spectrum. Figure 3 shows all three components in a single X-Pulse ^{19}F spectrum. The presence of LiF in the mixture corroborates both the assignment and the proposed breakdown mechanism.
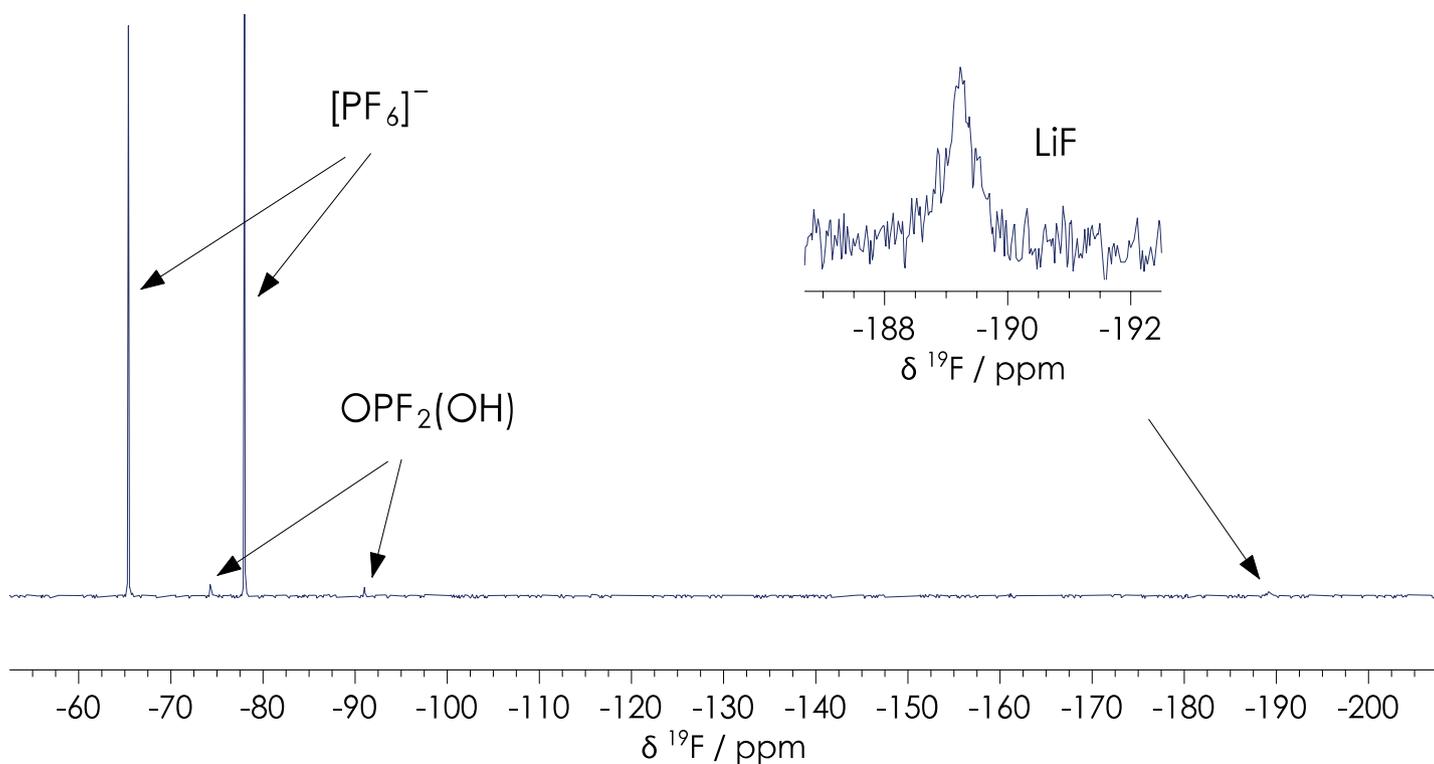

Figure 3: Wider range view of the ^{19}F 1D NMR spectrum of the suspect sample shows an additional peak at approximately -189 ppm. Peaks were assigned by chemical shift and J-coupling constants.

Monitoring Breakdown Rates

Beyond identification and quantification of breakdown products, another critical factor in lithium-ion battery electrolyte quality control is the rate at which those breakdown products are produced. Benchtop NMR can provide this information by monitoring degradation reactions, either via a flow cell or in a single tube containing a reaction mixture.

Figure 4 shows a set of spectra, acquired over the course of 3 hours, of a sample of Li[PF$_6$] in an organic electrolyte with a single drop of water added. The initial composition reaction proceeds very quickly, as shown in Figure 4 by the rapid decrease of the [PF$_6$]– peak integral during the first 30 minutes.

By integrating the spectral peaks obtained in a time course series of ^{19}F 1D NMR experiments, the rate of increase or decline of individual components can be determined, since the area of an NMR peak is directly proportional to the number of nuclei producing that peak. In a R&D setting, it may be desirable to calculate rate constants and even thermodynamic parameters from NMR data. However, in a QA/QC setting, it is generally more important to know whether the breakdown products are present and in what quantities, which can easily be determined from simple inspection and integration of the 1D NMR spectra.

Taking QA/QC analysis further, monitoring capabilities can be enhanced using a flow cell to provide real-time data. In addition, for some electrolytes, such as those using boron-based anions, the additional nuclei available on a broadband X-Pulse may be necessary to provide data for the complete determination of all breakdown products and reaction rates.
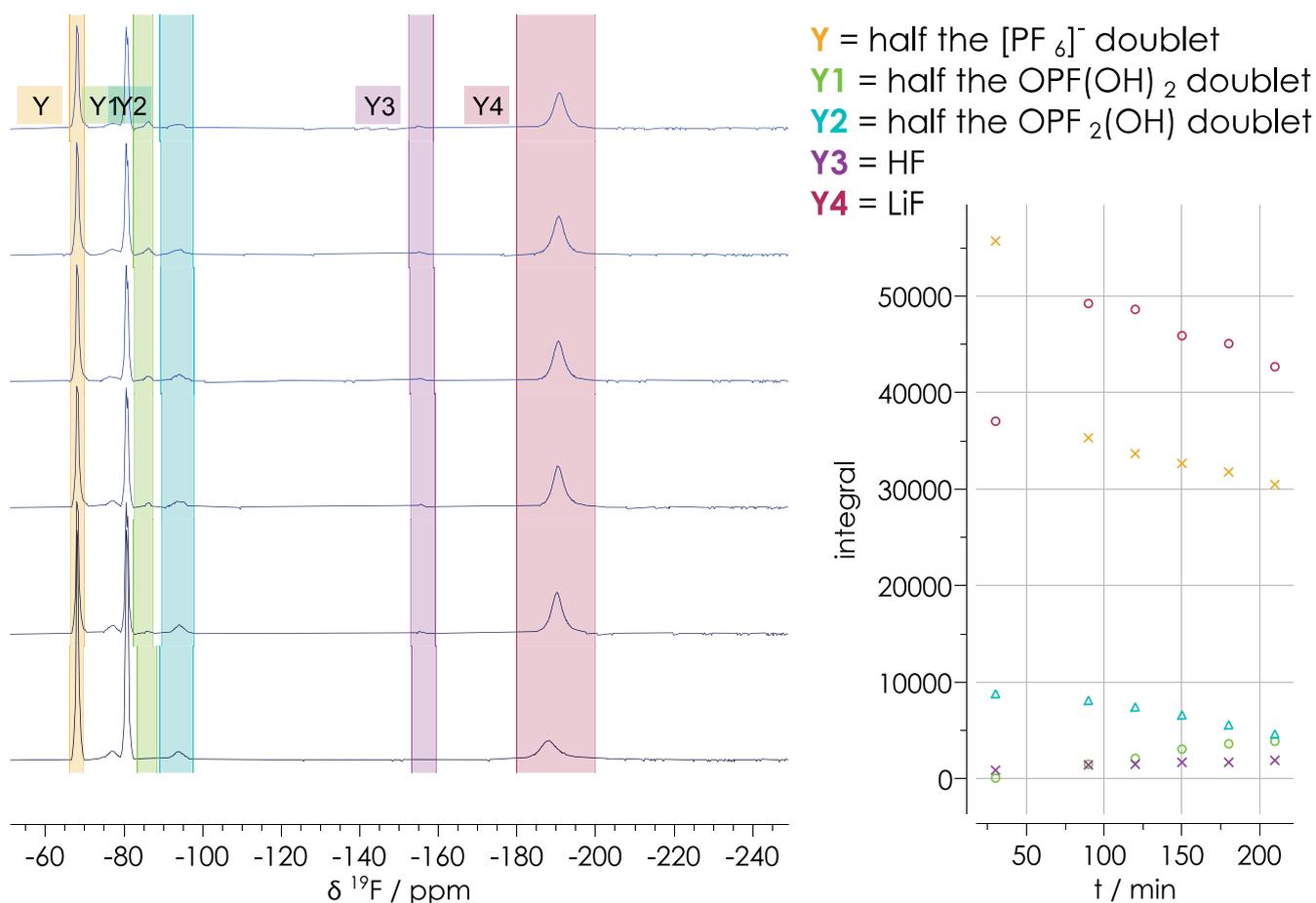

Y = half the [PF$_6$]$^-$ doublet
Y1 = half the OPF(OH)$_2$ doublet
Y2 = half the OPF$_2$(OH) doublet
Y3 = HF
Y4 = LiF

Figure 4: Stacked plot of [19]F 1D spectra acquired over 3 hours to monitor progression of the decomposition reaction and plot of the associated integrals of the spectral peaks over time.

Determining Effects on Electrolyte Properties

In addition to producing unwanted and potentially hazardous compounds, electrolyte breakdown can also affect overall battery performance. As a result, once breakdown products have been confirmed, performance effects should be analysed. The Pulsed Field Gradient Spin Echo (PGSE) experiment, which is described in more detail in Application Note 16: "Multinuclear Benchtop NMR for Electrolyte Design", can be used to provide information on diffusion of electrolyte components, also allowing calculation of ionic conductivity and transference number.

PGSE spectra were acquired for the sample in Figure 4, before (blue) and after (orange) exposure to H_2O. Because the downfield (left) peak of the hexafluorophosphate doublet was fully resolved from all other species produced during the experiment, it was integrated and displayed in a Stejskal-Tanner plot in Figure 5. The diffusion coefficient of a substance is the negative of the slope of the line in the Stejskal-Tanner plot. The change in slope after the degradation reaction, quantified in the inset of Figure 5, clearly demonstrates significant effects on electrolyte properties. The change in self-diffusion rates will affect both the ionic conductivity and cation transference, highlighting the importance of understanding and preventing electrolyte degradation.
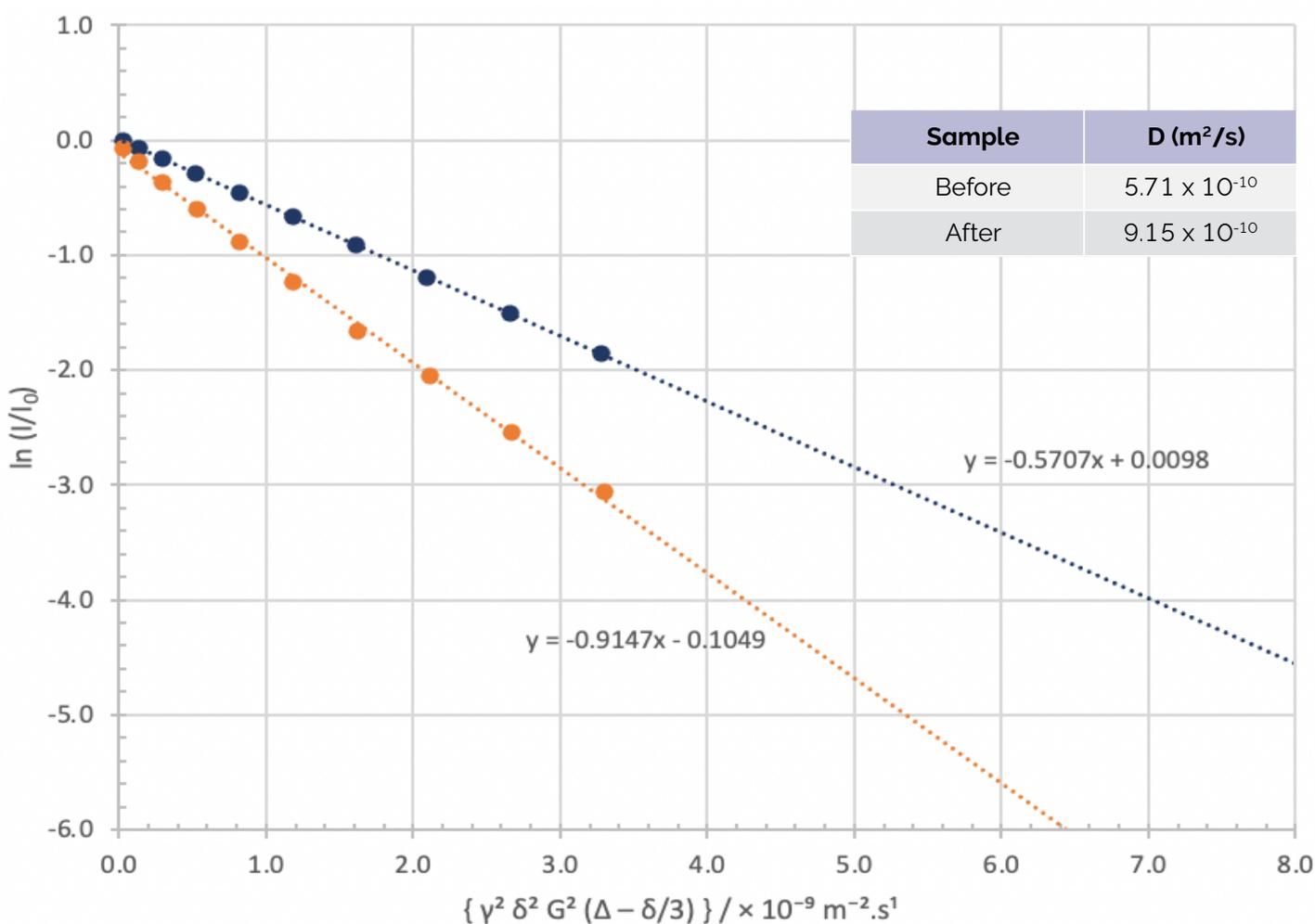
Sample	D (m²/s)
Before	5.71×10^{-10}
After	9.15×10^{-10}

$$y = -0.5707x + 0.0098$$

$$y = -0.9147x - 0.1049$$

Y-axis: $\ln (I/I_0)$

X-axis: $\{ \gamma^2\, \delta^2\, G^2\, (\Delta - \delta/3) \} / \times 10^{-9}\ m^{-2}.s^1$

Figure 5: Stejskal-Tanner plot of integrals from a series of ^{19}F PGSE NMR spectra of the sample from Figure 4. The blue circles and line (R^2=1.000) are from spectra taken before exposure to H_2O, while the orange circles and line (R^2=0.998) are from spectra acquired starting 40 minutes after exposure to H_2O. Inset: Self-diffusion coefficients calculated for the electrolyte sample from the Stejskal-Tanner plot before and after exposure to water.

Conclusion

The X-Pulse benchtop NMR spectrometer quickly and accurately monitors, measures, and characterises Lithium-ion battery breakdown products. Fast, simple standard 1D NMR spectra are often enough to identify and quantify breakdown products. In addition, the X-Pulse can monitor breakdown reactions, allowing determination of breakdown rates, providing crucial information about the stability of a system. Moreover, the PGSE experiment can be used to determine the effects of breakdown reactions on critical electrolyte properties. The multinuclear capabilities of the X-Pulse also allow the analysis of multiple electrolyte components, by enabling collection of ^{1}H, ^{7}Li, ^{11}B, ^{13}C, ^{19}F, ^{23}Na and ^{31}P data on a single instrument. The X-Pulse broadband benchtop NMR spectrometer brings easy, fast electrolyte analysis into any laboratory.

If you have any questions about this application note, please contact our experts:
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