Application Note 20

Quantitative benchtop NMR optimises battery electrolytes

NMR spectroscopy characterises the chemical structure of battery electrolyte solvents and additives. Importantly, quantitative broadband benchtop NMR additionally determines the precise concentrations of solvents, trace impurities, additives, and decomposition products. In this application note, we highlight the relevant quantitative NMR (qNMR) experiments and their importance for optimising next generation battery performance, raw materials checking and improving quality control.

Introduction — NMR spectroscopy

For non-destructive investigations of the chemical nature of materials in the liquid state, NMR spectroscopy is an extremely versatile method employed extensively in research and development. NMR provides information about individual atoms within the compounds, including not only their chemical environment and molecular structure, but also on their quantity. This makes the technique an ideal tool for rapid reaction monitoring and quality control. However, due to the high cost as well as demanding staff and environmental requirements, traditional high-field NMR instruments with their high maintenance superconducting magnets are difficult to integrate into an existing workflow.

By employing modern benchtop NMR instruments instead, those disadvantages can be eliminated. These instruments use a low maintenance permanent magnet, are much easier to operate and, due to their mobile and compact nature, can be easily located in existing workspaces. In particular, the X-Pulse broadband benchtop NMR spectrometer delivers high resolution and sensitivity, suitable for qualitative as well as quantitative measurements, with many applications taking just a few minutes.

In an NMR spectrum, the areas under peaks are directly proportional to the number of the atom(s) they are generated from. Quantitative NMR (qNMR) uses this property to determine the ratios or absolute concentrations of species in a sample. Accurate quantitation can easily be done, when the signals of interest are discrete and well defined, emphasising the importance of spectral resolution.

Introduction — lithium-ion batteries

The increasing number of mobile devices as well as the switch away from fossil fuels towards sustainable energy solutions has turned the development of efficient batteries into a critical challenge of our times. Lithium-ion batteries have proven to be commercially successful, with ongoing improvements to their components making them increasingly sophisticated and powerful. The electrolyte is one key component with many opportunities for optimisation. In most current commercial batteries, the electrolyte is a liquid consisting of an organic solvent in which lithium salts are dissolved to enable movement of charge carriers between the electrodes. In addition, chemical additives may also be present in the mixture to enhance properties such as chemical stability and battery life cycle. A schematic version of such a battery is shown in figure 1.

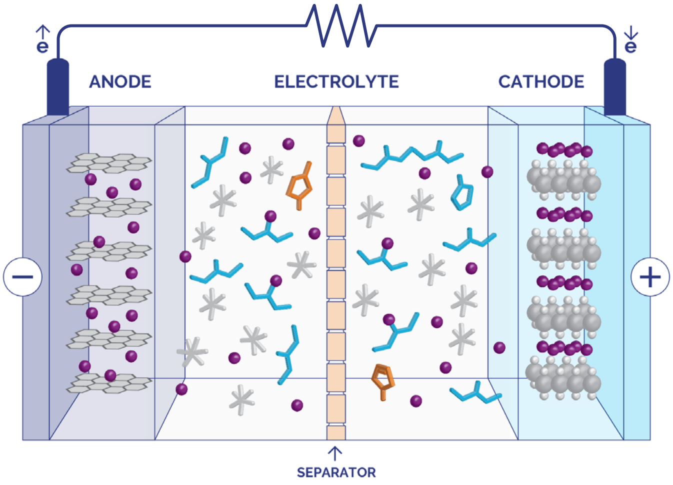

Figure 1: Schematic of a lithium-ion battery

For research and quality control alike, exact knowledge about the composition and concentration of the electrolyte is of paramount importance to achieve maximum performance. The X-Pulse is an ideal instrument for quick and reliable analysis of such systems. As the only benchtop spectrometer with broadband capabilities, the X-Pulse provides all the capabilities necessary for the investigation of a variety of X-nuclei such as phosphorous, lithium or boron present in electrolytes, as has already been shown previously in Application Note 16: "Multinuclear Benchtop NMR for Electrolyte Design". The X-Pulse is also capable of exact concentration measurements of more traditional hydrocarbons, like alkyl carbonates, that are used both for the solvent as well as additives in batteries.

Quantifying mixtures of solvents

Alkyl carbonates like ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are widely used aprotic polar solvents in electrolytes for lithium-ion batteries. Knowledge of the precise compositions of these solvents, together with various additives is required to optimise properties such as viscosity or permittivity, as well as their long-term chemical stability. The composition of such mixtures can be quantified in a few minutes on the X-Pulse using simple one-dimensional ^1H spectra, with sufficiently long relaxation time between each scan. Such an electrolyte mixture of an approximate 1:1:1 ratio by mass was analysed by such an experiment with 16 scans. To achieve accurate quantitative results in qNMR, you need to allow the nuclei to return to the equilibrium state before each scan. Therefore, we are using a 20 second relaxation delay between the scans for optimal accuracy. The resulting spectrum is shown in figure 2 below.

We can clearly see the separate singlet signals of EC and DMC, as well as the two distinct multiplets stemming from the chemically inequivalent protons in DEC splitting into a triplet and a quartet, respectively due to coupling between them.

In addition to this chemical and structural information, the area under each of those signals is proportional to the number of nuclei producing them, enabling us to quantify the compounds and determining their ratio R by measuring the signals integrals intensity I. The EC signal intensity is normalized to a value of 4 protons, which leads to a value of 6.05 protons for DMC, 3.16 for the CH_2 site of DEC and 4.60 for its CH_3 group. Considering the number of hydrogen atoms at those sites per molecule (six for DMC and four and six respectively for DEC), dividing the integral intensity by those values gives us a molar ratio of 1.00 : 1.01 : 0.78 or of roughly 4:4:3, with the value for EC being obtained by the average of its two signals.

$$R_{molar} = \frac{I_{measured}}{I_{expected}}$$

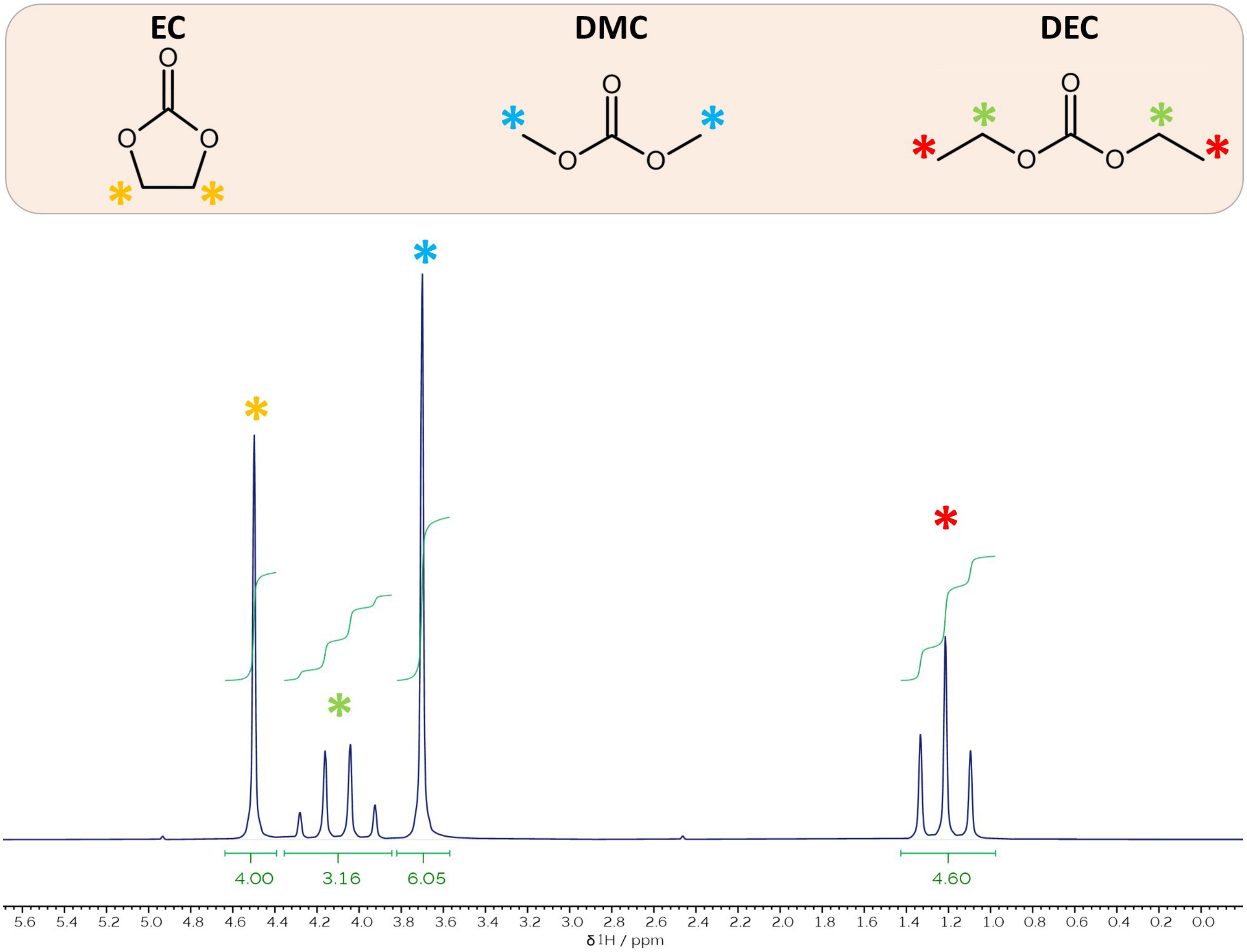

Figure 2: ^{1}H-NMR spectrum of a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate.

When weighing those ratios with the molecular mass *M* of each molecule, their ratio by weight as well as their weight percentage can be obtained.

$$R_{weight} = R_{molar} \cdot M$$

The deviation of the values obtained compared to the mass ratios given by the manufacturer of the solvents is less than two percent in each case, which proves the high accuracy obtainable in such a short amount of time and effort (see Table 1).

	Normalised integral ($I_{measured}$)	**Molar ratio (R_{molar})**	**Molecular Mass/g.mol^{-1} (M)**	**Weight % (measured)**	**Weight % (given)**
EC	4.00	1.00	88.06	32.51	32.97
DMC	6.05	1.01	90.08	33.54	33.69
DEC	3.16 (CH_2) 4.60 (CH_2)	0.78	118.13	33.95	33.34

Table 1: Molar and mass ratios of the carbonate mixture obtained via the integral area beneath their NMR signals and their molecular mass.

Investigating impurities and trace additives

Apart from quantifying majority components in mixtures, the X-Pulse is also capable of determining the amount of trace impurities in a sample. As a model, one, two or four drops of vinylene carbonate (VC) were added to samples of the same electrolyte used previously. VC is a compound used as an additive in electrolytes to generate an insoluble polymer film at the solid-electrolyte-interface (SEI).

While the positive effects of the film formation include a decrease of the self-discharge rate of the batteries, as well as improving the coulombic efficiency, a higher concentration of VC can lead to an unfavourable increase of the cell's impedance. The concentration range optimal for such applications may lie below 2%, which makes accurate analysis essential.[1]

By carrying out the same experiment as above, it is possible to obtain accurate results by integration of the distinct NMR signal of VC in the aromatic region around 7.5 ppm, as is shown in the spectra below (figure 3).

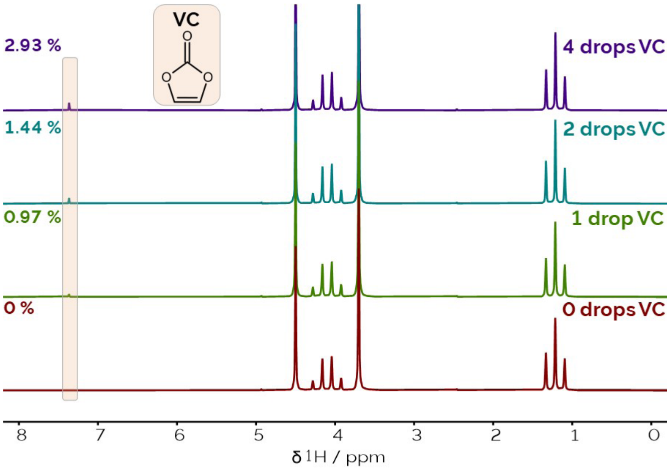

Figure 3: ^{1}H-NMR spectra of solvent mixtures with an increasing, yet small, amount of a VC additive.

Using the same method as described above, the concentrations of VC were determined to be 0.97%, 1.44% and 2.39% by weight in the three samples. (see Table 2).

Advanced sequences — eliminating ^{13}C-satelites

When trying to accurately quantify closely spaced signals, the carbon satellites present in the usual one-dimensional ^{1}H NMR experiments may not be able to be integrated easily together with their main signals and may overlap with signals from other protons, causing small inaccuracies in measurements. Because those peaks only arise from ^{13}C, which naturally comprises just 1.1% of carbon nuclei, the effects are generally very small. However, when quantifying a very small peak, such as a minor impurity, that is adjacent to a much larger solvent peak, the effects can be more significant. This source of error can be eliminated on the X-Pulse by a carbon decoupled experiment, using techniques such as **G**lobally optimized **A**lternating-phase **R**ectangular **P**ulses (**GARP**). By removing the coupling between the hydrogen nuclei and the small percentage of ^{13}C nuclei that bind to them, the satellite peaks are eliminated, with the proton signals all contained within the main peak (figure 4). This method slightly increases accuracy without prolonging measurement time.

	Normalised integral ($I_{measured}$)	Molar ratio (R_{molar})	Molecular Mass/g. mol^{-1} (M)	Weight % (measured)
1 drop of VC	0.08	0.04	86.05	0.97
2 drops of VC	0.13	0.07		1.44
4 drops of VC	0.17	0.09		2.39

Table 2: Quantification data of vinylene carbonate impurities in the carbonate mixture

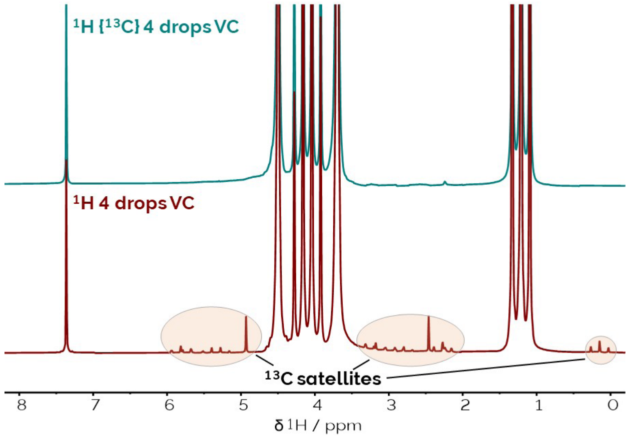

Figure 4: Zoomed in ^{1}H NMR spectra of the solvent mixture with four drops of VC without (bottom) and with (top) ^{13}C decoupling. The ^{13}C satellites in the lower spectrum are highlighted in orange.

Conclusion

Benchtop NMR is a practical method for use in quality and reaction control for its ease of use, non-destructive nature, and versatile applications. The X-Pulse enables rapid investigations of not only the chemical structure of electrolyte solvents and additives, but also the quantification of materials or impurities at much lower concentrations. This method has been applied to solvents and additives of interest for battery research. Moreover, eliminating the carbon satellites in ^{1}H-spectra by decoupling using a GARP sequence enables accurate measurements of even closely spaced signals.

While the examples in this Application Note use proton NMR spectra, qNMR experiments can also be performed on nuclei including: ^{19}F, ^{31}P, ^{11}B, ^{27}Al, ^{7}Li and ^{23}Na, on a single X-Pulse broadband benchtop NMR spectrometer. ^{19}F, ^{7}Li and ^{11}B qNMR is of particular significance for the analysis of electrolytes. ^{19}F quantifies concentrations of the anions, $[PF_6]^-$, $[BF_4]^-$, bis(fluorosulfonyl)imide (FSI) or bis(trifluoromethane)sulfonimide (TFSI), as well as fluorinated additive and decomposition products. ^{7}Li accurately determines the concentration of lithium cations in the solution which is crucial for understanding the energy density the final cell.

[1] J. C. Burns ***et al J. Electrochem. Soc.*** **2011**, *159*, A85

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