

Batteries: Quantifying Your Additives With qNMR



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Introduction

Over the last two decades, the use of lithium-ion batteries (LIBs) as an energy storage device has surged due to its uses in notebooks, cellular devices, and electric vehicles. As a result of its increasing popularity, interest in improving the performance of such batteries has proportionally increased. There are three components to LIBs that can change its performance, which include: the electrodes (anode and cathode), the separator, and the electrolyte (salt and solvent system). The LIB electrolyte plays a pivotal role as the medium enabling the movement of lithium ions between the anode and cathode. The electrolyte is often a complex mixture of non-aqueous solvents and lithium salt(s). To produce a successful electrolyte, factors such as salt dissociation, solubility, viscosity, ionic conductivity, chemical compatibility, and thermal stability need to be considered.^{1,2}

One common method of improving a battery's performance is with the addition of electrolyte additives. These additives usually make up less than 5-10% of the electrolyte. Electrolyte additives are chemical species added to the electrolyte mixture to improve functionality (dissolution facilitation, improving kinetics, etc.) or to prevent destabilization (HF scavenging, thermal stability, flame retarding properties, etc.).³ Commonly used electrolyte additives are shown in Figure 1. When it comes to electrolyte mixtures, it is crucial to ensure all chemical species are of high purity. Introducing impurities into a battery's electrolyte can interfere with the battery's performance, which may ultimately lead to the battery's failure.

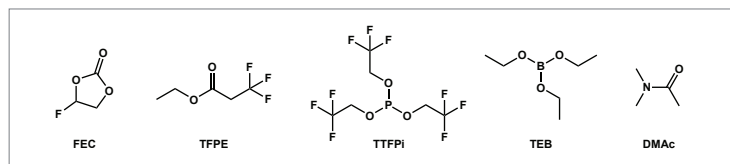


Figure 1. General structures of common electrolyte additives used for cathode protection/stabilization in lithium batteries: fluoroethylene carbonate (FEC), ethyl-3,3,3-trifluoropropanoate (TFPE), tris(2,2,2-trifluoroethyl)phosphite (TTFPI), triethylborate (TEB), and dimethylacetamide (DMAc).³

Analysis

The purity of almost any electrolyte additive can be conveniently determined using quantitative nuclear magnetic resonance (qNMR) spectroscopy. qNMR is most commonly used on nuclei such as ¹H, ¹⁹F, ³¹P. By collecting a 1D spectrum of the sample and internal calibrant in solution and integrating the relative regions associated with each compound, the purity of the sample can be determined with the equation below:

$$P_s = \frac{I_s}{I_{IC}} * \frac{N_{IC}}{N_s} * \frac{M_s}{M_{IC}} * \frac{m_{IC}}{m_s} * P_{IC}$$

Where:

P = Purity
 I = Integral area
 N = Number of protons*
 M = Molar mass
 m = Mass of compound used
 S = Sample
 IC = Internal calibrant

*Number of protons is used if the purity is calculated via ¹H qNMR. If ¹⁹F, ³¹P or other nuclei are used for quantification, the number of corresponding nuclei is taken into account for determining purity

As an example, ¹H and ¹⁹F qNMR were used to determine the purity of a sample of fluoroethylene carbonate using the 60PRO, and the results obtained were compared to those obtained on a high-field NMR spectrometer (400 MHz). 1,2,4,5-Tetrachloro-3-nitrobenzene (TraceCERT® certified ¹H NMR reference standard) was used as one of the internal calibrants for this application. A second internal

calibrant, high purity (>99%) 1,4-dibromotetrafluorobenzene, was used for ¹⁹F qNMR. All 3 species were weighed into a single vial using a Mettler Toledo analytical balance (model: MS105DU), and subsequently dissolved in chloroform-*d* and analyzed. Figure 2 shows the spectra obtained using the 60PRO and the high-field spectrometer. The experimental parameters used to acquire the data on the 60PRO are as follows: ¹H: spectral width: 40 ppm, number of points: 16384, number of scans: 16, scan delay: 25 seconds, spectral center: 10 ppm, pulse angle: 90°, receiver gain: auto. ¹⁹F: spectral width: 100 ppm, number of points: 8192, number of scans: 16, scan delay: 25 seconds, spectral center: -100 ppm, pulse angle: 90°, receiver gain: auto. The sample was run in triplicate to ensure precision.

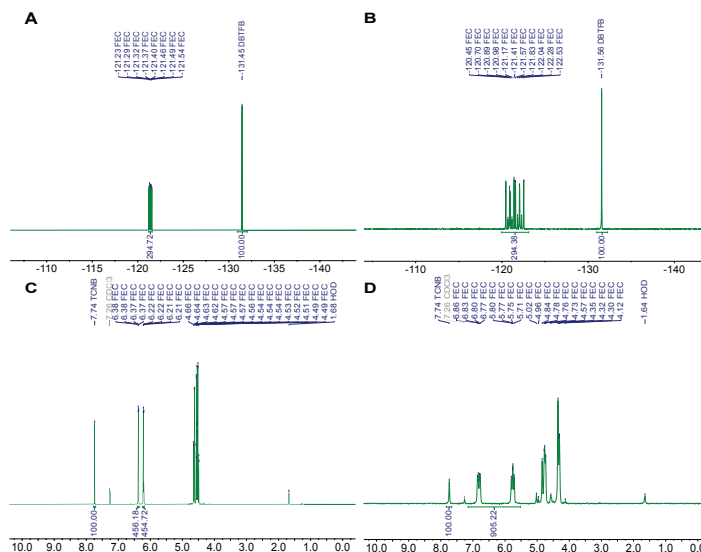


Figure 2. NMR spectra of fluoroethylene carbonate (FEC) and respective internal calibrant using the 60PRO and 400 MHz instruments. A) ¹⁹F NMR spectrum of FEC and 1,4-dibromotetrafluorobenzene (DBTFB) acquired on a 400 MHz instrument. B) ¹⁹F NMR spectrum of FEC and DBTFB acquired on a 60 MHz instrument. C) ¹H NMR spectrum of FEC and 1,2,4,5-tetrachloro-3-nitrobenzene (TCNB) acquired on a 400 MHz instrument. D) ¹H NMR spectrum of FEC and TCNB acquired on a 60 MHz instrument.

The results obtained using the 60PRO and the high-field spectrometer for the analysis of fluoroethylene carbonate are summarized in Table 1.

Table 1: Comparison between the purity obtained using the 60PRO and a high-field 400 MHz NMR spectrometer.

Instrument	¹ H Purity (%)*	¹⁹ F Purity (%)*
60PRO (Benchtop)	99.96 (0.35)	99.64 (0.61)
400 MHz (High-Field)	100.62 (0.43)	100.12 (0.12)

*RSD values shown in parentheses

As demonstrated in this study, the 60PRO compares quite well to high-field NMR spectroscopy when analyzing purity using ¹H and ¹⁹F qNMR. With increasing research being performed in energy storage, having a fast, efficient, and quantitative method at your disposal would be a huge asset. If you would like to know more about battery applications with NMR spectroscopy or are interested in how NMR spectroscopy could help you, please do not hesitate to contact us.

References

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