

## Batteries: Electrolyte Solvent Quantification With Deuterated Solvents

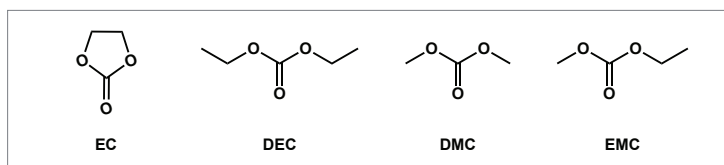


# Batteries: Electrolyte Solvent Quantification With Deuterated Solvents

## 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 affect its performance, which include: the electrodes (anode and cathode), the separator, and the electrolyte (salt and solvent system). The electrolyte in the LIB 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 aprotic 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.<sup>1,2</sup>

Currently, most commercially available LIBs have a metal oxide cathode (*i.e.*, lithium cobalt oxide) and a carbon anode (*i.e.*, graphite), containing an electrolyte which is a non-aqueous solution of LiPF<sub>6</sub> salt, dissolved in a combination of cyclic carbonates (*i.e.*, ethylene carbonate) and linear carbonates (*i.e.*, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate).<sup>2,3</sup> However, as battery research progresses, it is expected that more exotic and innovative electrolyte combinations will become available. Shown herein is a simple quantitative technique that can be used to analyze the solvents in LIB electrolytes using benchtop nuclear magnetic resonance (NMR).



**Figure 1.** General structure of the aprotic organic solvents ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC), commonly used in LIBs.

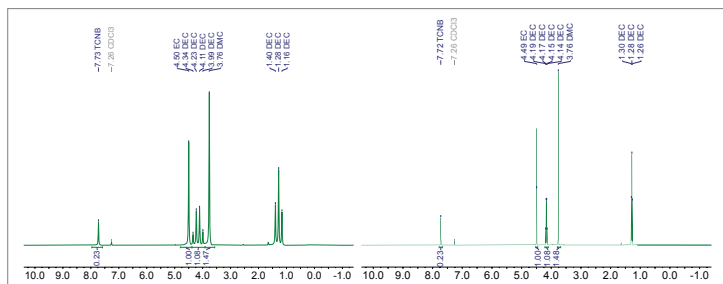
## Analysis

The relative amounts of each aprotic organic solvent in the electrolyte solution can be conveniently determined using <sup>1</sup>H quantitative NMR (qNMR) spectroscopy. By collecting a 1D spectrum of the sample solution in chloroform-*d* and integrating the relative regions associated with each compound, the relative amount of each chemical species can be determined using the equation below:

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

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

As an example, a <sup>1</sup>H NMR spectrum of a mixture of common aprotic solvents (ethylene carbonate, dimethyl carbonate, and diethyl carbonate) in CDCl<sub>3</sub> is shown in Figure 2. The experimental parameters used to acquire the data on the 60PRO are as follows: spectral width: 40 ppm, number of points: 16384, number of scans: 4, scan delay: 25 seconds, spectral center: 10 ppm, pulse angle: 90°, receiver gain: auto. Each sample was run in triplicate to ensure precision. Each experiment was completed in 2.2 minutes.



**Figure 2.** <sup>1</sup>H NMR spectrum at 60 MHz (left) and 400 MHz (right) of a mixture of aprotic organic solvents in CDCl<sub>3</sub> with the relative integration areas of each chemical species included, along with annotations above the signals.

The results acquired using the 60PRO benchtop spectrometer for the analysis of popular commercial aprotic solvents used in LIBs are summarized in Table 1. The relative amount of each species was determined from each spectrum using the average of triplicate values. The weight determined using the 60PRO was compared to the weight obtained from weighing using the Mettler Toledo analytical balance (model: MS105DU), and also compared to values obtained from high-field NMR spectroscopy (400 MHz). 1,2,4,5-Tetrachloro-3-nitrobenzene (TCNB) was used as a TraceCERT® certified internal calibrant for this application and was used as the reference point for integration values.

**Table 1:** Comparison between the masses obtained using the 60PRO, analytical balance, and high-field NMR.

Compound	Analytical Balance Mass (g)	60 MHz Predicted Mass (g)*	400 MHz Predicted Mass (g)*
1,2,4,5-Tetrachloro-3-nitrobenzene	0.02211	-	-
Ethylene carbonate	0.00789	0.008101 (1.9)	0.008101 (0)
Diethyl carbonate	0.01162	0.011823 (1.5)	0.011736 (0)
Dimethyl carbonate	0.00825	0.008229 (1.4)	0.008156 (0.39)

\*RSD values are shown in parentheses.

We have shown that the 60PRO provides results that compare quite well to analytical weighing when analyzing solvent compositions in LIBs. With increasing research in energy storage, having a fast, efficient, and quantitative method at your disposal is an important asset. If you would like to know more about battery applications using benchtop NMR spectroscopy or are interested in how NMR spectroscopy could help you, please do not hesitate to contact us.

## References

- [1] Mauger, A.; Julien, C.M.; Paolletta, A.; Armand, M.; Zaghbi, K. *Mater. Sci. Eng. R Rep.* **2018**, *134*, 1-21.
- [2] Younesi, R.; Veith, G.M.; Johansson, P.; Edström, K.; Vegge, V. *Energy Environ. Sci.* **2015**, *8*, 1905-1922.
- [3] Nitta, N.; Wu, F.; Lee, J.T.; Yushin, G. *Mater. Today.* **2015**, *18*, 252-264.