

APPLICATION NOTE

Batteries: Electrolyte Solvent Quantification Without Deuterated Solvents



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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 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.^{1,2}

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 LiPF₆ salt, dissolved in a combination of cyclic carbonates (i.e., ethylene carbonate) and linear carbonates (i.e., dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate).^{2,3} 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).

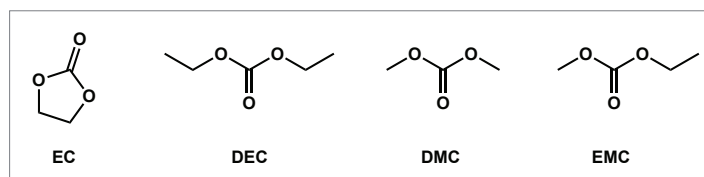


Figure 1. General structure of the aprotic organic solvents ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) from left to right, respectively.

Analysis

The relative amounts of each aprotic organic solvent can be conveniently determined using ¹H quantitative NMR (qNMR) spectroscopy. By collecting a 1D spectrum of the sample solution (without added solvent) and integrating the relative regions associated with each compound, the relative weight percentage (wt%) of each chemical species can be determined using the equation below:

$$wt\%_{x1} = \frac{\frac{I_{x1} * MW_{x1}}{N_{x1}}}{\frac{I_{x1} * MW_{x1}}{N_{x1}} + \frac{I_{x2} * MW_{x2}}{N_{x2}} + \dots}$$

Where,
 $wt\%_{x1}$ = the weight percentage of $x1$
 I_{x1} = the integration area of $x1$
 MW_{x1} = the molecular weight of $x1$
 N_{x1} = the number of protons in $x1$
 $x1, x2, \dots$ = represents a different chemical species in solution

The ¹H NMR spectrum of a mixture of aprotic solvents (ethylene carbonate, dimethyl carbonate, and diethyl carbonate) is shown as an example in **Figure 2**. The experimental parameters used to acquire the data using 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.

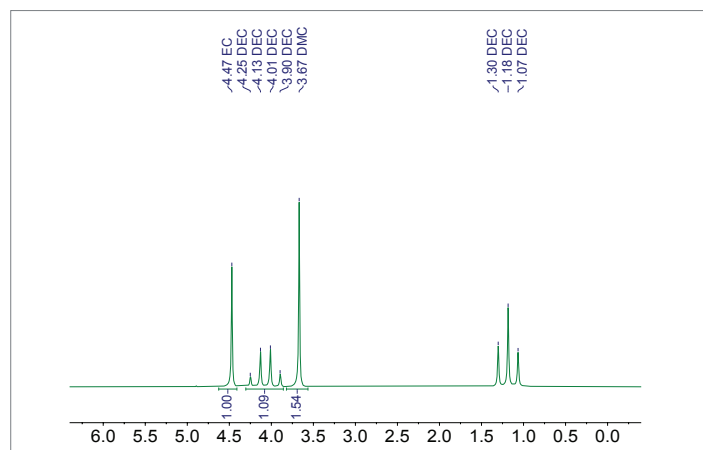


Figure 2. ¹H NMR spectrum at 60 MHz of a mixture of aprotic organic solvents without deuterated solvent showing the relative integration areas of each chemical species included, along with annotations above the signals.

The results acquired using the 60PRO benchtop spectrometer on popular commercial aprotic solvents are summarized in **Table 1**. The relative amount of each species was determined from each spectrum using the average value. The weight determined was compared to the approximate weight percentage obtained from weighing using a Mettler Toledo analytical balance (model: MS-105DU).

Table 1: Comparison between the wt% obtained using the 60PRO and analytical balance.

Compound	Analytical Balance Mass (g)	Analytical balance wt%	60 MHz Calculated wt%*
Ethylene carbonate	0.210930	0.284	0.284 (0)**
Diethyl carbonate	0.310570	0.419	0.417 (0.501)
Dimethyl carbonate	0.220360	0.297	0.300 (0.540)

*RSD values are shown in parentheses. **Ethylene carbonate has an RSD of 0 because it was used as a reference.

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.; Zaghib, 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.