Analysis of Organic Carbonate Solvent Components in Lithium Batteries

Using the Agilent 1290 Infinity II LC System with the Agilent 6546 LC/Q-TOF

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Abstract

This application note establishes a method for the identification and quantitative analysis of organic carbonate solvent components in lithium battery electrolytes using liquid chromatography coupled to high-resolution quadrupole time-of-flight mass spectrometry (Agilent 1290 Infinity II LC system with Agilent 6546 LC/Q-TOF). In this method, the electrolyte sample is diluted with acetonitrile, filtered, and directly injected for LC/Q-TOF analysis. The sample components are separated by an Agilent InfinityLab Poroshell 120 Bonus-RP column with a methanol-water (containing formic acid) mobile phase system and then detected by high resolution mass spectrometry. Four organic solvent components, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC), were successfully identified. EC and PC were quantitatively analyzed in three electrolyte samples. The simple, fast, efficient, and accurate method provides reliable information for the qualitative and quantitative analysis of organic carbonate solvents in lithium battery electrolytes.

Introduction

In recent years, energy issues have attracted much attention worldwide, especially the development and application of lithium batteries, which has become a focus in the field of renewable energy. Compared with traditional batteries, lithium batteries have the advantages of high energy density, low consumption, no memory effect, and more cycles, making them more suitable for providing energy for portable electronic devices and electrically powered vehicles.[1] Lithium batteries are mainly composed of positive electrode materials, negative electrode materials, electrolytes, and separators. The electrolyte - the "blood" of lithium batteries - is mainly composed of high-purity organic solvents, lithium salts, necessary additives, etc.[2, 3] The organic solvent in the electrolyte is mainly used to dissolve and ionize the lithium salts. Carbonate solvents are widely used in lithium battery production due to their high conductivity, high dielectric constant, and strong solubility for lithium salts. The type and ratio of solvent components will directly affect battery performance.[4] Therefore, methods that enable analysis of the carbonate solvents in lithium batteries are important. The combination of liquid chromatography (LC) and high-resolution quadrupole time-of-flight mass spectrometry (Q-TOF) can quickly provide the accurate mass and secondary fragment information for unknown substances, thereby reducing interferences from impurity peaks and improving the qualitative and quantitative analysis of electrolyte components.

Here, the Agilent 1290 Infinity II LC system coupled with the Agilent 6546 LC/Q-TOF was used to identify four organic carbonate solvents, EC, PC, DMC, and EMC (Figure 1 provides their structural formulas) in the electrolyte. In addition, EC and PC were quantitatively analyzed in three electrolyte samples.
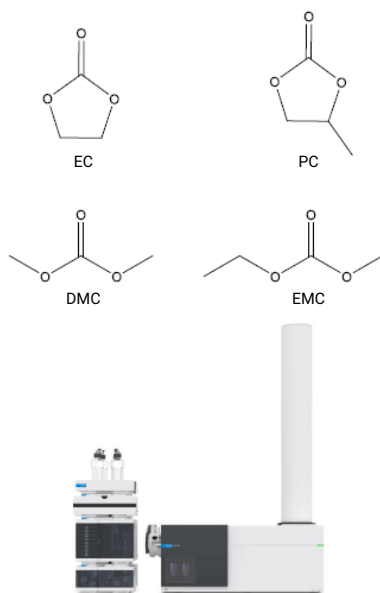

Figure 1. Structural formulas of the four organic carbonate solvents.

Experimental

Reagents and samples

Acetonitrile and methanol were MS grade and purchased from Merck. Formic acid was MS grade and purchased from Dikma. High-purity de-ionized water was prepared using a Millipore Milli-Q ultrapure water system. The samples were lithium battery electrolytes. Both the standards and samples were provided by a customer. The samples were diluted with acetonitrile in a certain ratio, filtered, and then directly injected for analysis.

Instrumentation

An Agilent 1290 Infinity II LC system used for the analysis was equipped with: 1290 Infinity II High-Speed Pump (p/n G7120A), 1290 Infinity II Multisampler (p/n G7167B), 1290 Infinity II Multicolumn Thermostat (p/n G7116B). The chromatograph conditions used are provided in Table 1.

The Agilent 6546 LC/Q-TOF was equipped with an Agilent Jet Stream Technology Ion Source (AJS) with the Dual spray Jet Stream Upgrade, and controlled by Agilent MassHunter Acquisition software version 10.1. The LC/Q-TOF MS instrument parameters are provided in Table 2.

Data analysis was performed using Agilent MassHunter Quantitative Analysis version 10.1, and Agilent MassHunter Qualitative Analysis version 10.0. Agilent MassHunter Molecular Structure Correlator (MSC) version 8.2 and Agilent ChemVista with LC/Q-TOF Spectral Libraries and Databases were used for identification.

Calibration curve preparation

EC and PC stock solutions were accurately prepared at a concentration of 100 µg/mL using acetonitrile as solvent. The stock solutions were diluted serially with acetonitrile to prepare a series of standard working solutions with concentrations of 50, 200, 500, 1000, and 2000 ng/mL for calibration curve development.

Table 1. Chromatographic conditions.

Parameter	Value	
LC System	Agilent 1290 Infinity II LC system	
Column	Agilent InfinityLab Poroshell 120 Bonus-RP, 3.0 × 100 mm, 2.7 µm (p/n 695968-301 (T))	
Flow Rate	0.4 mL/min	
Injection Volume	2 µL	
Temperature	35 °C	
Mobile Phase	A: Water with 0.1% formic acid B: Methanol	
MGradient Program	Time (min)	B (%)
	0.0	0.0
	2.0	0.0
	8.0	50.0
	10.0	100.0
	12.0	100.0
Stop Time	12 min	
Post Time	3 min	

Table 2. LC/Q-TOF MS instrument parameters.

Parameter	Value
MS System	Agilent 6546 LC/Q-TOF
Ion Mode	Positive mode (ESI+)
Gas Temperature	250 °C
Gas Flow	8 L/min
Nebulizer	45 psi
Sheath Gas Temperature	350 °C
Sheath Gas Flow	12 L/min
Capillary Voltage	2,500 V
Nozzle Voltage	500 V
Fragmentation Voltage	70 V
Scan Mode	Full spectra and Target MS/MS Acquisition

Results and discussion

Structural identification of organic carbonate solvents

Agilent Bonus-RP LC columns can tolerate 100% aqueous mobile phase systems, which is beneficial for enhancing the retention and separation of carbonates on the chromatographic column (Figure 2). The Agilent 6546 LC/Q-TOF was used to collect MS and MS/MS data for the main chromatographic peaks, and the unknown substances were identified by searching both the Agilent ChemVista with LC/Q-TOF Spectral Libraries and Agilent MSC. Four main organic solvents in the lithium battery samples were identified, including EC, PC, DMC, and EMC.
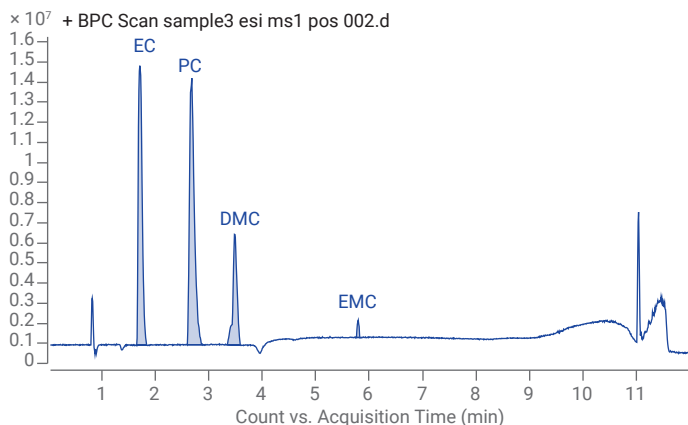

Figure 2. Base peak chromatograms of four organic carbonate solvents in lithium battery electrolyte.

Identification by searching Agilent ChemVista with LC/Q-TOF Spectral Libraries and Databases

Matching MS/MS data from unknown substances with existing database searches is commonly used for high-resolution MS analysis of unknown substances. Here, PC provides an example of compound identification using the Agilent ChemVista with LC/Q-TOF Spectral Libraries and Databases (Figures 3 and 4). Shown in Figures 3 and 4, the PC MS-level match score exceeds 99%, and the secondary fragment match score (obtained at a collision energy of 10 eV) is over 90%. The mirror image comparison of the measured MS/MS data with the library spectrum shows the accuracy and reliability of method results.
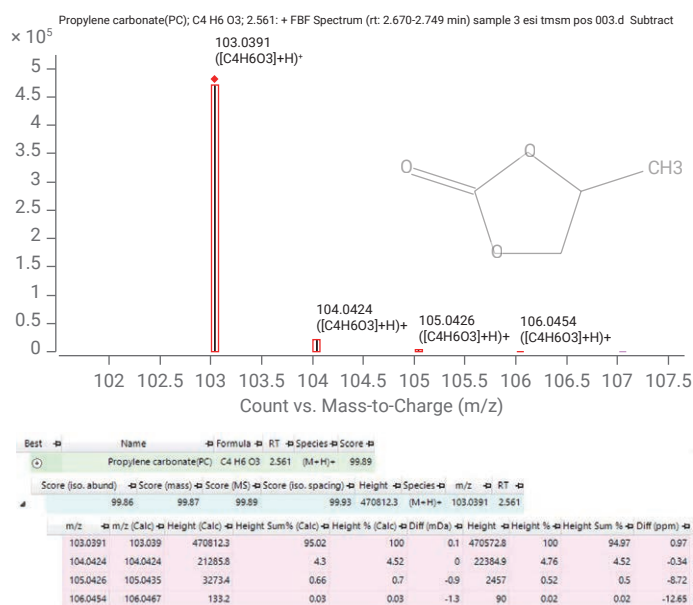

Figure 3. MS-level mass spectrum isotope peak matching results for PC.
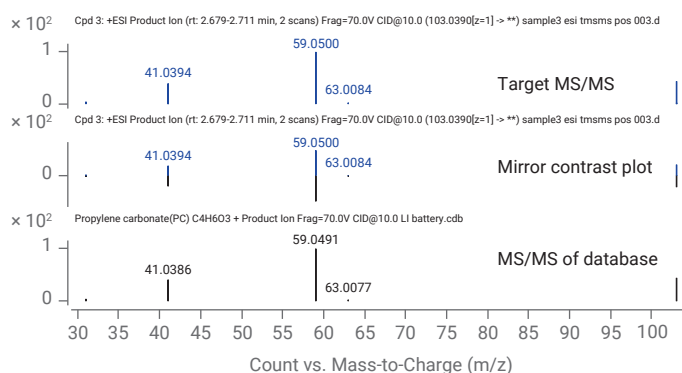

Figure 4. MS/MS spectrum and library spectrum mirror image comparison for PC.

Identification using the Agilent MSC

Agilent's MSC can automatically generate molecular formulas based on the MS and MS/MS data of unknown substances. The software can also link to ChemSpider or an Agilent PCDL database to search for one or more matching compound structures to help the user identifying the structure of the unknown. As shown in Figure 5, the structural formula of EC can be accurately matched using the Agilent MSC. As shown in Figure 6, the Agilent MSC can also perform fragment assignment and supports structure elucidation based on the MS/MS spectrum of EC, further improving the confidence of the qualitative analysis results for unknown substances.
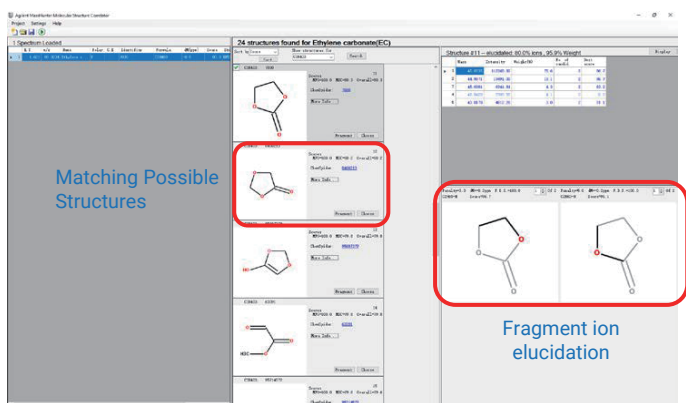

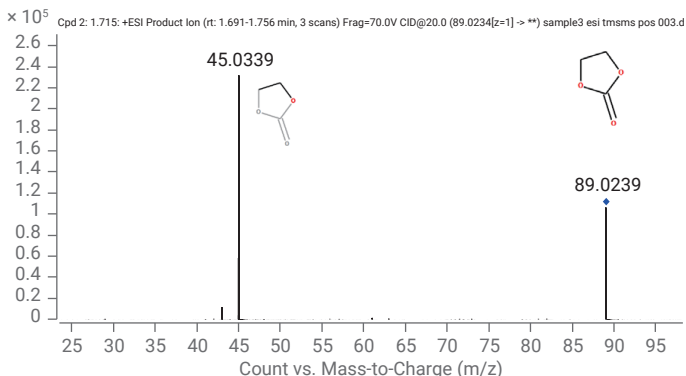**Figure 5.** Matching results obtained when using the Agilent MSC to identify EC.

Figure 6. MS/MS fragment ion structure elucidation results for EC obtained using the Agilent MSC.

Quantitative analysis of organic carbonate solvents

High-resolution MS can provide the accurate mass of compounds and reduce the impact of interfering substances. MS-level data was obtained in the Q-TOF full-spectra acquisition mode, and the characteristic ions of the corresponding compounds were extracted. These ions can be used for quantitative analysis of target compounds. The calibration curves for EC and PC are shown in Figure 7. As can be seen from Figure 7, the linear

correlation coefficient (R^2) of EC and PC is > 0.99 over the concentration range of 50-2000 ng/mL, indicating good linearity for both. The method was used to quantitatively analyze EC and PC in three lithium battery electrolyte samples (Table 3). As shown in Table 3, the EC content in the three samples was roughly two to five times the PC content. These data demonstrate the applicability of the method for optimizing the organic solvent ratio of battery electrolytes and improving battery performance.

Table 3. Quantitative results for EC and PC in three battery electrolyte samples.

Sample No.	EC Amount (µg/mL)	PC Amount (µg/mL)
1	2.0×10^5	1.1×10^5
2	2.5×10^5	5.0×10^4
3	2.6×10^5	5.0×10^4

* The sample was diluted with acetonitrile before injection into the instrument system.
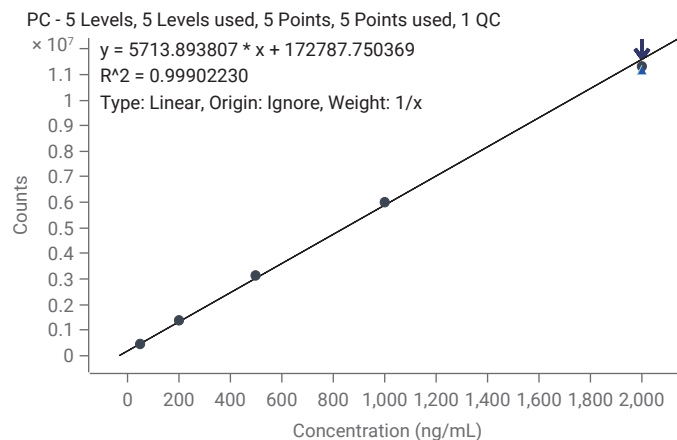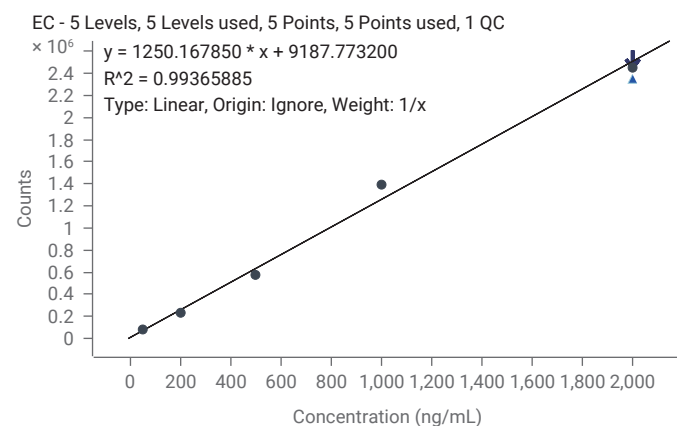

Figure 7. Calibration curves for EC and PC (50−2000 ng/mL).

Conclusion

In this application note, LC/Q-TOF was used to analyze the organic carbonate solvent components in lithium batteries. The method combined database and library searching using Agilent ChemVista with LC/Q-TOF Spectral Libraries and Databases and the Agilent MSC to identify four major organic solvents: EC, PC, DMC, and EMC. This method was also used to quantitatively analyze EC and PC in three lithium battery electrolyte samples. The results show that the amount of EC in the three lithium battery electrolyte samples was roughly two to five times the amount of PC. The results indicate that the method is suitable for the qualitative and quantitative analysis of organic carbonate solvent components in lithium battery electrolytes.

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