Application News

GC-MS GCMS-QP2050

Analysis of Carbonate Esters, Additives, and Phosphate Esters in Lithium-Ion Battery Electrolyte Using GCMS-QP2050

Shota Hayakawa, Misato Ishimoto

User Benefits

- The integration of GCMS-QP2050 and GC-2050 enables high-precision analysis of compounds in electrolytes while optimizing space utilization.
- The mass spectrometer enables the identification of unknown components.

■ Introduction

In recent years, lithium-ion batteries have rapidly gained traction in fields, including electric vehicles and portable electronic devices, owing to high energy density and long lifespan. This widespread adoption is largely driven by increasing demand for sustainable energy solutions and advancements in technology. The performance of lithium-ion batteries is significantly influenced by the composition and purity of carbonate esters and additives in the electrolyte, as well as by impurities introduced during manufacturing or formed during storage. Therefore, qualitative and quantitative analysis of these components is critically important.

In a previous publication1), quantitative analysis of carbonate esters and additives in electrolytes was demonstrated using the Brevis™ GC-2050 + FID. In this report, equivalent quantitative analyses were conducted using the GCMS-QP2050 (Fig. 1), and additional qualitative examinations of impurities were performed. GCMS-QP2050, with its high analytical performance and space-saving design, contributes to highly precise analyses. Furthermore, combining it with AOC™-30i auto-injector delivers enhanced accuracy, improved analytical stability, and increased productivity.

■ Analysis Conditions

The analytical conditions are shown in Table 1. For liquid injection, the Shimadzu Xtra Life Microsyringe (P/N 221-35400-01), equipped with a titanium alloy plunger and optimized for long-term analysis, was utilized.

Table 1 Analysis Condition

GC-MS Model	: GCMS-QP2050
Autoinjector	: AOC-30i
[GC]	
Collumn	: SH-I-5MS (P/N 221-75940-30) (30 m × 0.25 mm I.D., 0.25 µm)
Inj. Temp.	: 250 °C
Inj. Mode	: Split
Split Ratio	: 50
Carrier Gas	: He, constant linear velocity (40 cm/sec)
Collumn Temp.	: 40 °C (3 min) → 10 °C/min → 160 °C (5 min)
[MS]	
Ion Source Temp.	: 200 °C
Interface Temp.	: 230 °C
Pumping speed	: 255 L/s
Acquisition Mode	: SIM
SIM monitoring *m/z*	: Refer to Table 2

Fig. 1 AOC™-30i+GCMS-QP2050

■ Chromatogram of Mixed Standard Solution of Eight Components

A mixed standard solution comprising eight carbonate esters and additives commonly utilized in electrolytes was prepared. The TIC chromatogram obtained from a 100 mg/L solution analyzed under the conditions of Table 1 is showed in Fig. 2.

Table 2 Eight target carbonate esters and additives with the selected ions for SIM

No.	Compound	Abb.	Quantitative ion (*m/z*)	Qualitative ion (*m/z*)
1	Dimethyl carbonate	DMC	45	59, 62
2	Ethyl methyl carbonate	EMC	45	59, 77
3	Vinylene carbonate	VC	86	42, 58
4	Diethyl carbonate	DEC	45	63, 91
5	Fluoroethylene carbonate	FEC	62	43, 47
6	Ethylene carbonate	EC	43	44, 88
7	Propylene carbonate	PC	57	43, 87
8	1,3-Propanesultone	PS	58	41, 57

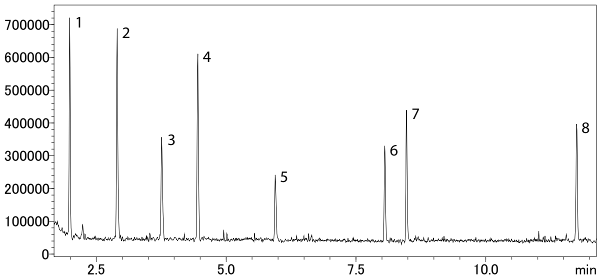

Fig. 2 Chromatogram of mixed standard sample of eight compounds (100 mg/L)

■ Calibration Curve and Repeatability of Mixed Standard Solution of Eight Components

Eight component mixed standard solutions were prepared in dichloromethane at six concentration levels (10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, and 500 mg/L) for the purpose of constructing calibration curves and assessing reproducibility. The calibration curves for each compound are depicted in Fig. 3, demonstrating excellent linearity ($R^2 > 0.999$). In addition, the repeatability (%RSD) of peak area values, determined from five consecutive injections of the 10 mg/L standard solution (Table 3). All compounds exhibited favorable repeatability.

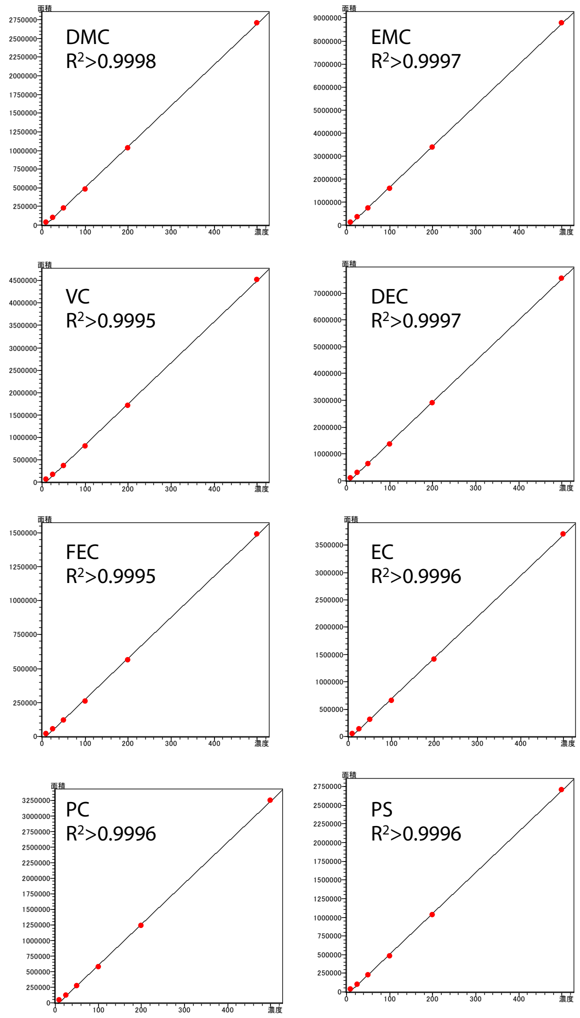

Fig. 3 Calibration Curves of eight compounds

Table 3 Peak area repeatability (%RSD) of 10 mg/L standard solution (n = 5)

Compound (Abb.)	%RSD
DMC	6.3
EMC	6.2
VC	6.4
DEC	6.2
FEC	6.4
EC	5.7
PC	6.0
PS	5.9

■ Quantitative Analysis of Actual Electrolyte samples

Based on the calibration curves described above, four types of commercially available lithium-ion battery electrolytes, each differing in electrolyte composition and contained carbonate esters, were subjected to quantitative analysis (Table 4).

In this study, the samples were diluted 1,000-fold with dichloromethane prior to analysis. If the samples are analyzed in the undiluted state, the effect of electrolyte precipitation will be excessive, and thus reducing analytical efficiency. In addition, such precipitation may lead to device failures.

Sample handling was conducted in a glove box because there is a risk of hazardous reactions between atmospheric moisture and the Li-based electrolyte.

The chromatograms for each sample are shown in Fig. 4, and the quantitative values for the carbonate esters in each undiluted sample are summarized in Table 5. Notably, for the samples containing $LiPF_6$, peaks suspected to be impurities were detected in addition to those of the included carbonate esters (Fig. 4, arrows).

Table 4 The characteristic of four actual samples

	Electolyte	Carbonate esters
Sample A	LiFSI	DMC、EMC、EC
Sample B	LiFSI	DMC、DEC、EC
Sample C	$LiPF_6$	DMC、EMC、EC
Sample D	$LiPF_6$	DMC、DEC、EC

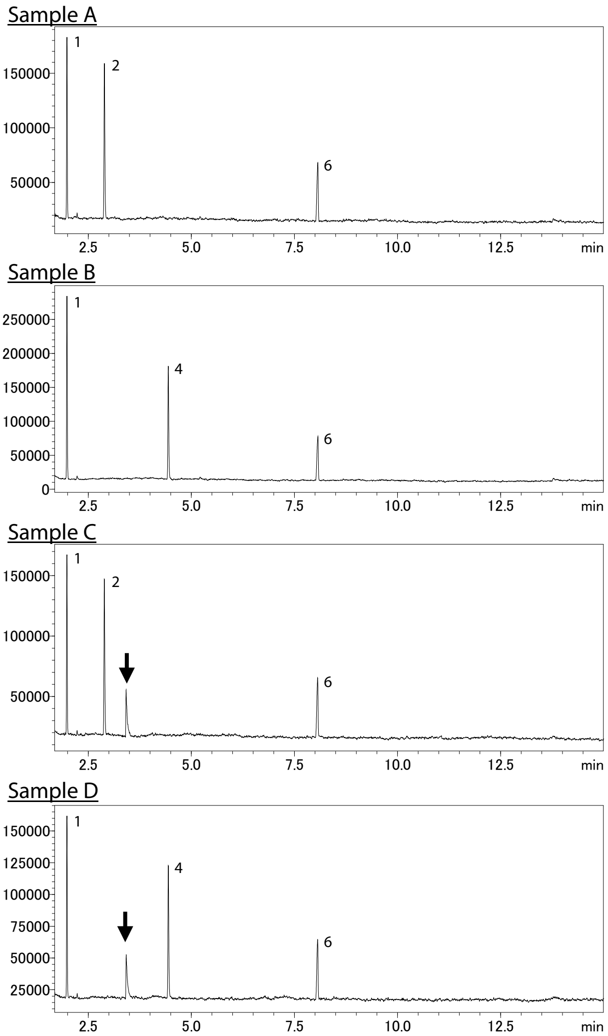

Fig. 4 Chromatograms of four samples

Table 5 Quantitative values of four samples（mg/L）

No.	Compound	Sample A	Sample B	Sample C	Sample D
1	DMC	507	496	527	551
2	EMC	450	—	470	—
3	VC	—	—	—	—
4	DEC	—	438	—	486
5	FEC	—	—	—	—
6	EC	560	539	585	576
7	PC	—	—	—	—
8	PS	—	—	—	—

■ Qualitative Analysis of Impurities in $LiPF_6$-Based Electrolytes using Low Ionization Energy (LEI)

Qualitative analysis was performed on an unknown component in the $LiPF_6$-based electrolyte indicated by the arrows in Fig. 4 using simultaneous Scan/SIM analysis (FASST) (Scan Event Time: 0.3 s, Scan *m/z* Range: 35–500).

Use of $LiPF_6$ as an electrolyte can lead to the formation of volatile phosphate esters, particularly at elevated operating voltages or over extended run times. Dimethyl fluorophosphate (DMFP), which has a molecular ion at *m/z* 128 and a principal fragment ion at *m/z* 98, is one of the phosphate esters[2)].

Although DMFP is not registered in the mass spectral library used in this study, qualitative analysis was conducted using information on the molecular ion, which is critically important for identification. However, in the mass spectrum acquired in Scan mode, the signal intensity for the molecular ion at *m/z* 128 was weaker than that of the fragment ions (upper part of Fig. 6, arrow).

To enhance detection of the molecular ion peak, a low-electron-ionization-energy (LEI) technique was employed. Specifically, the ionization voltage was lowered from 70 V (the standard EI setting) to 14 V. Under these conditions, the signal intensity for the molecular ion at *m/z* 128 increased by approximately four-fold (Fig. 6, bottom, arrow).

Based on prior investigations, the four-fold increase in the *m/z* 128 molecular ion signal in LEI, and the absence of this peak in the LiFSI-based electrolyte, the impurity was inferred to be DMFP. Notably, under standard qualitative workflows, mass spectral library searches and comparison of retention times against reference standards afford straightforward identification of unknown peaks.

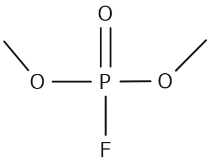

Fig. 5 Dimethyl fluorophosphate（DMFP）

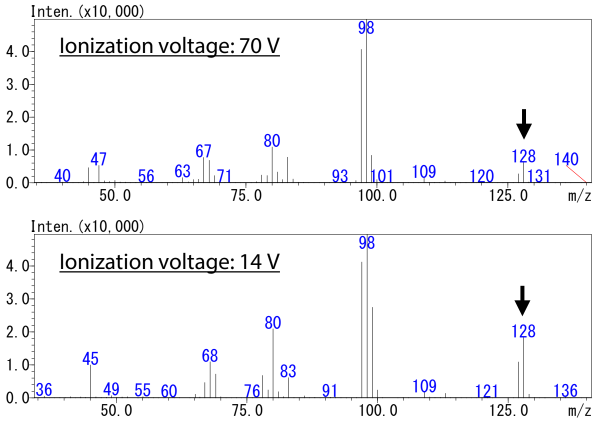

Fig. 6 Mass spectra of DMFP

■ Conclusion

In this study, eight commonly used carbonate esters and additives in lithium-ion battery electrolytes were quantified using the GCMS-QP2050. The standard mixture exhibited chromatographic separation, and the calibration curve indicated excellent linearity. Analysis of four commercial electrolyte samples detected and quantified multiple carbonate esters.

Additionally, impurities were detected in these samples. By applying low-electron-ionization (LEI) to strengthen the molecular ion signal, the impurity was identified as DMFP.

<Related Applications>

1) Analysis of Carbonic Esters and Additives in Lithium Ion Battery Electrolytes, Application News No.01-00708

<References>

2) Weber et al., Ion and gas chromatography mass investigations of organophosphates in lithium ion battery electrolytes by electrochemical aging at elevated cathode potentials. Journal of Power Sources. 306, 193-199 (2016).

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