Agilent
Trusted Answers

Poster Reprint

ASMS 2019
TP742

Investigation and Profiling of Organic Solvent Based Lithium Ion Battery Electrolytes and the Decomposition Products

.Nan Hu

Agilent Technologies (China), Beijing, CHINA

Introduction

The solvent in lithium ion batteries (LIBs) is typically a mixture of cyclic and linear organic carbonates, for example, ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) as shown in Figure 1, while $LiPF_6$ is used as the conducting salt.

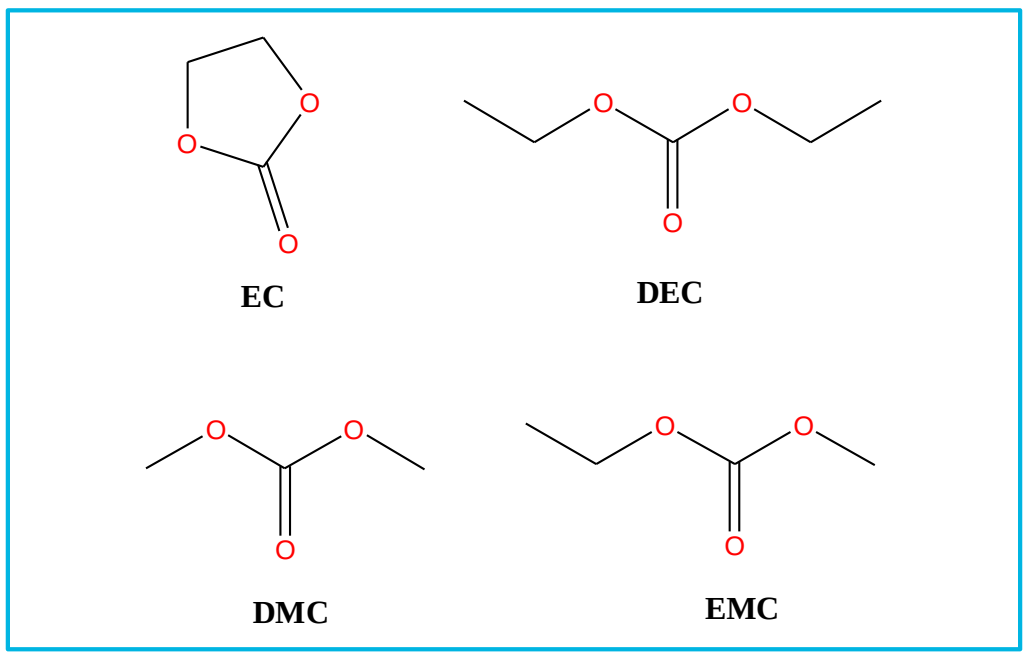


Figure 1. The Structures of organic carbonates.

The components change in different charge-discharge procedures and the decomposition products will give us some hints of aging mechanisms in order for us to improve the qualities of LIBs.

LC-Q/TOF, with high resolution and mass accuracy, is a very valuable tool in the investigation of electrolytes composition changes. It provides formulas and structural information even for PF_6^- and profiles the difference between the decomposition products.

Experimental

Sample preparation

The electrolytes of LIB and several decomposition products were diluted by 50/50 (v/v) Methanol/Water solution.

LC Conditions

1290 Infinity II UHPLC System		
Column	EC-C18 2.1X100 mm	
Mobile phase	A: 0.1% Formic acid in water B: Methanol	
Flow rate	0.3 mL /min	
Oven Temperature	30 ℃	
Injection	2 µL	
Gradient	Time	B
	0 min	5 %
	1 min	5 %
	3 min	50 %
	8 min	95 %
	9 min	95 %
	9.1 min	5 %
	10 min	5 %

MS Conditions

Agilent 6545 Q-TOF Mass Spectrometer	
Ion source	Dual AJS ESI
Polarity	Positive/Negative
VCap	3500 V
Gas Temp	250 ℃
Dry gas	8 L/min (N_2)
Nebulizer pressure	40 psi (N_2)
Sheath Gas Temp	325 ℃
Sheath Gas Flow	11 L/min (N_2)

Component Confirmation in the LIB Solvent

In our electrolytes sample, the solvent mainly contains DEC, EMC and FEC. $LiPF_6$ is used as the conducting salt and a trace of additives contain S and N.

Although the carbonates is usually suitable for GC analysis, the LC-Q/TOF system is also powerful by screening $[M+H]^+$ and $[M+Na]^+$ ions with score>80 and mass error<1mDa (Figure 2). The fragment ions, even small as $CH_3O_3^+$, can be detected which provide structural information. The signal of salt PF_6^- can also be observed with good mass accuracy.

We also find some minor components such as EC and additives containing N. Their formulas are proved by accurate mass and isotope patterns. The structural information is provided by accurate MS/MS analysis.

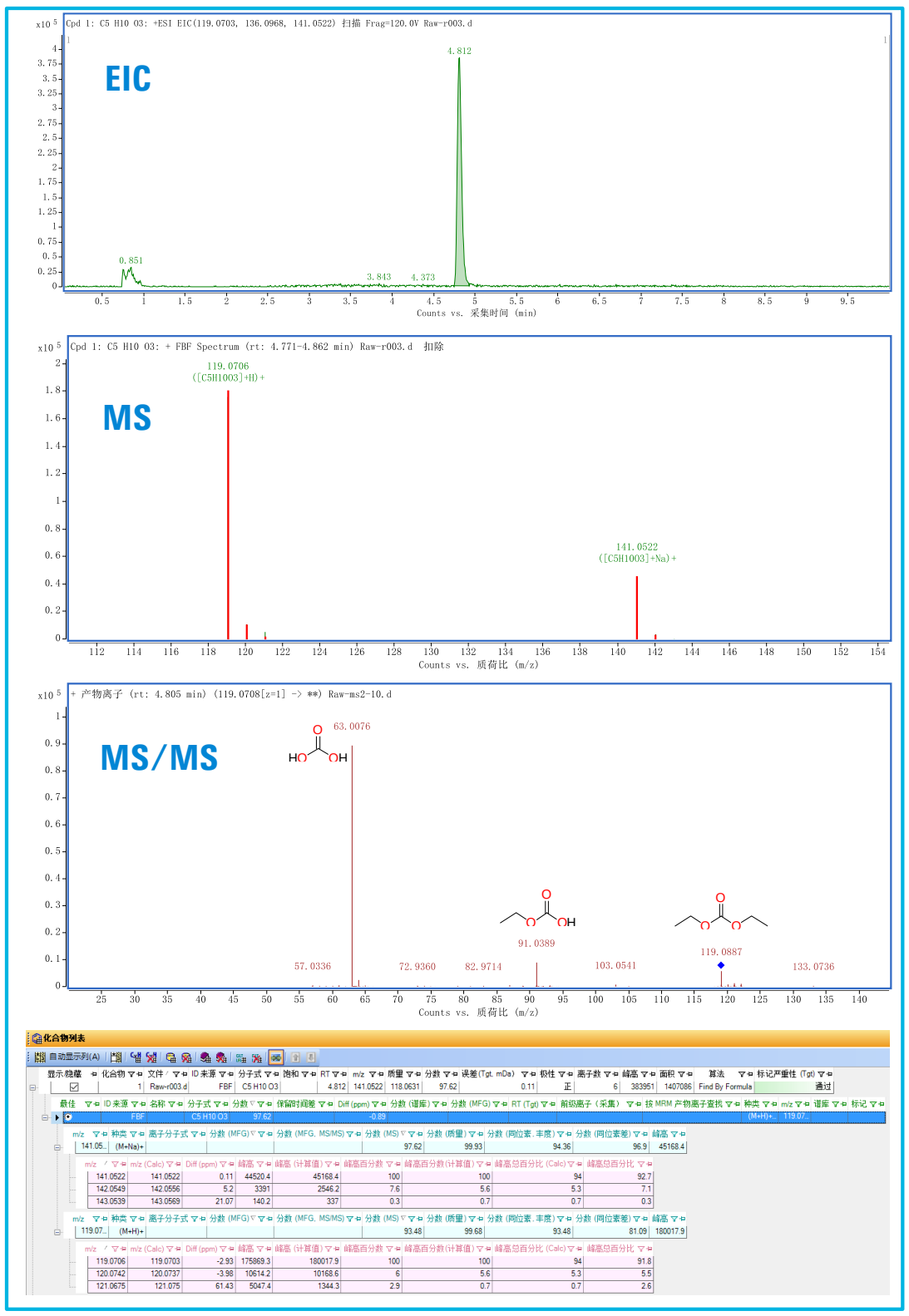


Figure 2. The Chromatograph and Mass spectra of DEC.

Profiling of Decomposition Products

4 of the decomposition products with different charge-discharge procedures were analyzed by LC-Q/TOF system (3 technical replicates) and profiled by Mass Profiler Professional (MPP) and related software.

From clustering analysis (Figure 3), decomposition products show obvious differences from original electrolyte.

TMP is a major component that cause the difference. The structure and EIC chromatograph are shown in Figure 4. The concentration is higher in product 1 and 2, lower in product 3 and 4 and rarely in original electrolyte.

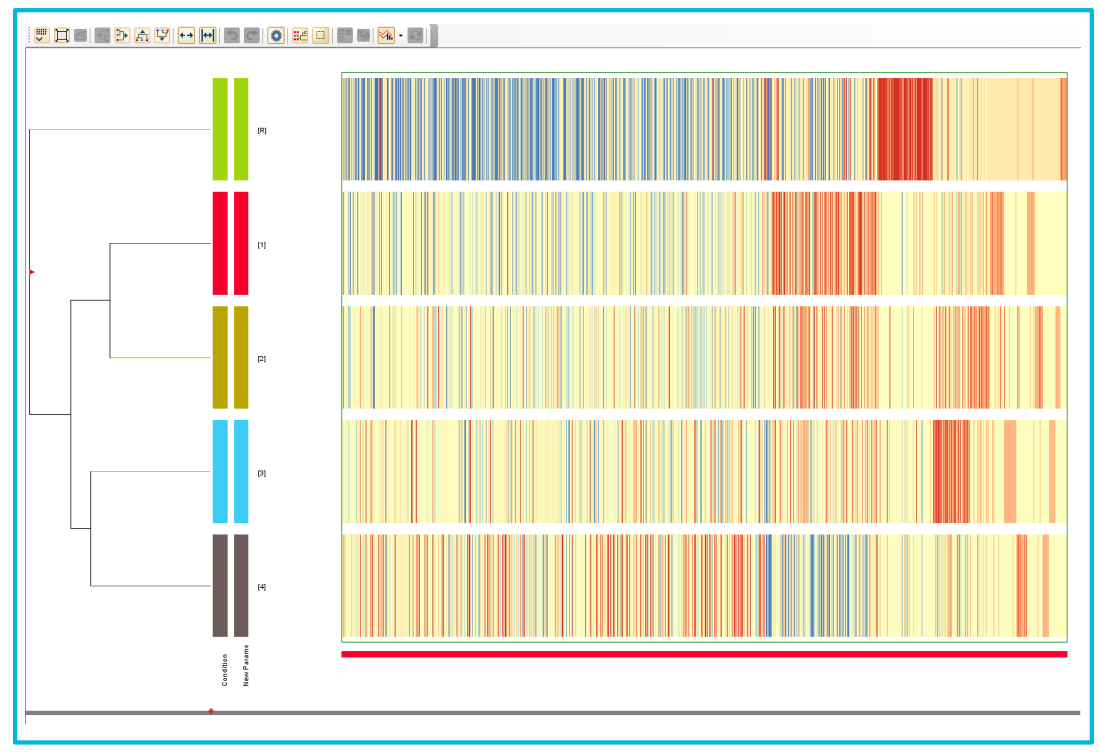


Figure 3. Clustering analysis of LIB solvent and the decomposition products.

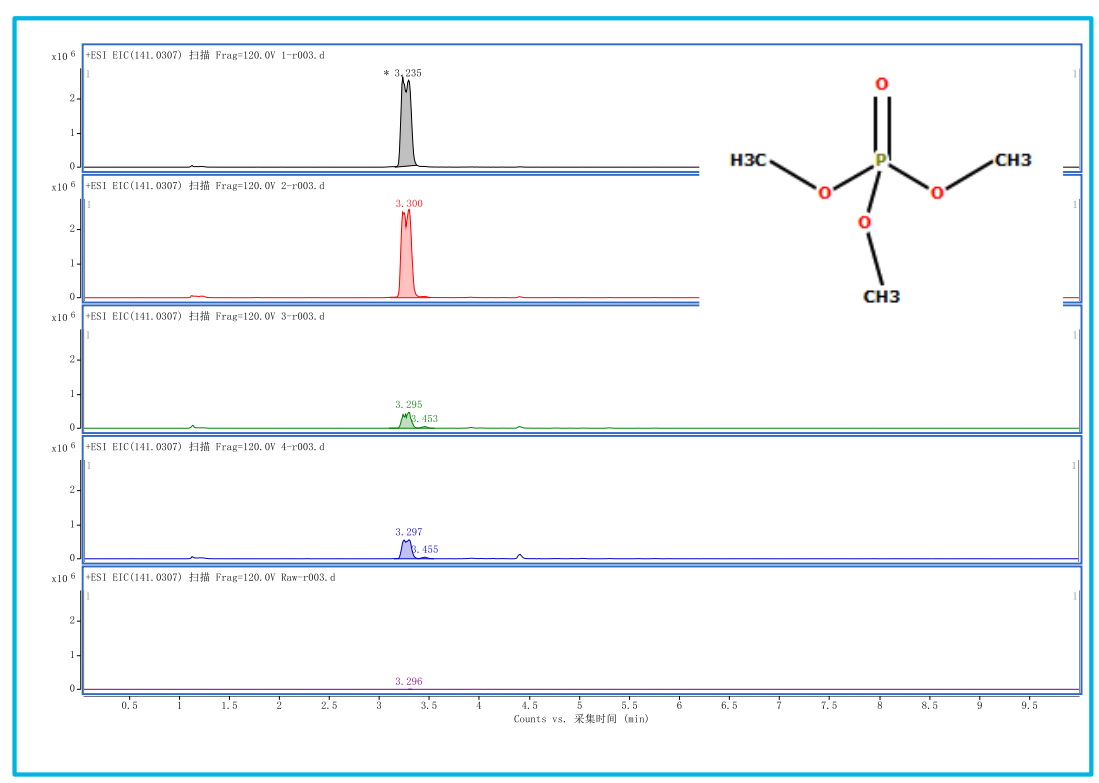
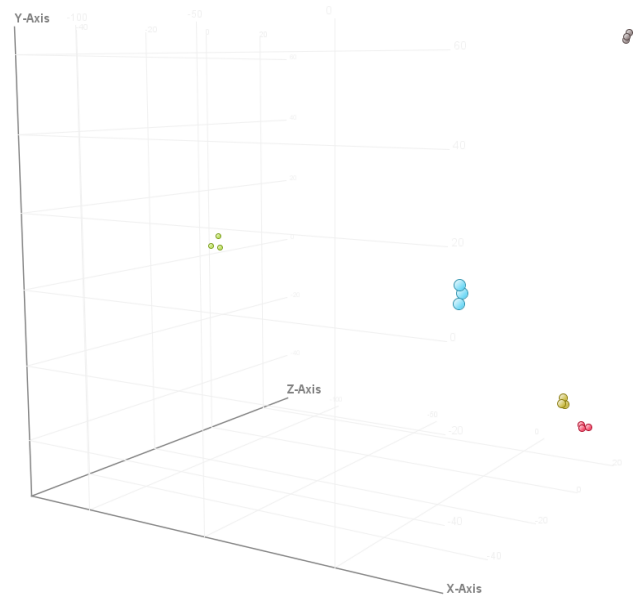
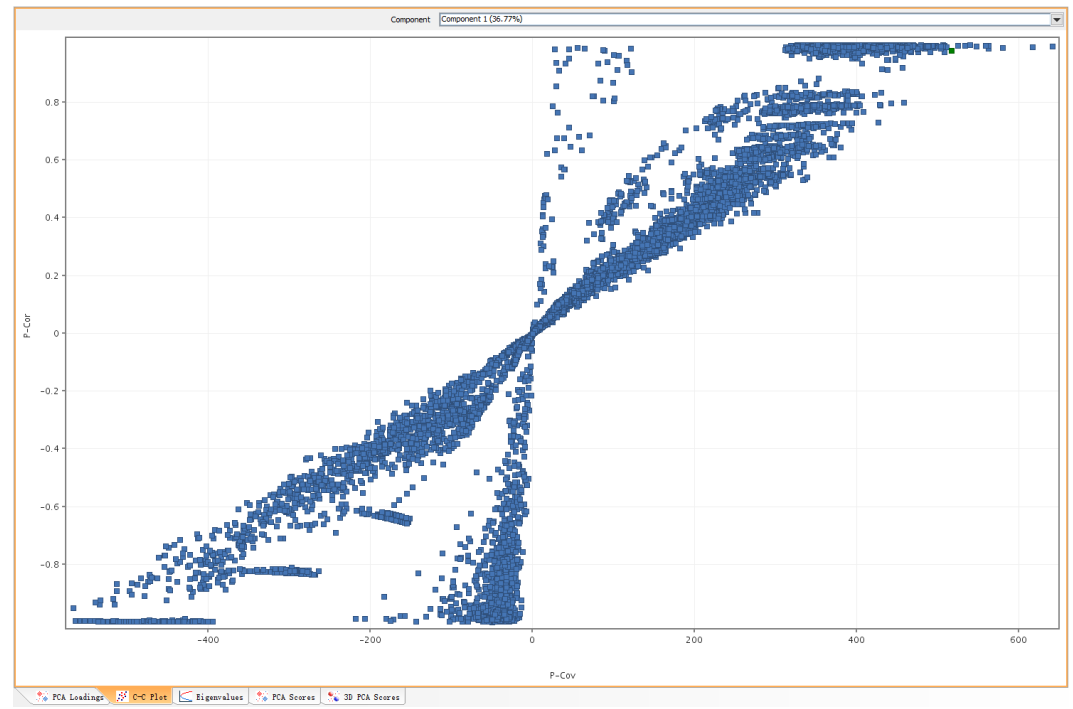


Figure 4. The structure and EIC chromatograph of major different compound TMP.

Results and Discussion



3D PCA



C-C Plot

Figure 5. Principal component analysis (PCA) of four decomposition products and the original electrolyte.

Principal component analysis (PCA, Figure 5) was applied to find the varying compounds in decomposition products. Figure 6 shows an interesting compound, $C_9H_{19}O_7P$, which exists only in product 4. According to the literature, this compound is related to high temperature processes.

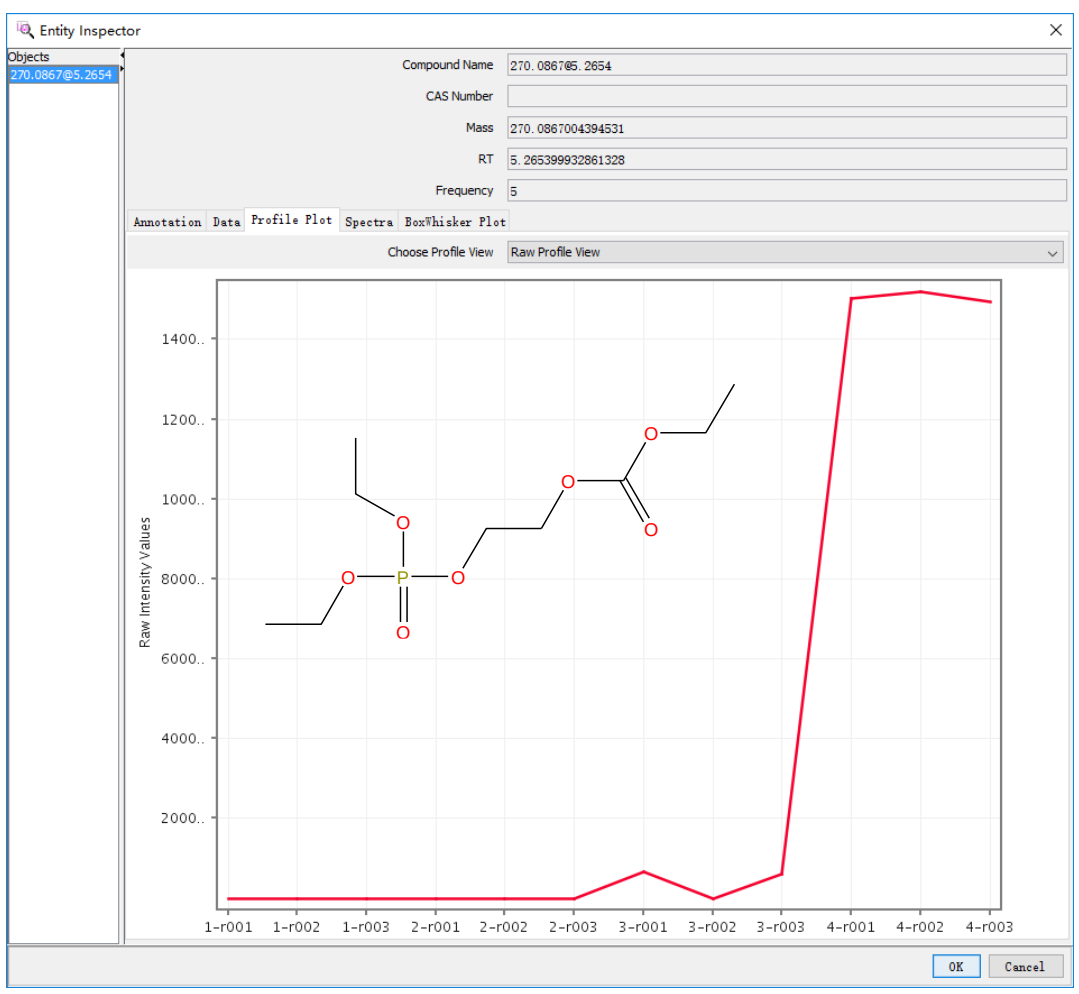


Figure 6. The possible structure of the compound existing only in product 4.

Conclusions

- The LC/Q-TOF is suitable for LIB electrolytes analysis.
- With high resolution and a high mass accuracy, LC/Q-TOF provides formulas and structural information for the organic carbonates.
- The decomposition products profiling provides some hints of aging mechanisms and helps understand as well as improve the qualities of LIBs.

References

[1] Carola Schultz, et al. *Anal. Chem.* 2016, **88**, 11160–11168.

[2] Carola Schultz, et al. *RSC Adv.* 2017, **7**, 27853–27862.

[3] ZHUANG Quang-chao, et al. *Electrochemistry*, 2001,**7**, 4, 403–410.

[4] Hirofumi Moriwaki, et al. The TRC News No. 117, 2013, 17-20.

Published in USA, June 2, 2019

Agilent
Trusted Answers