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Analysis of degradation products in electrolyte for rechargeable lithium-ion battery through high mass accuracy MS^n and multivariate statistical technique

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Introduction

Rechargeable lithium-ion batteries (LiB) are one of the major power sources for portable electronic devices and electric vehicles because of their high voltage and high energy density (Fig. 1-(a)). The electrolyte of a LiB is consisting of a lithium salt in an aprotic organic solvent. The typical operational potential of a LiB is between 0 and 5 V. Therefore, solvent can be reduced or oxidized at the negative and positive electrodes during the battery charging process. As a result, various degradation products are generated in the electrolyte and cause some problems such as a decrease in the capacitance of battery (Fig. 1-(b)). Here, we present the analysis method of degradation products generated in electrolyte using high mass accuracy MS^n and multivariate statistical technique.

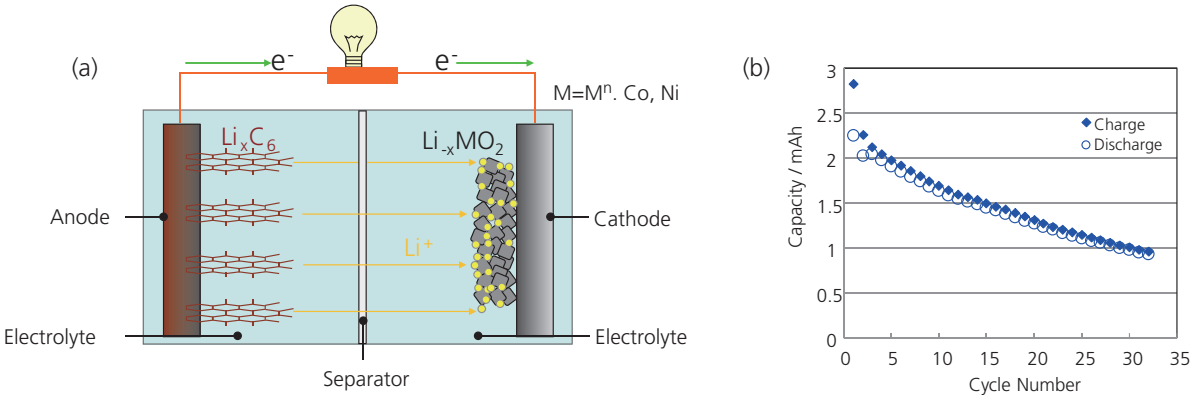


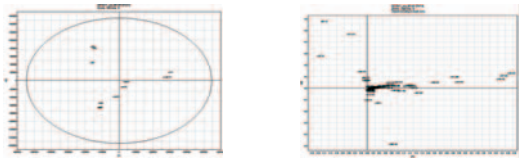
Fig. 1 Rechargeable lithium-ion battery component of lithium-ion battery (a), a decrease in the capacitance of battery (b).

Experiment

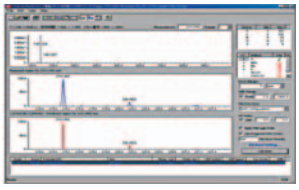
The electrolyte was a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC : DEC = 1 : 1 vol%) containing 1M lithium hexafluorophosphate ($LiPF_6$). The electrolyte A taken from unused lithium-ion battery and the electrolyte B taken from lithium-ion battery repeated charge and discharge cycles (60℃, 30 times) were used as samples. Those samples were prepared 1/10 dilution with methanol for LCMS-IT-TOF (Shimadzu Corporation) measurement. Orthogonal Partial Least Squares Discriminant Analysis (OPLS-DA) was performed using data acquired by LCMS-IT-TOF measurement of electrolyte A and electrolyte B (n=3) to find the compounds generated in electrolyte B. Then, those compounds were identified chemical formula using software "Formula Predictor" (Shimadzu Corporation). SIMCA-P+ (Umetrics) and Profiling Solution (Shimadzu Corporation) were used for OPLS-DA (Scheme).

1. Acquisition of the high mass accuracy MS^n data (LCMS-IT-TOF)

2. Peak alignment and generation of peak list (Profiling Solution)



3. Searching of degradation products (SIMCA-P+)



4. Prediction of chemical formula (Formula Predictor)

Structual estimation

Scheme Work flow of the analysis of degradation product in electrolyte for LiB

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Results and discussion

MS data of electrolyte A and electrolyte B were acquired using LCMS-IT-TOF under the analytical conditions shown Table 1. On the score plot of OPLS-DA, the group of electrolyte A and electrolyte B were located at left side and right side, respectively (Figure 2-(a)). 15 unique ions of electrolyte B were observed at right side on S-plot (Figure 2-(b)). And, those ions were not detected on the extracted ion chromatogram (EIC) of electrolyte A (Fig. 3). These results suggested that those ions were degradation products generated in the electrolyte of lithium-ion battery repeated charge and discharge 30 cycles.

Table 1 LCMS analytical conditions

Column	: Shim-pack FC-ODS (2.0 mmI.D.x150 mm, 3 mm)
Flow rate	: water
Column temp.	: 0.2 mL/min
Mobile phaseA	: 40°C
Mobile phaseB	: methanol
Time prog.	: 5%B (0 min) → 55%B (30 min) → 5%B (30.01 min)
Injection volume	: 1 µL
Ionization mode	: ESI(+)
Probe voltage	: 4.5 kV
CDL temperature	: 200°C
BH temperature	: 200°C
Nebulizing gas	: 1.5 L/min
Drying gas	: 0.1 MPa
Scan range	: *m/z* 80 - 1000

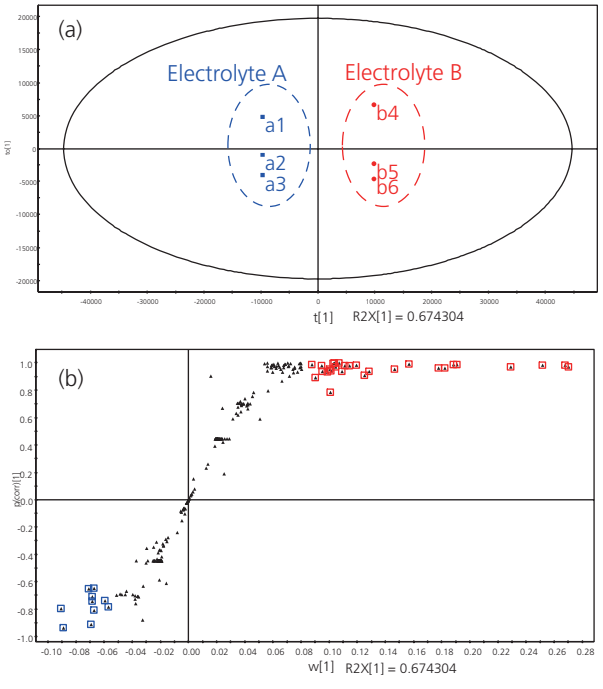

Fig. 2 The result of OPLS-DA, score plot (a), S-plot (b)

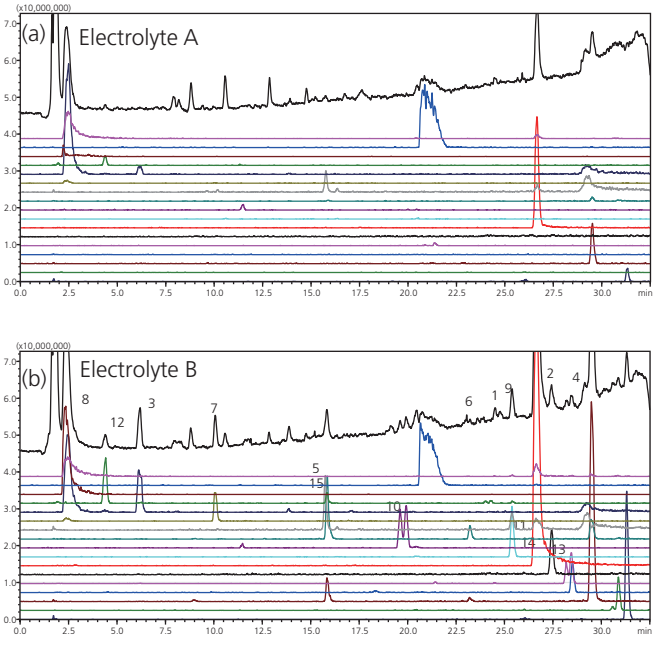

Fig. 3 EICs of ions detected in Electrolyte B (b)
These ions were not detected on EIC of electrolyte A (a).

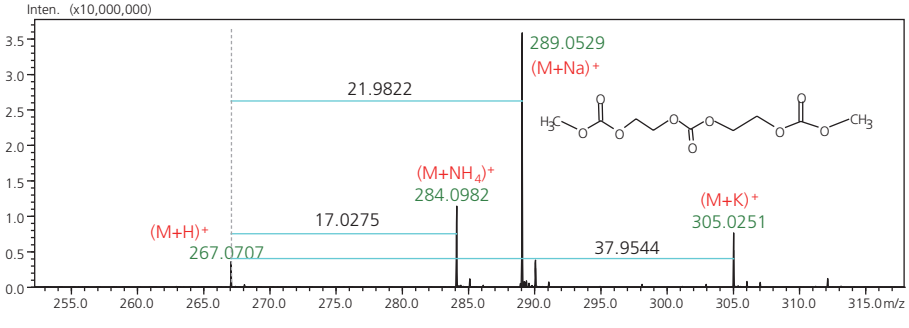

Fig. 4 MS data and predicted structure of peak number 2 (*m/z* 284.0982) being one of 15 unique ions of electrolyte B

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The formula of peak number 2 (*m/z* 284.0982) being one of 15 unique ions of electrolyte B was predicted as $C_9H_{14}O_9$ (polycarbonate) using high mass accuracy MS data and formula predictor. Indeed, the structure of $C_9H_{14}O_9$ was predicted as H_3C-(OCO_2-C_2H_4)$_2$-OCO-CH_3 referring to some articles on degradation products in electrolyte. MS^n of the ion (*m/z* 284.0982) also was measured to determine the validity of the predicted chemical structure. Each product ions and neutral loss in MS^2 and MS^3 data showed that the predicted structure of $C_9H_{14}O_9$ was correct.

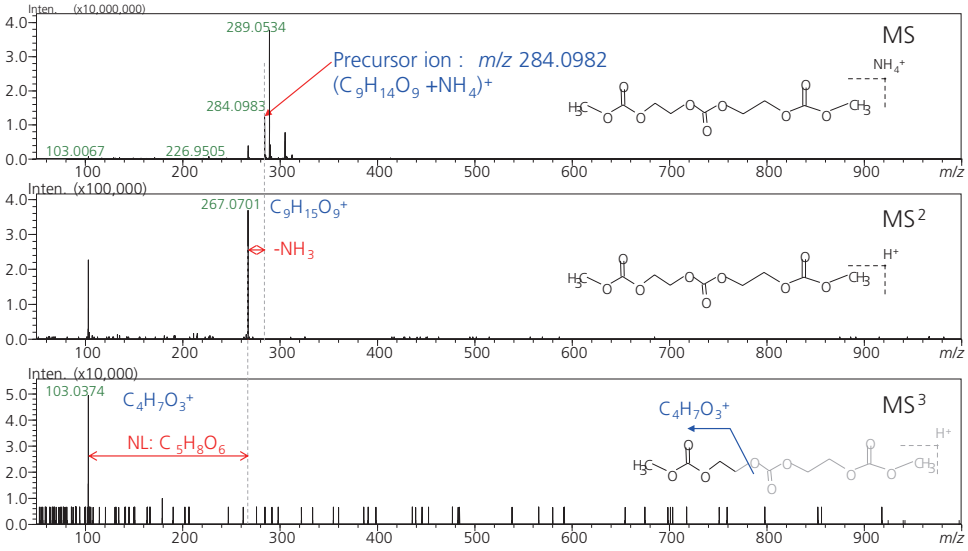

Fig. 5 MS^n data of peak number 2 (*m/z* 284.0982) detected in electrolyte B

By the same method, formula of peak number 13 (*m/z* 283.0336) was identified as $C_3H_7O_4P$. Structure of it was determined as phosphate shown in Fig. 6.

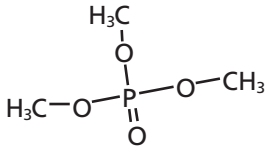

Fig. 6 of Structure peak number 13

Conclusion

- It was clear that the chemical species of degradation products generated in the electrolyte with increasing charge and discharge cycles were carbonate and phosphate from result of this study.
- The formulae of 15 degradation products detected in Electrolyte B were identified as below.

Peak No.	*m/z*	R.T.(min)	Ion species	M.W	Predicted formula	Mass accuracy (ppm)
1	229.0678	26.645	$(M+Na)_+$	206	$C_8H_{14}O_6$	-2.62
2	284.0982	20.401	$(M+NH_4)_+$	294	$C_9H_{18}O_9$	-0.35
3	295.1032	29.482	$(M+H)_+$	170	$C_{11}H_{18}O_9$	+1.69
4	177.0512	6.178	$(M+Li)_+$	382	$C_4H_{11}O_5P$	+2.92
5	400.1458	31.294	$(M+NH_4)_+$	272	$C_{14}H_{22}O_{12}$	+2.50
6	295.056	15.833	$(M+Na)_+$	244	$C_8H_{17}O_8P$	-1.36
7	262.0853	25.374	$(M+NH_4)_+$	184	$C_{10}H_{13}O_5P$	+1.53
8	185.0577	10.054	$(M+H)_+$	250	$C_5H_{13}O_5P$	+4.32
9	251.1111	27.416	$(M+H)_+$	268	$C_8H_{17}O_5F_3$	+2.39
10	269.0162	19.879	$(M+H)_+$	332	$C_7H_7O_2F_6P$	-2.60
11	350.1003	28.426	$(M+NH_4)_+$	138	$C_8H_{17}O_7F_4P$	+1.14
12	283.0336	4.385	$(2M+Li)_+$	358	$C_3H_7O_4P$	+4.32
13	381.0938	30.857	$(M+Na)_+$	270	$C_{12}H_{23}O_{10}P$	-1.57
14	293.0777	28.487	$(M+Na)_+$	222	$C_9H_{19}O_7P$	+1.36
15	245.0641	15.713	$(M+Na)_+$	266	$C_8H_{14}O_7$	-0.41

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