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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 MSn and multivariate statistical technique.

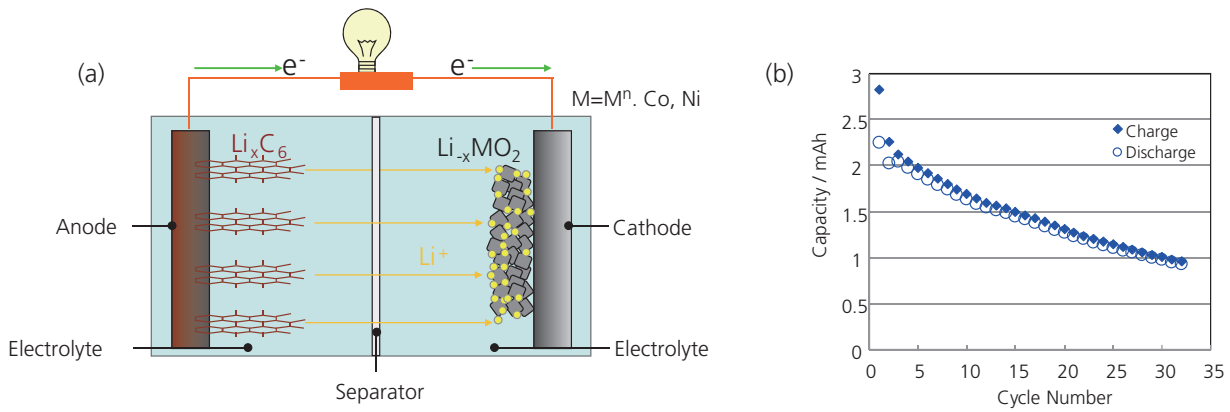
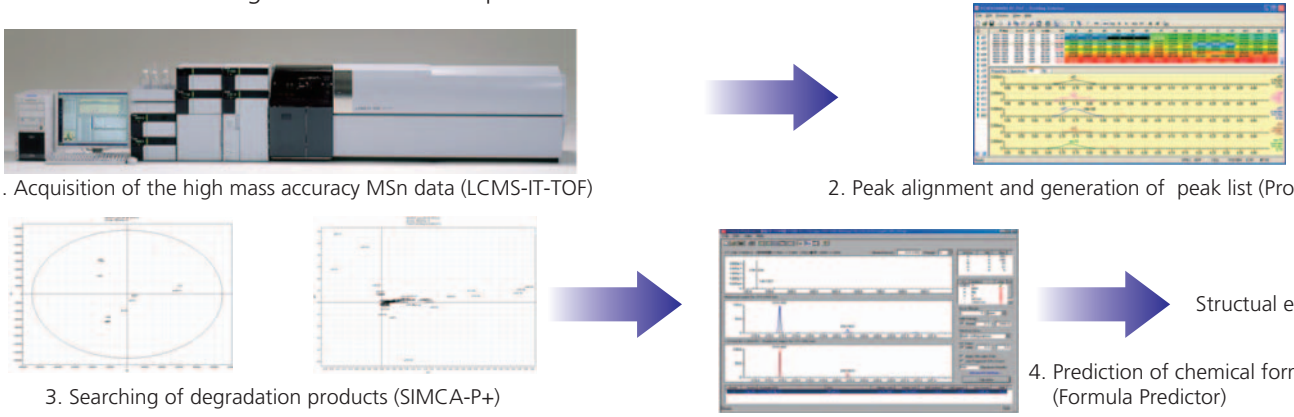



Fig. 1 Rechargeable lithium-ion battery component of lithium-ion battery (a), a decrease in the capacitance of battery (b).

## 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).




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 |

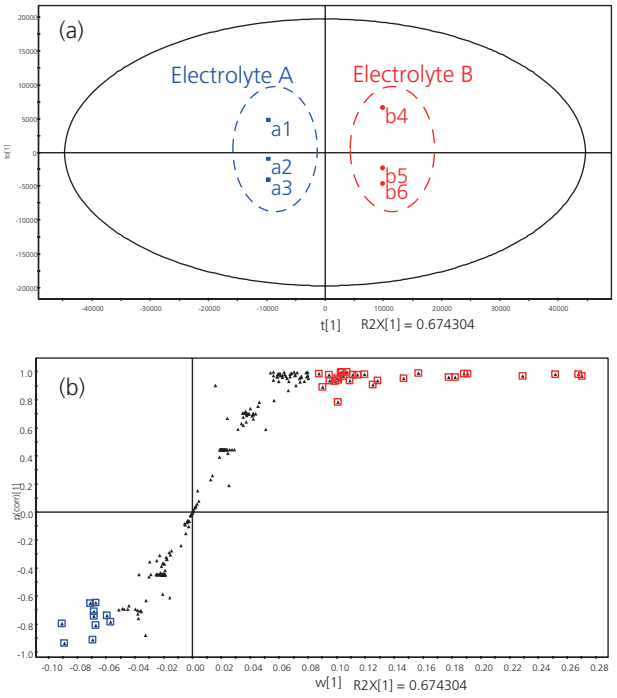


Fig. 2 The result of OPLS-DA, score plot (a), S-plot (b)

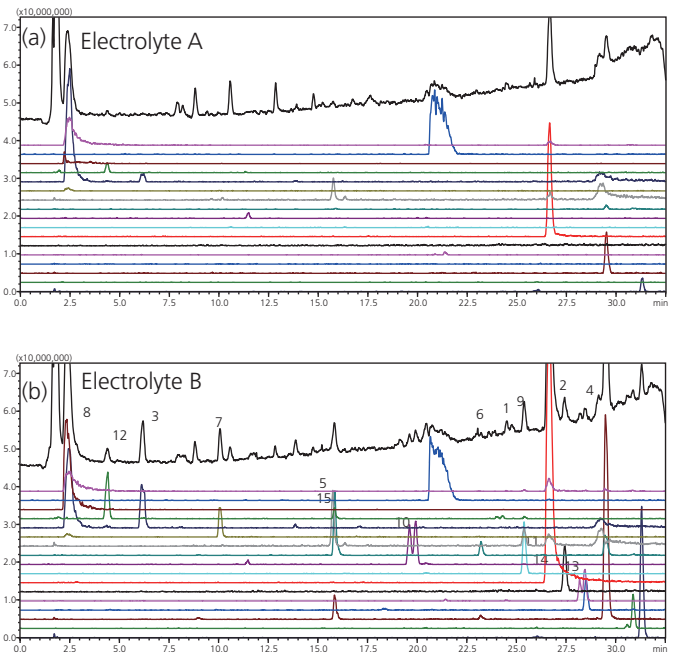


Fig. 3 EICs of ions detected in Electrolyte B (b)
These ions were not detected on EIC of electrolyte A (a).

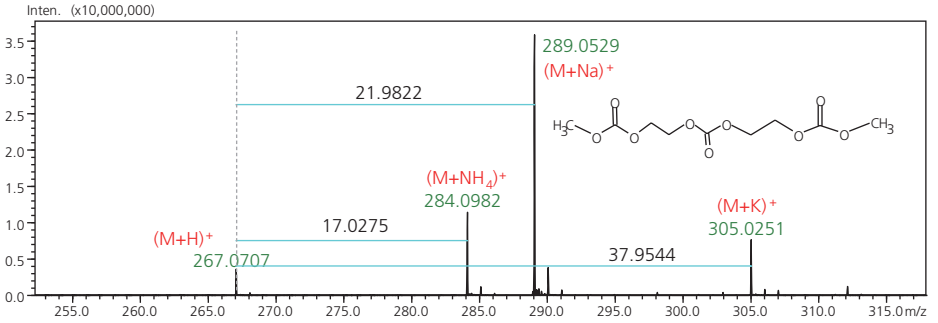


Fig. 4 MS data and predicted structure of peak number 2 (m/z 284.0982) being one of 15 unique ions of electrolyte B

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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.

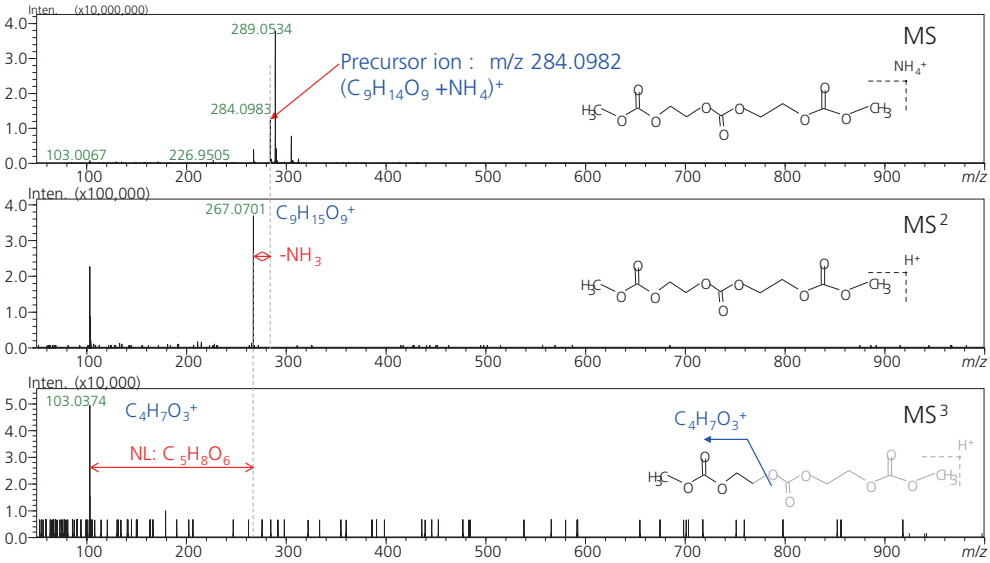


Fig. 5 $MS^n$ data of peak number 2 (*m/z* 284.0982) detected in electrolyte B

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.

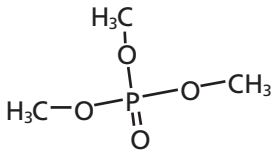

Fig. 6 of Structure peak number 13

# 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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