Liquid Chromatography-Quadruple Time of Flight Mass Spectrometry Analysis of Products in Degraded Lithium-Ion Batteries

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The electrode surfaces of degraded lithium-ion batteries (LIB) were analyzed by liquid chromatography-quadrupole time of flight mass spectrometry (LC-QTOF/MS). The solid-electrolyte interphase (SEI) layer influences the performance of LIBs. Therefore, we conducted a study aimed at clarifying the deterioration mechanism of LIBs by examining the components in the SEI before and after degradation due to cycling. We believe that the change in the mass transfer characteristics at the electrode interface influenced by SEI deterioration can be clarified via LC-QTOF/MS, which would allow elucidation of the deterioration mechanism. The analysis results showed that the degradation products contain multiple components, including polymers of carbonate compounds and phosphate esters, which are formed via electrochemical and chemical reactions, resulting in remarkably reduced capacity. The results suggest that LC-QTOF/MS is a valuable technique for the degradation analysis of LIBs.

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Since the invention of lithium-ion batteries (LIB), many research groups have actively conducted research on improving the battery performance.1–3 Excellent properties, including high capacity and high energy density, have been achieved owing to the work conducted so far. As a result, LIBs are not only used as power sources for mobile devices such as phones and personal computers, but are also used as power sources in electric vehicles, aviation, etc., as well as large-scale stationary power sources for smart grids.4–6 Owing to the remarkable expansion in their applications, it is necessary that LIBs are highly durable and safe in various environments; as a result, durability tests for LIBs have been conducted under diverse settings. In addition, the battery deterioration mechanisms in various cases have been widely studied.1–4

To accurately understand the deterioration mechanism, it is necessary to utilize precise mass spectrometry techniques to determine the structure and composition of materials present at the electrode interface, including the electrode surface layer (i.e., solid electrolyte interface or SEI). By conducting a proper structural analysis, the deterioration mechanism can be discussed in terms of the exact reactions occurring at the interface. The chief analytical techniques that are used to structurally analyze the SEI layer include X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, and nuclear magnetic resonance spectroscopy (NMR).7–21 All of these techniques enable the estimation of the skeletal structures of the compounds present in the SEI. However, since the structural formula obtained by these techniques is not supported by precise mass information, the exact reactions governing the deterioration mechanism cannot be deduced from these techniques. On the other hand, the use of precise mass spectrometry for analyzing the electrode interface, including the SEI layer, may allow accurate elucidation of the degradation behavior at the electrode interface by distinguishing between the degradation components and the components of the intrinsic SEI layer. Further, methods for suppressing degradation may be proposed based on stoichiometric considerations. Therefore, in the present study, we examined the degradation behavior of the electrode interface using liquid chromatography-quadrupole time of flight mass spectrometry (LC-QTOF/MS), from which precise mass spectrometry data can be obtained. In the LC/MS analysis, mass spectrometry data can be measured with four orders or higher accuracy by introducing the quantitative time-of-flight (QuanTOF) technique, along with several other techniques (accurate calibration and optimization of column configuration, etc.) that complement QuanTOF for improving the accuracy and sensitivity. As a result, mass of the order of 1 mDa can be detected. Owing to this level of sensitivity, structures of compounds for which no reference data exist can be elucidated. In addition, trace amounts of organic components with molecular weights of up to approximately 100,000 or high-boiling-point substances that cannot be analyzed by GC/MS can be analyzed with LC-QTOF/MS. In summary, LC-QTOF/MS has allowed the detection of a wider range of material. In battery research, a number of studies have been conducted by employing LC-QTOF/MS for the degradation analysis of electrolytes.22,23 However, to the best of our knowledge, no study has reported on the degradation analysis of electrode interfaces, including the SEI layer, by using the LC-QTOF/MS technique. Therefore, in the present study, we have examined the feasibility of using LC-QTOF/MS for identifying the products formed near the electrode interface during the degradation of a battery. In addition, we have explored pretreatment methods for recovering the degradation products in a form suitable for analysis by LC-QTOF/MS.

The degradation mode was selected to replicate the typical use environments of commercial batteries. Therefore, we selected a mode in which cycle deterioration occurs at high temperatures. For commercial LIBs, temperatures on the order of 45–60 °C during use are normally considered to be high temperatures24 and degradation in a 45 °C environment resembles the degradation behavior at room temperature (∼25 °C). However, the degradation reaction that occurs at temperatures over 80 °C is considered to be different because the temperature dependence of the capacity drop at elevated temperatures deviates from the Arrhenius equation.25,26 Owing to the expanded applications of the batteries and the increasing global temperatures in recent years, the service environments for batteries are becoming increasingly severe and the temperatures are shifting to higher values. Therefore, in this study, 60 °C was set as the upper temperature limit for normal battery use and the battery degradation behavior was examined. We chose this temperature because we believe that the temperature of the battery cases of automotive batteries and stationary batteries in outdoor summer-time environments reach 60 °C.

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Experimental

Outline of analytical methods and devices.— Fourier transform infrared (FT-IR) spectrometry analysis.— Although materials cannot be precisely identified with FT-IR spectrometry, the main functional groups can be determined, from which the basic structure of compounds can be deduced. It is also a convenient technique, since trace amounts of both solid and liquid samples can be measured without any pretreatment. The LIB electrodes and liquids such as electrolytes were directly introduced in a sealed cell in a glove box and the micro amount of both solid and liquid samples can be measured without any pretreatment. The data from 200 scans were integrated to obtain the final spectra. While measurements at aperture sizes ranged from 100 μm × 100 μm to 10 μm × 10 μm are possible with this instrument, in this study, the measurements were conducted at an aperture size of 50 μm × 50 μm only, since it has been previously confirmed that stable spectra can be obtained with this aperture size.27 A transmission BaF2 window (diameter: 10 mm) was used on the top of the sealed cell used for micro-FTIR measurements to observe the electrode surface. Thus, the measurement positions could be determined by observing the sample.

LC-QTOF/MS analysis.— For the LC-QTOF/MS analysis, Xevo G2-S TOF (Waters Corporation) was used. The analytical conditions are shown in Tables I–III. Briefly, this device consists of an LC section, an ionization device, a QTOF/MS section, and a detector. The components of the sample are separated by the LC column. Next, in the ionization device, which is installed in the first stage of the QTOF/MS section, the sample was ionized with either positive or negative ions by the electrospray (ESI) method. The ionized molecules were then passed through a quadrupole mass filter to enhance the mass detection accuracy, followed by fragmentation by impact with inert gas molecules (Ar). After dissociation, the molecular ions were introduced into the TOF section. In the TOF section, the ions were accelerated to high speeds under the influence of a large electric field and passed through a dual-stage-type reflectron to achieve high sensitivity and resolution. Subsequently, the ions flew through the drift tube and reached an ion detector, depending on the dynamic range.

Sample preparation.— Fabrication of laminated LIBs.— Lithium cobalt oxide (LiCoO2) and graphite were used as the active materials for the positive and negative electrodes, respectively. For the positive electrode, LiCoO2 was mixed with acetylene black and polyvinylidene difluoride (PVDF) in the ratio of 90:5:5 by weight, whereas for the negative electrode, graphite and PVDF were mixed in the ratio of 95:5 by weight. N-Methyl pyrrolidinone (NMP) was added to the mixtures as the solvent, forming slurries, which were coated on one side of an aluminum foil in the case of the positive electrode (15 mg/cm2) and a copper foil in the case of the negative electrode (5.5 mg/cm2). The coated metal foils were then heated and vacuum dried at 120 °C, with 10% pressing. The positive and negative electrodes were cut to sizes of 70 mm × 70 mm and 74 mm × 74 mm, respectively. Aluminum and nickel tabs were welded to the positive and negative electrodes, respectively, as leads for passing current. Porous polypropylene film (74 mm × 74 mm) were used as separators. A cell consisting of a positive electrode, separator, and negative electrode was then assembled in a dry room and placed in aluminum-laminated bags. The electrolyte used was 1 M lithium hexafluorophosphate (LiPF6) in a 1:1 (v:v) mixture solvent of ethylene carbonate (EC) and diethyl carbonate (DEC). This electrolyte was introduced into the bag, and after permeation under reduced pressure, the aluminum-laminated bag was sealed in a way that allowed leads of proper length to extend from the bag. Since the purpose of this experiment was to clarify the basic degradation behavior of the electrodes, the fundamental compositions of the electrode slurries and electrolyte were not changed and no performance-enhancing additives were used nor any physical or chemical pretreatment of the current-collecting foil was conducted to improve the adhesion between the foil and the active materials. The configuration of the laminated cell is shown in Figure 1. We added one extra separator on the electrode side of the laminate cell when assembling the cell. This way, the reaction product on the surface of the electrode during charging and discharging that accumulated around the electrode surface can be sampled separately from the electrolyte.

Electrochemical measurements and cycle deterioration tests.— The electrochemical characteristics of the laminated battery were measured using a battery charge/discharge system (Hokuto Denko Corporation). Prior to the initial capacity measurements, the cells were subjected to two charge/discharge cycles as the aging treatment. Charging was conducted in the constant current-constant voltage (CC-CV) mode at 0.1 C with an end-of-charge voltage of 4.2 V, whereas the discharge was conducted in the CC mode with an end-of-discharge voltage of 3 V and at a rate of 0.1 C at 25 °C. The discharge capacity obtained in the second cycle is reported as the initial.
capacity of the battery. A rest time of 5 min was allowed between each charging and discharging operation. In the cycle deterioration tests, the cells were subjected to up to 200 charging/discharging cycles. The charging cycles were conducted in the CC-CV mode with an end-of-charge voltage of 4.2 V at a rate of 1 C, whereas the discharge was conducted in the CC mode, with an end-of-discharge voltage of 3 V at a rate of 1 C at 60 °C. Rest time of 5 min was allowed between each charging and discharging operation. For measuring the capacity after each cycle test, the cells were subjected to one charge/discharge cycle with an end-of-charge voltage of 4.2 V in the CC-CV mode (charging rate of 0.1 C) and an end-of-discharge voltage of 3 V in the CC mode (discharge rate of 0.1 C) at 25 °C. The discharge capacity obtained after this cycle was regarded as the capacity after the cycle test.

Surface analysis of the electrodes.— A method for recovering the degradation products for use in the LC-QTOF/MS system was studied by qualitative analysis via FT-IR. First, the laminated cell was opened in the glove box. The cathode and the anode were then cut to sizes of 10 mm × 10 mm, and the electrodes were immediately placed separately in vials in the glove box. The samples were then rinsed with 3 mL of acetonitrile, after which they were placed in an ultrasonic cleaner with acetonitrile. An extraction treatment was performed for various durations up to 30 min. The extracts, containing substances from the electrode surfaces, the electrolyte in the vicinity of the electrodes, and the product were recovered in the acetonitrile solvent and used as samples. These samples were qualitatively analyzed using FT-IR. The electrode surfaces, before and after cycle deterioration, were analyzed using micro-FT-IR measurements. The laminated cell was opened in a glove box, and the cathode and the anode were cut to sizes of 10 mm × 10 mm. The samples were immediately introduced in a sealed cell for micro-FT-IR measurements in the glove box under conditions described in section Fourier Transform Infrared (FT-IR) spectrometry analysis.

The electrode and the product samples for mass spectrometric analyses using LC-QTOF/MS were prepared as follows. First, the laminated cell subjected to the deterioration tests was opened in the glove box. The positive and negative electrodes were removed and separated by the separate sheets and removed from the laminated cell. The positive and negative electrodes were mixed in equal amounts in the glove box, placed in a vial, and used as LC-QTOF/MS samples.

Results and Discussion

Electrochemical analysis of the laminated cell.— Figure 2 shows the charging and discharging curves, corresponding to the capacity measurements of the laminated cell. The cell capacity was measured at 25 °C after subjecting the cell to 200 cycles at a rate of 0.1 C at 60 °C. For comparison, the charging and discharging curves measured at 25 °C at a rate of 0.1 C obtained before the deterioration tests are also shown.

In the initial charging curve obtained before the deterioration tests, plateaus were observed at approximately 3.72, 3.85, and 4.10 V during the initial voltage increase. Similarly, in the discharging curve, plateaus were seen at approximately 4.05, 3.80, and 3.68 V. Interestingly, the voltage plateaus observed during discharge are 0.05 V lower than the corresponding plateaus observed during charging, in all the cases. The appearance of the plateaus in the charging and discharging curves is a distinctive feature of cells with LiCoO₂ as the positive electrode. Since plateaus were observed at very close voltage values during both the charging and discharging cycles, they can be attributed to reversible reactions, including reactions at the positive electrode such as diffusion of Li ions in the interior of the positive electrode material and the solid/liquid interface (surface layer), solvation or desolvation of Li ions in the electrolyte, and rearrangement of the positive electrode lattice. On the other hand, after 200 cycles at 60 °C, no plateaus were observed in the charging and discharging curves of the cell, which possibly indicates that the intrinsic LiCoO₂ structure may have changed as a result of cycling.

A comparison of the voltages observed during charging and discharging showed that the charging voltage after 200 cycles at 60 °C shifted to higher values, whereas the discharge voltage shifted to the low side. Based on these changes, the internal resistance of the cell can be expected to increase.

Figure 3 shows the capacity retention ratios measured for the cells subjected to up to 200 cycles at 60 °C. At 60 °C, the capacity retention ratio relative to the initial capacity decreased to 40% and 22% after 100 and 200 cycles, respectively. In both the cases, no anomalous phenomena such as significant swelling was observed in the external appearance of the cell. Since no visible swelling or similar anomalies could be observed in the laminated cell after 200 cycles at 60 °C, it was assumed that there was no abnormal decomposition of the solvent. Therefore, the remarkable decrease in capacity is likely to be related to the changes on the electrode surface.

Comparison of electrode surfaces before and after cycle deterioration.— Qualitative analysis of the electrode surface by FT-IR.— The surface layers on the anode and cathode of the degraded
The laminated cells were charged and discharged under the following conditions. Charging rate: 1C, end voltage during charging: 4.2 V, charging mode: CC-CV; discharging rate: 1C, cutoff voltage: 3 V, discharging mode: CC; number of charge/discharge cycles: 200; temperature: 60°C.

The samples must be in the liquid form for LC-QTOF/MS analyses. Therefore, we first studied a solvent-extraction method for recovering the degradation products from the electrode surfaces. Figure 5 shows the results of a study in which the product at the electrode surface was recovered using acetonitrile. The degradation products present on the electrode surfaces were recovered either by light rinsing or ultrasonic treatment for 30 min, and the samples obtained by the two methods were analyzed and compared using FT-IR analyses. In the case of light rinsing, no signals corresponding to the recovered substance were observed. The main component of the spectrum was acetonitrile. Characteristic peaks of acetonitrile are located in the vicinity of 750 cm⁻¹, 920 cm⁻¹, 1000 cm⁻¹, 1350–1500 cm⁻¹, 2200 cm⁻¹, and 3000 cm⁻¹. Since most peaks are detected, and we determined that these were the spectra of acetonitrile. In the case of ultrasonic treatment, in contrast, several peaks corresponding to the recovered substance were observed (Figs. 5a, 5b). Therefore, we decided on the way to recover the degradation products from the electrode surfaces. Figure 6 shows the results of a study in which the product at the electrode surface was recovered by ultrasonic treatment using acetonitrile. ROCOOLi and RCOOLi, as well as phosphate and fluorine compounds, were observed in the liquid samples from electrode surfaces (Figures 6a and 6b), and were believed to originate from the degradation products formed at the electrode interface. Further, in the case of the negative electrode surface, in addition to ROCOOLi, RCOOLi, and Li₂CO₃, a peak at 900–1000 cm⁻¹ was also observed, which was attributed to ROLi and LiOH (Figures 6c and 6d). In the case of the positive electrode surface, RCOOLi and additional peaks corresponding to the generation of substances derived from the change in the active material surfaces itself is the main reaction at the cathode, and the main reaction at the anode is denaturalization of organic materials such as electrolytes and their alteration products. Therefore, though FT-IR can predict a molecular structure, it cannot determine the composition and structure of the generated substances. Therefore, we utilized LC-QTOF/MS for more accurately identifying the degradation products on the electrode surfaces.

**Figure 4.** FT-IR difference spectra obtained by subtracting the spectrum recorded before the cycle test from those recorded after cycle tests for (a) anode sample and (b) cathode sample. The laminated cells were subjected to charge and discharge cycles under the following conditions. Charging rate: 1C, end voltage during charging: 4.2 V, charging mode: CC-CV; discharging rate: 1C, cutoff voltage: 3 V, discharge mode: CC; number of charge/discharge cycles: 200; temperature: 60°C.

**Figure 5.** FT-IR spectra of the solutions extracted by the two methods of light rinsing and ultrasonic treatment, after the cycle tests from (a) anode and (b) cathode. The laminated cells were subjected to charge/discharge cycles under the following conditions. Charging rate: 1C, end voltage during charging: 4.2 V, charging mode: CC-CV; discharging rate: 1C, cutoff voltage: 3 V, discharge mode: CC; number of charge/discharge cycles: 200; temperature: 60°C.
LiOH, Li₂O, or a fluorine compound originating from the binder were observed. These compounds exist at the surface layer of the active substance, and are believed to be part of the SEI, which is difficult to dissolve in organic solvents and does not delaminate even with ultrasonic treatment. Therefore, based on the above results, the components extracted by ultrasonic treatment using acetonitrile were believed to be either degradation products built up on the electrode surface, or modified SEI products formed during the initial cell operation. The fact that some of the components recovered by ultrasonic treatment resembled the persistent residue on the electrode surface that remains even after ultrasonic treatment lends further credence to our hypothesis that a portion of the SEI layer formed during the initial cycling period was also recovered by ultrasonic treatment.

**Analysis of mass spectrometry by LC-QTOF/MS.**—Figure 7 shows the total ion chromatograms (TIC) from the LC/MS measurements before cycling and after 200 cycles at 60°C. To activate all the samples, the laminated cells were subjected to two charging and discharging cycles at 25°C. It is important to note that the samples labeled as “Before cycle test” in the figure were in fact subjected to two cycles of charging and discharging for activation.

A plot of the LC retention time and MS intensity for each component separated by LC is shown in Figure 7. Since a decrease in separation by the LC column was a concern for retention times exceeding 9.5 min, the peaks obtained before 9.5 min were used for the analyses.

Six main peaks could be identified on the TIC graph of the sample before cycling, whereas 27 main peaks could be distinguished in the samples subjected to 200 cycles at 60°C. Since each of the separated peaks can be regarded as originating from different components, a large number of substances appear to be formed as a result of degradation. Moreover, peaks 1–6 observed in the sample before cycling were also observed in the sample subjected to 200 cycles, with decreased intensities. In other words, the amount of material corresponding to these peaks present before cycling decreased after the cycle tests. Precise mass spectrometry analyses of the components separated in the LC-QTOF/MS system were next performed using the Q-TOF/MS function.

In this study, the main peaks on the TIC graphs were analyzed. However, owing to the sharp separation in LC, all the peaks could be accurately detected in the samples both before and after cycling. The degradation products can be analyzed by applying principal component analysis (PCA), which is a statistical technique, to the data.

Table IV summarizes the mass spectrometry results of the 27 main components obtained after the cycle tests. The distinctive peaks 1–6 identified before the cycle tests were also present after the cycle test with the same retention time. The peak No. column for the “After cycle test” cell also shows the peak Nos. corresponding to the respective peak Nos. ①–⑥ in the “Before cycle test” sample. An increase in the peak intensity after the cycle test is indicated by an upward arrow (↑), whereas a decreased peak intensity is indicated by a downward arrow (↓).

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**Figure 6.** FT-IR spectra of the extracted solution and that of the electrode surface after the cycle test (60°C, 200 cycles). (a) solution extracted from the anode by ultrasonic treatment using acetonitrile, (b) solution extracted from the cathode by ultrasonic treatment using acetonitrile, (c) surface of the anode surface after ultrasonic treatment, and (d) surface of the cathode after ultrasonic treatment.

**Figure 7.** LC/MS (ESI+) chromatograms of the solution extracted by ultrasonic treatment. The laminated cells were subjected to charge/discharge cycles under the following conditions. Charging rate: 1C, end voltage during charging: 4.2 V, charging mode: CC-CV; discharging rate: 1C, cutoff voltage: 3 V, discharging mode: CC; number of charge/discharge cycles: 200; temperature: 60°C.
From the mass spectrometry data, it is evident that all the components that appeared or increased in concentration after the cycle tests contained C, H, O, and P, possibly originating from phosphate esters, and some F. On the other hand, polymers of carbonate compounds, composed of C, H, and O, decreased in concentration after cycling. The composition ratios of all the components were determined with a high homology rate.

Next, structural analysis was conducted based on the mass spectrometry results of the degradation products, and the results are summarized in Table IV. Monomers, dimers, and trimers of phosphate esters were detected with a high homology rate. These products resulted from the decomposition of carbonate compounds and LiPF$_6$. Several MS$^5$ data are shown in Figure 8. Several representative structural formulae are shown in Figure 9. Substance No. 1 identified in the degraded sample is likely to have formed over the course of the cycle tests, whereas the dimers and trimers of the phosphate ester, such as substances 6, 18, and 21, or polymers of carbonate compounds and dimers and trimers of the phosphate ester, are likely to have subsequently originated from 1. A comparison of the areas under the peaks of the spectra before and after the cycle tests showed significant changes for peaks 6, 18, and 21. The carbonate polymers (22 and 27), which were identified both before and after the cycle tests, showed a decrease in the peak intensity after the cycle tests.

From past knowledge, we believe that C$_2$H$_5$OLi may be formed as an intermediate product by the decomposition of lithium alkyl carbonate (C$_2$H$_5$OCOOLi) (a component of the SEI formation process or the SEI layer) under a reducing environment, whereas H$_2$[PO$_3$F] is formed by the hydrolysis of LiPF$_6$ and repeated elimination reaction of halogen F. Substance No. 1 becomes an intermediate product with reactive sites at both terminals under reducing conditions.

![Figure 8](https://example.com/figure8.png)

**Figure 8.** MS$^5$ data of the degradation products recovered after the cycle tests (200 cycles, 60°C). The solutions were extracted from the electrodes by ultrasonic treatment. MS$^5$ (a) is data of Structural formulae No.1 and MS$^5$ (b) is data of Structural formulae No.18. The Structural formulae number is Peak Number in Table IV.
Figure 9. LC/MS analysis of the degradation products recovered after the cycle tests (200 cycles, 60°C). The solutions were extracted from the electrodes by ultrasonic treatment. Structural formulae Number (No. 1, No. 6, No. 18, No. 21, No. 22, No. 27) are Peak Number in Table IV.

(1) The reaction of deterioration products from EC.
\[
2 \text{O} + 2\text{Li}^+ + 2\text{e}^- \rightarrow (\text{CH}_2\text{OCOOLi})_2 + \text{C}_2\text{H}_4\text{CH}_3
\]
\[
(\text{CH}_2\text{OCOOLi})_2 + 2\text{Li}^+ + \text{e}^- \rightarrow (\text{CH}_2\text{OLi})_2 + 2\text{LiOCO}^-
\]
\[
(\text{CH}_2\text{OLi})_2 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{OH} + \text{LiOH} + (1/2)\text{O}_2
\]
\[
(\text{CH}_2\text{OCOOLi})_2 + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{CO}_3 + (\text{CH}_2\text{OH})_2 + \text{CO}_2
\]

(2) The reaction of deterioration products from DEC.
\[
\sqrt{2} \text{O} + 2\text{Li}^+ + 2\text{e}^- \rightarrow 2(\text{CH}_2\text{OCOOLi}) + \text{C}_2\text{H}_4\text{CH}_3
\]
\[
\rightarrow \text{CH}_2\text{OCOOLi} + \text{Li}^+ + \text{e}^- \rightarrow \text{CH}_2\text{OLi} + \text{LiOCO}^-
\]
\[
2(\text{CH}_2\text{OCOOLi}) + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{CO}_3 + 2(\text{CH}_2\text{OH}) + \text{CO}_2
\]
\[
2\text{Li}^+ + 2\text{e}^- + (1/2)\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{LiOH}
\]

Scheme 1. Cycle deterioration reaction in the EC/DEC electrolyte [29–35].

\[
\text{Li}^+ + \text{PF}_6^- \rightleftharpoons \text{LiPF}_6 \rightleftharpoons \text{LiF} + \text{PF}_3
\]
\[
\text{PF}_6^- + 3\text{Li}^+ + 2\text{e}^- \rightarrow 3\text{LiF} + \text{PF}_3
\]
\[
\text{PF}_3 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF}
\]
\[
2\text{HF} + 2\text{Li} \rightarrow 2\text{LiF} + \text{H}_2
\]
\[
\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} \cdot \text{HF} + \text{HF} + \text{POF}_3
\]
\[
\text{POF}_3 + \text{H}_2\text{O} \rightarrow [\text{HPO}_2\text{F}] + \text{H}_2\text{O} \rightleftharpoons \text{H}_2[\text{PO}_2\text{F}]
\]
\[
\text{H}_2[\text{PO}_2\text{F}] + \text{HF} \rightarrow [\text{HPO}_2\text{F}]
\]
\[
\text{H}_2[\text{PO}_2\text{F}] + \text{H}_2\text{O} \rightleftharpoons \text{H}_2[\text{PO}_4\text{F}] + \text{HF}
\]

Scheme 2. Cycle deterioration products in the LiPF6 electrolyte [35].

Environmental, repeated polymerization occurs by successive reactions of the monomers. In addition, a reaction also occurs with the initially formed carbonate polymer, which is considered to be part of the SEI film; as a result of the reaction, a resistance component is formed on the electrode surface.

The carbonate polymers and phosphate esters detected in the vicinity of the electrode surface of the degraded cell by the LC-QTOF/MS analysis were considered to be substances formed during the degradation process. In other words, since the amount of carbonate polymers decreased after cycling, it can be assumed that the carbonate polymers are modified compounds originating from ROCOOLi and ROOCOLi, which are components of the SEI film formed during the initial cycling period (Schemes 1 and 2). Owing to the high polarity of acetonitrile,

Deterioration product: No. 1

Scheme 3. Cycle deterioration products obtained in this study for the product No. 1.


Scheme 4. Cycle deterioration reaction inferred in this study for the product No. 18.

In this study, we examined the feasibility of analyzing the degradation products of LIBs using LC-QTOF/MS. The substances at the electrode interface before and after deterioration by cycling were analyzed. The results of the analysis showed that multiple products, including the polymers of carbonates and phosphate esters, were formed via electrochemical and chemical reactions at the electrode interface, as a result of which the cell capacity was remarkably decreased. In the present study, LC-QTOF/MS was demonstrated as a suitable method for identifying the degradation products on the electrode surfaces, which allows the deterioration mechanism of the batteries to be traced. In this study, we considered the degradation of LIBs by cycling under certain conditions, which is a type of battery degradation mode. LC-QTOF/MS may also be an important technique for obtaining information on the state of the electrode surface. For example, the effect of products at the electrode surface on the extent of cycle deterioration may be determined. In addition, the products resulting from cycle deterioration can be compared with those formed in the preservation deterioration mode.

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References

1. T. Osaka, T. Momma, D. Mukoyama, and H. Nara, J. Power Sources, 205, 483 (2012).
2. D. Mukoyama, T. Momma, H. Nara, and T. Osaka, Chem. Lett., 44, 444 (2012).
3. M. Lazzari and B. Scrosati, J. Electrochem. Soc., 127, 773 (1980).
4. S. Megahed and B. Scrosati, J. Power Sources, 51, 79 (1994).
5. D. Guerard and A. Herold, Carbon, 13, 337 (1975).
6. J. O. Besenhard and H. P. Fritz, J. Electroanal. Chem., 53, 329 (1974).
7. M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mitate, S. Nakajima, M. Yoshida, Y. Yoshimoto, T. Suzuki, and H. Wada, J. Power Sources, 26, 545 (1989).
8. Z. Yan, C.-Y. Yang, and T. Kidong, J. Power Sources, 196, 1513 (2011).
9. H. Yoshida, N. Imamura, T. Inoue, K. Takeda, and H. Naito, Electrocatalysis, 78, 482 (2010).
10. H. Ishikawa and T. Kusudo, Panasonic Technical Journal, 60(1), 18 (2014) [in Japanese].
11. L. S. Kanevskii and V. S. Dubasova, Russ. J. Electrochem., 41, 1 (2005).
12. H. Ota, Y. Sakata, A. Inoue, and S. Yamauchi, J. Electrochem. Soc., 151, A1659 (2004).
13. H. Yoshida, T. Fukanaga, T. Hazama, M. Terasaki, M. Mizutani, and Y. Yamachi, J. Power Sources, 68, 311 (1997).
14. E. Peled, J. Electrochem. Soc., 126, 2047 (1979).
15. D. Aubach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, and H. Yamin, J. Electrochem. Soc., 141, 603 (1994).
16. D. Aubach, B. Markovsky, A. Shechter, Y. Ein-Eli, and H. Cohen, J. Electrochem. Soc., 143, 3809 (1996).
17. K. Abe, K. Miyoshi, T. Hattoria, Y. Ushigoe, and H. Yoshitake, J. Power Sources, 178, 404 (2008).
18. T. Abe, H. Fukushima, Y. Iriyama, and Z. Ogumi, J. Electrochem. Soc., 151, A1120 (2004).
19. Y. Ein-Eli, S. R. Thomas, R. Chadha, T. Blakley, and V. Koch, J. Electrochem. Soc., 144, 823 (1997).
20. Y. Ein-Eli, B. Markovsky, D. Aubach, Y. Carmeli, H. Yamin, and S. Luski, Electrochim. Acta, 39, 2559 (1994).
21. K. Edstrom, M. Herstedt, and D.-P. Abraham, J. Power Sources, 151, A1202 (2004).
22. S. Laruelle, S. Pilard, P. Guenot, S. Grugeon, and J.-M. Tarascon, J. Power Sources, 68, 311 (1997).
23. G. Gachot, S. Grugeon, G. Gachot, D. Mathiron, M. Armand, J.-B. Leriche, S. Pilard, and S. Laruelle, Anal. Chem., 83, 478 (2011).
24. Specification For Laminated Sheet Lithium Ion Rechargeable Battery S Size Cell (ENS-XE36) (2009) http://www.enax.jp/pdf/data/s-size-cell-energy36.pdf [in Japanese].
25. K. Takei, K. Kumai, Y. Kobayashi, H. Miyashiro, N. Terada, T. Iwahori, and T. Tanaka, J. Power Sources, 97, 697 (2001).
26. Zeka Lithium Ion Denchi, Kyupashita no Issen Houyou Gijutu, 17, Technical Information Institute Co. Ltd (2009) [in Japanese].
27. M. Tochihara, H. Nara, T. Momma, and T. Osaka, The 62nd Annual Meeting of The Electrochemical Society of Electrochemistry, Niigata Japan, Poster Session s08-P-057 (2011).
28. M. Tochihara, H. Nara, T. Momma, and T. Osaka, The 62nd Annual Meeting of The Electrochemical Society of Electrochemistry, Yokohara, Japan, 3L28 (2011) [in Japanese].
29. G. G. Eshetu, S. Grugeon, G. Forough, M. Armand, and S. Laruelle, Electrochim. Acta, 603 (2004).
30. P. Lu and S. J. Harris, Electrochem. Commun., 13, 1035 (2011).
31. G. Gachot, S. Grugeon, M. Armand, S. Pilard, P. Guenot, J. Tarascon, and S. Laruelle, J. Power Sources, 178, 409 (2008).
32. K. Abe, K. Miyoshi, T. Hattoria, Y. Ushigoe, and H. Yoshitake, J. Power Sources, 184, 449 (2008).
33. L. Gireaud, S. Grugeon, S. Pilard, P. Guenot, J. Tarascon, and S. Laruelle, Anal. Chem., 78, 3688 (2006).
34. G. Gachot, S. Grugeon, G. G. Eshetu, D. Mathiron, P. Riberie, M. Armand, and S. Laruelle, Electrochim. Acta, 83, 402 (2012).
35. C.-L. Campion, W. Li, and B.-L. Luchi, J. Electrochem. Soc., 152, A2327 (2005).

C₃H₅COO⁻Li⁺ + e⁻ → C₂H₅OLi + CO₂

C₂H₅OH + H₂[P₃O₃] → HO⁻P⁻F⁺ + LiOH

H₂⁺ + C₂H₅OH → H₂O + P⁻O⁻C₂H₅ + LiF + 2H⁺

H₂C₅O₃O⁻O⁻CH₃ + Li⁺ + e⁻ → H₂C₅O₃O⁻O⁻C⁻ + LiH