Failure Analysis Testing of a Cycle Aged Automotive Lithium Ion Battery Electrolyte

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Overview

Purpose: Identify the chemical composition of electrolyte degradation products (deposited on the anode surface of a cycle aged lithium ion battery – LIB) via peaks resolved by ion chromatography (IC).

Method: Extract the electrolyte degradation products from the anode surface using DI water. Measure the retention time of the peaks of interest from the aqueous extract using an Ion Chromatography system with an Hydroxide-Selective Anion-Exchange Column, and correlate the results with IC-MS and IC-ICP-MS technologies to determine their respective mass and chemical composition.

Results: Characterization by IC-MS and ICP-MS identified the peaks of interest as organic and inorganic phosphates.

Introduction

Rechargeable LIBs are key components of portable electronics, medical devices, industrial equipment, and automobiles. Much research has been spent on improving product safety, cycle life, and power output, yet understanding fundamental processes and degradation mechanisms in LIBs remains a challenge.

While capable of exhibiting maximum output and prolonged cycle life under ideal conditions, a steady decrease in LIB performance is recognized to occur from the interaction between the electrolyte, anode, and cathode when exposed to contaminants, charge effects, or thermal effects. In particular, the anode undergoes a variety of mechanisms over prolonged contact with the electrolyte to produce degradation products such as organic and inorganic phosphates that can provide valuable information on the failure mechanism. Understanding a degradation process can lead to identification of key degradation pathways if blocked, can impart improved degradation resistance to the electrolyte that translates to safer and longer lasting LIBs.

Presented are results of the analysis of electrolyte degradation products formed on the anode surface of a cycle aged automotive battery. Results are compared with a calendar aged automotive battery. Battery components included a graphite anode, a lithium cobalt oxide cathode, and a lithium hexafluorophosphate electrolyte in dimethyl carbonate. Analysis of the degradation products was performed using Thermo Scientific ™ IC, IC-MS and IC-ICP-MS systems.

Methods

Sample Preparation: anode sample extracted for LIB
10 mL DI water, 30 min ultrasonic bath
10 mL DI water, stand for 30 min
10 mL DI water, stand for 30 min.
All extracts were combined and filtered (0.45 μm membrane)
Additional 1:20 dilution before measurement

Sample Introduction: Thermo Scientific™ iCAP™ Qc ICP-MS
PFA-LC nebulizer
Quartz glass spray chamber
Quartz 2.0 mm ID injector
Ni sample cone
Ni skimmer cone
    High matrix insert
Thermo Scientific™ QCell™ operated in KED mode
    4.8 ml/mL 100% He

Experimental: IC-MSQ Chromatographic Conditions
Ion Chromatography: Thermo Scientific™ Dionex™ ICS-5000™
Column: Thermo Scientific Dionex IonPac AS11; 2 mm I.D.
Eluent: 5 - 50mM KOH
Flow Rate: 0.35 mL/min
Temperature: 30^{o}C
Sample: 1:2 dilution
Detection: Thermo Scientific™ MSQ™ single quadrupole mass spectrometer
Detection method: Negative mode electrospray ionization
Scan Range: 38-800 *m/z*

Results

Figure 1. Analysis of Anode Electrolyte Degradation Products by IC

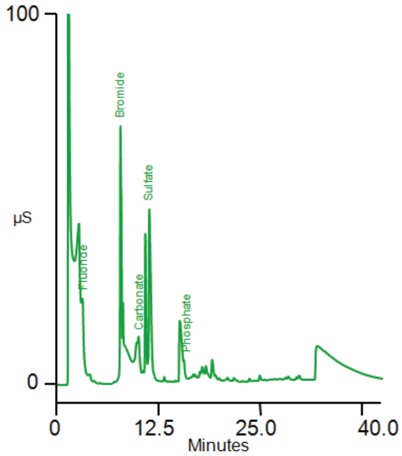

Figure 1 shows the analysis of an aqueous extract of a cycle aged graphite anode of a LIB (in a $LiPF_6$ dimethyl carbonate mixture) by ion chromatography. . Peak resolution of less than 20 minutes was achieved using an IonPac AS 11 hydroxide selective anion exchange column and suppressed conductivity detection. Of particular interest was identifying the peaks eluting between 5 – 12 min.

Figure 2. Identification of Anode Electrolyte Degradation Products by IC-MS

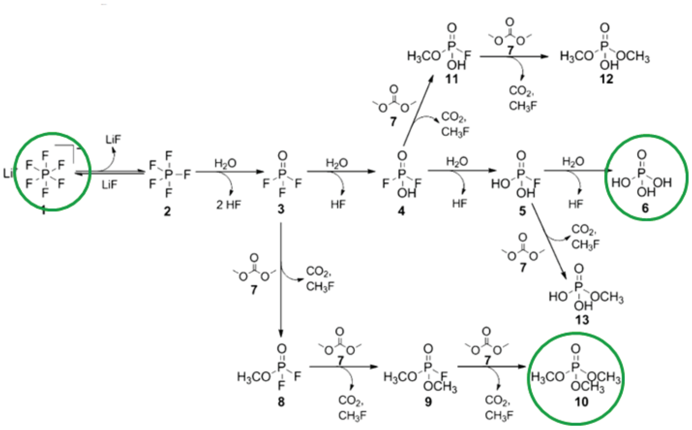

Figure 2 shown are IC-MS results using negative electrospray ionization from a cycle aged electrolyte that identifies three of the peaks eluting between 5 – 12 minutes as hexafluorophosphate, phosphoric acid, and trimethyl phosphate (circled). The hexafluorophosphate is the dissociated anion of the $LiPF_6$ electrolyte. The phosphoric acid and trimethyl phosphate are degradation products. The three products are overlaid on a proposed mechanistic map for a *thermally* aged electrolyte[1] to illustrate where they appear in the degradation process and show commonality with a complementary degradation process

Figure 3. Characterization of Anode Electrolyte Degradation Products by IC-MS

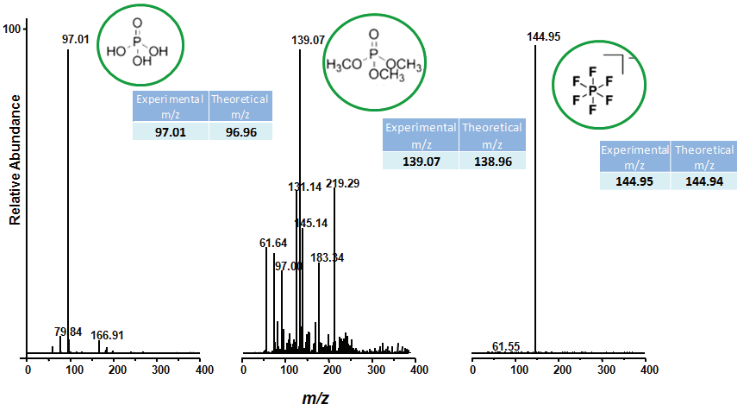

Figure 3 shows results from the characterization of the cycle aged electrolyte degradation products by IC-MS, reported as $[M\text{-}H]^-$ negative ion mode for the organic phosphates. The experimental mass to charge ratios for the three degradation products is shown to be in close agreement with the theoretical value. However the analysis is not inclusive. The above approach does not consider all the degradation products present in the aqueous extract. Only those present at specific retention times. To provide a comprehensive analysis, the anode extract was analyzed by ICP-MS to give total elemental concentration and IC-ICP-MS for species specific characterization.

Table 1. Total Element Quantification: ICP-MS

	Sample weight	^{7}Li [mg/L]	^{31}P [mg/L]	^{55}Mn [mg/L]	^{59}Co [mg/L]
Control	0.8802 g	213	139	0.26	0.04
Calendar Aged	0.8585g	331	127	4.4	0.30
Cycle Aged	0.8117 g	297	88	14.8	0.47

Table 1 shows results from the total element quantification of the cycle aged anode extract by ICP-MS. For comparison, a blank (water), a control (an anode sample not exposed to aging) and a calendar aged sample was included in the analysis.

The column on the far left lists the extracted sample weights. The columns to the right list the concentration for each of the elements. The Li sample concentration is shown to be approximately equal for all three samples, not what we expected. It is reasoned that the samples were not properly rinsed with dimethyl carbonate (used to remove excess $LiPF_6$) prior to DI water extraction. The omitted step explains a higher than expected sample weight for the control.

The P sample shows a steady decrease. The Mn and Co show an increase.

Figure 4. Trace Elemental Analysis: ^{31}P

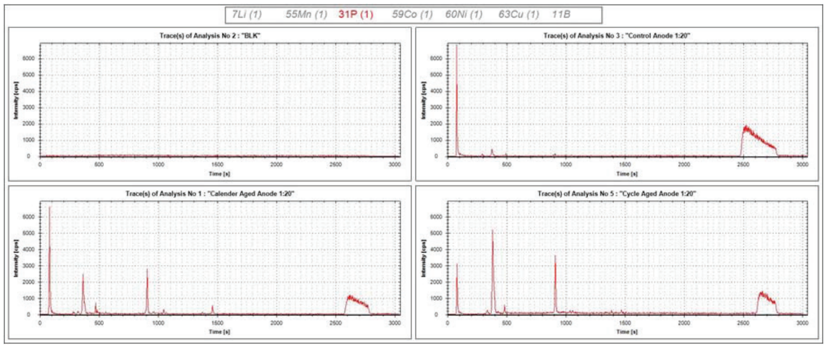

Figure 4 provides results of the analysis for P using IC-ICP-MS for species (or speciation) analysis. Analysis by IC using an IonPac AS 11 column shows four major peaks and several minor ones eluting in the first 1,000 sec (17 min). The slower eluting peak is suspected to be an ionic complex of unknown composition. Both the calendar and cycle aged anode samples appear to contain the same degradation products

Figure 5. Trace Elemental Analysis: ^{7}Li

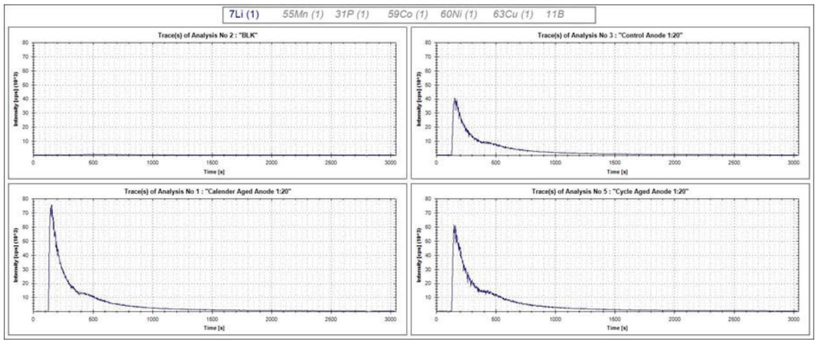

Figure 5 provides results of the analysis for Li containing products using IC-ICP-MS. Shown are the Li containing compounds eluting with the void volume. The reason the Li products are not retained by the column is the compounds are cations and the sample was run on an anion IonPac AS11 column. Separation of any Li products would require separate analysis using a cation column.

Figure 6. Trace Elemental Analysis: ^{55}Mn

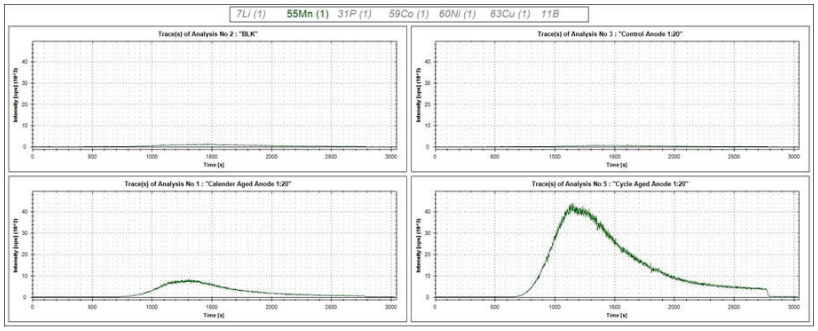

Figure 6 provides results of the analysis of Mn containing products using IC-ICP-MS. Of particular interest was retention of Mn products on an anion column. Given that Mn is a cation, it should have eluted with the void volume, in a similar manner to Li. Considering that Mn was retained by the column suggests an ionic complex.

Figure 7. Trace Elemental Analysis: ^{59}Co

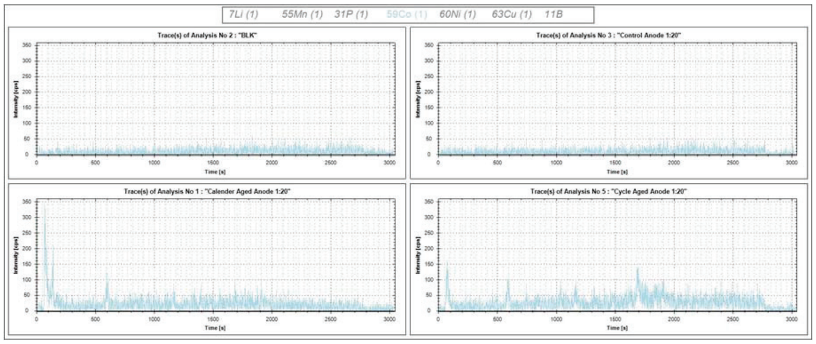

Figure 7 provides results of the analysis of Co containing products using IC-ICP-MS shows the majority of Co products eluting with the void volume. The minor components shown to be retained by the column suggest ionic complexes.

Conclusion

- Analysis of the extract of a cycle aged LIB anode by IC with an IonPac AS 11 column showed multiple unknown peaks eluting between 5-12 min.
- Characterization of the anode extract by IC-MS identified three products eluting between 5-12 min; the dissociated anion of the $LiPF_6$ electrolyte (hexafluorophosphate), and two phosphate degradation products, an inorganic phosphate (phosphoric acid) and an organic phosphate (trimethyl phosphate).
  - The three products were overlaid on a proposed mechanistic map of a *thermally* aged electrolyte that predicts the formation of the same three products. This finding suggests the cycle aged anode LIB process produces similar products as the thermally aged electrolyte process.
- Elemental analysis of the cycle aged anode extract by IC-ICP-MS provided a more comprehensive characterization of the electrolyte degradation products by enabling identification of compounds that contain a particular element in the presence of other elements for the duration of the entire run, not just for 5-12 min.
  - Elemental analysis of Mn revealed the formation of an unknown ionic complex
- Understanding the degradation process provides an insight into failure mechanism and can offer a means to prevent their formation.
  - The proposed degradation mechanism in Figure 2 shows phosphorus oxyfluoride (compound 3) being key to catalyzing a host of further degradation products. It is interesting to speculate that preventing the formation of compound 3 could avoid the formation of downstream products, enhance degradation resistance of the electrolyte resulting in longer LIB cycle life.

References

B. Vortmann, S. Nowak, and C. Engelhard, Anal.Chem., 85, 2013, 3433-3438

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