Comprehensive Analysis of Lithium Ion Battery Anode Samples by Ion Chromatography Coupled with High Resolution Mass Spectrometry

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Overview

Purpose: To demonstrate a workflow using ion chromatography and high resolution mass spectrometry for lithium ion battery (LIB) anode degradation product analysis.

Results: LIB anode degradation products were identified from four anode samples..

Introduction

The lithium ion battery (LIB) is the key component for electric vehicles (EV) and many other electronic devices. The LIB quality directly affects the performance of EV and other devices. Much research has been done in order to improve the performance and increase the efficiency of LIB.

In this study, comprehensive analysis of LIB anode degradation products was conducted using Ion Chromatography (IC) coupled with High Resolution Mass Spectrometry (HRMS).

Methods

Sample Preparation

The four LIB anode samples[1] were sonicated and rinsed in deionized water. Extracts were filtered through Whatman PP 0.45 μm filters.

Ion Exchange Chromatography
The ionic separations were carried out on Thermo Scientific™ Dionex™ ICS-2100 IC System using Thermo Scientific™ Dionex™ IonPac™ AG11, AS11 (2 mm) column.
Eluent: KOH from 1 to 65 mM in 45 min with gradient.
Eluent source: Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge
Thermo Scientific™ Dionex™ AERS™ 500 (2 mm) Suppressor [2].

Mass Spectrometry

The MS analyses were carried out on Thermo Scientific™ Q Exactive™ hybrid quadrupole-Orbitrap mass spectrometer using electrospray ionization in negative mode.

High resolution full-scan MS and top3 data-dependent MS/MS data were collected at resolving power of 70,000 and 35,000 at FWHM m/z 200 respectively. Stepped HCD normalized collision energy (NCE): 30, 45 , 60.

Result

The anode samples were separated by ICS-2100 system based on conductivity, and ions were eluted from the ion-exchange column based on their valences. The eluent was introduced to a Q Exactive mass spectrometer for High Resolution Accurate Mass (HRAM) measurement. The HRAM full scan and ms/ms data provided rich information for confident elemental composition determination and structure characterization. The data was processed using SIEVE for component extraction, followed by ChemSpider and Thermo Scientific HR compound database searching for structure identification. Small molecule structure analysis software (Thermo Scientific™ Mass Frontier™ software) was used to aid with known and unknown structure elucidation.

High Resolution Accurate Mass Ensured Accurate and Confident Results

Sulfate (SO_4^-) and phosphate ($H_2PO_4^-$) have the same unit mass 97.0 amu. High Resolution Accurate Mass (HRAM) data clearly distinguish these two compounds, which ensured unambiguous identification of ion species, especially for unknown degradation product, see Table1. HRAM MS/MS fragments facilitated structure characterization through accurate fragment ions elemental composition determination, see Figure 2. In addition, HRAM MS/MS readily distinguished co-eluting compounds. See Figure 3.

TABLE 1. Unit mass vs. High Resolution Accurate Mass (HRAM).

m/z (-) Unit mass	m/z (-) HRAM	Formula (-)	Ionic Species
97.0	96.9601	SO_4	Sulfate
97.0	96.9696	H_2PO_4	Phosphate
139.0	139.0166	$C_3H_8O_4P$	Phosphate Ester
139.0	139.0071	$C_3H_7O_4S$	Sulfonate

FIGURE 1. Ion Exchange Chromatography and High Resolution Mass Spectrometry Workflow for Lithium Ion Battery Anode Impurity Analysis
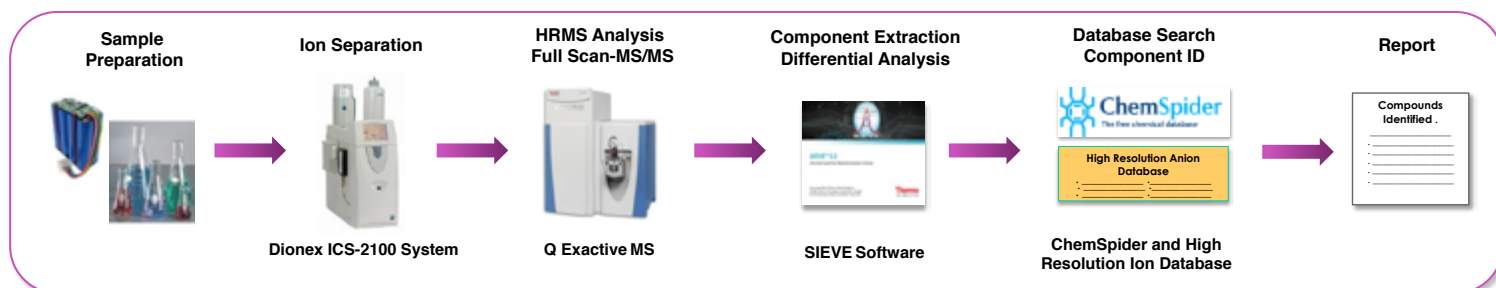
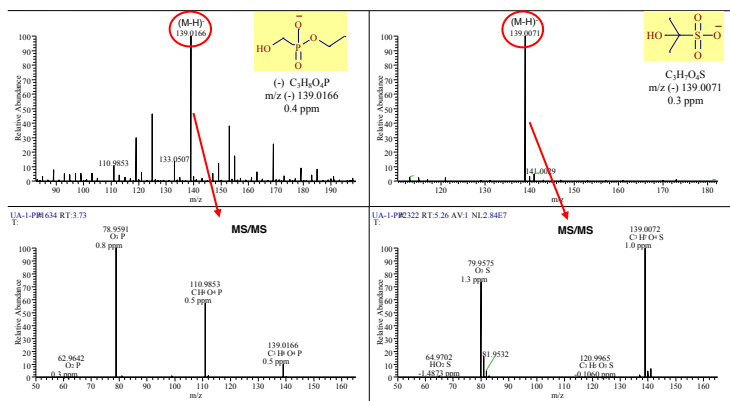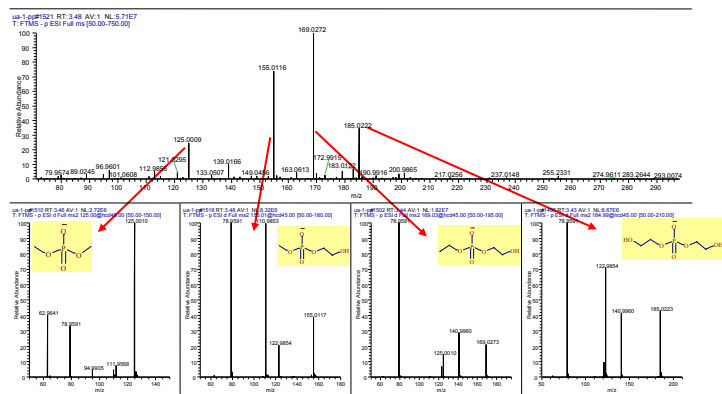**FIGURE 2. HRAM MS/MS Fragments Ensure Confident Structure Characterization**

FIGURE 3. HRAM MS/MS Fragments Facilitate Identification of Co-eluting Compounds

HRAM MS/MS Fragments Facilitate Identification of Co-eluting Compounds

The MS negative mode base peak chromatograms of four LIB anode samples with solvent blank and process control are shown in Figure 4 (same scale). Compared with control sample, there were noticeable changes for the other three samples: the peak intensity was either increased or reduced. The data was processed using differential analysis software (Thermo Scientific™ SIEVE™ software) for component extraction and database searching.

FIGURE 4. MS Base Peak Chromatograms (-) of Sample Group
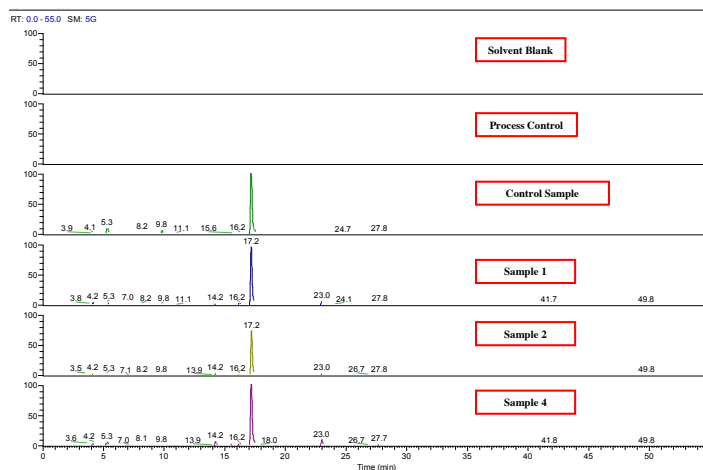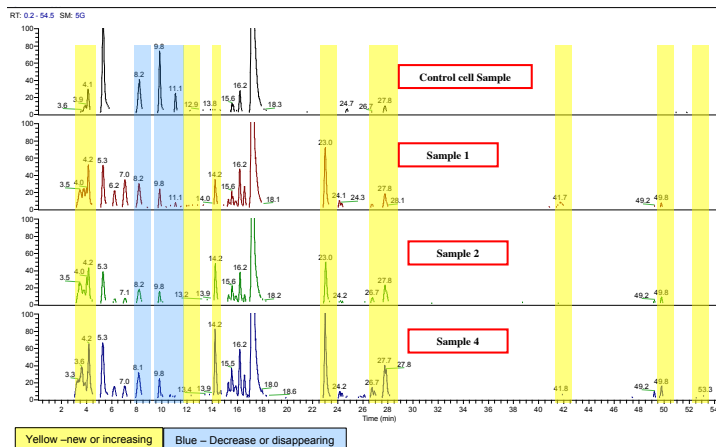

FIGURE 5. Zoomed-in View for Details

SIEVE software results show the extracted components, also the trend intensity and it's details. Figure 6 shows trend intensity of m/z 124.9912 at RT 11.0 min with Elemental Formula $C_2H_5O_4S$.

FIGURE 6. Trend Intensities View for m/z 124.9912 at RT 11.0 minute

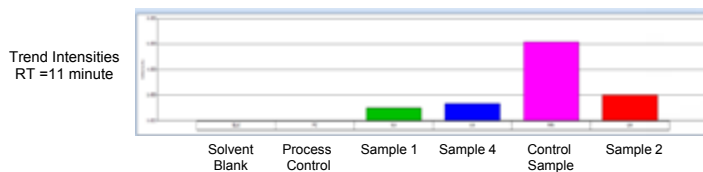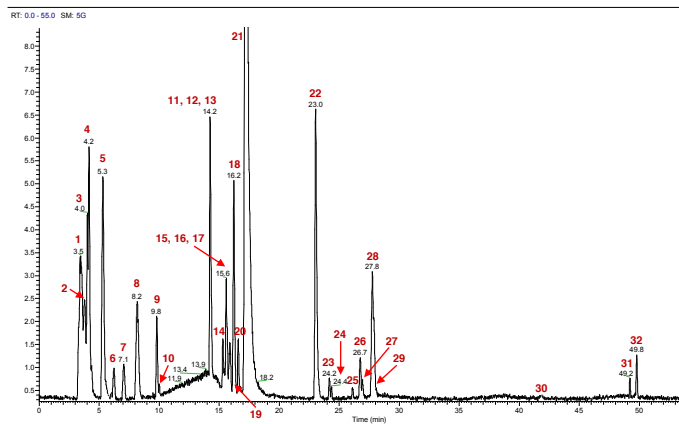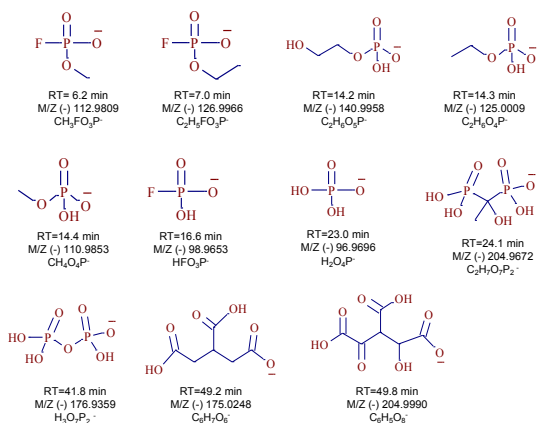**Figure 7. MS Base Peak Chromatogram of Sample 3**

FIGURE 7. Components Identified from Sample 3

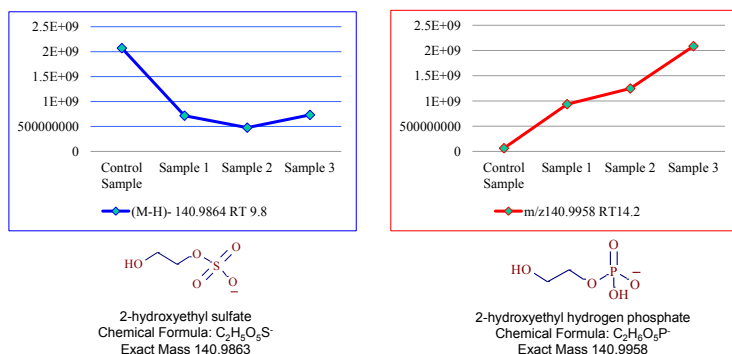| Peak #	RT (min)	m/z	Formula (-)	Delta ppm	Name (Based on MS results)*
1	3.2-3.6	125.0009	C2H6O4P	0	Phosphate Esters
		155.0116	C3H8O5P	0.6	
		169.0272	C4H10O5P	0.6	
		185.0222	C4H10O6P	0.6	
2	3.8	139.0166	C3H8O4P	0.4	Phosphoric acid
3	4.0	89.0244	C3H5O3	0.1	
4	4.2	75.0088	C2H3O3	-0.2	Methyl Carbonate
5	5.3	139.0071	C3H7O4S	0.4	Propyl sulfate
6	6.2	112.9810	CH3O3FP	0.3	Methyl Phosphorofluoridate
7	7.1	126.9966	C2H5O3FP	0.1	Ethyl phosphorofluoridate
8	8.2	123.0122	C3H7O3S	0.3	Propyl sulfonate
9	9.8	140.9864	C2H5O5S	0.3	2-hydroxyethyl sulfate
10	10.0	155.0020	C3H7O5S	-0.3	
11	14.2	140.9958	C2H6O5P	0.1	2-hydroxyethyl hydrogen phosphate
12	14.3	125.0009	C2H6O4P	-0.1	ethyl hydrogen phosphate
13	14.4	110.9853	CH4O4P	-0.2	methyl hydrogenphosphate
14	15.3	131.0350	C5H7O4	0	3-carboxy-2-methylpropanoate
15	15.6	117.0193	C4H5O4	0.2	methyl malonate
16	15.7	133.0143	C4H5O5	0.2	3-carboxy-3-hydroxypropanoate
17	15.9	117.0194	C4H5O4	0.2	Succinate
18	16.2	103.0037	C3H3O4	0.3	2-carboxyacetate
19	16.6	98.9653	HO3FP	0	hydrogen phosphorofluoridate
20	17.1	118.9986	C3H3O5		
21	17.2	96.9601	HO4S	-0.2	hydrogen sulfate
22	23.0	96.9696	H2O4P	-0.5	dihydrogen phosphate
23	24.2	204.9674	C2H7O7P2	0.7	hydrogen (1-hydroxy-1-phosphono-ethyl)-phosphonate
24	24.4	190.9517	CH5O7P2	1.1	Methyl trihydrogen diphosphate
25	26.1	131.0349	C5H7O4	-0.4	
26	26.7	175.0249	C6H7O6	0.3	
27	26.9	147.0299	C5H7O5	0.3	4-carboxy-3-hydroxybutanoate
28	27.8	161.0092	C5H5O6	0.1	Ethanetricarboxylate
29	27.9	103.0037	C3H3O4	0	
30	41.7	176.9360	H3O7P2	0.3	Trihydrogen diphosphate
31	49.2	175.0249	C6H7O6	0.3	Tricarballyllate
32	49.8	204.9312	C6H5O8	0.1	

Table title: Components Identified in Cycle Aged Exhibited 20% Loss in Capacity Sample 3

FIGURE 7. Components Identified from Sample 3

RT= 6.2 min
M/Z (-) 112.9809
$CH_3FO_3P^-$

RT=7.0 min
M/Z (-) 126.9966
$C_2H_5FO_3P^-$

RT=14.2 min
M/Z (-) 140.9958
$C_2H_6O_5P^-$

RT=14.3 min
M/Z (-) 125.0009
$C_2H_6O_4P^-$

RT=14.4 min
M/Z (-) 110.9853
$CH_4O_4P^-$

RT=16.6 min
M/Z (-) 98.9653
HFO_3P^-

RT=23.0 min
M/Z (-) 96.9696
$H_2O_4P^-$

RT=24.1 min
M/Z (-) 204.9672
$C_2H_7O_7P_2^-$

RT=41.8 min
M/Z (-) 176.9359
$H_3O_7P_2^-$

RT=49.2 min
M/Z (-) 175.0248
$C_6H_7O_6^-$

RT=49.8 min
M/Z (-) 204.9990
$C_6H_5O_8^-$

Components Profile and Battery Performance

Figure 7 shows the intensity variations in different anode samples of two compounds selected. Because these four anodes were aged under different conditions, the correlation between the compounds and their intensities could be used as an indicator for battery performance.

FIGURE 7. The Intensity Variations of Two Selected Compounds

2-hydroxyethyl sulfate
Chemical Formula: $C_2H_5O_5S^-$
Exact Mass 140.9863

2-hydroxyethyl hydrogen phosphate
Chemical Formula: $C_2H_6O_5P^-$
Exact Mass 140.9958

Conclusion

- Ion chromatography coupled with a Q Exactive mass spectrometer provides a powerful platform for li-ion battery anode impurity and degradant analysis.
- Phosphate degradation products in three aged lithium ion batteries were identified.
- This IC-HRMS platform can be used for QA/QC for lithium-ion battery manufacturers and performance evaluations.
- Further study will be conducted to investigate the relationship of the compounds identified and their intensities with the batteries performance.

Reference

[1] The LIB anode samples were provided by a major transportation company.

[2] See Rosanne Slingsby's AABC2015 poster for in depth IC analysis.

Acknowledgements

The authors would like to thank the transportation company for providing the lithium ion battery anode samples.