Thermo Fisher
SCIENTIFIC

Comprehensive analysis of lithium-ion battery anode samples by ion chromatography coupled with high resolution mass spectrometry

Kate Comstock[1], Rosanne Slingsby[2], Charanjit Saini[2], Paul Voelker[2], Chris Pohl[2]
[1]Thermo Fisher Scientific, San Jose, CA, USA; [2]Thermo Fisher Scientific, Sunnyvale, CA, USA

Overview

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

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

Introduction

The 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 IC coupled with HRMS.

Methods

Sample preparation

The four LiB anode samples[1] were sonicated and rinsed in deionized (DI) 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 top 3 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.

Results and discussion

The anode samples were separated by the 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
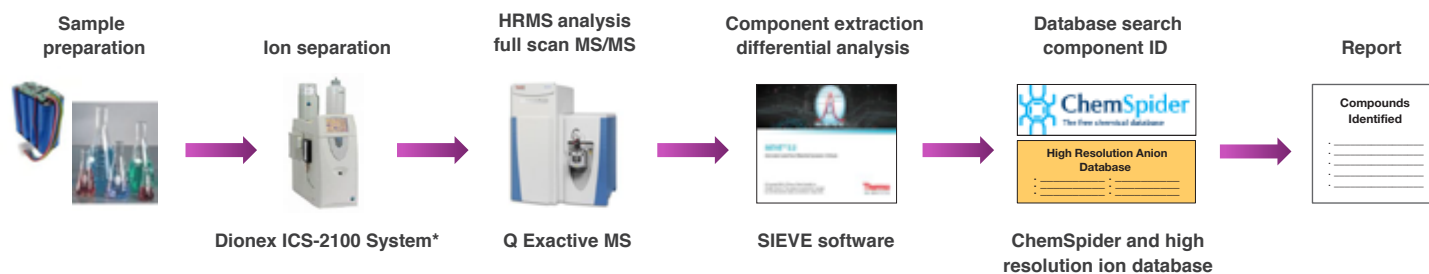

Figure 1. Ion exchange chromatography and high resolution mass spectrometry workflow for lithium-ion battery anode impurity analysis

* or equivalent Thermo Scientific™ Dionex™ Integrion™ HPIC System

thermo scientific

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 Thermo Scientific™ SIEVE™ software 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 Table 1. 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)

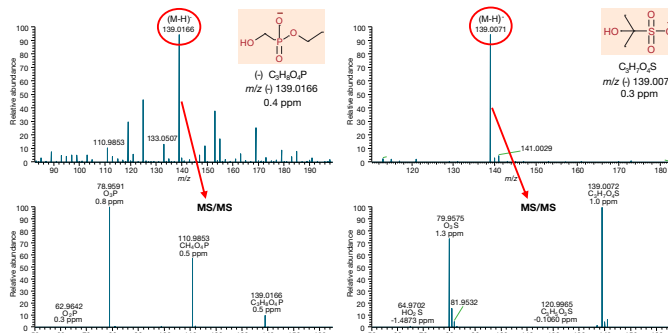| m/z (-) Unit mass	m/z (-) HRAM	Formula (-)	Ionic species
97.0	96.9601	SO_4	Sulfate
97.0	96.9696	H_2PO_4	Phosphate
139.0	139.0166	$C_3H_8O_4P$	Phosphate ester
139.0	139.0071	$C_3H_7O_4S$	Sulfonate

Figure 2. HRAM MS/MS fragments ensure confident stracture characterization
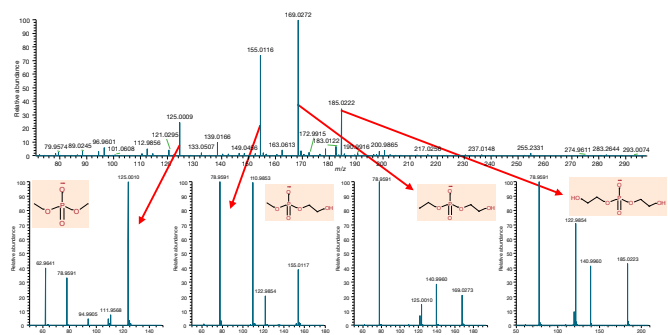

Figure 3. HRAM MS/MS fragments facilitate identification of co-eluting compounds

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 (such as SIEVE software) for component extraction and database searching.
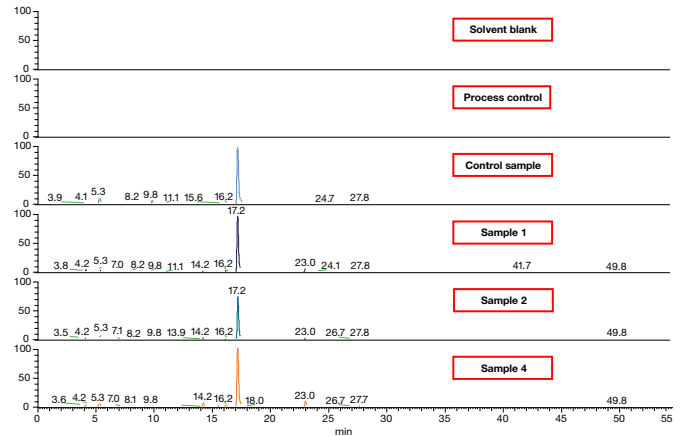

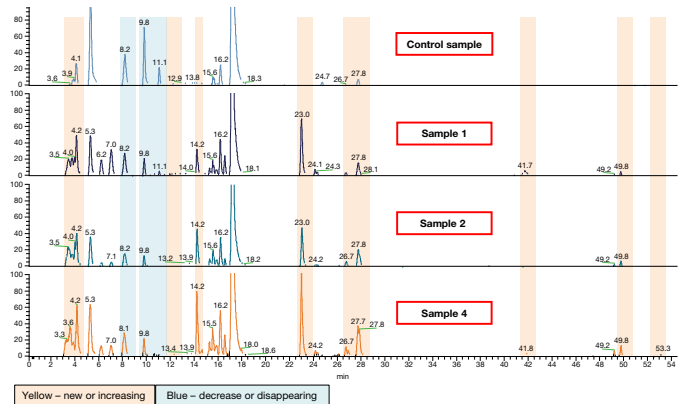Figure 4. MS base peak chromatograms (-) of sample group

Figure 5. Zoomed-in view for details

SIEVE software results show the extracted components, also the trend intensity and its details. Figure 6 shows trend intensity of m/z 124.9912 at RT 11.0 min with elemental formula $C_2H_5O_4S$.
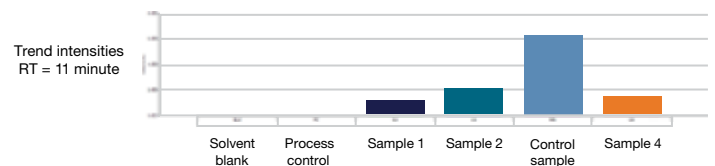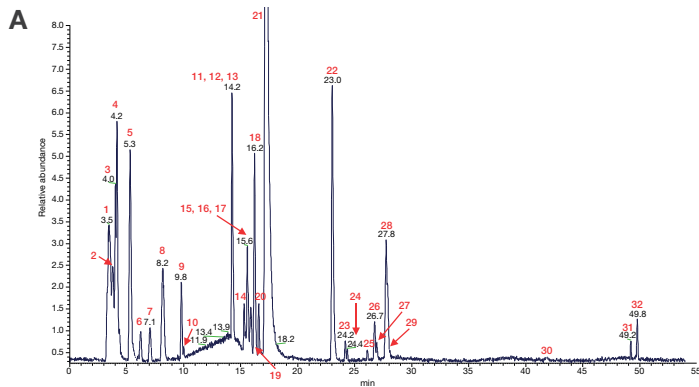

Figure 6. Trend intensities view for m/z 124.9912 at RT 11.0 minute

A

B

Components identified in cycle aged exhibited 20% loss in capacity—Sample 3					
Peak #	RT (min)	m/z	Formula (-)	Delta ppm	Name (based on MS results)*
1	3.2 - 3.6	125.0009	$C_2H_6O_4P$	0	Phosphate esters
		155.0116	$C_3H_8O_4P$	0.6	
		169.0272	$C_4H_{10}O_4P$	0.6	
		185.0222	$C_4H_{10}O_5P$	0.6	
2	3.8	139.0166	$C_3H_8O_4P$	0.4	Phosphoric acid
3	4.0	89.0244	$C_3H_5O_3$	0.1	
4	4.2	75.0088	$C_2H_3O_3$	-0.2	Methyl carbonate
5	5.3	139.0071	$C_3H_7O_4S$	0.4	Propyl sulfate
6	6.2	112.9810	CH_3O_3FP	0.3	Methyl phosphorofluoridate
7	7.1	126.9966	$C_2H_5O_3FP$	0.1	Ethyl phosphorofluoridate
8	8.2	123.0122	$C_3H_7O_3S$	0.3	Propyl sulfonate
9	9.8	140.9864	$C_2H_5O_5S$	0.3	2- hydroxyethyl sulfate
10	10.0	155.0020	$C_2H_7O_5S$	-0.3	
11	14.2	140.9958	$C_2H_6O_5P$	0.1	2-hydroxyethyl hydrogen phosphate
12	14.3	125.0009	$C_2H_6O_4P$	-0.1	ethyl hydrogen phosphate
13	14.4	110.9853	CH_4O_4P	-0.2	methyl hydrogenphosphate
14	15.3	131.0350	$C_5H_7O_4$	0	3-carboxy-2-methylpropanoate
15	15.6	117.0193	$C_4H_5O_4$	0.2	methyl malonate
16	15.7	133.0143	$C_4H_5O_5$	0.2	3-carboxy-3-hydroxypropanoate
17	15.9	117.0194	$C_4H_5O_4$	0.2	Succinate
18	16.2	103.0037	$C_3H_3O_4$	0.3	2-carboxyacetate
19	16.6	98.9653	HO_3FP	0	hydrogen phosphorofluoridate
20	17.1	118.9986	$C_2H_4O_4P$		
21	17.2	96.9601	HO_4S	-0.2	hydrogen sulfate
22	23.0	96.9696	H_2O_4P	-0.5	dihydrogen phosphate
23	24.2	204.9674	$C_2H_7O_5P_2$	0.7	hydrogen (1-hydroxy-1-phosphono-ethyl)-phosphonate
24	24.4	190.9517	$CH_4O_7P_2$	1.1	Methyl trihydrogen diphosphate
25	26.1	131.0349	$C_5H_7O_4$	-0.4	
26	26.7	175.0249	$C_6H_7O_6$	0.3	
27	26.9	147.0299	$C_5H_7O_5$	0.3	4-carboxy-3-hydroxybutanoate
28	27.8	161.0092	$C_5H_5O_6$	0.1	Ethanetricarboxylate
29	27.9	103.0037	$C_3H_3O_4$	0	
30	41.7	176.9360	$H_3O_7P_2$	0.3	Trihydrogen diphosphate
31	49.2	175.0249	$C_6H_7O_6$	0.3	Tricarballylate
32	49.8	204.9312	$C_6H_5O_8$	0.1	

C

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
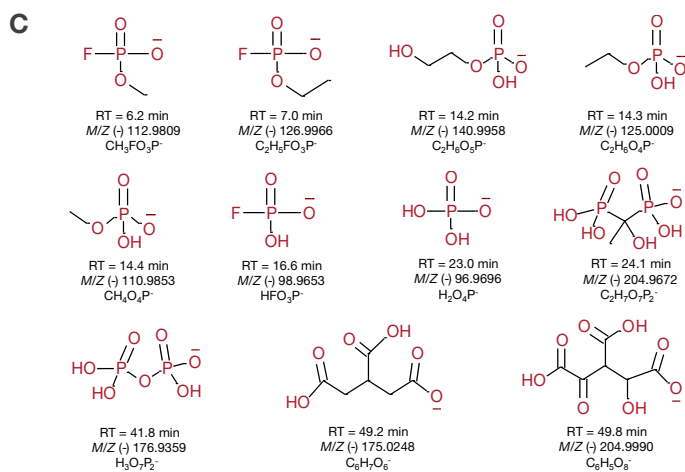M/Z (-) 204.9990
$C_6H_5O_8^-$

Figure 7. A) MS base peak chromatogram of sample 3; B) and C) components identified from sample 3

Components profile and battery performance

Figure 8 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.
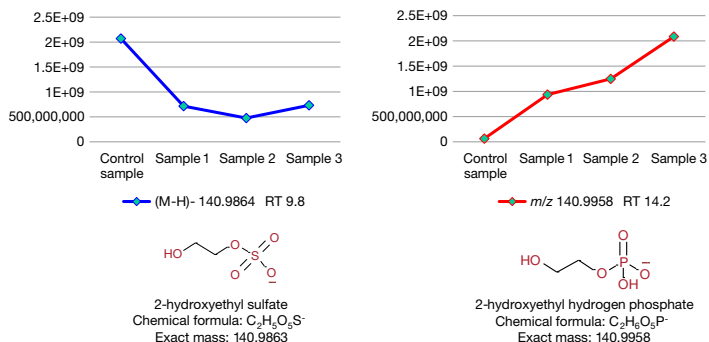

—◆— (M-H)- 140.9864 RT 9.8

2-hydroxyethyl sulfate
Chemical formula: $C_2H_5O_5S^-$
Exact mass: 140.9863

—◆— m/z 140.9958 RT 14.2

2-hydroxyethyl hydrogen phosphate
Chemical formula: $C_2H_6O_5P^-$
Exact mass: 140.9958

Figure 8. The intensity variations of two selected compounds

Conclusion

- Ion chromatography coupled with a Q Exactive mass spectrometer provides a powerful platform for LiB anode impurity and degradant analysis

- Phosphate degradation products in three aged LiB were identified

- This IC-HRMS platform can be used for QA/QC for LiB manufacturers and performance evaluations

- Further study will be conducted to investigate the relationship of the compounds identified and their intensities with the batteries performance

References

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

Find out more at **thermofisher.com**

thermo scientific