

Ion chromatography

Identification of phosphorus-containing degradation products obtained from surface deposits on lithium-ion battery anodes using ion chromatography coupled to high resolution accurate mass MS/MS

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Overview

Purpose: This poster note will focus on work our group has done to identify phosphorus-containing degradation products obtained from surface deposits on lithium-ion battery (LiB) anodes showing varying degrees of capacity loss.

Methods: Ion chromatography (IC) separates analytes based on ion-exchange selectivity, which provides information on the ionizable functional groups present in each analyte. A hydroxide eluent gradient was used to separate anionic sample components on an anion-exchange column and the analytes were detected both by electrical conductivity and high resolution accurate-mass (HRAM) MS/MS.

Results: Compound classes and specific compounds that were found in these samples include methyl carbonate, ubiquitous anionic contaminants such as chloride and sulfate, electrolyte breakdown products such as fluoride, phosphate and pyrophosphate, organic acids derived from degradation of the anode as well as ionic materials derived from reactions between various ion classes found in the samples including: sulfate esters, phosphate esters and fluorophosphate esters. This poster note focuses on the phosphorus-containing species.

Introduction

Identifying key electrolyte degradation products by chemical analysis can provide insight into elucidating mechanistic pathways that, if blocked, could potentially impart improved degradation resistance and lead to safer, longer lasting LiBs. Chemical analysis may also complement electrochemical measurements by providing a more complete solution to areas of interest such as charge transfer.

Using IC on samples containing complex mixtures of anionic species can help in the elucidation of chemical structures of unknown components. The use of HRAM mass spectrometry provides high confidence analyte identification while use of

IC provides confirmatory information about ionizable functional groups. Together these two techniques bring a new view into the search for the identity of anionic degradation products in LiBs.

Methods

Sample preparation

Anodes showing 45% loss in capacity were received from a major transportation company and cut to known weight. They were then sonicated and rinsed in deionized (DI) water three times and brought to volume. The extracts were filtered through Whatman® 0.45 µm polypropylene filters before injection into the IC-HRAM MS system.

Ion chromatography

Thermo Scientific™ Dionex™ ICS-2100 System*

Column	Thermo Scientific™ Dionex™ IonPac™ AG11/AS11 (2 mm)
Eluent	1 mM KOH from 0 to 5 minutes, 1–30 mM KOH from 5 to 25 minutes, 30–65 mM KOH from 25.1–45 minutes
Eluent source	Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge
Flow rate	0.25 mL/min
Injection volume	2.5 µL
Temperature	30 °C
Detection	Suppressed conductivity, Thermo Scientific™ Dionex™ AERS™ 500 (2 mm) Suppressor
Post column solvent	90/10 acetonitrile/water, 0.25 mL/min

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

Mass spectrometry

Thermo Scientific™ Q Exactive™ Orbitrap™ MS: ESI negative ion mode, AGC target 1e06, HRAM full scan MS and data dependent top 3 MS/MS were collected at resolution 70K and 17.5K, respectively; Stepped NCE settings were: 30, 45, 60. Scan range 50–750 *m/z*.

Data analysis

Thermo Scientific™ Xcalibur™ and Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software.

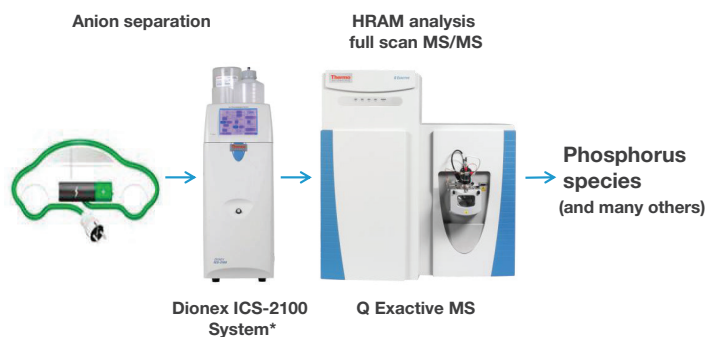
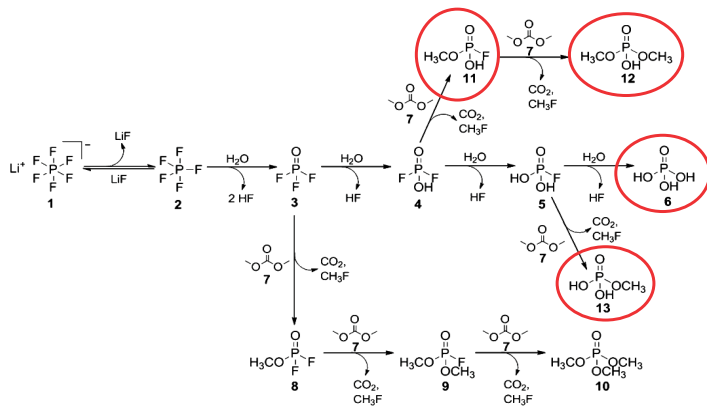


Figure 1. Overview of IC-HRAM MS system

The IC includes an eluent generator, an anion-exchange column, a suppressor and a conductivity detector. The suppressor follows the analytical column, neutralizes the KOH eluent and pairs the analytes with hydronium ion. The analytical stream is then mixed with solvent before entering the ESI interface to the mass spectrometer.



Species no. from Figure 2	Retention time (min)	Ion exchange valency	Exact mass (<i>m/z</i>)	ID
12	3.42	-1	125.0009	Dimethylphosphate C ₂ H ₆ O ₄ P
11	6.21	-1	112.9810	Monofluorophosphate, methyl ester CH ₃ O ₃ FP
13	14.43	-2	110.9853	Methylhydrogenphosphate CH ₄ O ₄ P
6	23.03	-3	96.9696	Phosphate

Figure 2. Proposed decomposition pathway¹

Several anionic species are highlighted in Figure 2 for the proposed decomposition pathway of the electrolyte lithium hexafluorophosphate in a mixed solvent of ethylcarbonate and dimethylcarbonate. These species were separated and identified by IC-HRAM MS in our current work.

Results and discussion

Figure 3 shows the anion-exchange separation of components from the wash of an anode exhibiting 45% loss in capacity, using the conditions outlined under Methods. Many of these analytes increase in concentration with anode capacity loss. Anions elute in this separation in order of valency on the anion exchange column but are detected as singly-charged ions in the mass spectrometer. Inorganic anions sulfate (-2 charge), phosphate (-3 charge) and pyrophosphate (-4 charge) are noted.

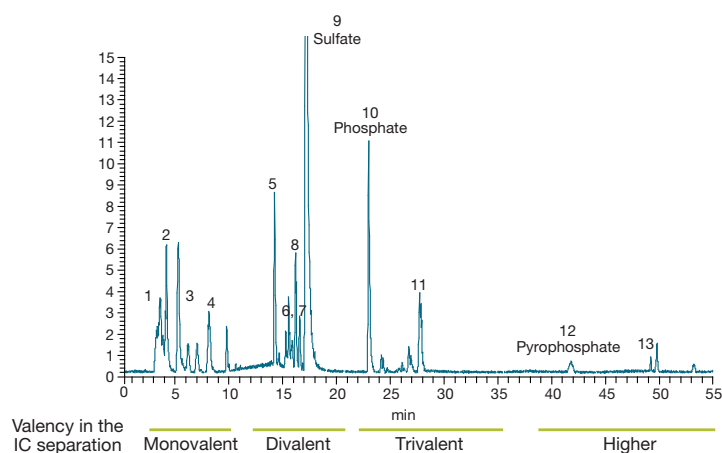


Figure 3. Full scan chromatogram of anode (45% capacity loss) wash sample

Table 1 provides the peak identifications for some species found in this sample HRAM MS/MS detection.

* or equivalent Thermo Scientific™ Dionex™ Integriion™ HPLC System

Table 1. HRAM results for species shown in Figure 3

Peak number	Retention time (min)	Exact mass (m/z)	Mass accuracy delta (ppm)	Possible ID (as -1 charged species)
1	3.3–3.8	several		Phosphate esters
2	4.20	75.0088	0.4	CH ₃ O ₃ Methyl carbonate
3	6.21	112.9810	0.6	CH ₃ O ₃ FP Monofluorophosphate, methyl ester
4	8.15	123.0121	-0.3	C ₃ H ₇ O ₃ S Propylsulfonate
5	14.2–14.5	several		Phosphate esters
6	15.55	117.0193	0.3	C ₄ H ₅ O ₄ Succinate
7	16.19	103.0036	-0.2	C ₃ H ₃ O ₄ Malonate
8	15.62	133.0137	0.4	C ₄ H ₅ O ₅ Malate
9	17.22	96.9601	0	HSO ₄
10	23.03	98.9696	-0.2	H ₂ PO ₄
11	27.73	161.0092	0.2	C ₅ H ₅ O ₆
12	41.79	176.9360	0.3	H ₃ P ₂ O ₇
13	49.19	175.0249	0.5	C ₆ H ₇ O ₆

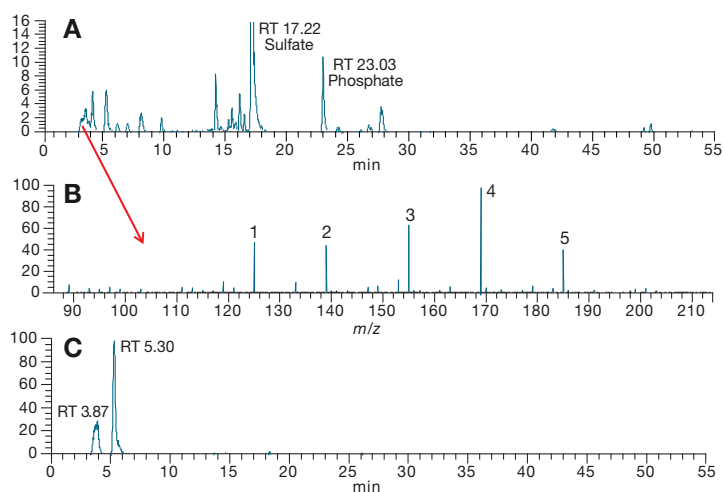


Figure 4. Early-eluting phosphate esters. A) the full scan chromatogram generated by the anion-exchange separation of components from the wash of an anode exhibiting 45% loss in capacity, using the conditions outlined under Methods. B) the MS results generated from the extracted masses of full scan in the time window of 3.6–3.8 minutes. C) the extracted ion chromatogram of mass to charge 139.01, showing that this ion elutes primarily in two peaks, meaning it can be a fragment from a slightly larger phosphate ester.

Table 2 contains a collection of the largest m/z ions found and the associated mass accuracy information.

It is important to correlate mass accuracy of a found mass to the proposed chemical formula in order determine if the proposed chemical formula is reasonable. For example, the anion with a m/z of 125.0009 must be monovalent at the found retention time, so the probable species is the monovalent phosphate ester, dimethylphosphate, as opposed to a divalent species ethylhydrogenphosphate.

Table 2 HRAM MS results for species shown in Figure 4

Peak no. (Figure 4, spectrum B)	Exact mass (m/z)	Mass accuracy delta (ppm)	Possible chemical formula
1	125.0009	-0.1	C ₂ H ₆ O ₄ P dimethylphosphate
2	139.0166	0.2	C ₃ H ₈ O ₄ P methylethylphosphate
3	155.0115	0.1	C ₃ H ₈ O ₅ P
4	169.0272	0.4	C ₄ H ₁₀ O ₅ P
5	185.0221	1.1	C ₄ H ₁₀ O ₆ P

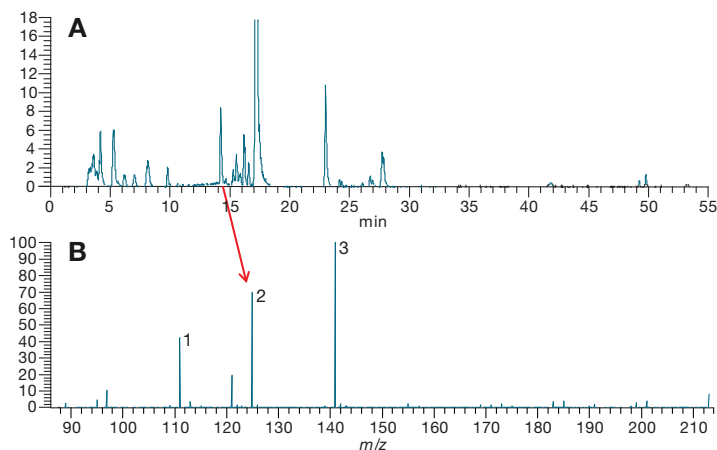


Figure 5. Phosphate esters eluting in the divalent region of the anion-exchange chromatogram. A) the full scan chromatogram generated by the anion-exchange separation of components from the wash of an anode exhibiting 45% loss in capacity, using the conditions outlined under Methods. B) shows the MS results generated from the extracted masses of full scan in the time window of 14.14–14.45 minutes. These ions are described in Table 3. The divalent ethylhydrogenphosphate elutes in this region.

Table 3. HRAM MS results for species shown in Figure 5

Peak no. (Figure 5, spectrum B)	Exact mass (<i>m/z</i>)	Mass accuracy delta (ppm)	Possible chemical formula
1	110.9853	0	CH ₄ O ₄ P methyl- hydrogenphosphate
2	125.0009	-0.1	C ₂ H ₆ O ₅ P ethyl- hydrogenphosphate
3	140.9958	0.1	C ₂ H ₆ O ₅ P hydroxyethyl- hydrogenphosphate

Conclusion

- Ion chromatography provides ion-exchange separations of anionic (or cationic) sample components
- The IC with a conductivity detector is coupled to an HRAM MS to provide information in the elucidation of unknowns
- Analytes are eluted in the order of monovalent < divalent < trivalent < higher by ion-exchange separation so information is provided on key structural features
- To date we have found components from the aging of LIB anodes in several chemical classes including carboxylic acids, esters, phosphate esters, fluorophosphate esters, sulfate esters, as well as inorganic anions
- The proposed decomposition pathway in Figure 2 is supported by our independent identification of the circled products

Reference

1. Vortmann, B. S. Nowak and C. Engelhard, *Anal. Chem.*, **2013**, *85* (6), pp 3433–3438.

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