Identification of Phosphorus-Containing Degradation Products Obtained from Surface Deposits on Li-Ion Battery Anodes Using Ion Chromatography Coupled to High Resolution Accurate Mass MS/MS

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Overview

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

Methods: Ion chromatography 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 (HR/AM) 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 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 Li-ion batteries. Chemical analysis may also complement electrochemical measurements by providing a more complete solution to areas of interest such as charge transfer.

Using ion chromatography (IC) on samples containing complex mixtures of anionic species can help in the elucidation of chemical structures of unknown components. The use of HR/AM 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 lithium ion batteries.

Methods

Sample Preparation (Figures 3, 4, 5)

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 thru Whatman 0.45 µm polypropylene filters before injection into the IC-HR/AM MS system.

Ion Chromatography

Thermo Scientific[™] Dionex[™] ICS-2100 System: Column: Thermo Scientific[™] Dionex[™] lonPac[™]AG11/AS11 (2 mm); Eluent for Figures 3,4,5: 1mM 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; Inj. Volume: 2.5 μ L; 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.

Mass Spectrometry

Thermo Scientific[™] Q Exactive[™] Orbitrap[™] MS: ESI negative ion mode, AGC target 1e06, HR/AM 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[™] Dionex[™] Chromeleon[™] Chromatography Data System (CDS) Software.

FIGURE 1. Overview of IC-HR/AM 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.





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-HR/AM MS in our current work.

Species number from Fig. 2	Retention time (minutes)	lon Exchange Valency	Exact Mass (m/z)	ID
12	3.42	-1	125.0009	Dimethylphosphate C2H6O4P
11	6.21	-1	112.9810	Monofluorophosphate, methyl ester CH3O3FP
13	14.43	-2	110.9853	Methylhydrogenphosphate CH4O4P
6	23.03	-3	96.9696	Phosphate

Results

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



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.

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

Table 1 HR/AM results for species shown in figure 3.

Peak number	Retention time (minutes)	Exact Mass (<i>m/z</i>)	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	CH3O3 Methyl carbonate
3	6.21	112.9810	0.6	CH3O3FP Monofluororphosphate, methyl ester
4	8.15	123.0121	-0.3	C3H7O3S Propylsulfonate
5	14.2-14.5	several		Phosphate esters
6	15.55	117.0193	0.3	C4H5O4 Succinate
7	16.19	103.0036	-0.2	C3H3O4 Malonate
8	15.62	133.0137	0.4	C4H5O5 Malate
9	17.22	96.9601	0	HSO4
10	23.03	98.9696	-0.2	H2PO4
11	27.73	161.0092	0.2	C5H5O6
12	41.79	176.9360	0.3	H3P2O7
13	49.19	175.0249	0.5	C6H7O6

FIGURE 4. Early-eluting phosphate esters.



Figure 4A shows 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

Figure 4B shows the MS results generated from the extracted masses of full scan in the time window of 3.6-3.8 minutes.

Figure 4C shows 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 Table 3 HR/AM MS results for species shown in figure 5. 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 HR/AM MS results for species shown in figure 4.

Peak number (Fig. 4, Spectrum B)	Exact mass (<i>m/z</i>)	Mass Accuracy Delta (ppm)	Possible Chemical formula
1	125.0009	-0.1	C2H6O4P dimethylphosphate
2	139.0166	0.2	C3H8O4P methylethylphosphate
3	155.0115	0.1	С3Н8О5Р
4	169.0272	0.4	C4H10O5P
5	185.0221	1.1	C4H10O6P

FIGURE 5. Phosphate esters eluting in the divalent region of the anion-exchange chromatogram.



Figure 5A shows the full scan chromatogram generated by the anion-exchange separatio of components from the wash of an anode exhibiting 45% loss in capacity, using the conditions outlined under Methods. Figure 5B 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.

Peak number (Fig. 5, Spectrum B)	Exact mass (<i>m/z</i>)	Mass Accuracy Delta (ppm)	Possible Chemical formula
1	110.9853	0	CH4O4P methylhydrogenphosphate
2	125.0009	-0.1	C2H6O5P ethylhydrogenphosphate
3	140.9958	0.1	C2H6O5P hydroxyethylhydrogenphospha

Conclusions

- Ion chromatography provides ion-exchange separations of anionic (or 1 cationic) sample components
- 2. The IC with a conductivity detector is coupled to an HR/AM MS to provide information in the elucidation of unknowns
- 3. Analytes are eluted in the order of monovalent<divalent<trivalent<higher b ion-exchange separation so information is provided on key structural features
- 4. To date we have found components from the aging of LiB anodes in severa chemical classes including carboxylic acids, esters, phosphate esters, fluorophosphate esters, sulfate esters, as well as inorganic anions
- 5. The proposed decompositon 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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