

Ion chromatography

Analysis and identification of ionic manganese containing degradation products from the anode surface of cycle & calendar aged lithium-ion batteries

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Overview

Purpose: Identify the chemical composition of manganese 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 deionized (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 using IC with suppressed conductivity detection (IC-CD), IC coupled with high resolution accurate mass spectrometry (IC-HRAM MS), and direct infusion HRAM MS.

Results: Identification of a proposed permanganate containing degradation product by IC-HRAM MS (-ESI mode) by component identification software was consistent with the expected elution profile and supported with an m/z to two decimal point accuracy. However, an m/z ratio to four decimal point accuracy disproved the proposed product.

Introduction

Manganese-based LiBs are environmentally friendly, have a good safety record, and can be made at a lower cost than other metal based LiB. However, they have a shorter lifetime. A common source of battery failure includes dissolution of a manganese based cathode and deposition of electrolyte and manganese containing degradation products on the anode.

Presented are results from the chemical analysis of manganese degradation products on the anode surface of cycle and calendar aged LiBs using ion exchange chromatography (IC) with suppressed conductivity detection (IC-CD), IC coupled to high resolution accurate mass spectrometry (IC-HRAM MS), and direct infusion HRAM MS.

Battery components included a graphite anode, a lithium nickel manganese cobalt oxide (NMC) cathode, and a lithium hexafluorophosphate electrolyte in a dimethyl carbonate solvent.

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 DI water three times and brought to volume. The extracts were filtered thru Whatman® 0.45 µm polypropylene filters before injection into the IC-HRMS system.

Ion chromatography

Thermo Scientific™ Dionex™ ICS-2100 IC 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	(MS detection) 90/10 acetonitrile/water, 0.25 mL/min

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

Mass spectrometry

Thermo Scientific™ Q Exactive™ Orbitrap™ MS: ESI negative ion mode, AGC target 1e06, HRAM full scan MS and data dependent 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.

Results and discussion

Figure 1 shows results from the analysis of the aqueous extract of a cycle aged graphite LiB anode in a LiPF_6 dimethyl carbonate mixture by IC. Peak resolution was achieved using an IonPac AS 11 hydroxide selective anion exchange column, KOH eluent gradient, and suppressed conductivity detection.

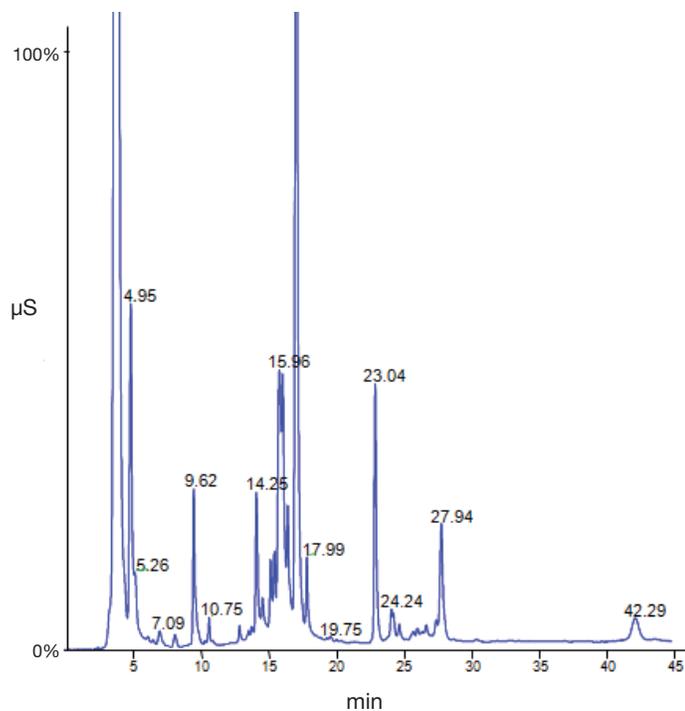


Figure 1. Analysis of electrolyte degradation products by IC

Figure 2 provides results of the analysis of Mn containing products using IC-ICP-MS. Of particular interest was retention of Mn containing products appearing as a broad peak between 17–25 min using an anion exchange column. Since Mn is a cation, the expectation was it should have eluted with the void volume. Mn containing products retained by the column suggests an anionic complex of unidentified composition.¹

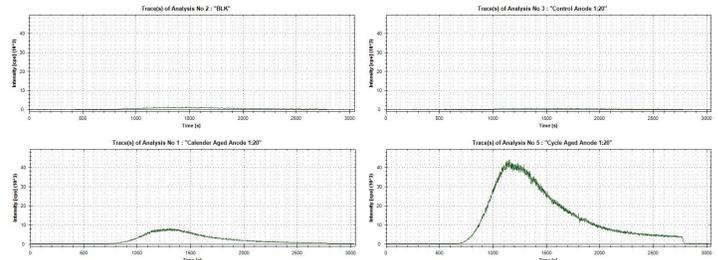


Figure 2. Analysis of ^{55}Mn containing degradation products by IC-ICP-MS

Figure 3 depicts a pathway on the formation of a presumed anionic Mn complex. A Mn based cathode begins dissolving under acidic conditions, catalyzed by the presence of trace water. The dissolved Mn forms Mn^{3+} which disproportionates to Mn^{2+} and Mn^{4+} . Mn^{2+} is soluble in the electrolyte and migrates to the anode where it deposits on the anode surface.

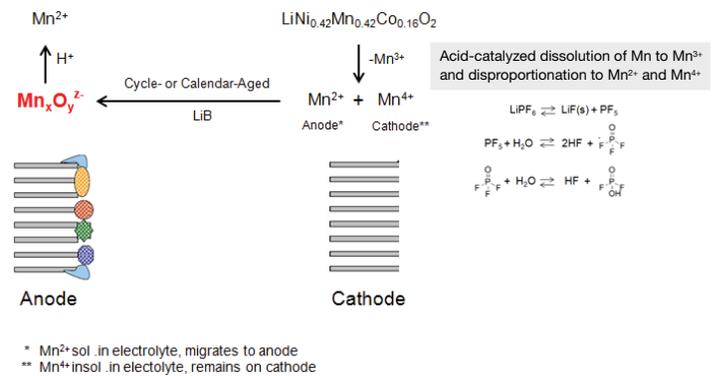


Figure 3. Manganese dissolution mechanistic pathway

Figure 4 provides an overlay of a permanganate standard, a manganate standard, a mixture of anions standards, and a calendar aged LiB sample. Results show permanganate includes a major peak that elutes at approximately 2 minutes and a smaller peak that co-elutes with manganate at approximately 18 min. The manganate standard is shown to elute with carbonate. In addition the calendar aged sample has peaks that co-elute with both the permanganate and manganate standards.

Initial results suggest neither permanganate nor manganate are stable on the anion exchange column. A possible explanation is permanganate may be reacting on the column and the degradation products are eluting in the vicinity of carbonate.

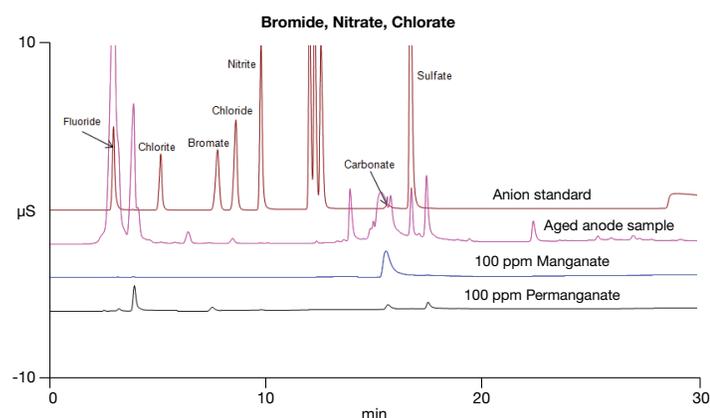


Figure 4. Analysis of manganate, permanganate, anion standards, and calendar aged anode samples by IC

Figure 5 shows results from the analysis of a permanganate standard by direct infusion -ESI HRMS MS and by -ESI IC-HRAM MS. Results produce a positive response to permanganate by direct infusion HRAM MS, but a negative response to IC-HRAM MS. A negative response by IC-HRAM MS supports the premise that permanganate is not stable on the anion column.

Analysis of the cycle aged LiB sample by direct infusion HRAM MS produce a negative response, indicating the absence of permanganate.

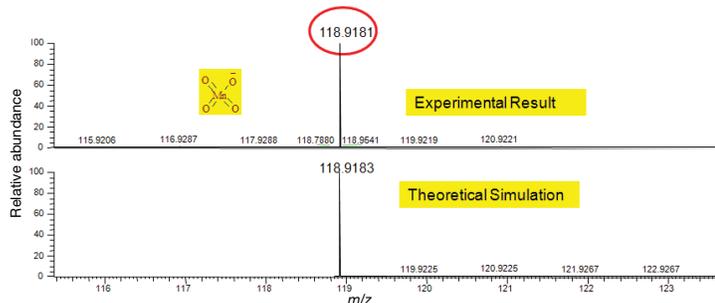


Figure 5. Analysis of permanganate standard by direct infusion HRAM MS

Figure 6 considers a Mn oxide species (labeled 1) as a candidate anionic degradation product of interest.² The product is NOT permanganate but a complex incorporating permanganate. Formation of the product is consistent with observed divalent carboxylic acid degradation products by -ESI IC-HRAM MS (in a separate study) that could serve as the starting material. In addition the product degrades under acidic conditions which is consistent with the mechanism and observed behavior.

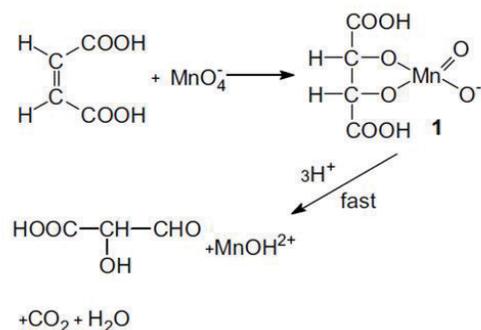


Figure 6. Proposed anionic Mn containing product mechanistic pathway

Figure 7 provides results from a full scan of a cycled aged sample by direct infusion -ESI HRAM MS for possible Mn containing components. Component identification of the MS data provided a positive response to a proposed Mn containing product (labeled 1 in Figure 6) and was consistent with a retention time of 18–25 min. When *m/z* is measured to 2 decimal point accuracy, the data supports the proposed species. However when measured to 4 decimal points, it disproved the proposed species, based on the variation at the outer decimal points.

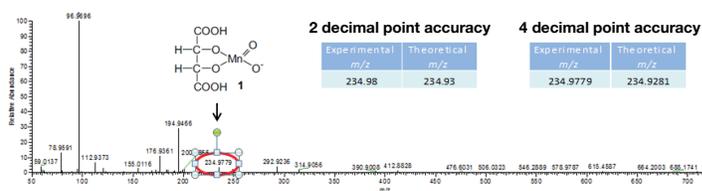


Figure 7. Mis-identification of cycle aged (45% capacity loss) Mn containing degradation product by direct infusion HRAM MS

Conclusion

Analysis of water soluble electrolyte degradation products (deposited on the anodesurface of aged LiB samples) for Mn using anion exchange IC-ICP-MS were retained under alkaline eluent conditions suggesting an anionic Manganese oxide complex such as $Mn_xO_y^z$.

A comparison between a permanganate standard (considered a likely degradation product) and the calendar aged LiB sample by anion exchange IC shows a major peak from the calendar aged sample co-eluting with the permanganate standard. However the permanganate standard also included smaller peaks that co-elute with manganate and carbonate standards suggesting permanganate may not be stable on the column. Analysis of a permanganate standard by direct infusion -ESI HRAM MS provided a positive response, but a negative response to -ESI IC-HRAM MS. The results support the premise that permanganate may not be stable on the column.

Elemental composition based on HRAM data of the cycle aged sample produced a negative response to permanganate but a positive response to a proposed Mn containing compound ($C_4H_4O_8Mn$) that corresponded to a structure containing a permanganate moiety. The proposed structure was consistent with the observed retention time, and matched a m/z to 2 decimal point accuracy. But not to 4 decimal point accuracy. As a result, the proposed chemical structure was dismissed as the identified compound, saving time and resources that could have been spent pursuing it further based on 2 decimal point accuracy. No other Mn containing product were proposed.

Results from the study including elution behavior by IC, possible interaction with the column, and compound identification by HRAM MS, suggest the Mn compound observed by IC-ICP-MS is not Mn oxide based but may instead be carboxylate or carbonate based, such as $MnC_xO_y^z$.

References

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