

Analysis of Main Components of Lithium Salts in Lithium-Ion Battery Electrolytes Using Ion Chromatography-Quadrupole Time-of-Flight High-Resolution Mass Spectrometry

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Abstract

In this study, a method for identifying the main components of lithium salts in lithium-ion battery electrolytes was established using a Metrohm 930 ion chromatography system (IC) coupled with an Agilent 6546 LC/Q-TOF. Electrolyte samples were diluted and filtered before direct injection. The main anion components of lithium salts were separated with acetonitrile and a mixed solution system of $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$, and then analyzed by high-resolution mass spectrometry. Various anions (including difluorophosphate, tetrafluoroborate, hexafluorophosphate, and bisfluorosulfonimide) and a degradation product (oxalate) of lithium salts were successfully identified using this method.

Introduction

The lithium-ion battery industry has been experiencing rapid growth, driven by the surge in production of new energy vehicles. Electrolytes, one of the four key materials of lithium batteries, generally take nonaqueous solvents as lithium-ion carriers. Their components mainly include organic solvents, lithium salts, and some additives. The organic solvents frequently used in lithium batteries are polar aprotic solvents, predominantly carbonates and carboxylates. The lithium salt used in the electrolyte provides a large amount of free lithium ions in the process of charge and discharge. The electrochemical properties of the electrolyte, such as charge-discharge efficiency, stability, and lifetime, are dependent on the type and nature of the lithium salt. Therefore, the analysis and identification of lithium salt components and related degradation products in lithium-ion battery electrolytes are of significant importance for mechanistic research.

Lithium salts in the electrolyte generally exist in the form of lithium ions and various anions. Ion chromatography, a branch of high-performance liquid chromatography (HPLC), has unique advantages in the separation and determination of anions and cations. It allows for simultaneous analysis of multiple ions and is widely applied in various fields such as environmental¹, food², pharmaceutical³, and new energy⁴ industries. Currently, the most common analysis method is based on ion chromatography coupled with a conductivity detector. However, this method is mainly applicable to known compounds and is unable to support the determination of unknown lithium salt components and related degradation products in the electrolyte. The quadrupole time-of-flight (Q-TOF) high-resolution mass spectrometry system monitors the accurate mass of compounds over a wide mass range and calculates the elemental composition using the accurate mass and isotopic pattern. This makes it well-suited for the extensive screening, comprehensive analysis, and accurate identification of unknown compounds. The combination of IC high-efficiency multi-ion separation and the powerful capabilities of the Q-TOF provide an important and effective method for analyzing unknown components in lithium-ion battery electrolytes.

In this study, a Metrohm 930 ion chromatography system was used to separate the main anion components of lithium salt samples in the electrolyte through a Metrosep A supp 5–250/4.0 anion column. The separated analyte ions flowed along with the eluent to the ion suppressor and then were sent to a conductivity detector for detection. In addition, the mobile phase processed by the suppressor is compatible with Q-TOF, allowing for the direct identification of the main anions in samples by Q-TOF. The overall analysis process is illustrated in Figure 1.

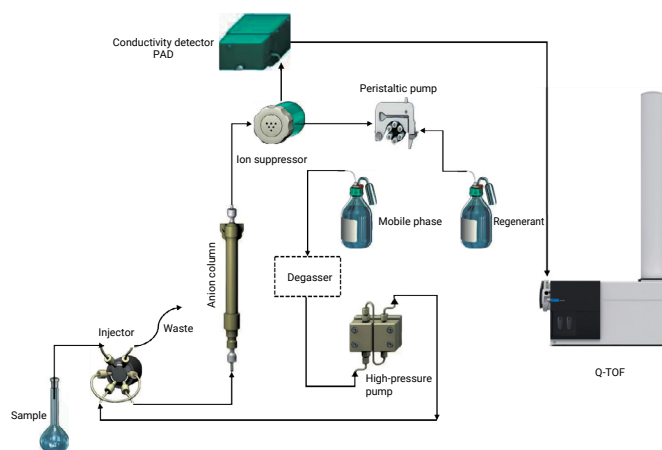


Figure 1. Schematic diagram of IC-PAD-QTOF analysis process.

Experimental

Reagents and samples

Acetonitrile was MS grade, purchased from Merck. Sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) were analytical grade, purchased from Guangzhou Chemical Reagent Factory. High-purity deionized water was freshly prepared using a Millipore Milli-Q ultrapure water system. The 2 mol/L sulfuric acid standard solution was analytical grade, purchased from Shenzhen Bolinda Technology Co., Ltd. Lithium battery electrolyte samples were provided by the user, diluted with acetonitrile at a predetermined ratio and filtered before direct injection.

Instruments and equipment

A Metrohm 930 Compact IC Flex ion chromatograph and an Agilent 6546 LC/Q-TOF system with an Agilent Dual AJS ESI source were used.

Agilent MassHunter workstation software (version 10.1) was used for data acquisition and qualitative analysis on the Agilent 6546 LC/Q-TOF system. Metrohm MagIC Net software (version 3.3) was used for ion chromatography data acquisition and analysis.

Instrument parameters

IC Conditions	
Column	Metrohm Metrosep A supp 5–250/4.0 anion column
Flow Rate	0.5 mL/min
Injection Volume	20 μ L
Column Temperature	30 $^{\circ}$ C
Mobile Phase A	Water containing 3.2 mmol/L Na_2CO_3 and 1.0 mmol/L NaHCO_3
Mobile Phase B	Acetonitrile
Gradient	Isocratic elution (mobile phase A:mobile phase B = 60:40, v:v)
MS Conditions	
Ion Mode	Negative (ESI $^{-}$)
Gas Temperature	250 $^{\circ}$ C
Drying Gas Flow	8 L/min
Nebulizer	35 psi
Sheath Gas Temperature	350 $^{\circ}$ C
Sheath Gas Flow	11 L/min
Capillary Voltage	2,500 V
Nozzle Voltage	500 V
Fragmentor	120 V
Cone Voltage	65 V
Octopole RF	750 V
Mass Range (MS)	50 to 1,100
Mass Range (MS/MS)	20 to 1,100
Acquisition Rate	6 spectra/second
Isolation Width	Narrow (~ 1.3 m/z)
Collision Energy	20, 40, and 60 V

Results and discussion

Ion chromatographic separation

The anions hexafluorophosphate (PF_6^-), bisfluorosulfonimide ($\text{F}_2\text{NS}_2\text{O}_4^-$), and oxalate (C_2HO_4^-) analyzed in this study are highly polarizable ions. They exhibit strong retention on conventional anion exchange columns, making their elution challenging. In this experiment, a high-capacity anion column of Metrosep A supp 5–250/4.0 was used, and 40% acetonitrile was added to the eluent of the mixed system of Na_2CO_3 and NaHCO_3 . This improves the elution of anions such as PF_6^- and shortens the retention times (RTs) of these ions on the anion exchange column.

The separation results of six anions in unknown electrolyte samples after three replicate injections are depicted in Figure 2. The figure shows that at a flow rate of 0.5 mL per minute, six identified anions in the sample, including a fluoride ion, difluorophosphate, tetrafluoroborate, hexafluorophosphate, and bisfluorosulfonimide, were completely eluted within 45 minutes and well-separated.

The resolution (R_s) between target peaks was significantly greater than 1.5, as shown in Table 1. Furthermore, the RTs and responses of the six anions in the sample were stable in three replicate injections, with their RSDs being less than 0.8% and 5.5%, respectively. The results demonstrate the stability of this separation method.

Table 1. Resolution and stability of six anions in unknown electrolyte ($n = 3$).

Target peak	Average RT (min)	RT RSD (%)	Peak Area RSD (%)	Resolution (R_s)
1	8.70	0.5	2.1	NA
2	10.73	0.7	1.2	5.17
3	13.53	0.5	3.6	7.32
4	20.25	0.5	3.2	8.85
5	33.20	0.5	5.2	9.86
6	38.32	0.8	5.5	7.08

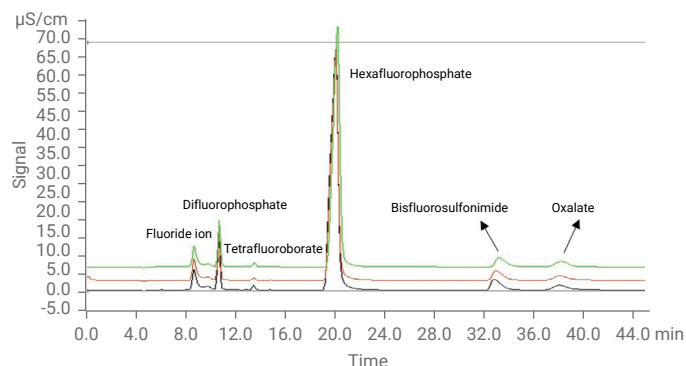


Figure 2. Separation and identification of six anions in unknown electrolyte ($n = 3$).

Mass spectrometry identification

The sample components separated by ion chromatography were introduced into the ion suppressor along with the mobile phase for desalting, and then directly injected into the Q-TOF for qualitative analysis. Taking bisfluorosulfonimide ($\text{F}_2\text{NS}_2\text{O}_4^-$) in Figure 2 as an example, the primary ion (quasi-molecular ion) of the target peak (RT \sim 33.2 minutes) collected by Q-TOF had an m/z of 179.9243. Then, using the Agilent MassHunter Qualitative Analysis software, the molecular formula of the target was calculated as $\text{F}_2\text{NO}_4\text{S}_2$ based on the collected accurate mass and its isotope (intensity/spacing) distribution. The deviation between the measured value and the theoretical value of the accurate mass was 0.09 ppm, and the comprehensive match score was 99.64 (see Figure 3). The secondary spectra are shown in Figure 4. At collision energies of 40 and 60 V, the S-N bond of the ion m/z 179.9243 was broken, generating associated characteristic fragment ions m/z 82.9607 (FSO_2^-).

and m/z 96.9633 (FNSO_2^-); and with the loss of the F ion, these two characteristic fragment ions in turn generated fragment ions m/z 63.9612 (SO_2^-) and m/z 77.9657 (NSO_2^-), respectively. Therefore, it was deduced that the target was lithium bisfluorosulfonimide.

Following this process, the other components were identified as difluorophosphate (PF_2O_2^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), and oxalate (C_2HO_4^-) (see Figure 2). The target peak at RT \sim 8.7 minutes was identified as the fluoride ion (F^-) by comparison with the retention time of the standard in the ion chromatography analysis. It is noteworthy that oxalate (C_2HO_4^-) could potentially be a degradation product of lithium oxalate difluoroborate (LiODFB), a common component of lithium salts. According to the relevant literature⁵, LiODFB readily forms LiODFB·H₂O with a stable six-fold coordination structure with water molecules in the air. As the exposure time in air increases, LiODFB·H₂O hydrolyzes slowly, yielding oxalic acid as one of its hydrolysis products. Therefore, it can be deduced that the analyzed electrolyte samples contain LiODFB and that LiODFB has degraded.

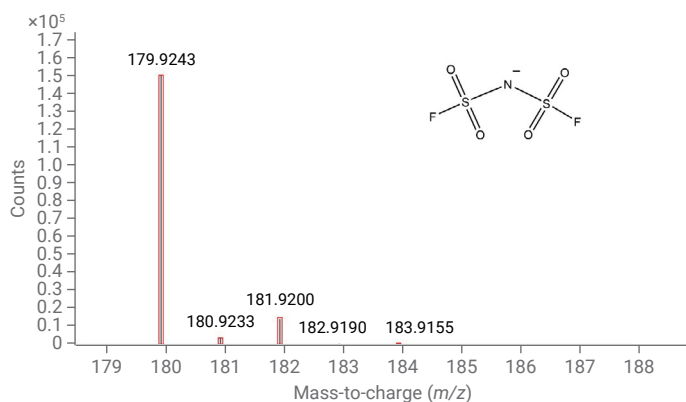


Figure 3. Accurate mass and isotope distribution of primary ion of target peak (RT = 32.5 minutes).

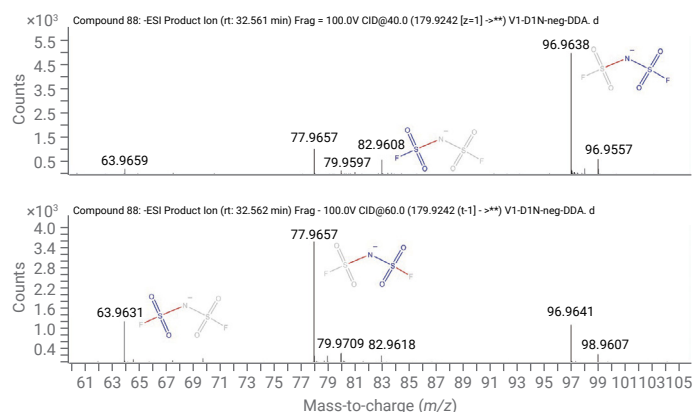


Figure 4. Secondary fragment ion spectra of target peak (RT = 32.5 minutes) at collision energies of 40 and 60 V.

Conclusion

In this study, a Metrohm 930 ion chromatography system (IC) coupled with an Agilent 6546 LC/Q-TOF was used to separate and qualitatively identify the main anions of lithium salts in lithium-ion battery electrolytes. The results showed that after the sample components were separated by ion chromatography, the six anions obtained from the analysis were completely eluted within 45 minutes and well separated, with a resolution significantly greater than 1.5. After identification, it was found that the unknown electrolyte sample contained fluoride ions, lithium difluorophosphate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium bisfluorosulfonimide, and oxalic acid, a hydrolysis product of lithium oxalate difluoroborate. Compared to the conventional LC/Q-TOF technique, the IC/Q-TOF method established in this study can effectively address the issues of weak retention and difficult separation of highly polar substances on the chromatographic column, fulfilling the needs of identifying unknown anion components in lithium-ion battery electrolytes. It provides an effective approach for further investigation into the degradation mechanism of lithium-ion battery electrolytes.

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DE76468443

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© Agilent Technologies, Inc., 2023
Printed in the USA, December 8, 2023
5994-6122EN

