Identification for Anion in Electrolyte of Lithium Battery Using Ion Chromatography – Quadrupole -Time of Flight Mass Spectrometry

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Introduction

Electrolyte, as one of the four key materials of lithium batteries, generally takes non-aqueous solvents as lithium-ion carriers, and its components mainly include organic solvents, lithium salts and some additives. The lithium salt used in the electrolyte provides a large amount of free lithium ions in the process of charge and discharge. They generally exist in the form of lithium ions and various anions in the electrolyte. Ion chromatography (IC) detection technology has unique advantages in the separation and determination of anions and cations. and it can realize simultaneous analysis of multiple ions. Quadrupole – time of flight high-resolution mass spectrometry (Q-TOF) system can be used for extensive screening, comprehensive analysis and accurate identification of unknown compounds. Therefore, combination of IC high-efficiency multi-ion separation and Q-TOF powerful qualitative function provides an important and effective method for analyzing unknown components in lithium battery electrolyte.

In this study, the Metrohm 930 ion chromatography system was used to separate the main anion components of the lithium salt in the electrolyte through the Metrosep A supp 5–250/4.0 anion analysis column. The separated analyte flowed along with the eluent to the ion suppressor, and then was sent to conductivity detector for detection. In addition, the mobile phase processed by the suppressor can be compatible with Q-TOF, which can be used to identify the main anions in samples directly. Schematic diagram of IC-QTOF analysis process is shown in Figure 1.
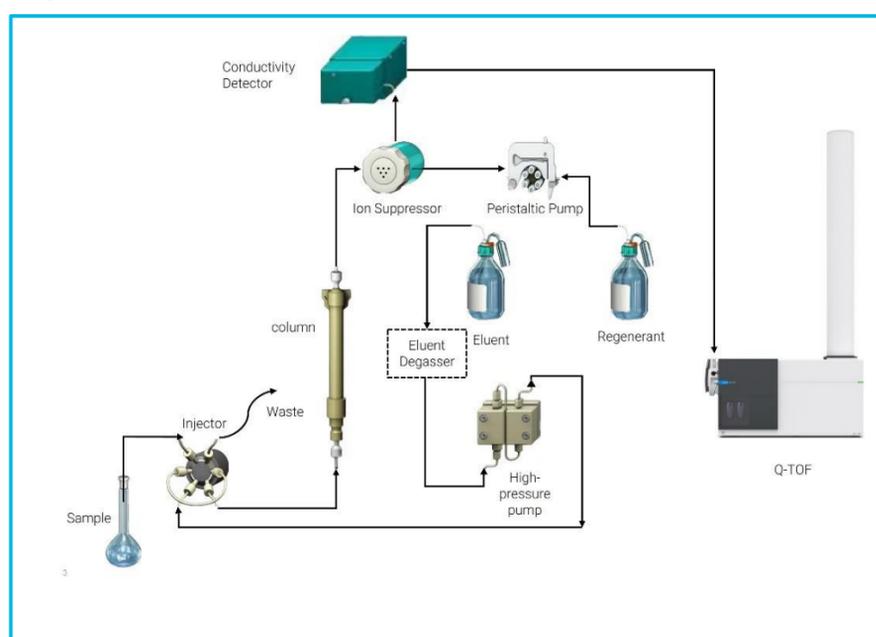

Figure1:Schematic diagram of IC-QTOF analysis process

Experimental

Sample Preparation

Lithium battery electrolyte samples were diluted with acetonitrile in a certain proportion and filtered before direct injection analysis.

Method

IC Conditions	
Column:	Metrohm Metrosep A supp 5–250/4.0
Column Temperature:	30 ℃
Injectiong Volume:	20 μL
Regeneration Eluent:	2 mmol/L sulfuric acid
Flow Rate:	0.5 mL/min
Mobile Phase A:	3.2 mmol/L Na_2CO_3 + 1.0 mmol/L $NaHCO_3$ in water
Mobile Phase B:	Acetonitrile
Gradient:	Mobile phase A: Mobile phase B = 60 : 40, v: v
Run time:	45 min

MS Conditions	
Ion mode:	Negative
Gas Temperature:	250 ℃
Gas Flow:	8 L/min
Nebulizer:	35 psi
Shealth Gas Temperature:	350 ℃
Shealth Gas Flow:	11 L/min
Capillary Voltage:	2500 V
Nozzle Voltage:	500 V
Fragmentor:	120 V
MS mass range:	50 – 1100 m/z
MS/MS mass range:	20 – 1100 m/z
Collision Energy:	20, 40, 60 eV

Ion chromatography separation

The anions such as hexafluorophosphate (PF_6^-), bisfluorosulfonimide ($F_2NS_2O_4^-$) and oxalate ($C_2HO_4^-$) analyzed in this study belong to easily polarized ions, and their retention on conventional anion exchange columns is extremely strong ,which is difficult to be eluted. In order to solve this problem, a high-capacity anion analysis column of Metrosep A supp 5−250/4.0 was used in this experiment. What's more, 40% acetonitrile was adopted to the eluent of the mixed system of Na_2CO_3 and $NaHCO_3$ to improve the eluent's ability to elute anions such as PF_6^- and shorten retention times of these ions on anion exchange column. The separation results of unknown electrolyte samples after ion chromatography analysis are shown in Figure 2. It can be seen from the figure that at a flow rate of 0.5 mL/min, six identified anions in the sample were completely eluted within 45 min and achieved good separation, and the resolution Rs between each target peak was much greater than 1.5.
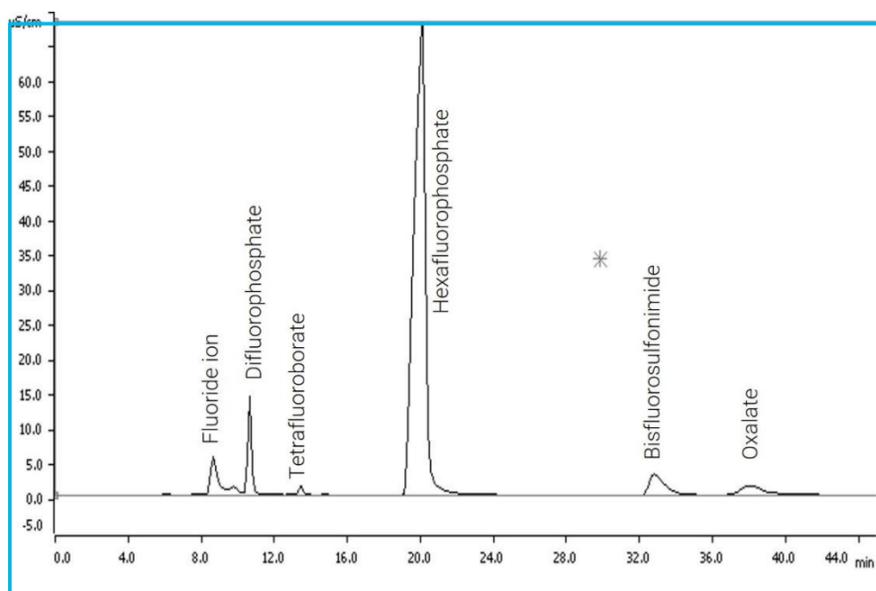

Figure 2: Separation of Six Anions in Unknown Electrolyte

Identification

The sample components separated by IC enter the ion suppressor with the mobile phase for desaltion, and then directly inject into the Q-TOF for qualitative analysis. Taking bisfluorosulfonimide ($F_2NS_2O_4^-$) in Figure 3 as an example, the primary ion (quasimolecular ion) m/z of this target peak (RT = 32.5 min) collected by Q-TOF is 179.9243. Then, using MassHunter qualitative analysis software, according to the collected accurate mass number and its isotope (intensity/spacing) distribution (Figure 3)., the molecular formula of the target is calculated as $F_2NO_4S_2$, and the deviation between the measured value of the accurate mass number and the theoretical value is 0.09 ppm, and the matching comprehensive score is 99.64.

The MS/MS spectrum is shown in Figure 4. At 40 eV and 60 eV collision energies, the S-N bond of the ion m/z 179.9243 was broken, generating the 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, this Two characteristic fragment ions in turn generate fragment ions m/z 63.9612 (SO_2) and m/z 77.9657 (NSO_2), respectively. Therefore, it was deduced that the target object was bisfluorosulfonimide.
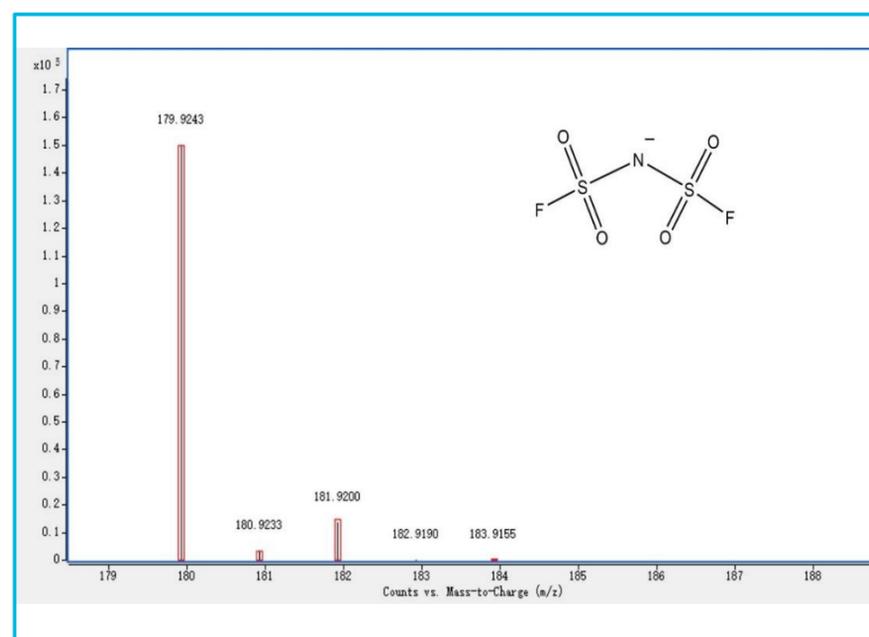

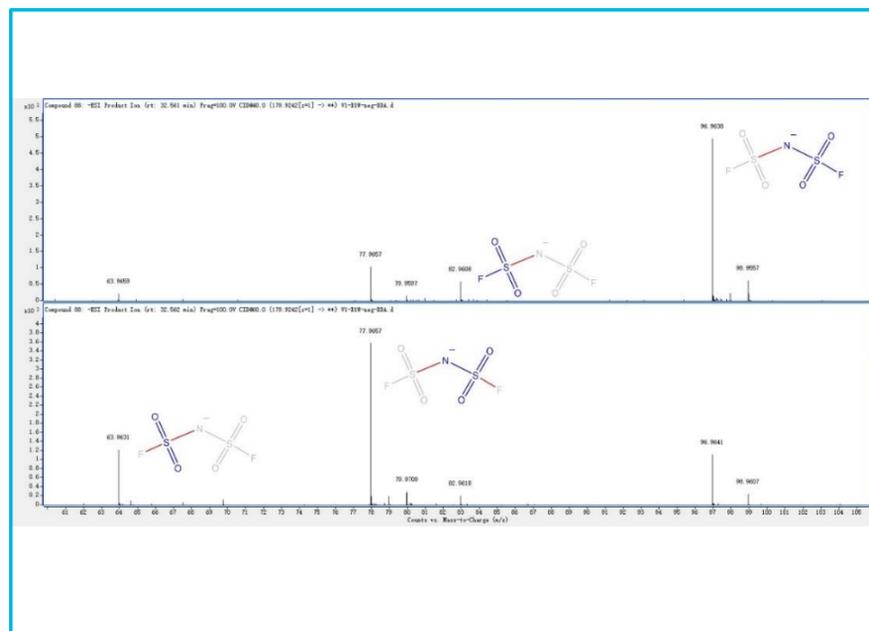Figure 3: Accurate Mass and Isotope Distribution of Primary Ion of Target Peak (RT =32.5 min)

Figure 4: Secondary Fragment Ion Maps of Target Peak (RT =32.5 min)) at 40 eV and 60 eV Collision Energies

Results and Discussion

According to this process, the other components in the sample were identified as difluorophosphate ($PF_2O_2^-$), tetrafluoroborate (BF_4^-), hexafluorophosphate ($PF6^-$) and oxalate ($C_2HO_4^-$) .The target peak at RT = 9.2 min was identified as the fluoride ion (F^-) by comparison with the retention time of the standard in ion chromatography analysis . It is worth mentioning that oxalate ($C_2HO_4^-$) may be a degradation product of lithium oxalate difluoroborate (LiODFB), which is a common lithium salt component. According to the relevant literature[1], LiODFB tend to be formed as LiODFB·H2O with a stable six-fold coordination structure with water molecules in the air, and one of its hydrolysis products is oxalic acid. From this, it can be deduced that the analyzed electrolyte samples contain LiODFB and that LiODFB has been degraded.
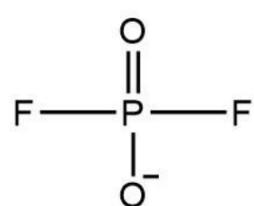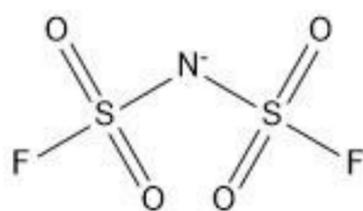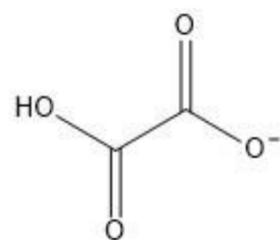

Difluorophosphate
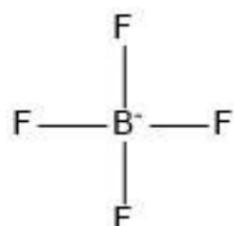
Tetrafluoroborate
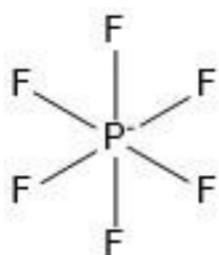
Hexafluorophosphate

Bisfluorosulfonimide

Oxalate

Conclusions

- In this paper, a Metrohm 930 ion chromatography system (IC) coupled with an Agilent 6546 quadrupole time-of-flight high-resolution mass spectrometry system (Q-TOF) was used to separate and qualitatively identify the main anions of lithium salts in lithium battery electrolytes. The results showed that after the sample was separated by ion chromatography, the six anions obtained in the analysis were completely eluted within 45 minutes, and a good separation was obtained.

- After identification, the unknown electrolyte sample contained fluoride ions, lithium difluorophosphate, lithium hexafluorophosphate, lithium tetrafluoroborate and lithium bisfluorosulfonimide, and oxalic acid, a hydrolysis product of lithium difluoroborate oxalate. Compared with conventional LC-QTOF technology, the IC-QTOF method established in this paper can effectively solve the problems of weak retention and difficult separation of strong polar substances on the chromatographic column, and can meet the needs of identifying unknown anion components in lithium battery electrolytes. It provides an effective technical means for further research on the degradation mechanism of lithium battery electrolyte.

References

[1]Sandra Zugmanna, Dominik Moosbauera, et al. Electrochemical characterization of electrolytes for lithium-ion batteries based on lithium difluoromono(oxalato)borate. Journal of Power Sources, 2011, 196: 1417-1424.

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