Application Brief

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Characterization of the Electrochemical Differences Between Sulfur Isotopes in Lithium-Sulfur Batteries Using the Agilent 8900 ICP-MS/MS

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Introduction

A lithium-sulfur (Li-S) battery is a secondary battery with metallic lithium (Li) as the anode and sulfur (S) as the cathode. Compared to conventional lithium-ion batteries, Li-S batteries offer a significantly higher theoretical energy density and are therefore considered one of the candidate technologies for the next-generation high-energy storage systems. Despite this potential, Li-S batteries still face several challenges, such as the "shuttle effect" of polysulfides. During charging and discharging, sulfur is converted into soluble polysulfides, which can diffuse to the electrolytes and migrate to the lithium metal anode and react with lithium. This side reaction degrades cycle life and overall battery performance. In nature sulfur exist as two major isotopes, i.e., ^{32}S and ^{34}S. Both isotopes are very similar in chemical properties, but may behave somewhat differently in some physical and chemical processes due to different masses, a phenomenon known as the "isotope effect".

To explore this, the authors conducted a modeling study on Li-S batteries to investigate the difference in electrochemical properties between ^{32}S and ^{34}S. Despite both isotopes forming the same eight-atom ring structure (S8), notable variation was observed. Specifically, the S-S bonds in the cyclic ^{34}S$_8$ molecule were found to be stronger than those in the cyclic ^{32}S$_8$ molecule, resulting in greater tendency to react with lithium. The soluble lithium polysulfides generated by the Li-^{34}S conversion reaction, compared with the products based on Li-^{32}S, showed stronger cation–solvent interactions and weaker cation–anion interactions, which facilitated the rapid dissolution of the polysulfides but hindered their migration from the cathode to the anode. Therefore, Li-^{34}S batteries showed improved cathode reaction kinetics at the solid–liquid interface and suppressed shuttling of the polysulfides through the electrolyte, resulting in better cycle performance than Li-^{32}S batteries. In this application brief, an electrochemical separation method for ^{34}S/^{32}S isotopes is proposed based on the different shuttling kinetics of isotopic sulfur-based polysulfides. Compared to traditional isotopes separation methods such as chemical exchange or distillation, this method achieves higher separation factors and brings opportunities for low-cost manufacture, utilization, and research of heavy chalcogen isotopes.

The Agilent 8900 ICP-MS/MS was used to characterize ^{34}S and ^{32}S. Conventional single quadrupole ICP-MS faces challenges in sulfur determination due to low sensitivity and spectral interferences from polyatomic ions such as O_2^+ and NO^+. In contrast, the Agilent 8900 ICP-MS/MS uses a dual-quadrupole configuration to eliminate these interferences, enabling accurate detection of ^{34}S and ^{32}S at ppb levels or lower.

Analysis

The Agilent 8900 ICP-MS/MS was used for this analysis, with operating parameters listed in Table 1.

Table 1. Operating parameters of ICP-MS/MS

Parameter	Value
RF power (W)	1,550
Sampling depth (mm)	8
Nebulizer gas flow rate (L/min)	1.03
Extract 1 (V)	−4
Extract 2 (V)	−210
Omega bias (V)	−100
Omega lens (V)	10
Cell gas flow rate (oxygen mode) (mL/min)	0.45

Because of intense polyatomic ion interference of $^{32}S^+$ (major isotope of S) from $^{16}O_2^+$ at *m/z* 32, an oxygen addition reaction was performed to make S^+ far away from interfering ions O_2^+ before detection. In the reaction cell of the ICP-MS/MS, sulfur ions readily react with oxygen to form SO^+ ions (e.g., $^{32}S^{16}O^+$ at *m/z* 48), which are free from common interferences and allow more accurate detection.

The key reaction is as follows:

$$^{32}S^+ + O \longrightarrow {}^{32}S^{16}O^+ \ (m/z = 48)$$

Using a cathode composed of equal amounts of ^{34}S and ^{32}S as a model system, the study specifically investigated differences in the polysulfides shuttling behavior of two sulfur isotopes in Li-S batteries. After cell cycling, the concentrations of both S isotopes were measured on the anode side and in the electrolyte.

The results obtained using ICP-MS/MS (Table 2) show that after cycling, the contents of ^{32}S at the anode and in the electrolyte were higher than for ^{34}S, and $^{32}S/^{34}S$ ratios varied within the range from 1.5 to 2.0, indicating that the ^{34}S cathode can effectively slow down the shuttling of polysulfides.

Table 2. Concentrations of two S isotopes at the anode and in the electrolyte after cell cycling, determined using the 8900 ICP-MS/MS

Name	^{32}S (CPS*)	^{34}S (CPS)	$^{32}S/^{34}S$
Standard blank	2.764×10^6	1.215×10^5	——
S isotope standard solution	6.958×10^6	3.257×10^5	20.54
Correction factor	**1.128****		
Sample blank	1.150×10^7	5.404×10^5	——
Sample 1	2.780×10^7	1.045×10^7	**1.86****
Sample 2	2.526×10^7	1.079×10^7	**1.52****
Sample 3	3.166×10^7	1.171×10^7	**2.04****

* CPS is an abbreviation of counts per second.
** The data in bold were calculated from the original data, as detailed below:
For the S isotope standard solution, $^{32}S/^{34}S$ ratio (20.54) was obtained after subtracting the counts of the standard blank
The correction factor was obtained by dividing the actual $^{32}S/^{34}S$ ratio of the S isotope standard solution (23.17) by the tested $^{32}S/^{34}S$ ratio (20.54)
The $^{32}S/^{34}S$ ratio of a test sample was obtained by subtracting the sample blank and then multiplying by the correction factor

This study revisits the impact of isotopes on the thermodynamic and kinetic properties in electrochemical systems by revealing the isotope effect in lithium-sulfur batteries. Compared with ^{32}S, ^{34}S effectively slowed down the shuttling of polysulfides while improving the reaction kinetics, thus achieving a more stable Li-S electrochemical process. Based on this electrochemical isotope effect, efficient sulfur isotope separation can be achieved, with a separation ratio much higher than those of conventional isotope separation methods. This method also promises to be extendable to the isotope separation of elements involved in other electrochemical systems (for example, chalcogen elements Se and Te as well as halogens). It also draws attention to isotope electrochemistry, a new interdisciplinary field, which not only sheds new light on existing electrochemical systems but also promotes the development of isotope-related technologies.

References

1. Li XT, Zhao Y, Zhu YH, et al. The Electrochemistry of Stable Sulfur Isotopes versus Lithium. Proc Natl Acad Sci USA. 2024 Apr 2;121(14): e2316564121. doi: 10.1073/pnas.2316564121. Epub 2024 Mar 25. PMID: 38527200; PMCID: PMC10998575

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