



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Reduction mechanism of sulfur in lithium–sulfur battery: From elemental sulfur to polysulfide



Dong Zheng^a, Xuran Zhang^b, Jiankun Wang^c, Deyu Qu^{b, **}, Xiaoqing Yang^d,
Deyang Qu^{a, *}

^a Department of Mechanical Engineering, College of Engineering and Applied Science, University of Wisconsin Milwaukee, Milwaukee, WI 53211, USA

^b Department of Chemistry, School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan 430070, Hubei, PR China

^c Department of Applied Chemistry, School of Advanced Materials and Nanotechnology, Xidian University, Xi'an 710126, Shaanxi, PR China

^d Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

HIGHLIGHTS

- S_4^{2-} and S_5^{2-} were the major species at the first reduction wave of elemental sulfur.
- The polysulfides during the discharge of Li–S batteries were captured instantly.
- The polysulfides were accurately in-situ determined.

ARTICLE INFO

Article history:

Received 21 August 2015

Received in revised form

13 September 2015

Accepted 2 October 2015

Keywords:

Reduction of sulfur
Lithium–sulfur battery
Polysulfide
HPLC

ABSTRACT

The polysulfide ions formed during the first reduction wave of sulfur in Li–S battery were determined through both *in-situ* and *ex-situ* derivatization of polysulfides. By comparing the cyclic voltammetric results with and without the derivatization reagent (methyl triflate) as well as the *in-situ* and *ex-situ* derivatization results under potentiostatic condition, *in-situ* derivatization was found to be more appropriate than its *ex-situ* counterpart, since subsequent fast chemical reactions between the polysulfides and sulfur may occur during the timeframe of *ex-situ* procedures. It was found that the major polysulfide ions formed at the first reduction wave of elemental sulfur were the S_4^{2-} and S_5^{2-} species, while the widely accepted reduction products of S_8^{2-} and S_6^{2-} for the first reduction wave were in low abundance.

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1. Introduction

Recently, rechargeable lithium sulfur (Li–S) and lithium air (Li–Air) batteries have drawn significant attention due to their high theoretical energy density [1]. Both batteries are considered to be potential candidates to replace state-of-art Li-ion batteries in electric vehicles (EVs). Although oxygen and sulfur are in the same group on the periodic table, the electrochemical redox reactions of these two are quite different. It's well known that the redox reaction of sulfur is one of the most complicated redox reactions and its mechanism is still not fully understood. It's believed that the reduction of the most stable form of elemental sulfur,

cyclooctasulfur (S_{8c}), is a multistep reduction. The cyclooctasulfur is first electrochemically reduced into long chain linear polysulfides by the cleavage of the sulfur ring. The long chain sulfides are then further reduced into shorter chain polysulfides at a different potential [2–12]. Correspondingly there are two reduction waves observed in the cyclic voltammetry and two discharge plateaus observed between 1.5 and 3.0 V vs. Li/Li⁺ in the discharge profile of a Li–S battery. We demonstrate in this paper that the stepwise sulfur reduction mechanism may not be accurate.

Unlike Li-ion cathode materials which are based on Li ion insertion, the redox reaction of sulfur involves polysulfides dissolution and re-deposition. Therefore, the sulfur cathode experiences compositional, structural, and surface alteration during charge and discharge. Due to the lack of a reliable analytical method for the quantitative and qualitative determination of the soluble polysulfides formed during the various stages of cell operation, the

** Corresponding author.

* Corresponding author.

E-mail addresses: deyuquwuhan@163.com (D. Qu), qud@uwm.edu (D. Qu).

mechanism for the sulfur redox reaction is still debatable; for example, whether the very first charge transfer reaction is the electrochemical reduction of S_{8C} yielding linear S_8^{2-} [8]. To fully understand the stepwise reduction of elemental sulfur in the Li–S battery, substantial fundamental research has been done by means of electrochemistry [4,6,13–15], UV–Vis spectroscopy [2,3,5,7–9,12,16,17], Raman [10,11,18], ESR [19], XRD [10,19–22], XAS [19,22], as well as the theoretical calculations [23–25]. These studies revealed the complexity associated with the reduction of sulfur. Different mechanisms of reduction were proposed although most of them lacked direct and clear experimental proof. There are three mainstream mechanisms proposed to explain the first reduction wave at around 2.3 V vs. Li as shown in Schemes 1–3: 1) 2-electron electrochemical reduction process followed by chemical reactions (abbreviated 2EC) [5,6,9,13,16,18]; 2) 1-electron electrochemical reduction process followed first by a chemical reaction and then by another one-electron electrochemical reduction (abbreviated ECE) [7,17]; and 3) two successive 1-electron electrochemical reduction processes followed by a chemical reaction (abbreviated EEC) [4,8,14,15]. Although similar analytical and electrochemical methods were used, different observations were reported, thus the different mechanisms described above were proposed according to the corresponding results. It is worth to emphasize that the existence of $S_8^{\cdot -}$ radicals have never been proven experimentally, although the radicals with shorter sulfur chain length e.g. $S_3^{\cdot -}$ were detected by ESR experiments [19].

In the investigation of polysulfide species in an aqueous system, Lev et al. reported a derivatization method tandem with separation and identification by HPLC [26–29]. Through reaction with methyl triflate, or methyl iodide, the polysulfide anions were derivatized into different dimethyl polysulfides. Based on the sulfur chain length in the dimethyl polysulfides, the baseline separation of different dimethyl polysulfides can be achieved by HPLC and each dimethyl polysulfide in the chromatogram can be identified based on the relationship between retention time and sulfur chain length. Both Barchasz et al. [30] and our group [31] recently reported the investigation of the discharge mechanism of the Li–S battery using *ex-situ* derivatization coupled with HPLC-MS. All eight polysulfide ions and elemental sulfur can be separated and identified by HPLC-MS after derivatization.

In this work, for the first time *in-situ* derivatization with HPLC was used to investigate the mechanism of sulfur reduction. By comparing the *in-situ* and *ex-situ* derivatization results under potentiostatic condition, the electrochemical mechanism of the first reduction wave of sulfur was discussed.

2. Experimental

2.1. Chemicals

Sulfur (from Fisher Scientific), lithium metal, lithium sulfide (Li_2S), HPLC grade methanol, HPLC grade water, methyl triflate, anhydrous Dimethoxyethane (DME) (from Sigma Aldrich), and lithium bis(trifluoromethane) sulfonimide (LiTFSi, battery grade from FERRO) were purchased and used without further treatment.

2.2. Sample preparation and methods

Three catholyte solutions were prepared. Catholyte A and B were made by mixing excess amount of Li_2S with different amounts of elemental sulfur (A = 0.0194 g, B = 0.0973 g) in 20 ml 1M LiTFSi/DME. Catholyte C was a sulfur saturated LiTFSi/DME solution.

Cyclic voltammetry (CV) was carried out using an AutoLab PGSTAT30 and recorded by the Nova software (version 1.7 from Metrohm). The electrochemical cell, with three-electrode configuration, was assembled and operated under Ar. The working electrode was a glassy carbon disk electrode, the reference and counter electrodes were lithium metal. The potential range for the CV was 1.5 V–3.3 V (vs Li/Li⁺) and DME was used as the solvent.

The discharge of the Li–S battery was performed with an 8-channel Arbin battery tester. The cylindrical Li–S batteries consisted of three electrodes: the cathode was carbon felt with a geometric area of 3.14 cm² (BET surface area is about 111.4 cm²), the anode and the reference electrode were lithium metal. The total volume for electrolyte in the Li–S battery was 10 ml. Catholyte C was used as the electrolyte and the source of sulfur. For the *in-situ* derivatization, methyl triflate was added into the electrolyte with sulfur and the final concentration of methyl triflate was about 20 mM. The Li–S battery was then discharged under potentiostatic conditions (2.3 V vs Li/Li⁺). For *ex-situ* derivatization, Li–S battery without methyl triflate in the sulfur saturated electrolyte was discharged under potentiostatic condition (2.3 V vs Li/Li⁺). After the discharge, the methyl triflate-added electrolyte (*in-situ* derivatization) was directly analyzed by HPLC UV and MS without any further treatment; and the electrolytes without methyl triflate (*ex-situ* derivatization) were derivatized by methyl triflate before analysis by HPLC UV and MS. The Li–S batteries were assembled and tested in an Ar-filled glovebox, as was the *ex-situ* derivatization.

Agilent 1200 quaternary pump with Agilent G1329A autosampler was used to deliver methanol/water mobile phase through a Waters Symmetry C₁₈ column (from Waters, C₁₈, 4.6*50 mm, 5μm) at flow rate of 0.70 mL/min. The injection volume was 4μL. A binary gradient mobile phase was used to elute the injected sample out under the following conditions: at 0 min 25% methanol (75% water); at 10 min 100% methanol; at 20 min 100% methanol; at 21 min 25% methanol. All flow from the HPLC was first introduced through an Agilent 1260 Diode Array Detector (DAD) and then introduced into the Agilent 6130 quadrupole mass spectrometer (MS) with an Atmospheric Pressure Chemical Ionization (APCI) source. For the DAD detector, the chromatograms of five sets of different wavelength were recorded at: 210 nm, 230 nm, 254 nm, 280 nm, and 300 nm. Only results from the 254 nm recording were shown and discussed in this work, since all other results at other wavelengths show similar chromatograms (shown in Fig. S-3 in the supplemental information). For the MS detector, APCI negative mode was set as follow: Capillary Voltage 3 kV, Corona Current 15μA, Drying gas temperature 250 °C, Vaporizer temperature 250 °C, nitrogen gas flow was 12 L/min for Drying gas flow, Nebulizer pressure was 35 psi. The *m/z* ratio was recorded from 50 to 600. All HPLC UV and MS data were recorded by Agilent Chemstation.

3. Results and discussion

After keeping catholyte A and B in an Ar-filled glove-box for at



Scheme 1. Proposed mechanism of 2-electron electrochemical reduction process followed by chemical reactions (2EC).

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