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Electrochemical reactions of lithium-sulfur batteries: an analytical study using the organic conversion technique

Ayako Kawase*a, Soichi Shirai, Yoshinari Yamoto, Ryuichi Arakawa and Toshikazu Takata

This investigation elucidates the electrochemical reaction process occurring within lithium-sulfur battery cells in detail, which have been unclear even after a half century of study primarily due to the very high reactivity of the polysulfide species. The polysulfide intermediates were deactivated by organic conversion – benzylization, and LC/MS and NMR analyses were first applied. The results demonstrate that the second voltage plateau in the discharge profile, which is the most important step in practical use because of its constant voltage, is dominated by the reduction of Li2S3 intermediate. The first voltage plateau and the transition state between the plateaus, in which the voltage varies with the capacity, are associated with multiple reactions including the decomposition of S8 to Li2Sx (x = 1 to 7) and the transformation of Li2Sy (y = 4 to 8) to Li2Sz (z = 1 to 3). It is also revealed that longer polysulfide species, Li2Sx (i = 6 to 8) are responsible for redox shuttle phenomenon, which cause serious capacity degradation.

Introduction

The research and development of rechargeable batteries with sufficient energy storage is becoming one of the most active aspects of the automobile and the power industry, due to the rapidly increasing demands for environmentally-friendly electric vehicles and load leveling systems. One potential candidate for next-generation rechargeable batteries is the lithium-sulfur battery, which offers high theoretical specific capacity of 1680 mAh/g in addition to a specific energy value of 2570 Wh/kg. Its capacity is more than six times that of lithium ion batteries based on LiCoO2.1 Lithium-sulfur battery technology is also attractive since sulfur is a plentiful natural resource and thus is low in cost. Compared to the lithium-air cell, lithium-sulfur batteries can be compactly packaged and thus can be used to replace currently-used lithium ion battery systems with less difficulty. However, there are still challenges in practical applications of lithium-sulfur batteries such as low sulfur utilization due to sulfur’s insulating properties and capacity degradation resulting from dissolution-deposition cycling or redox shuttle phenomenon.2 Additional insights into the electrochemical reactions within a lithium-sulfur cell are of critical importance with regard to mitigating these shortcomings.

The polysulfide compounds generated in a lithium-sulfur cell have been intensively studied over a half century3–5 because identification of the reactants, intermediates and products in the cell is a fundamental step in understanding the electrochemical reactions. The following reaction scheme has been suggested by ultraviolet-visible absorption (UV-vis) spectroscopic studies.5

\[
\begin{align*}
S_8 + 2e^- & \rightarrow S_8^{2-} \quad (1) \\
S_8^{2-} + 2e^- & \rightarrow 2S_4^{2-} \quad (2) \\
S_{6i}^{2-} & \rightarrow S_{6i}^{2-} + \frac{1}{2}S_8 \quad (3) \\
S_{6i}^{2-} & \rightarrow 2S_3 \quad (4)
\end{align*}
\]

The details of these reactions are still unclear, however, because the UV-Vis absorption bands of some polysulfide molecules including unidentified species may overlap. The absence of reference spectra for isolated polysulfide compounds further complicates the situation. Equations 5 through 8 with Equations 1 and 2 are also widely accepted.1,6

\[
\begin{align*}
3S_{8i}^{2-} + 2e^- & \rightarrow 4S_{4i}^{2-} \quad (5) \\
2S_{6i}^{2-} + 2e^- & \rightarrow 3S_{4i}^{2-} \quad (6) \\
S_{6i}^{2-} + 2e^- & \rightarrow 2S_{3i}^{2-} \quad (7) \\
S_{3i}^{2-} + 2e^- & \rightarrow 2S_{2i}^{2-} \quad (8)
\end{align*}
\]

These equations are based on the hypothesis that the eight-membered ring sulfur is reduced with respect to an even number of sulfur atoms. However, the hypothesis has not been authenticated by experimental studies. In-situ measurements of reactions within a cell are associated with difficulties since some polysulfide molecules readily transform in solution. IR and Raman spectroscopic studies have been performed, but these analyses have faced difficulties in peak assignments as well as UV-Vis.4 In particular, IR and Raman peak assignments for polysulfide species larger than S4− have rarely been reported. Although, in principle, the number of sulfur atoms in a polysulfide molecule can be determined by mass spectrometry (MS), some polysulfide molecules transform even during the injection and ionization due to their high reactivity. The sensitivity of 33S nuclear magnetic resonance spectrometry (NMR) is insufficient for elucidation of the structures of polysulfide molecules. Thus, ingenious methods of analysis are required to overcome these
shortcomings and to obtain additional insights into the detailed reaction mechanism.

It has recently been reported that sodium polysulfide species (Na2Sx) can be converted to benzylized polysulfide (Bz2Sx) molecules without changing the number of S atoms. The Bz2Sx species can be analyzed via proton NMR (1H NMR).7 This organic conversion technique can be also applied to lithium polysulfide (Li2Sx) species and therefore enable us to follow electrochemical reactions in battery cells using 1H NMR. Furthermore, liquid chromatography-mass spectrometry (LC/MS) become also applicable, since the benzylized polysulfide species are sufficiently stable in the LC/MS environment.8 Since, to the best of our knowledge, 1H NMR spectra of isolated benzylized polysulfide species are rarely available, we instead utilize ab initio molecular orbital (MO) calculations for peak assignments. Ab initio MO calculations can be also useful in peak assignment and interpretation of ambiguous UV-Vis spectra.9

In this study, the polysulfide species within a lithium-sulfur cell have been identified utilizing LC/MS and NMR following application of the organic conversion technique, in order to elucidate the electrochemical reactions in more detail. UV-Vis spectra were also obtained to confirm consistency of the results of this work with those of previous studies.

Results and discussion

LC/MS Analysis

The charge-discharge profile of the lithium-sulfur cell during first cycle, showing the specific measurement points, is presented as Fig. 1. Distinctive plateaus appear at approximately 2.3 and 2.1 V, and the slope between 2.3 and 2.1 V can be regarded as the transition state. It is notable that the voltage varies with the capacity in the first plateau and the transition state, while the voltage is almost constant in the second plateau.

The LC data associated with the discharge process are shown in Fig. 2(a), along with reference data for Bz2S2, Bz2S2 and S8. LC peaks for Bz2Sx were successfully identified by MS (see Supporting Information, Fig. S1), and peak for S8 was identified by reference. The amount of each species relative to its original concentration at each point is estimated from the peak area and summarized in Table 1. The amount change of Bz2Sx (x = 1 to 6) is shown in Fig. 2(b).

It is evident that the concentration of S8 decreases between points 1 and 3-2, and that all possible species produced by the decomposition of S8, including Li2S2, Li2S4, Li2S6, Li2S4 and Li2S6 are detected at point 2-1. These species were undetected in previous studies.6-8 Li2S4, Li2S6 and Li2S8 are major, while Li2S2 is minor. The increasing rate of Li2Sx (x = 4 to 8) species makes a downward turn between points 2-1 and 3-1, and these species completely disappear at point 3-3. Li2S8, which is dominant at point 3-2, gradually decreases up to point 4, and Li2S6 and Li2S4 increase over this same span. Beginning at point 3-4, Li2S increases at an accelerated rate, while the increasing rate of Li2Sx is reduced.

These results suggest that the overall electrochemical reaction can be divided into four major stages. The first stage is between points 1 and 3-1 (in the first plateau and the transition state). The second stage is between points 2-1 and 3-3 (in the transition state and the beginning of the second plateau). The third stage is from points 3-1 to 4 (in the second plateau). The fourth stage is from points 3-4 to 5 (in the latter half of the second plateau and after the plateau).

In the first stage, S8 is either reduced to Li2S4 or smaller species directly, and this decomposition of S8 likely continues up to point 3-1. The first stage (from point 1 to point 3-1) is described by Equations 9 through 13.

\[
\text{Li}_2\text{S}_8 + 2e^- \rightarrow \text{Li}_2\text{S}_4 + 2\text{S}^2- \quad (9)
\]

\[
\text{Li}_2\text{S}_4 + 4e^- \rightarrow \text{Li}_2\text{S}_6 + 2\text{S}^2- \quad (10)
\]

\[
\text{Li}_2\text{S}_6 + 4e^- \rightarrow \text{Li}_2\text{S}_8 + 2\text{S}^2- \quad (11)
\]

\[
\text{Li}_2\text{S}_4 + 4e^- \rightarrow \text{S}^2- + 2\text{S}^2- \quad (12)
\]

\[
\text{Li}_2\text{S}_6 + 4e^- \rightarrow 2\text{S}^2- \quad (13)
\]

The increase in Li2Sx (x = 1 to 3), concurrent decline of Li2Sx (y = 4 to 8) and disappearance at point 3-3 suggest that the Li2Sx (y = 4 to 8) is reduced to Li2Sx (x = 1 to 3) in the second stage. The second stage (from point 2-1 to point 3-3) is denoted by Equations 14 through 20.

\[
\text{S}^2- + 2e^- \rightarrow \text{S}_2^2- + \text{S}^2- \quad (14)
\]

\[
\text{S}_2^2- + 2e^- \rightarrow \text{S}_2^2- + \text{S}^2- \quad (15)
\]

\[
\text{S}_2^2- + 2e^- \rightarrow 2\text{S}_2^2- \quad (16)
\]

\[
\text{S}_2^2- + 2e^- \rightarrow \text{S}_2^2- + \text{S}^2- \quad (17)
\]

\[
\text{S}_2^2- + 2e^- \rightarrow 2\text{S}_2^2- \quad (18)
\]

\[
\text{S}_2^2- + 2e^- \rightarrow \text{S}_2^2- + \text{S}^2- \quad (19)
\]

\[
\text{S}_2^2- + 2e^- \rightarrow 2\text{S}_2^2- \quad (20)
\]

The Li2Sx produced in the first and second stage is subsequently reduced to Li2S2 and Li2S in the third stage. The third stage (from point 3-1 to point 4) is represented by Equation 21.

\[
\text{S}^2- + 2e^- \rightarrow \text{S}_2^2- + \text{S}^2- \quad (21)
\]

In the latter half of the second plateau and subsequent plateau, the Li2S2 is partly reduced to Li2S in the fourth stage. The
fourth stage does not complete, judging from the observation that most of the Li₃S₂ remains intact. The fourth stage (from point 3-4 to point 5) is represented by Equation 22.

\[ S_{2}^{2-} + 2e^- \rightarrow 2S^{2-} \]  
(22)

It is worth noting that the second plateau with a constant voltage is associated with simple reaction – the reduction of Li₂S₃. On the other hand, in the first plateau and the transition state in which the voltage changes drastically, multiple reactions occur simultaneously. The quantities of polysulfide species in those regions in which multiple reactions overlap can be considered as the sum total generated by the simultaneous reactions.

Equations 9, 16, 20 and 22 correspond to the previously proposed reactions, which are shown above as Equations 1, 2, 7 and 8 respectively. The other reactions are newly proposed in this study.

Reverse reactions occur in the charging process. It is evident, however, that Li₃S₄ \((x = 4 \text{ to } 8)\) increase and Li₂S₃ keeps its amount from points 8 to 9. This phenomenon is attributed to the redox shuttle phenomenon, in which the polysulfide migrate onto the anode and reduced on the spot, resulting in the endless charge of such cells. The shuttle phenomenon occurs between points 8 and 9 (in the first plateau in charging process), in which longer Li₃S₄ \((y = 6 \text{ to } 8)\) appear. The results suggest that longer Li₃S₄ \((y = 6 \text{ to } 8)\) are responsible for shuttle phenomenon, and they are reduced to shorter Li₂S₃ \((z = 3 \text{ to } 5)\) on the Li anode. The shuttle phenomenon can be suppressed by electrolyte additives or protection layers of Li anode.

The \(^1\)H NMR spectra of benzylized polysulfide species in the electrolyte solutions are shown in Fig. 3(a), along with spectra for Bz₂S and Bz₂S₄ as reference. The peaks, which appear in the region from 3 to 5 ppm, correspond to methylene H of the benzylized polysulfides. The peak at 3.60 ppm, which can be assigned to either Bz₂S or Bz₂S₄, is the most prominent at point 5 and is observed at all points except point 1. Three major peaks at 4.02, 4.15 and 4.20 ppm can be assigned to Bz₂S₃ \((x = 3, 4, 5)\) according to the LC/MS results. The calculated relative chemical shifts for Bz₂S₃ \((y = 3 \text{ to } 8)\) summarized in Fig. 3(a) suggest the following peak assignments: 4.02 ppm to Bz₂S₃, 4.15 ppm to Bz₂S₄, and 4.20 ppm to Bz₂S₅.

The relative concentrations of the species estimated from peak areas are shown in Fig. 3(b). These results demonstrate that Li₂S₅, Li₂S₆, Li₂S₇, along with small amounts of Li₂S₂ and/or Li₂S, were generated between points 1 and 2-1, and that both Li₂S₄ and Li₂S₅ have disappeared by point 3-4. Li₂S₃ is the dominant species at point 3-2 and then fragments into Li₃S₂ and/or LiS from point 3-1 to point 5. These findings are qualitatively consistent with the LC/MS results.

In the case of Bz₂S₃ \((x = 1 \text{ to } 5)\), the calculated chemical shift increases with the number of S atoms, as a result of withdrawal of the electrons from benzyl group by the polysulfur moieties (due to the high electronegativity of S). The electron withdrawing strength of the polysulfur moiety increases with increasing number of S atoms because the negative charge can be more widely distributed and hence stabilized throughout the expanded orbitals. Conversely, however, the chemical shift decreases in the order of Bz₂S₃ > Bz₂S₄ > Bz₂S₅ > Bz₂S₆. In the optimized Bz₂S₃ geometry, one of the methylene H is located

**NMR Analysis**

\[ \text{Li} + \text{S} \rightarrow \text{Li}_2\text{S}_3 \]

**Fig. 2**: LC/MS results at points during cell discharge-charge. (a) LC data for points 1 to 5, including Bz₂S, Bz₂S₄ and Sₓ as references. (b) Relative remaining quantity of Bz₂Sₓ \((x = 1 \text{ to } 6)\) at points 1 to 9 as estimated from LC data.
close to the fifth S atom, resulting in a H bonding-type interaction (see Supporting Information, Fig. S3). It has been shown that the chemical shift of the H closest to the S atom in Bz$_2$S$_5$ is remarkably high because of the deshielding by S atoms with the electron withdrawing property. In the case of Bz$_2$S$_5$ (x = 6 to 8), the methylene H is further removed from the sulfur atom, resulting in the lower chemical shift.

**UV-Vis Analysis**

The UV-Vis spectra of the electrolytes in the cell are shown in Fig. 4(a). No peaks are observed in the region above 300 nm at point 1, whereas a peak appears at 430 nm at point 2-1, and a prominent peak at 400 nm along with a smaller peak at 610 nm are both observed at point 3-1. Both the 400 and 610 nm peaks gradually decrease during the second plateau (from points 3-1 to 5). In the charging process, reverse reactions are observed except for point 9 (see Supporting Information, Fig. S4), as well as LC/MS results. The simulated UV-Vis spectra incorporating the solvent effect of dimethoxyethane (DME) are shown in Figs. 4(b) to (g). The simulated spectra indicate that some of the Li$_x$S$_y$ species produce characteristic peaks in the region above 300 nm; both Li$_4$S$_8$ and Li$_3$S$_7$ have absorption bands at 430 nm and Li$_2$S$_5$ has a band at 400 nm. Most radical species show significantly red-shifted peaks, and the Li$_3$S$_7$ radical has a peak at 610 nm. These calculated results suggest that Li$_3$S$_7$ and/or Li$_5$S$_9$ are produced at point 2-1 and Li$_2$S$_5$ and the Li$_3$S$_7$ radical is generated at point 3-1. The large absorption band which appears between 300 and 400 nm can be assigned to a mixture of Li$_x$S$_y$ (x = 1 to 8) species and/or radicals. The results of the analysis are consistent with LC/MS and NMR results.

The absorption wavelengths obtained in both experimental and calculated results incorporating the solvent effects of DME and dimethylformamide (DMF) are compared in Table 2. This comparison shows that the calculation results are largely consistent with both present and previous experimental results.

**Experimental**

**Experimental details**

Cathodes were composed of 60 wt% sulfur, 30 wt% carbon (Ketjenblack EC-600 JD), 8 wt% polytetrafluoroethylene binder and 2 wt% carboxymethyl cellulose thickener. A slurry made from these cathode materials mixed with water was applied to etched Al foil and then dried, after which the cathode sheets were cut into disks (φ = 10 mm) and pressed. The finished sulfur cathodes (80 μm thickness, 8 g/cm²) were assembled in coin-type cells (CR2032) along with polyethylene separators (S6722, Asahi Kasei), Li foil (150 μm thickness) and electrolyte solutions (60 μl) consisting of 1.5 M lithium bis(trifluoromethanesulfonyl) imide in DME and dioxolane. The discharge-charge profiles were obtained using a current density of 0.8 mA cm⁻² and voltages between 1.5 and 2.7 V at 25 °C.

All the subsequent sample preparation procedures were conducted under an Ar atmosphere. During the discharge-charge reaction, the cathodes were removed from the cells at various points within the process. The cathode, still wet with...
electrolytes, was immersed in 1 ml of DME and the resulting solution was transferred into a 1 mm path length quartz cell and examined by UV-Vis spectroscopy using a Shimadzu UV-3100PC.

For LC/MS and \(^1\)H NMR measurements, cathodes taken from cells in the same manner were instead immersed in a mixture of DME and benzyl chloride, after which the cathode was pulverized by ultrasonication. Each sample was then allowed to sit for three hours to convert the lithium polysulfide (Li\(_2\)S\(_x\)) to benzylized polysulfide (Bz\(_2\)S\(_x\)). The conversion of Li\(_2\)S\(_3\) (x = 3 to 8) is almost complete in three hours (see Supporting information, Fig. S6 and Fig. S7). On the other hand, three-hour conversion is supposed to be insufficient for Li\(_2\)S\(_1\) (x = 1 to 2) because of these poor solubility. Therefore, the half of each sample was allowed to sit for four days to get the highest conversion rate for Li\(_2\)S (see Supporting information, Fig. S8). The conversion ratio of Li\(_2\)S\(_1\) (x = 1 to 2) is supposed to be higher than 66%. Though the chain length of Bz\(_2\)S\(_x\) (x = 6 to 8) can be shortened during the long-time conversion, obtained Bz\(_2\)S\(_x\) (x = 3 to 8) by three-hour conversion should reflect the relative amounts of Li\(_2\)S\(_x\) in cathodes (see Supporting information, Fig. S7). S\(_x\) dissolved in the solution remain unreacted during the time. The residual carbon matrix and current collector were subsequently removed by filtration, after which the solvent was evaporated. Sulfur and Bz\(_2\)S\(_x\) were dissolved in either tetrahydrofuran (THF) or deuterated chloroform. Sulfur and Bz\(_2\)S\(_x\) samples that were dissolved in THF were analyzed via LC/MS, and the samples that were dissolved in deuterated chloroform were analyzed using \(^1\)H NMR. LC/MS experiments were carried out on a Thermo Scientific Exactive mass spectrometer, equipped with an atmospheric pressure chemical ionization (APCI) source, and interfaced to a Dionex Ultimate 3000 LC system with a 254 nm UV detector. Samples were first diluted with methanol and then injected onto an Intersil ODS-3 (150 x 2.1 mm, 5 µm) column, using a mobile phase composed of 10% aqueous ammonium acetate (5 mM) and 90% methanol at a constant flow rate of 200 µL/min. MS data were collected in positive ion mode as the ammonium adduct. To allow quantitative analysis, LC peak area for S\(_6\), Bz\(_2\)S and Bz\(_2\)S\(_x\) were converted to a relative analyte amount using calibration curves derived from standard solutions, and peak area for Bz\(_2\)S\(_x\) (x = 3 to 8) were converted based on the calculated relative absorbance at 254 nm. NMR data were recorded on a JEOL AL-400 spectrometer.

**Computational details**

Lithium-polysulfide molecules, which can be generated in the electrochemical reactions within the lithium-sulfur cell, were prepared. The closed-shell species were S\(_6\), Li\(_2\)S\(_6\), Li\(_2\)S\(_7\), Li\(_2\)S\(_8\), Li\(_2\)S\(_{10}\), Li\(_2\)S\(_{12}\), Li\(_2\)S\(_{14}\), Li\(_2\)S\(_{15}\) and Li\(_2\)S, while the open-shell radical...
species were LiS₈, LiS₇, LiS₆, LiS₅, LiS₄, LiS₃, and LiS₂. Bz₂Sₓ models were prepared by replacing the Li atoms in these species with a benzyl group (C₆H₅CH₂-).

The molecular geometries were first optimized using density function theory (DFT) calculations. The ¹H NMR chemical shifts for Bz₂Sₓ were calculated using DFT combined with the gauge-independent atomic orbital (GIAO) technique. The shielding constant of tetramethylsilane (TMS) was calculated to be 31.7947 ppm using the same theoretical approach and this was employed as the standard. The calculated chemical shifts for the four methylene H were represented by the average of their individual values. The excited states of polysulfide compounds were calculated using time dependent DFT (TD-DFT) calculations in order to simulate their UV-Vis spectra, and each peak was represented by a Gaussian function with a maximum height proportional to the oscillator strength, using a 6-311+G (2d,p) basis set. All calculations were performed using the Gaussian03 program.

Conclusions
The lithium polysulfide species generated in a lithium-sulfur cell were analyzed by LC/MS and NMR combined with organic conversion technique. The results suggested that electrochemical reactions in the cell proceed through four distinct stages. It is of particular interest that the second plateau in the discharge profile, which is the most important reaction state in practical use because of its constant voltage, is dominated by the reduction of Li₂S₈, while the first plateau and the transition state, in which the voltage varies with the capacity, is associated with multiple reactions. It also revealed that longer polysulfide, Li₂S₈ (x = 6 to 8) are responsible for redox shuttle phenomenon, which cause serious capacity degradation. These new analytical method is also useful in study of sulfur based redox flow cells and catholyte cells, because dissolved polysulfide are used as an active material in such cells. This work is the first step of understanding the influence of current density and electrolyte components on the reaction scheme, which is connected with cell performances. Therefore these understanding lead to enhancement in input-output capability, cell capacity, and discharge-charge cycle durability.

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