Lithium Polysulfide Radical Anions in Ether-Based Solvents

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ABSTRACT: Lithium sulfur batteries have a theoretical specific energy 5 times greater than current lithium ion battery standards, but suffer from the issue of lithium polysulfide dissolution. The reaction mechanisms that underlie the formation of lithium polysulfide reaction intermediates have been studied for over four decades, yet still elude researchers. Polysulfide radical anions formed during the redox processes have become a focal point of fundamental Li-S battery research. The formation of radical species has even been shown to be advantageous to the electrochemical pathways. However, whether polysulfide radical anions can form and be stabilized in common Li-S battery electrolytes that are ether-based is a point of contention in Li-S battery research. The goal of this work was to examine the presence of radical polysulfide species in ether-based solvents. Lithium polysulfide solutions in tetraethylammonium dimethyl ether and poly(ethylene oxide) are probed using a combination of ultraviolet–visible (UV–vis) and electron paramagnetic resonance (EPR) spectroscopy. EPR results confirm the presence of radical species in ether-based electrolytes. Comparison of the UV–vis spectra to EPR spectra establishes that the UV–vis absorbance signature for radical species in ether-based solvents occurs at a wavelength of 617 nm, which is consistent with what is observed for high electron pair donor solvents such as dimethylformamide and dimethyl sulfoxide.

INTRODUCTION

Lithium sulfur (Li-S) batteries are attractive for energy storage applications because they have a theoretical specific energy of 2600 (Wh)/kg, and because sulfur is affordable and naturally abundant. Unfortunately, Li-S cells are plagued by issues related to the reaction intermediates, collectively called lithium polysulfides, that are formed during charge and discharge. As the redox reactions proceed, these polysulfides dissolve in the electrolyte and diffuse out of the cathode, causing the battery capacity to fade. Additionally, if diffusion to the cell anode occurs, polysulfides may react with lithium, forming insulative layers of Li2S and Li2S2, and leading to parasitic shuttles if soluble species are formed.

While lithium polysulfides molecules are most commonly thought to be dianion species (Li2Sx, 2 ≤ x ≤ 8), evidence of polysulfide radical anions (LiSx, 3 ≤ x ≤ 5) in Li-S batteries has also been obtained. Recent studies have even suggested that radical anions may be of benefit to Li-S reaction pathways. It has been argued that the presence of radical species (here we refer to polysulfide radical anions as radicals or radical species for simplicity) in a particular lithium sulfur cell depends primarily on the electron pair donor (EPD) number of the electrolyte. Solvents with high EPD numbers may stabilize radical polysulfides, while solvents with low EPD numbers do not.

The long-term stability of polysulfide radicals in some environments is well-established. This is demonstrated most clearly by lapis lazuli, a blue mineral that is pulverized to form a pigment commonly known as ultramarine. Through extensive studies involving electron paramagnetic resonance (EPR) spectroscopy, Raman spectroscopy, ultraviolet–visible (UV–vis) light spectroscopy, and X-ray absorption spectroscopy (XAS), the blue color of ultramarine/lapis lazuli has been attributed to the S3•− trisulfur radical anion. The crystalline tectosilicate cage structure of the mineral stabilizes the radical anion, apparently isolating the individual molecules and preventing recombination of these reactive species. Additional studies on the chemical composition of ultramarine/lapis lazuli suggest that S3•− may also be present. The S3•− radicals that give the blue color of ultramarine pigments have been stable for thousands of years.

Polysulfide radicals have been reported to be stable in solvents such as DMF and DMSO that have high EPD numbers.

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numbers. Radical species such as LiS₄ and LiS₅ were detected in equilibrium with dianion species (e.g., Li₂S₆) in these systems by XAS, EPR spectroscopy, and UV−vis absorbance spectroscopy. Solutions of polysulfide species in solvents with high EPD numbers are typically blue in color, owing to the presence of LiS₅₋. 

It is not clear if polysulfide radicals are present in solvents with low EPD numbers, such as dimethyl ether (DME), 1,3-dioxolane (DOL), tetraethylene glycol dimethyl ether (TEGDME), and poly(ethylene oxide) (PEO). Some studies indicate the presence of radicals in these ether-based systems, while others do not. Establishing the stability of radicals in these ether-based electrolytes is important because these solvents are often used in Li−S batteries.

In this study, we quantify the presence of radicals in chemically synthesized lithium polysulfides in TEGDME and PEO using a combination of UV−vis and EPR spectroscopy. Our results provide unambiguous proof of the existence of polysulfide dianions in these solvents, and show that the concentration of radical species is a complex function of the polysulfide type and concentration. On the basis of the observed EPR g factors, the identification of the radical species present in the ether-based solvents is discussed, but further work is needed to confirm the exact radical species present in solutions.

### EXPERIMENTAL SECTION

#### Materials.

Lithium sulfide (Li₂S) and elemental sulfur (S₈) were purchased from Alfa Aesar and were received under argon. Tetraethylene glycol dimethyl ether (TEGDME) (99.0%) was purchased from Sigma-Aldrich and was obtained under argon. Poly(ethylene oxide) (PEO) was purchased from Polymer Source Inc. and had a molar mass of 600 g/mol. The PEO was dried overnight at 90 °C under vacuum and then brought into the glovebox. All materials were stored in an argon-filled glovebox.

#### Lithium Polysulfide Solutions.

Lithium polysulfide solutions were prepared by adding stoichiometric amounts of S₈ and Li₂S to the solvent of interest as described by Rauh et al. The amounts of S₈ and Li₂S added to solutions were controlled by the following formula:

\[
\text{Li}_2\text{S} + \frac{x_{\text{mix}} - 1}{8} \text{S}_8 \rightarrow \text{Li}_2\text{S}_{x_{\text{mix}}}
\]

Here \(x_{\text{mix}}\) is used to denote the polysulfide dianion that would be obtained if a single dianion polysulfide type were formed by the reaction. In reality, the solution is likely a mixture of various polysulfide species in equilibrium, formed through various disproportionation reactions. This distribution of polysulfide species can include both diions (of the form Li₂S₆⁻) and radical species (of the form LiS₄⁻). Here \(x_{\text{mix}}\) is used simply as a descriptor of the atomic ratio of lithium to sulfur. Solutions were mixed for at least 24 h at 90 °C in a sealed vial within an argon-filled glovebox.

Solution sulfur concentrations (referred to as \(C_s\)) used here represent the overall atomic moles of sulfur per volume of solution. For instance, a 10 mM concentration solution contains 10 mmol of atomic S per liter of solution. The millimoles of S atoms represents the sulfur added in the form of S₈ and Li₂S.

To maintain consistent \(x_{\text{mix}}\) values throughout the study, “bulk,” high-concentration solutions were made for each \(x_{\text{mix}}\) value which were then used to produce the lower concentration solutions through dilution. For instance, the TEGDME \(x_{\text{mix}} = 6\) solutions were made by first preparing a bulk \(x_{\text{mix}} = 6, 300 \text{mM}\) solution. This 300 mM solution was then diluted to create the 100, 50, and 10 mM solutions. This procedure was used for all \(x_{\text{mix}}\) values. Additions of TEGDME and PEO were performed using a micropipette.

#### UV−Vis Spectroscopy.

Liquid lithium polysulfide solutions were loaded into quartz cuvette sample holders inside an argon-filled glovebox. The quartz cuvettes had a path width of 1 mm. After loading, the cuvettes were sealed and then placed in closed vials with Teflon tape wrapped between the glass threading of the vial and the cap. The vials were then brought out of the glovebox and to the UV−vis spectrophotometer. There cuvettes containing the samples were taken out of the vials and immediately measured. An Agilent Cary 5000 UV−vis−NIR spectrophotometer was used to measure the samples in a range of wavelengths spanning 200−820 nm. Data were obtained in transmission mode. Within the range of sulfur concentrations probed here (\(C_s = 10, 50, \text{and } 100 \text{mM}\)), absorbance spectra became oversaturated below 300 nm. For that reason, our analysis of the UV−vis results is restricted only to the absorbance above 300 nm for all samples. This is of importance given that the absorbance of elemental sulfur occurs in the 200−300 nm range. The measured spectra thus may not represent all of the sulfur-containing species in the samples. Measurement of 300 mM sulfur concentration solutions was attempted, but spectra were oversaturated in the 200−820 nm wavelength range. Spectra were taken for each solvent (TEGDME and PEO); solvent spectra were subtracted from the polysulfide solution spectra shown throughout the rest of this paper. All solutions were measured at room temperature.

#### Electron Paramagnetic Resonance Spectroscopy.

Lithium polysulfide solutions were loaded into borosilicate capillary tubes obtained from Active Spectrum, having an outer diameter of 2.3 mm. Roughly 0.1 mL of solution was loaded into each capillary tube. This volume surpassed the volume of solution present in the measurement cavity of the EPR instrument, meaning that the sample geometry and total solution volume probed for each measurement were identical from sample to sample. Capillary tubes were sealed using a Cha-seal tube sealing compound. The small capillary tubes were then placed inside larger 5 mm outer diameter quartz tubes (Wilmad-LabGlass) that were capped with standard NMR tube caps. Kapton tape was then wrapped around the top of the tube and over the cap to ensure an airtight seal. All sample preparation was performed in an argon-filled glovebox.

Continuous wave (CW) EPR was performed in the X-band frequency range, approximately 9.69 GHz, using an Active Spectrum extended range benchtop EPR instrument. All spectra were obtained at room temperature. The microwave power was set to be 15 mW for all samples. This power was in the linear regime of the power saturation curve obtained for the samples, indicating a quantitative relationship between the double integral of the EPR peaks and sample concentration. The magnetic field had a modulation frequency of 100 kHz and a modulation amplitude of 2 G. Spectra were taken between 2900 and 3900 G at a sweep rate of 7.18 G/s. Two batches of samples were prepared for the set of polysulfide solutions (each solution thus had two separately prepared samples). Five scans were performed and averaged together for each sample. The spectra shown herein are the spectra obtained for one of the sample batches. Raw spectra were smoothed using a second-order Savitsky−Golay filter algorithm, with a frame size of 4 G.
Spectra were obtained for the capillary tubes, TEGDME, and PEO. These background spectra were subtracted from the lithium polysulfide mixture spectra.

## RESULTS AND DISCUSSION

Figure 1 shows UV-vis spectroscopy results for TEGDME lithium polysulfide solutions at a variety of $x_{\text{mix}}$ values and sulfur concentrations ($C_S$). Here $x_{\text{mix}}$ denotes the ratio of sulfur to lithium ($Li_2S_{x_{\text{mix}}}$), as described in reaction 1 in the Experimental Section. UV-vis spectra were obtained for $x_{\text{mix}}$ values of 4, 6, 8, and 10 and sulfur concentrations of 10, 50, and 100 mM. For ether-based solvents, the peaks in the 300–550 nm range are generally attributed to polysulfide dianions.\textsuperscript{8,9,38} The identity of the peak at 617 nm has not been confirmed for ether-based polysulfide solutions. While some have attributed the peak to radical polysulfides,\textsuperscript{8,9} others have attributed the peak to polysulfide dianions.\textsuperscript{38} Since our primary interest is to characterize radical anions in ether-based solvents, we focus on the peak at 617 nm.

At a 10 mM sulfur concentration, the $x_{\text{mix}} = 4$ solution has the highest absorbance at 617 nm, followed by $x_{\text{mix}} = 6$, $x_{\text{mix}} = 8$, and $x_{\text{mix}} = 10$. At 50 mM (Figure 1b), $x_{\text{mix}} = 4$ and $x_{\text{mix}} = 6$ appear to have similar absorbances at 617 nm, followed by $x_{\text{mix}} = 8$ and $x_{\text{mix}} = 10$. At 100 mM (Figure 1c), an identical trend is observed. The highest absorbance at 617 nm in DMF solutions of lithium polysulfides occurs at $x_{\text{mix}} = 6$.\textsuperscript{20} Our results for TEGDME are thus slightly different, but consistent with

<table>
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<tr>
<th>$x_{\text{mix}}$</th>
<th>$C_S = 10$ mM</th>
<th>$C_S = 50$ mM</th>
<th>$C_S = 100$ mM</th>
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<tr>
<td></td>
<td>amplitude</td>
<td>area</td>
<td>amplitude</td>
</tr>
<tr>
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<td>0.242</td>
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<tr>
<td>8</td>
<td>0.026</td>
<td>3.4</td>
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<tr>
<td>10</td>
<td>0.022</td>
<td>2.6</td>
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</tbody>
</table>

Figure 2. UV-vis spectra obtained for PEO lithium polysulfide ($C_S = 10$ mM) solutions.
data obtained for DMF solutions. The spectra shown in Figure 1 were fit using a series of Gaussian functions. Results of this fitting procedure for the 617 nm peak are shown in Table 1. (Parameters corresponding to the other peaks are given in Supporting Information.)

PEO solutions at \(x_{\text{mix}}\) values of 4, 6, and 8 at a concentration of 10 mM were also examined using UV-vis spectroscopy. The resulting spectra for these solutions are shown in Figure 2. Similar to the results obtained for TEGDME, the \(x_{\text{mix}} = 4\) solution shows the largest absorbance at 617 nm, followed by \(x_{\text{mix}} = 6\) and \(x_{\text{mix}} = 8\).

Polysulfide mixtures in DMF, DMSO, and like solvents are typically blue in color. Photographs of the TEGDME and PEO solutions examined in this study are shown in Table 2. TEGDME solutions with \(x_{\text{mix}}\) values equal to 4 were green in color for all concentrations. For \(x_{\text{mix}} = 6\), solutions were light yellow/green at 10 mM, and then became a dark olive/brown.
color at high concentrations. The \( x_{\text{mix}} = 8 \) solutions were light yellow/green in color at 10 mM, orange/brown at 50 mM, and dark red at 100 mM. The \( x_{\text{mix}} = 10 \) solutions were light yellow at 10 mM, orange/brown at 50 mM, and dark red at 100 mM. Low concentration \( x_{\text{mix}} = 4 \) PEO solutions were light green/yellow at low concentrations and dark yellow/brown at higher concentrations, \( x_{\text{mix}} = 6 \) solutions were light yellow at low concentration and red at higher concentrations, and \( x_{\text{mix}} = 8 \) solutions were light yellow at low concentration and red at higher concentration.

While the attribution of the 617 nm peak in the UV−vis spectra to a radical anion is consistent with what has been established for DMF and DMSO, the TEGDME and PEO solutions are not blue in color, as is typically the case for radical-containing polysulfide solutions. The low EPD number of TEGDME and PEO (compared to DMF and DMSO), and lack of blue color in these solutions, thus brings to question whether the 617 nm peak truly represents a radical anion.

Figures 3 and 4 show the EPR spectra obtained for TEGDME and PEO solutions, respectively, at a variety of \( x_{\text{mix}} \) values and concentrations. Radical species are detected in all TEGDME and PEO solutions at the range of concentrations probed. Additionally, the concentration of radical species increased as the sulfur concentration increased, which is most clearly shown by the \( x_{\text{mix}} = 4 \) and 6 TEGDME solutions (Figure 3).

To obtain more insight regarding the behavior of the EPR spectra in relation to the concentration and \( x_{\text{mix}} \) value, the EPR spectra were fit using a Tsallian first-derivative peak function, which was then double integrated to obtain an integrated peak area (here referred to as the “double integral”) proportional to the overall concentration of radical species present. Integration of the Tsallian fitting reduces the error due to noise and unsteady baselines in the raw data. Additional spin-counting experiments necessary to obtain absolute radical concentrations by EPR were not attempted.) Our analysis enables a comparison of radical concentrations in the solutions of interest. The results of the peak fitting are summarized in Table 3. The fitting of each spectrum and detailed parameters for each Tsallian fit can be found in the Supporting

Table 3. Peak Areas Obtained by Double Integration of TEGDME and PEO EPR Spectra for \( x_{\text{mix}} = 4, 6, 8, \) and 10 at Sulfur Concentrations (\( C_S \)) of 10, 50, 100, and 300 mM

<table>
<thead>
<tr>
<th>( x_{\text{mix}} )</th>
<th>( C_S ) = 10 mM</th>
<th>( C_S ) = 50 mM</th>
<th>( C_S ) = 100 mM</th>
<th>( C_S ) = 300 mM</th>
<th>( C_S ) = 10 mM</th>
<th>( C_S ) = 300 mM</th>
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<tbody>
<tr>
<td>4</td>
<td>328 ± 218</td>
<td>740 ± 13</td>
<td>1797 ± 59</td>
<td>3797 ± 702</td>
<td>140 ± 106</td>
<td>2389 ± 1735</td>
</tr>
<tr>
<td>6</td>
<td>108 ± 70</td>
<td>632 ± 133</td>
<td>1536 ± 25</td>
<td>4438 ± 78</td>
<td>35 ± 49</td>
<td>510 ± 214</td>
</tr>
<tr>
<td>8</td>
<td>35 ± 25</td>
<td>329 ± 185</td>
<td>574 ± 131</td>
<td>1668 ± 200</td>
<td>17 ± 15</td>
<td>294 ± 110</td>
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<td>10</td>
<td>23 ± 15</td>
<td>203 ± 3</td>
<td>337 ± 124</td>
<td>1216 ± 218</td>
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</tbody>
</table>

Figure 5. (a) Peak area obtained for the UV−vis 617 nm absorbance peak and (b) double integral of the EPR spectra as a function of the lithium to sulfur ratio (\( x_{\text{mix}} \)) at sulfur concentrations (\( C_S \)) between 10 and 100 mM. Lines connecting the data points are provided as a guide for the eye.

Figure 6. UV−vis peak area (617 nm) versus the double integral of the EPR spectra for TEGDME and PEO solutions. Peak areas obtained from UV−vis and the EPR double integrals are proportional, indicating a direct relationship between the 617 nm UV−vis feature and the presence of radical anions.
The average g factor obtained for the TEGDME solutions was 2.0294 ± 0.0011, while that obtained for the PEO solutions was 2.0323 ± 0.0021. A comprehensive list of each solution factor is provided in the Supporting Information. These g factors are similar to those previously obtained for the S\textsuperscript{4+} radical (2.029)\textsuperscript{12,18,20,28,46} and the S\textsuperscript{3+} radical (2.031).\textsuperscript{21}

Conclusive identification of the radicals present in the TEGDME and PEO solutions will be a focus of future work, as it is difficult to determine given the broad line width and low signal-to-noise ratio of the spectra. For now, the general agreement between g factors obtained here and those previously obtained for polysulfide solutions serves to show that the radical species elucidated by EPR are most likely polysulfide species.

The EPR results show that radical species are certainly present in the TEGDME and PEO polysulfide solutions, despite their green, red, and brown colors and despite their low EPD numbers. Other researchers have also detected polysulfide radicals in ether-based solvents by EPR. However, the correspondence between EPR signals and UV–vis data for ether-based polysulfide solutions has not been established. We do this in Figure 5. In Figure 5a, we plot the peak areas obtained at the 617 nm UV–vis wavelength versus the x\textsubscript{mix} value for three concentrations. In Figure 5b, we plot the peak area obtained by double integration of the EPR spectra versus x\textsubscript{mix} for the same concentrations. The lines connecting the data points in Figure 5 are presented only as a guide for the eye. The trends observed in Figure 5 are nearly identical. Furthermore, we plot the UV–vis peak areas versus the EPR double integral in Figure 6. To a first approximation, the UV–vis 617 nm peak area is directly proportional to the EPR double integral. It is evident that the UV–vis peak at 617 nm of TEGDME and PEO solutions is due to the presence of polysulfide radical anions.

To gain insight into the concentration of radical species present in the TEGDME polysulfide solutions, the UV–vis data were used to calculate radical concentrations according to the Beer–Lambert law:

\[
A = εC_gl
\]  

Figure 7 shows that the polysulfide radical concentration is a complex function of C\textsubscript{S} and x\textsubscript{mix}. In general, the radical concentration increases with C\textsubscript{S}, but the increase is dramatic for
low values of $x_{\text{mix}}$ (e.g., $x_{\text{mix}} = 4$). At constant $C_R$, the radical concentration ($C_S$) is a sigmoidal function of $x_{\text{mix}}$, increasing rapidly in the vicinity of $x_{\text{mix}} = 7$. The fact that the radical concentration increases with the sulfur concentration is not surprising. One can use these data to elucidate the fraction of sulfur present as radical species in these solutions, $f$. To do this, one needs information about the distribution of radical anions in solutions. While conclusive identification of the radical species present in the TEGDME solutions will be a focus of future work, we calculate $f$ assuming that the radical species were present in the form of LiS$_x$. This assumption is supported by the similarity of the EPR $g$ factors obtained for the TEGDME solutions and those previously obtained for LiS$_x$. One may thus view $f$ as a crude estimate of the fraction of sulfur atoms in radical form:

$$f = \frac{3C_R}{C_S}$$

(3)

This fraction, $f$, calculated according to eq 3, is plotted in Figure 8 as a function of the sulfur concentration ($C_S$) and $x_{\text{mix}}$. The values of $f$ lie between 0.005 and 0.080 depending on the sulfur concentration and lithium to sulfur ratio. The radical fraction, $f$, is highest at low values of $x_{\text{mix}}$ and low sulfur concentrations. The physiochemical properties of lithium polysulfide solutions will depend on both $C_S$ and $f$; solutions with large $f$ have low values of $C_S$. The increase of $f$ with decreasing $C_S$ is consistent with what has previously been observed in DMF solutions, and is evidence of the dianion/radical anion dissociation equilibrium. Radical species are favored at low concentrations, while recombination of radicals to form dianion polysulfides is favored at higher sulfur concentrations.

**CONCLUSIONS**

We conclude that polysulfide radical anions are present in ether-based solvents, TEGDME and PEO. This conclusion is based on both UV–vis and EPR spectroscopy. We demonstrate quantitative relationships between the UV–vis and EPR signals in our solutions. We determine both the total radical concentration and fraction of sulfur in radical form. These parameters are complex functions of the sulfur concentration and lithium to sulfur ratio, as shown in Figures 7 and 8. The fraction of radical species is high in dilute solutions and when the lithium to sulfur ratio is high.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b04264.

Parameters and description for fitting of UV–vis and EPR spectra as well as EPR $g$ factors (PDF)

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Notes

The authors declare no competing financial interest.

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