Direct Observation of Sulfur Radicals as Reaction Media in Lithium Sulfur Batteries

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ABSTRACT: Lithium sulfur (Li-S) battery has been regaining tremendous interest in recent years because of its attractive attributes such as high gravimetric energy, low cost and environmental benignity. However, it is still not conclusively known how polysulfide ring/chain participates in the whole cycling and whether the discharge and charge processes follow the same pathway. Herein, we demonstrate the direct observation of sulfur radicals by using *in situ* electron paramagnetic resonance (EPR) technique. Based on the concentration changes of sulfur radicals at different potentials and the electrochemical characteristics of the cell, it is revealed that the chemical and electrochemical reactions in Li-S cell are driving each other to proceed through sulfur radicals, leading to two completely different reaction pathways during discharge and charge. The proposed radical mechanism may provide new perspectives to investigate the interactions between sulfur species and the electrolyte, inspiring novel strategies to develop Li-S battery technology.

KEYWORDS: Electron paramagnetic resonance (EPR), Radicals, Reaction mechanism, Li-S batteries, Energy storage

Lithium sulfur (Li-S) cells have been intensively revisited in recent years due to the demand on high-energy density batteries for vehicle electrification and large-scale energy storage.^{1, 2} The main obstacle in Li-S battery, e.g. the dissolution of intermediate long-chain polysulfides Li_2S_x ($4 \leq x \leq 8$) in the electrolyte leads to the gradual loss of active sulfur from the cathode³ which continuously “corrode” the lithium anode⁴ and contaminate the whole system. Severe “shuttle reaction” is identified along with low Coulombic efficiency, fast capacity degradation and significant self-discharge.^{5, 6} Various approaches have been proposed to address the polysulfide

dissolution issue from different perspectives.⁷⁻⁹ Although reports on Li-S batteries are quickly accumulated,^{10, 11} the fundamental understanding on the sulfur reaction mechanism and the interactions among dissolved polysulfides, electrolyte and electrodes are still unclear and under debate.

The mechanistic study of sulfur chemistry has been performed by applying various characterization techniques to probe polysulfide in terms of the crystalline structure,¹² morphology evolution¹³ and the coordination with the electrolyte¹⁴ in an attempt to understand the sulfur activities under the electrical field. Simply, scanning electron microscope (SEM) is used to compare sulfur electrodes after repeated cycling in different amounts of electrolytes.¹⁵ The ratio between sulfur and electrolyte is then identified to be the key to reproduce consistent results from Li-S batteries.^{15, 16} Reverse phase high performance liquid chromatography (RP-HPLC) and electrospray ionization mass spectroscopy (ESI/MS) are coupled to separate polysulfides with different chain lengths generated at different voltages.¹⁷ Compared to other characterization methods, X-ray diffraction (XRD) provides relatively less information for Li-S batteries due to the dissolution of the intermediate products and the poor crystallinity of reformed polysulfides after cycling.¹⁸ However, recent findings from *in situ* XRD uncovers the formation of monoclinic β -sulfur after the recrystallization of original sulfur, indicating the necessity of *in situ* characterizations.^{19, 20} The integration of in operando XRD and transmission X-ray Microscopy further reveal the variation of sulfur-derived discharge products, highlighting the importance of in operando characterizations for Li-S battery research.²¹ New analytical tools such as operando X-ray absorption near edge spectroscopy (XANES) and nuclear magnetic resonance (NMR) are also employed to promote the understanding of sulfur redox reaction mechanism,^{22, 23} although the lack of standard Li_2S_x series may raise some concerns. A more

recent work from Cornell correlates the XRD and XANES data with the electrochemical results and points out the participation of $s_3^{\bullet-}$ radicals in the discharge processes,²⁴ consistent with our recent discovery from *in situ* NMR analysis of Li-S batteries (unpublished work, see Supporting Information for Review Only). However, the peak assignment related to the radicals in XANES is still arguable.²⁵ Indeed, the existence of sulfur radicals such as $s_4^{\bullet-}$, $s_3^{\bullet-}$ and $s_2^{\bullet-}$ in nature has been recognized well and they are identified to be the different color centers of ultramarine pigments.²⁶ An earlier work using *ex situ* electron paramagnetic resonance (EPR) has discovered $s_4^{\bullet-}$ and $s_3^{\bullet-}$ radicals in Li_2S_x solution,²⁷ although others only observed EPR signals of $s_3^{\bullet-}$ radicals in the catholyte harvested from cells polarized at different potentials.²⁸ No doubt a series of dynamic equilibrium among various polysulfides proceeds when the potential changes, in which radicals could be generated through dissociation and disproportionation reactions. However, it is unknown how the radicals participate in the electrochemical reaction of sulfur and whether these radicals will be regenerated during charge. That is, will the reaction pathway keep the same during discharge and charge? Other puzzles include the interactions between the radicals and the electrolyte.

This work discusses the application of *in situ* EPR technique to directly monitor the formation and evolution of $s_3^{\bullet-}$ radicals during the electrochemical process. The concentration of sulfur radicals is found to change periodically at different potentials, providing important clues on the roles of radicals in the interplay between chemical and electrochemical reactions in Li-S batteries.

Figure 1a illustrates the detailed dimension of the EPR cell. There are three possible sources that may contribute to the resonance signals obtained from the EPR cell: 1) sulfur radical, 2) carbon substrate and 3) Li metal.²⁹ According to the different line width and g-factors with sulfur

radicals, 2) and 3) were subtracted as the background information (See Supporting Information Figure S1). Figure 1b only shows the resonance signals from sulfur radicals, which demonstrate periodic changes with changing potentials (time) and are assigned to $S_3^{\bullet-}$ radicals based on its line shape/width and g-factor (2.029). Considering the extreme stability of $S_3^{\bullet-}$ in nature,³⁰ this work will mainly focus on the discussion of $S_3^{\bullet-}$ radicals, while other sulfur radicals such as $S_4^{\bullet-}$ or $S_2^{\bullet-}$ may coexist in a trace amount as well.

cell. Both c) and d) starts from the second cycle with the first cycle information in supplementary information.

The concentration of $S_3^{\bullet-}$ radicals is obtained by integrating the peak areas of each spectrum collected at different time (potential) from Figure 1b. To simplify the discussion, the amplitude of sulfur radical concentration is plotted together with the potential changes in Figure 1c. It is found that the concentration change of $S_3^{\bullet-}$ radicals during the first cycle (Figure S2a) is quite different with the subsequent ones (Figure 1c). The *in situ* EPR signals from Li-S cell (Figure 1b) are monitored during the cyclic voltammetry (CV) scan (see Figure 1d for CV curves). Because the effective electrode areas e.g. the electrode surfaces are directly facing each other (EPR cell thickness: 0.8 mm in Fig.1a), are very limited, the polarization is relatively large leading to the asymmetric redox peaks. However, a small reduction peak at 2 V is clearly seen with a second broad peak extended to 1 V due to the polarization. The CV curve of the first cycle (Figure S2b) displayed a much larger polarization than the following ones (Figure 1d). This is because that Teflon binder is used in the cathode with high sulfur loading (3-4 mg cm⁻²). The electrode is not fully wetted until after the first cycle thus there is a delay of sulfur radical enrichment (Figure S2a) due to the electrolyte flooding process. The relatively high polarization in the first cycle (Figure 1d) is caused by the electrolyte wetting issue. The discussion of the $S_3^{\bullet-}$ concentration variation in Figure 1c and 1d, therefore, starts from the second cycle. During the negative scan, the concentration of $S_3^{\bullet-}$ increases fast and reaches its maximum at ca. 2.0 V (Figure 1c). When the potential further decreases, radical concentration decreases indicating the consumption of sulfur radicals at lower potentials. When the positive scan begins, the concentration of $S_3^{\bullet-}$ still decreases but becomes stable for a short duration between 2.0 V and

2.75 V, probably suggesting a temporal balance between consumption and generation of sulfur radicals. A sharp drop of radical concentration is seen at the end of the positive scan. A delay is also noticed between the end of anodic scan and the minimum concentration of $s_3^{\bullet-}$ radicals at ca. 700 min in Fig.1c. This is because when the potential scan is reversed, the response current still keeps positive for a while before becoming negative (Fig.1d). Therefore, a delay is usually observed.

It is known that $s_3^{\bullet-}$ radicals are generated from the dissociation of S_6^{2-} anions.³¹ Therefore, the occurrence of $s_3^{\bullet-}$ can be used to index the existence of Li_2S_6 . Li_2S_x series are chemically synthesized by mixing stoichiometric amount of lithium metal and sulfur powders (Figure 2a). It is found that Li_2S_8 and Li_2S_6 are completely soluble in DOL/DME, while Li_2S_4 are suspension. Li_2S_2 still partially dissolves in the electrolyte, while Li_2S is completely insoluble. It has to be pointed out that the semi-solid behavior of Li_2S_4 depends on its concentration and solvent used (Figure S3). The electrolyte used in this work consists of DOL/DME, in which the solubility of Li_2S_4 is low. Considering the electrolyte amount in the real cells is very limited for practical application purpose, it is appropriate to assume Li_2S_4 generated in Li-S cells is in semi-solid phase. Interestingly, $s_3^{\bullet-}$ radicals are generally discovered in all polysulfide species from Li_2S_8 to Li_2S_2 except in commercial Li_2S (Figure 2b). This indicates that the nominally stoichiometric Li_2S_x is in fact a mixture of different species in which $S_6^{2-}(s_3^{\bullet-})$ must exist. Indeed S_8^{2-} , S_6^{2-} and S_4^{2-} all experience quick disproportionation once formed.^{22, 27} With that said, the ring cleavage process cannot be a “step-by-step” mechanism. Instead, once polysulfide, for example, Li_2S_8 , is produced, some of S_8^{2-} anions quickly disproportionate into S_6^{2-} ²⁷ and other polysulfide species simultaneously, according to the observed $s_3^{\bullet-}$ radicals from both *in situ* and *ex situ* EPR

measurement (Figure 1c and Figure 2b). Further, s_3^{*-} radicals are not consumed completely during the electrochemical process (Figure 1c) and even appear in “Li₂S₂” (Figure 2b). How those radicals participate in the electrochemical reactions and how the sulfur radicals interact with other polysulfide as well as the electrolyte in the system are further discussed in the following part.

Figure 2. a) Comparison of chemically synthesized Li₂S_x series in DOL/DME solvents.

Concentration of each sample is 0.2 M based on elemental sulfur. b) EPR spectra of Li₂S_x series.

s_3^{*-} radicals were detected in Li₂S₈, Li₂S₆, Li₂S₄ and Li₂S₂, while there is no resonance signals from commercial Li₂S.

Figure 3 plots a typical discharge-charge curve of Li-S battery with detailed electrochemical and chemical equations noted for each plateau or slope. Button cells are used to obtain the representative charge-discharge curves throughout this work. The current EPR cell cannot obtain representative charge-discharge curves for Li-S cells due to the large polarization from the limited cell space. During discharge, soluble long-chain polysulfides such as S₈²⁻ are generated firstly (step 1) but quickly undergo disproportionation reaction as described in step (1.1) of Figure 3 and produce S₆²⁻ anions. This explains the quick increase of s_3^{*-} concentration once cathodic scan begins (Figure 1c) since S₆²⁻ is always in equilibrium with s_3^{*-} radicals (Step 1.2).

Some of the “regenerated” S_8 in step (1.1) is electrochemically consumed by accepting electrons, if the scan rate is not very high. The inconsistent observation of S_8 in literature,¹² therefore, may depend on the real current densities, which is related with the carbon surface area, applied on the cell since the amount of “residual” S_8 in steps (1) and (1.1) largely varies at different rates. Dilute configuration e.g. thin-film sulfur cathode also minimizes the content of unreacted S_8 as explained by Cuisinier *et al* earlier.²² At the end of 2.3 V, S_8^{2-} , $S_6^{2-}(s_3^{\bullet-})$ and S_8 should temporarily reach an equilibrium. The dominant electrochemical reaction is a two-phase transition between S_8 and Li_2S_8 , while the conversion to Li_2S_6 is mainly through the chemical step. Thus only a single plateau is observed at 2.3 V. As the voltage continues to decrease, S_8^{2-}/S_6^{2-} is electrochemically reduced to S_4^{2-} through the electrochemical step (2) in Figure 3. Because Li_2S_8/Li_2S_6 are soluble and Li_2S_4 is semisolid (Figure 2a), this liquid-to-semisolid conversion forms a slope between 2.3 and 2.1 V in Figure 3, accompanied by the decrease of $s_3^{\bullet-}$ concentration (Figure 1c). Further scan to the lower potential leads to the electrochemical reduction of Li_2S_4 to Li_2S_2 and then to Li_2S (see step 3 in Figure 3), while chemical disproportionation of S_4^{2-} into S^{2-} and S_6^{2-} concurrently occurs (step 3.1 in Figure 3). The electrochemically derived Li_2S depends on the current density and cutoff voltage, while the chemically formed Li_2S is from the precipitation of S^{2-} (step 3.2 in Figure 3) dissociated from S_4^{2-} , which can be used to explain the semisolid state of chemically synthesized Li_2S_4 (Figure 2a). The proposed equilibria in step 3.1-3.2 are further supported by the resonance signals of $s_3^{\bullet-}$ in chemically synthesized Li_2S_4 emulsion (Figure 2b). At the end of discharge, a new equilibrium should be established among S_4^{2-} , $s_3^{\bullet-}(S_6^{2-})$ and Li_2S_2/Li_2S , with the dominant species being Li_2S_2/Li_2S mixtures. Therefore, the radical concentration does not drop to zero at the end of negative scan (Figure 1c). If the discharge process is terminated earlier by limiting the discharge

cutoff voltage, less amount of insulating Li_2S forms in the equilibrium thus improving the cyclability of the cell.³² The shuttle effect is also observed in Figure 3 suggesting the generation of soluble polysulfide which changes the electrolyte properties such as viscosity. The role of the sulfur radicals in the shuttle reaction is worth further investigation.

Figure 3. Proposed reaction mechanism for Li-S batteries during cycling. The equilibria between S_6^{2-} and S_3^{*-} always exists and shifts at different potentials. S_6^{2-} prefers to stay at relatively high potential (> 2.1 V) while S_3^{*-} is the preferred form at low potential (≤ 2.1 V). Different reaction pathways are suggested for discharge and charge processes. The Li-S cell was tested at C/5 rate between 1 V and 3 V in typical button cells.

The evidence that the final discharge product in Li-S cell is a radical-containing mixture instead of pure $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ is very critical to understand the charge reaction mechanism. During discharge (Figure 3), a distinct transition between 2.3 V and 2.1 V plateaus is commonly observed. However, this gap almost disappears in the charge process. In addition, the voltage jumps quickly to reach a long charge plateau at 2.3 V. Despite the current density, the polarization of charge curves change little from C/50 to C/5 (Figure S4). Another small plateau appears at ca. 2.4 V during charge, corresponds to the transition from S_8^{2-} to solid S_8 . Similar charge characteristics can be found in many literature,^{22, 33, 34} but have not been elaborated yet, in contrast to the extensive discussion on the discharge mechanism. As mentioned earlier, at the end of discharge, $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ equilibrates with $\text{s}_3^{\bullet-}$ (from S_6^{2-}) to form S_4^{2-} anions, as shown in steps 4.1-4.2. Once the over potential becomes sufficiently high, S_4^{2-} will be immediately converted into long-chain $\text{S}_8^{2-}/\text{S}_6^{2-}$ directly due to the fast kinetics of semisolid-to-liquid conversion as shown in step (5.1). Once new $\text{S}_8^{2-}/\text{S}_6^{2-}$ is produced, more $\text{s}_3^{\bullet-}$ radicals form which drive the chemical reaction of (4.1) and (4.2) to produce more S_4^{2-} to facilitate the conversion of insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$. Consequently, more insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ are consumed chemically, in addition to their electrochemical conversion. From this point of view, the polarization of a Li-S cell mainly comes from discharge curves instead of the over potential of the charge process. During charge, the speed of producing new $\text{s}_3^{\bullet-}$ radicals from $\text{S}_8^{2-}/\text{S}_6^{2-}$ (step 5.1) temporarily offsets the consumption speed of $\text{s}_3^{\bullet-}$ radicals in steps (4.1-4.2), leading to a short region of constant concentration in Figure 1c during the anodic scan until the final conversion to S_8 (Step 5.2 in Figure 3).

The reaction mechanism discussed in Figure 3 further helps to explain quite a few phenomena in Li-S batteries. For example, if the polysulfide chain is cleaved step-by-step, multiple plateaus

should appear at 2.3 V and 2.1 V plateaus due to the many two-phase transitions. However, even when the current density is lowered to C/50, the total number of plateaus did not increase (Figure S4), consistent with the conclusion that some of the polysulfide species are produced through chemical process. The proposed charge mechanism can also be used to explain the high over potential of commercial Li_2S . Usually when Li_2S is directly used as the starting cathode, a high over potential is required to activate the material during the first charge,³⁵ while the electrochemically formed Li_2S has no such issue. In addition to the particle size differences between the electrochemical derived Li_2S and commercial Li_2S ,¹⁵ another reason could be the lack of $\text{S}_3^{\bullet-}$ radicals in commercial Li_2S powders (Figure 2b) to establish the chemical equilibria in step (4.1). That is, there is no S_4^{2-} anions to shorten the charge reaction pathway, leading to a high over potential during the first charge. If $\text{S}_3^{\bullet-}$ radicals (from $\text{Li}_2\text{S}_8/\text{Li}_2\text{S}_6$) are mixed with Li_2S cathode in the beginning, the similar equilibrium as in step 4.1-4.2 is built so the over potential of Li_2S cathode is lowered (Figure S5). A recent interesting work³⁶ also discovers that the addition of soluble polysulfide into Li-S cell helps to minimize the formation of Li_2S probably because of the same proposed mechanism here. Finally, the observation of $\text{S}_3^{\bullet-}$ radicals also helps to select electrolyte for Li-S batteries. The majority of the reported work on Li-S batteries uses ether-based electrolyte such as 1,3-dioxolane (DOL) and dimethoxyethane (DME) as the solvents with the reason not well understood.³⁷ If alkyl-carbonate solvent such as ethyl carbonate (EC)/dimethyl carbonate (DMC) is used, $\text{S}_3^{\bullet-}$ will immediately react with the alkyl carbonates, which is known to be vulnerable to the radicals.³⁸ In the chemically synthesized Li_2S_8 solution, after adding a small amount of carbonate-based electrolyte, all resonance signals disappear after 40 min (Figure S6). The voltage profile (Figure S7a) and CV curves (Figure S7b) of Li-S cells in EC/DMC-based electrolyte further confirm that the parasitic reactions between sulfur radicals

and the alkyl-carbonate solvents generate non-active byproducts, making the cell non-rechargeable. Similarity can be found in Li-O₂ batteries, in which carbonate solvents intensively react with intermediate O₂^{•-} radicals through nucleophilic attack, converting discharge products to inactive carbonates.³⁹ On the other hand, ether-based electrolytes or glymes are relatively more stable towards radicals.²⁷ Considering the similar oxidation ability between s_3^{*-} and O₂^{•-}, the commonly used DOL/DME electrolyte is more suitable in the presence of s_3^{*-} , although the long-term stability may still remain a question mark especially considering the vulnerability of SEI on the lithium metal anode. Of note, if sulfur was bonded to polymer backbones by forming S-containing polymer, or organosulfides, then alkyl-carbonate solvents can still be used due to the absence of sulfur radicals or dissociable S₆²⁻ anions.^{40, 41} However, those cells consisting of organosulfides, strictly, are different from typical Li-S batteries as the voltage profiles have been significantly changed and a large amount of carbon has to be incorporated to stabilize the cycling.

In summary, the generation and concentration variation of sulfur radicals have been monitored in a functioning Li-S cell by using *in situ* EPR technique. s_3^{*-} is identified throughout the whole cycling, indicating the temporal equilibrium among different polysulfides, instead of producing a single polysulfide component, at each different potential. The chemical and electrochemical reactions in the Li-S cell are driving each other to move forward via using sulfur radicals as the media. Different reaction pathways have been revealed for the discharge and charge processes of Li-S battery, which matches well with their voltage profiles and helps to elaborate the high over potential of pure Li₂S. It is also suggested in this work that the electrolyte selection for Li-S system should consider the reactivity of sulfur radicals to enable the long-term cycling stability of the cells.

ASSOCIATED CONTENT

Supporting Information. Experimental details, EPR spectra, Cyclic Voltammograms (CV), and Electrochemical charge/discharge data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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