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Investigation of Li-S Battery Mechanism by Real-Time Monitoring the Changes of Sulfur and Polysulfide Species during the Discharge and Charge

Dong Zheng[†], Dan Liu[§], Joshua B. Harris[†], Tianyao Ding[†], Jingyu Si[†], Sergei Andrew[†], Deyu Qu[§], Xiao-Qing Yang[‡], Deyang Qu^{†}*

[†] Department of Mechanical Engineering, College of Engineering and Applied Science,
University of Wisconsin Milwaukee, Milwaukee, WI 53211, USA

[§] Department of Chemistry, School of Science, Wuhan University of Technology,
Wuhan 430070, Hubei, P.R. China.

[‡] Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

* qud@uwm.edu

ABSTRACT

The mechanism of the sulfur cathode in Li-S batteries has been proposed. It was revealed by the real-time quantitative determination of polysulfide species and elemental sulfur by means of the high performance liquid chromatography in the course of the discharge and recharge of a Li-S battery. A three-step reduction mechanism including two chemical equilibrium reactions was proposed for the sulfur cathode discharge. The typical two-plateau discharge curve for sulfur cathode can be explained. A two-step oxidation mechanism for the Li_2S and Li_2S_2 with a single chemical equilibrium among soluble polysulfide ions was proposed. The chemical equilibrium among S_5^{2-} , S_6^{2-} , S_7^{2-} and S_8^{2-} throughout the entire oxidation process resulted for the single flat recharge curve in Li-S batteries.

KEYWORDS: Li-S battery, polysulfide and sulfur determination, charge and discharge mechanisms, HPLC, polysulfide equilibrium

1. INTRODUCTION

To minimize the green-house gas emission from the combustion engines of vehicles, the substitution of fossil fuels with other energy and power sources is of great importance. State-of-art Li-ion batteries (LIBs) have been successfully applied in hybrid and plug-in electric vehicles for several years. However the energy density of a LIB cannot satisfy the increasing demand for the driving distance per charge for a pure electric vehicle (EV). Rechargeable lithium sulfur (Li-S) batteries are considered as one of the potential candidates to replace state-of-art Li-ion batteries in EV, due to their high theoretical energy density ($1672\text{mAh}\cdot\text{g}^{-1}$), safety, and low cost. Substantial amount of work has been done on Li-S batteries.

Under certain restricted conditions e.g. continuous cycling, a freshly made Li-S battery can be cycled over hundreds times and with at least over half of the theoretical capacity being retained.¹ Unlike Li-ion materials in which the Li ion insertion mechanism is well studied and understood, the sulfur redox reaction mechanism in Li-S batteries is still not well understood due to the fact that the sulfur redox reaction is one of the most complicated redox reactions.² It has commonly accepted that after accepting the first electron, the reduced elemental sulfur on a cathode (cyclooctasulfur, S_8) becomes a long chain linear polysulfides through the cleavage of the sulfur ring, then the long chain polysulfide ions are further reduced into short chain polysulfide ions at lower electrochemical potentials; during recharge, the short chain polysulfide ions are oxidized into long chain polysulfide ions first, then the long chain linear polysulfide ions are oxidized back into elemental sulfur.³ To better understand the stepwise redox process of sulfur in a Li-S battery, various analytical techniques have been deployed, including UV-Vis,⁴⁻¹⁰ Raman,¹¹⁻¹⁴

ESR,¹⁵⁻¹⁶ XRD,^{14,17-20} XANES,²¹ XRF,²² TEM,^{13,20} SEM,^{9,20,23} as well as NMR^{24,25}. However none of the above analytical techniques are adequate for the quantitative and qualitative determination of dissolved polysulfides due to their overlapping absorbance spectrum and the lack of the polysulfide standard solutions.

High performance liquid chromatography (HPLC) is a powerful separation tool and widely used in qualification as well as quantitation. Recently, this technique was successfully used for the analysis of dissolved polysulfide ions^{7,26,27} and elemental sulfur²⁸ in Li-S batteries. The uniqueness of the HPLC analysis of polysulfides is the derivatization of unstable polysulfides into stable alkyl polysulfides as shown in the following reaction through which the fast redistribution of different polysulfides is eliminated and the original distribution of polysulfides is captured.^{26,27} Also only the derivatized alkyl polysulfides have suitable retention and separation on widely used reverse-phase HPLC column and the ionic polysulfides have no retention and separation on reverse-phase HPLC column.²⁹ Based on our success in the development of this HPLC-MS method for the polysulfides and sulfur analysis, it is now the only reliable analytical method for the determination of polysulfides in the Li-S battery electrolyte. In this work, for the first time we reported a systematic study of the real-time changes of polysulfides and sulfur during discharge and charge of a Li-S battery. To our knowledge, no such systematic work has been done before, and most important the findings in this work could be a good supplement to the results from other analytical techniques to assist in understanding the redox mechanism comprehensively and clearly.

2, Experimental

2.1. Chemicals

Sulfur (99.98%), lithium metal, lithium nitrate (LiNO_3 , 99.99%), HPLC grade methanol, HPLC grade water, methyl triflate (98%), anhydrous dimethoxyethane (DME) (from Sigma Aldrich), and lithium perchlorate (LiClO_4 , battery grade from FERRO) were purchased and used without further treatment.

2.2. Sample preparation and methods

0.0295g S_8 was dissolved in 50mL 0.5M LiClO_4 /DME solution (with 0.1 M LiNO_3) to prepare the catholyte with elemental sulfur (concentration about 2.3mM). The Li-S cell was prepared in a 25mL 4-neck round bottom flask: the cathode was a carbon felt electrode (30x10x4.6mm, SIGRACELL KDF 4.6, from SGL group in Germany), the anode was made of lithium metal, lithium metal was also used as a reference electrode and 15 ml of the catholyte was used as both the supporting electrolyte and sulfur source. Since the carbon felt electrode has an extremely low surface area (mainly carbon fiber, as shown in figure S-1), the use of a carbon felt electrode can greatly minimize the specific or nonspecific absorption of both elemental sulfur and polysulfide species which could influence the homogeneity of the electrolyte. To minimize the concentration and diffusion polarizations (due to the low surface area of carbon felt cathode and the high volume of electrolyte), the cell was stirred and cycled at 0.2mA (the C rate is about C/70). The 4th neck of the flask was used as a sampling port for real-time HPLC analysis.

All of the following operations including the electrochemical cycling and sample preparations were done in an Ar-filled glove-box with the oxygen and moisture less than 0.1 ppm. The catholyte was taken out of the cell at various depths of discharge and recharge and derivatized in

an HPLC vial with the following procedure: 525 μL of DME with 25 μL of methyl triflate (0.22 mmol) was added into a 1.5 mL HPLC vial and vortexed for 1 minute, 75 μL of electrolyte was extracted out of the Li-S cell under operation and was then added into the DME/ methyl triflate solution, and immediately the HPLC vial with the mixture was capped by an air-tight cap and vortexed for 5 minutes. The derivatized electrolyte samples in the air-tight HPLC vials were then removed from the glove-box for HPLC analysis.

A Shimadzu LC-20AD quaternary pump with a Shimadzu SIL-20A auto-sampler was used to deliver a methanol/water mobile phase through an Agilent Zobrax C_{18} column (from Agilent, C_{18} , 4.6*50 mm, 5 μm) at a flow rate of 0.70 mL/min. The injection volume was 20 μL . A binary gradient of mobile phases were used to elute the injected sample out with the following condition: at 0 min 25% methanol (75% water); at 10 min 100% methanol; at 25 min 100% methanol; at 26 min 25% methanol. All flows from the HPLC were introduced into the Shimadzu SPD-M20A detector, full wavelength range from 190 nm to 800 nm was recorded by Shimadzu LabSolutions Lite software, and the chromatograms discussed in this work were based on the data collected at 230 nm.

The electrochemical experiment was done by electrochemical station (PARSTAT 2273, Princeton Applied Research) and recorded by PowerSuite (version 2.58, from Princeton Applied Research).

3. RESULTS AND DISCUSSION

Most of the electrochemical experiments for Li-S batteries were conducted in a typical coin cell configuration in which the high surface porous carbon materials with preloaded sulfur (solid) were used as cathode.¹ Moreover, the total electrolyte used in coin cell configuration was limited,

it's reported that for the best cell performance the electrolyte to sulfur ratio in coin cell configuration is about 10-20 μl (electrolyte)/mg (sulfur).³⁰ Thus the coin cell configuration was not suitable for real-time analysis by HPLC due to the limited volume of electrolyte and the existence of insoluble elemental sulfur in cathode. Figure 1 shows the discharge and charge profiles of the S in the catholyte. The discharge capacity and charge capacity were 1168.1 and 1213.0 mAh g^{-1} , respectively. The discharge and recharge profiles shown in figure 1 are similar to a typical discharge and recharge profiles obtained from Li-S batteries with coin cell configurations.^{30,31}

Figure 1. Discharge/charge profile for three-electrode Li-S cell in this work with carbon felt as cathode, lithium metal as anode and reference electrode, and 2.3 mM elemental sulfur in 0.5 M $\text{LiClO}_4/\text{DME}$ electrolyte. The magenta dash lines indicate the stoichiometric species of polysulfides (also labeled on top of the dash lines) based on theoretical stepwise reduction.

Figure 2(A) shows the real-time sampling points of the Li-S cell during discharge. While the Li-S cell was still under operation, a specific amount electrolyte was sampled from the cell and derivatized by methyl triflate in a DME solution. After derivatization, the sample was analyzed by HPLC. Figure 2 (B) shows the comparison of the chromatograms for the samples taken from all the sampling points during the discharge. The retention times of each derivatized polysulfide and elemental sulfur are indicated with the dash lines (refer Table S-1 in Supporting Information for detailed information, and the assignment of each species on the chromatogram can be found in reference 32). Evidentially, elemental sulfur was reduced to polysulfides between 2.5 and 2.3 V, the rapid potential drop from 2.4 V to below 2.3 V indicated the exhausting of elemental sulfur. As shown in the chromatogram D4 in figure 2(B), the elemental sulfur was almost completely consumed and polysulfide species became abundant with the majority of the polysulfides being S_5^{2-} and S_6^{2-} balanced by a minority of S_7^{2-} and S_4^{2-} . It is worth emphasizing that a small amount of S_8^{2-} was observed, e.g. in chromatogram D4, but it was not a result of the electrochemical reduction of sulfur, rather from the subsequent chemical reactions.²⁷ In the region between 2.3 V to 2.1 V where a sloped discharge curve appeared, polysulfide ions with chain length longer than five became reduced to shorter chain polysulfide ions e.g. S_4^{2-} as shown in the chromatographs D7-D12. At 2.1 V, little polysulfide ions with chain length longer than five existed. During the discharge plateau between 2.1 and 2.0 V, the only abundant polysulfide ions in the electrolyte were S_5^{2-} and S_4^{2-} . It was interesting that limited amount of S_3^{2-} existed in the solution and almost no dissolved S_2^{2-} and S^{2-} was detected. This is consistent with previous observations^{26,27} that the solubility of S^{2-} and S_2^{2-} are low, and the final products were Li_2S and Li_2S_2 precipitates. The existence of Li_2S and Li_2S_2 was also confirmed by *in-situ* XRD,¹⁷⁻¹⁹ XANES,²¹ and NMR²⁵ at the final stage of discharge. It is interesting to observe from table S-2

Figure 2. The discharge profile of Li-S cell with sampling points (red squares from D1 to D13) during operation (A) and the corresponding HPLC chromatograms (B). The chromatographic peak for each derivatized polysulfide species ($R=CH_3$) is labeled as the magenta dash lines in (B) as well as elemental sulfur.

in the supplemental materials that the ratio of the peak area between RS_4R and RS_5R remained the same during the discharge plateau between 2.1 and 2.0 V (D7 – D10) (the chromatographic peak areas in figure 2 (B) were integrated and tabulated). It is reasonable to assume that the

chemical equilibrium between S_4^{2-} and S_5^{2-} remained during the discharge between 2.1 to 2.0 V, which explains the flat discharge curve in the potential range.

Due to the different molar efficiencies of absorbance for different derivatized polysulfide species ($CH_3S_nCH_3$), direct comparison of the peak intensities of $CH_3S_nCH_3$ with different n values may be not appropriate. However the peak areas of the same derivatized polysulfide in different discharge stages are comparable. In table S-3 (in the Supplemental Materials) and figure 3, the peak areas for each derivatized polysulfide ion at different discharge stages were normalized to its highest value. The change of polysulfide ions in the electrolyte from elemental sulfur, long chain polysulfides to short chain polysulfides can be clearly demonstrated as the discharge proceeded. The vertical dash lines indicate the stoichiometric polysulfide calculated from the discharge capacity. Previously, the reduction mechanism of elemental sulfur was proposed as a 2-electron electrochemical reduction of S_8 to S_8^{2-} and followed by fast decomposition of S_8^{2-} into S_6^{2-} .^{1,2} Such a mechanism was proven not actuate since in our *in-situ* investigation, S_8^{2-} was not generated electrochemically but through subsequent chemical reactions.²⁷ It can be observed in figure 3 that the change of the abundance for S_8^{2-} , S_7^{2-} and S_6^{2-} were almost identical in the first discharge plateau, which was evident from the chemical equilibrium among those polysulfide species. The first flat discharge plateau could be a result from the equilibrium. Another interesting observation from figure 3 is that even when the discharge reached the stoichiometric S_2^{2-} stage the most abundant polysulfides in the electrolyte were S_4^{2-} , S_5^{2-} and S_3^{2-} . To the very end of the discharge, even though the concentration decrease, the relative distribution of the three polysulfides remained.

Figure 3. The normalized chromatographic peak for each derivatized polysulfide species ($R=CH_3$) from real-time HPLC results during discharge of Li-S cell (from table S-3). The magenta dash lines indicate the stoichiometric species of polysulfides (also labeled on top of the dash lines) based on theoretical stepwise reduction.

Based on the above discussion, scheme 1 shows the mechanism of the 3-stage sulfur reduction reaction. The elemental sulfur became reduced to long chain polysulfide ion (mainly S_7^{2-} , S_6^{2-} and S_5^{2-}) and S_8^{2-} was formed through the subsequent reaction between the long chain polysulfide ions and sulfur²⁷. During this period, a chemical equilibrium was maintained among S_7^{2-} , S_6^{2-} and S_5^{2-} until a substantial amount of S_7^{2-} , S_6^{2-} were consumed around 2.3 V, then the potential started to decrease. A sloped discharge profile was demonstrated between 2.3 to 2.1 V. Evidentially, as shown in figure 3, almost all the polysulfides S_n^{2-} with $4 \leq n \leq 7$ were co-existing in the electrolyte during the reduction reaction; the concentration of the polysulfide changed

independently, so no apparent equilibrium can be observed. The second reduction plateau started when almost all the polysulfide species S_n^{2-} with $n \geq 6$ were consumed at about 2.1 V. During the second flat reduction plateau, the reduction rate of S_5^{2-} , S_4^{2-} and S_3^{2-} remained almost the same as shown by the parallel curves for these three species in figure 3 which indicates a chemical equilibrium between these three species. Even though the ratio of the concentrations of these three polysulfides remained almost unchanged during the flat reduction region, the total amount of dissolved polysulfide ions decreased as shown in table S-2 in the supplemental information. The products were insoluble Li_2S_2 and Li_2S , which were observed at this stage of reduction by *in-situ* XRD,¹⁷⁻¹⁹ XANES,²¹ and NMR²⁵.

Scheme 1. The proposed discharge mechanism of sulfur in Li-S battery.

The slope discharge between 2.3 and 2.1V, which was typically assigned to the formation of medium chain length polysulfides, was proposed to be the formation of both medium chain length polysulfides and the precipitates of Li_2S_2 and Li_2S . The hypothesis could be proven based on the two following evidences. Firstly, Li_2S was observed in the beginning of the second discharge plateau with *in-situ* XRD¹⁷⁻¹⁹ and XANES²¹. Chiang *et al*²³ also pointed out that the

nucleation of the new aggregations of Li_2S on the carbon electrode needed about 100 mV overpotential and the morphology of the formed Li_2S aggregations was rate dependent.

Therefore, it's reasonable to assume the co-existence of Li_2S_2 and Li_2S on the carbon electrode surface due to the slow kinetics for the formation of Li_2S . Secondly, it's evident that the relative peaks of the polysulfides (Li_2S_n with $n \geq 5$) were peaked in the vicinity of the corresponding stoichiometric value. However, the relative peaks of the polysulfide with $n=3$ and 4 were peaked far away from the corresponding stoichiometric values, which indicated the formation of other species and in this case only Li_2S_2 and Li_2S were possible.

Figure 4 shows the points of sampling during the recharge of the Li-S cell (figure 4A) and the corresponding chromatograms (figure 4B). The most significant conclusion from figure 4 was that almost all the solid lithium sulfide and dissolved polysulfides became oxidized back to elemental sulfur at 2.9 V. By comparing the initial chromatographic peak area for S_8 before discharge (table S-2) and the peak area in table S-4 at 2.902 V after recharge, it was found that over 95% sulfur was recovered at 2.9 V. Due to the limitation of other analytical methods, this is the first time the reduction and re-oxidation efficiency for a sulfur redox reaction was determined not with electrochemical analysis but with quantitative chemical analysis, which is more accurate. It is worth pointing out that there were still some polysulfide species (S_n^{2-} $4 \leq n \leq 7$, referring to table S-4 in supplemental materials) in the fully charged catholyte at 2.9 V. The same observation was also reported by studying the color changes of the electrolyte in a Li-S cell by optical microscope.³⁴ Similar color changes can be observed in the Li-S catholyte during discharge and recharge, as shown in figures S-2 and S-3 in the supplemental material. During discharge, the color of the catholyte changed from light to dark and back to light at the end of discharge; during recharge, the color of the same catholyte changed from light to dark back to

light at the end of charge. The light yellow color in the fully charged catholyte was the evidence for the existence of low concentration of the polysulfide species, whose composition was now fully revealed as shown in table S-4.

The charge mechanism for a Li-S cell has been widely reported, but due to the lack of the analytical techniques for dissolved polysulfide ions, the charge mechanisms in the literature were ambiguous and sometimes conflicted with each other. In the early electrochemical study of the redox of sulfur, Levillain *et al*³ ascribed three oxidation waves in the cyclic voltammograms (CV) to the oxidations of S_3^{2-} , S_4^{2-} , S_6^{2-} , and S_8^{2-} . The solvent used in this pioneering work was dimethylformamide instead of ether solvents and the condition in CV studies was different from the operating conditions of a Li-S battery. Dominko and Patel⁵ investigated the sulfur redox mechanism by in operando UV-Vis spectroscopy, and they reported the increase of long chain polysulfides (S_8^{2-} , and S_6^{2-}), first an increase and then decrease of medium chain polysulfides (S_4^{2-} , and S_3^{2-}), and a similar trend for short chain polysulfide (S_2^{2-}). The assignments of the polysulfides in UV-Vis spectra has been debatable due to the overlay of the peaks, for example, absorbance at 620nm is assigned to S_3^- radical¹⁰ instead of S_8^{2-} as in Dominko and Patel's work⁵. Nazar *et al*²¹ also investigated the oxidation mechanism in a Li-S battery during charge by XANES. They reported that the S_6^{2-} species instead of S_8^{2-} species were the main species to be oxidized into α -sulfur and the S_4^{2-} species were the transient species for oxidation of Li_2S into Li_2S_6 . Barchasz and Alloin *et al*¹⁹ studied the charge of Li-S battery by *in situ* and operando

Figure 4. The charge profile of Li-S cell with sampling points (red squares from C1 to C11) during operation (A) and the corresponding HPLC chromatograms (B). The chromatographic peak for each derivatized polysulfide species (R=CH₃) is labeled as the magenta dash lines in (B) as well as elemental sulfur.

XRD. They reported that the oxidation of Li₂S was a two-step process and the formation of β -sulfur only happened at the end of the charge process. The second step of the oxidation of Li₂S was slow due to the parallel oxidation of Li₂S₄.¹⁹ Overall the oxidation mechanism in a Li-S

battery reported in the literature can be summarized into a step-wise oxidation mechanism from short sulfide to medium chain polysulfides and finally long chain polysulfides to elemental sulfur, although this mechanism may not exactly be the reverse of the reduction mechanism.

Figures 4 and 5 offer detailed insights for the oxidation reaction. Due to Li_2S and Li_2S_2 precipitation, the conductivity of the fully discharged electrode ought to be low, which only recovered as the Li_2S and Li_2S_2 became oxidized to dissolved polysulfide ions. The change of electrode conductivity resulted from the initial potential dip in figure 4. It was evident that the concentration of S_3^{2-} and S_4^{2-} remained constant while the concentration of S_5^{2-} and S_6^{2-} kept increasing during the potential dip. It appears that the initial oxidation of Li_2S and Li_2S_2 yielded soluble S_5^{2-} and S_6^{2-} polysulfide ions either through S_3^{2-} and S_4^{2-} as intermediates or directly. After the potential dip, the concentrations of S_3^{2-} and S_4^{2-} took sharp drops, the concentration of S_3^{2-} started to continuously decrease while the concentration of S_4^{2-} remained constant until elemental sulfur started to form at 2.4 V. In the meantime, S_5^{2-} , S_6^{2-} , S_7^{2-} and S_8^{2-} were formed and the ratio among the four polysulfide ions remained constant, as shown in figure 5. It appears that the chemical equilibrium among these polysulfides remained. The increasing concentrations of S_5^{2-} , S_6^{2-} , S_7^{2-} and S_8^{2-} reversed coinciding with the increase of elemental sulfur concentration at about 2.4 V, while the concentration of S_4^{2-} took a nose dive. It is interesting that the concentration of S_3^{2-} and S_4^{2-} were never above their concentrations at the end of reduction (or beginning of oxidation), which could mean that either S_3^{2-} and S_4^{2-} were not the products for the electrochemical oxidation of Li_2S and Li_2S_2 , or they were the intermediates for the formation of longer chain polysulfide. Therefore, we suspected that the sharp decrease of S_3^{2-} and S_4^{2-} concentration resulted from the chemical reaction with newly formed elemental sulfur rather than electrochemical oxidation on the electrode. On the other hand, of course, the decrease of S_5^{2-} ,

S_6^{2-} , S_7^{2-} and S_8^{2-} concentration correlated very well with the production of elemental sulfur until the almost disappearance of polysulfide ions, so it must be an electrochemical oxidation process. It is also interesting to notice that during the decline, S_5^{2-} , S_6^{2-} , S_7^{2-} and S_8^{2-} still remained in a chemical equilibrium. Therefore, unlike the stepwise reduction process, the oxidation of polysulfide ions was conducted through the electrochemical formation of polysulfide ions S_n^{2-} ($5 \leq n \leq 7$) and sulfur while the chemical equilibrium among S_5^{2-} , S_6^{2-} , S_7^{2-} and S_8^{2-} remained throughout the whole oxidation process. That was the reason the oxidation curve was a single flat one. The oxidation reaction mechanism is shown in scheme 2.

Figure 5. The normalized chromatographic peak for each derivatized polysulfide species ($R=CH_3$) from real-time HPLC results during charge of Li-S cell (from table S-5).

Scheme 2. The proposed charge mechanism on the cathode in a Li-S battery.

Table 1, The highest chromatographic peak areas and the corresponding cell potentials for different polysulfide species during charge and discharge of a Li-S cell.

	Charge		Discharge		Ratio of peak area of Charge/Discharge
	Potential (V)	Peak area	Potential (V)	Peak Area	
RS ₃ R	2.300	49904	2.068	219102	0.23
RS ₄ R	2.420	754517	2.091	1865579	0.40
RS ₅ R	2.420	1603892	2.207	1965162	0.82
RS ₆ R	2.375	1387329	2.266	1400488	0.99
RS ₇ R	2.401	537688	2.266	550688	0.98

Table 1 tabulates the potential for the highest concentration (highest chromatographic area) of each polysulfide species during the reduction and oxidation. It was interesting to observe that the maximum concentrations of S₆²⁻, S₇²⁻ and S₈²⁻ polysulfide species were almost the same (ratio close to one) during the reduction and oxidation reactions. The potentials for the corresponding maximum concentrations were within 200 mV. On the contrary, the maximum concentrations of

S_3^{2-} and S_4^{2-} species and their corresponding potentials were much more different in reduction and oxidation reactions.

It should be emphasized that the redox mechanism proposed for the Li-S battery was based on the determination of polysulfide species at steady or possible equilibrium states. Fast reacting species and free radicals were not taken into consideration. Further investigations with e.g. *in-situ* ESR are in progress and more details will be revealed in conjunction with the *in-situ* HPLC results reported in this paper. Also it is worth pointing out that the additive of $LiNO_3$ in the electrolyte is pivotal especially in the charge process. It's been demonstrate that the $LiNO_3$ additive in the electrolyte could greatly minimize the “shuttle effect” during charge.^{35,36} In our preliminary trial of Li-S cell without $LiNO_3$ additive, the complete oxidation of polysulfides back to elemental sulfur was never achieved due to the shuttle reactions.

4. CONCLUSION

Again the reliable and quantitative HPLC method we developed for the analysis of the dissolved polysulfide species and sulfur was demonstrated as a vital technique for the investigation of Li-S batteries. A three-step reduction mechanism was proposed for the sulfur cathode during the discharge, while a continuous oxidation of lithium sulfide and polysulfide ions to elemental sulfur was revealed. The two flat discharge plateau and a single flat recharge curve can be explained by the fast reaching chemical equilibrium of dissolve polysulfide ions, S_7^{2-} , S_6^{2-} and S_5^{2-} for the discharge plateau >2.3 V; S_5^{2-} , S_4^{2-} and S_4^{2-} for the discharge <2.1 V and S_5^{2-} , S_6^{2-} , S_7^{2-} and S_8^{2-} during recharge.

AUTHOR INFORMATION

Corresponding Author

* D.Y. Qu. E-mail: qud@uwm.edu

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REFERENCES

- (1) Zhang, S.S. Liquid Electrolyte Lithium/Sulfur Battery: Fundamental Chemistry, Problems, and Solutions. *J. Power Sources*, **2013**, *231*, 153-162.
- (2) Xu, R.; Lu, J.; Amine, K. Progress in Mechanistic Understanding and Characterization Techniques of Li-S Batteries. *Adv. Energy Mater.*, **2015**, *5* (16).
- (3) Leghie, P.; Lelieur, J.-P.; Levillain, E. Comments on the Mechanism of the Electrochemical Reduction of Sulphur in Diemthylformamide. *Electrochem. Commun.*, **2002**, *4*, 406-411
- (4) Patel, M.U.M.; Demir-Cakan, R.; Morcrette, M.; Tarscon, J.-M.; Gaberscek, M.; Dominko, R. Li-S Battery Analyzed by UV/Vis in Operando Mode. *ChemSusChem*, **2013**, *6*, 1177-1181
- (5) Patel, M.U.M.; Dominko, R. Application of in Operando UV/Vis Spectroscopy in Lithium-Sulfur Batteries. *ChemSusChem*, **2014**, *7*, 2167-2175.
- (6) Canas, N.A.; Fronczek, D.N.; Wagner, N.; Latz, A.; Friedrich, K.A. Experimental and Theoretical Analysis of Products and Reaction Intermediates of Lithium-Sulfur Batteries. *J. Phys. Chem. C*, **2014**, *118*, 12106-12114.
- (7) Barchasz, C.; Molton, F.; Duboc, C.; Lepretre, J.-C.; Patoux, S.; Alloin, F. Lithium/Sulfur Cell Discharge Mechanism: an Original Approach for Intermediate Species Identification. *Anal. Chem.*, **2012**, *84*, 3973-3980.
- (8) Han, D.-H.; Kim, B.-S.; Choi, S.-J.; Jung, Y.J.; Kwak, J.; Park, S.-M. Time-resolved In Situ Spectroelectrochemical Study on Reduction of Sulfur in N,N'-dimethylformamide. *J. Electrochem. Soc.*, **2004**, *151*, E283-209.
- (9) Marceau, H.; Kim, C.-S.; Paoletta, A.; Ladouceur, S.; Lagace, M.; Chaker, M.; Vijh, A.; Guerfi, A.; Julien, C.M.; Mauger, A.; Armand, M.; Hovington, P.; Zaghbi, K. In Operando Scanning Electron Microscopy and Ultraviolet-Visible Spectroscopy Studies of Lithium/Sulfur Cells Using All Solid-State Polymer Electrolyte. *J. Power Sources*, **2016**, *319*, 247-254.

- (10) Manan, N.S.A.; Aldous, L.; Alias, Y.; Murray, P.; Yellowlees, L.J.; Lagunas, M.C.; Hardacre, C. Electrochemistry of Sulfur and Polysulfides in Ionic Liquids. *J. Phys. Chem. B*, **2011**, *115*, 13873-13879
- (11) Wu, H.L.; Huff, L.A.; Gewirth, A.A. In Situ Raman Spectroscopy of Sulfur Speciation in Lithium-Sulfur Batteries. *ACS Appl. Mater. Interfaces*, **2015**, *7*, 1709-1719.
- (12) Hagen, M.; Schiffels, P.; Hammer, M.; Doerfler, S.; Tuebke, J.; Hoffmann, M.J.; Althues, H.; Kaskel, S. In-Situ Raman Investigation of Polysulfide Formation in Li-S Cells. *J. Electrochem. Soc.*, **2013**, *160*, A1205-A1214.
- (13) Elazari, R.; Salitra, G.; Talyosef, Y.; Grinblat, J.; Scordilis-Kelley, C.; Xiao, A.; Affinito, J.; Aurbach, D. Morphological and Structural Studies of Composite Sulfur Electrode upon Cycling by HRTEM, AFM and Raman Spectroscopy. *J. Electrochem. Soc.*, **2010**, *157*, A1131-1138.
- (14) Yeon, J.-T.; Jang, J.-Y.; Han, J.-G.; Cho, J.; Lee, K.T.; Choi, N.-S. Raman Spectroscopic and X-ray Diffraction Studies of Sulfur Composite Electrodes during Discharge and Charge. *J. Electrochem. Soc.*, **2012**, *159*, A1308-1314.
- (15) Wang, Q.; Zheng, J.M.; Walter, E.; Pan, H.L.; Lv, D.P.; Zuo, P.J.; Chen, H.B.; Deng, Z.D.; Liaw, B.Y.; Yu, X.Q.; Yang, X.-Q.; Zhang, J.G.; Liu, J.; Xiao, J. Direct Observation of Sulfur Radicals as Reaction Media in Lithium Sulfur Batteries. *J. Electrochem. Soc.*, **2015**, *162*, A474-478.
- (16) Vijayakumar, M.; Govind, N.; Walter, E.; Burton, S.D.; Shukla, A.; Devaraj, A.; Xiao, J.; Wang, C.M.; Karim, A.; Thevuthasan, S. Molecular Structure and Stability of Dissolved Lithium Polysulfide Species. *Phys. Chem. Chem. Phys.*, **2014**, *16*, 10923-10932.
- (17) Nelson, J.; Misra, S.; Yang, Y.; Jackson, A.; Liu, Y.J.; Wang, H.L.; Dai, H.J.; Andrews, J.C.; Cui, Y.; Toney, M.F. In Operando X-ray Diffraction and Transmission X-ray Microscopy of Lithium Sulfur Batteries. *J. Am. Chem. Soc.*, **2012**, *134*, 6337-6343.
- (18) Walus, S.; Barchasz, C.; Colin, J.-F.; Martin, J.F.; Elkaim, E.; Lepretre, J.-C.; Alloin, F. New Insight into the Working Mechanism of Lithium-Sulfur Batteries: In Situ and Operando X-ray Diffraction Characterization. *Chem. Commun.*, **2013**, *49*, 7899-7901.

- (19) Walus, S.; Barchasz, C.; Bouchet, R.; Lepretre, J.-C.; Colin, J.-F.; Martin, J.F.; Elkaim, E.; Baehtz, C.; Alloin, F. Lithium/Sulfur Batteries Upon Cycling: Structural Modifications and Species Quantification by In Situ and Operando X-Ray Diffraction Spectroscopy. *Adv. Energy Mater.*, **2015**, 5 (16).
- (20) Xu, R.; Belharouak, I.; Zhang, X.F.; Chamoun, R.; Yu, C.; Ren, Y.; Nie, A.M.; Shahbazian-Yassar, R.; Lu, J.; Li, J.C.M.; Amine, K. Insight into Sulfur Reactions in Li-S Batteries. *ACS Appl. Mater. Interfaces*, **2014**, 6, 21938-21945.
- (21) Cuisinier, M.; Cabelguen, P.-E.; Evers, S.; He, G.; Kolbeck, M.; Garsuch, A.; Bolin, T.; Balasubramanian, M.; Nazar, L.F. Sulfur Speciation in Li-S Batteries Determined by Operando X-ray Absorption Spectroscopy. *J. Phys. Chem. Lett.*, **2013**, 4, 3227-3232.
- (22) Yu, X.Q.; Pan, H.L.; Zhou, Y.N.; Northrup, P.; Xiao, J.; Bak, S.; Liu, M.Z.; Nam, K.W.; Qu, D.Y.; Liu, J.; Wu, T.P.; Yang, X.-Q. Direct Observation of the Redistribution of Sulfur and Polysulfides in Li-S Batteries During the First Cycle by In Situ X-Ray Fluorescence Microscopy. *Adv. Energy Mater.*, **2015**, 5 (16).
- (23) Fan, F.Y.; Carter, W.C.; Chiang, Y.M. Mechanism and Kinetics of Li₂S Precipitation in Lithium-Sulfur Batteries. *Adv. Mater.*, **2015**, 27, 5203-5209.
- (24) Huff, L.A.; Rapp, J.L.; Baughman, J.A.; Rinaldi, P.L.; Gewirth, A.A. Identification of Lithium-Sulfur Battery Discharge Products Through Li⁻⁶ and S⁻³³ Solid-State MAS and Li⁻⁷ Solution NMR Spectroscopy. *Surf. Sci.*, **2015**, 631, 295-300.
- (25) Xiao, J.; Hu, J.Z.; Chen, H.H.; Vijayakumar, M.; Zheng, J.M.; Pan, H.L.; Walter, E.D.; Hu, M.; Deng, X.C.; Feng, J.; Liaw, B.Y.; Gu, M.; Deng, Z.D.; Lu, D.P.; Xu, S.C.; Wang, C.M.; Liu, J. Following the Transient Reactions in Lithium-Sulfur Batteries Using an In Situ Nuclear Magnetic Resonance Technique. *Nano Lett.*, **2015**, 15, 3309-3316.
- (26) Zheng, D.; Qu, D.Y.; Yang, X.-Q.; Yu, X.Q.; Lee, H.S.; Qu, D.Y. Quantitative and Qualitative Determination of Polysulfide Species in the Electrolyte of Lithium-Sulfur Battery Using HPLC ESI/MS with One-Step Derivatization. *Adv. Energy Mater.*, **2015**, 5 (16). DOI:10.1002/aenm.201401888.

- (27) Zheng, D.; Zhang, X.R.; Wang, J.K.; Qu, D.Y.; Yang, X.-Q.; Qu, D.Y. Reduction Mechanism of Sulfur in Lithium-Sulfur Battery: From Elemental Sulfur to Polysulfide. *J. Power Sources*, **2016**, *301*, 312-316.
- (28) Zheng, D.; Zhang, X.R.; Li, C.; McKinnon, M.E.; Sadok, R.G.; Qu, D.Y.; Yu, X.Q.; Lee, H.S.; Yang, X.-Q.; Qu, D.Y. Quantitative Chromatographic Determination of Dissolved Elemental Sulfur in the Non-Aqueous Electrolyte for Lithium-Sulfur Batteries. *J. Electrochem. Soc.*, **2015**, *162*, A203-A206.
- (29) Zheng, D.; Qu, D.Y. Chromatographic Separation of Polysulfide Species in Non-aqueous Electrolytes-Revisted. *J. Electrochem. Soc.*, **2014**, *161*, A1164-1166.
- (30) Zhang, S.S. Improved Cyclability of Liquid Electrolyte Lithium/Sulfur Batteries by Optimizing Electrolyte/Sulfur Ratio. *Energies*, **2012**, *5*, 5190-5197.
- (31) Ji, X.L.; Nazar, L.F. Advances in Li-S Batteries. *J. Mater. Chem.*, **2010**, *20*, 9821-9826.
- (32) Zheng, D.; Yang, X.-Q.; Qu, D.Y. Stability of the Solid Electrolyte Interface on the Li Electrode in Li-S Batteries. *ACS Appl. Mater. Interfaces*, **2016**, *8*, 10360-10366
- (33) Yang, Y.; Zheng, G.Y.; Cui, Y. Nanostructured Sulfur Cathodes. *Chem. Soc. Rev.*, **2013**, *42*, 3018-3032.
- (34) Sun, Y.M.; Seh, Z.W.; Li, W.Y.; Yao, H.B.; Zheng, G.Y.; Cui, Y. In-operando Optical Imaging of Temporal and Spatial Distribution of Polysulfides in Lithium-Sulfur Batteries. *Nano Energy*, **2015**, *11*, 579-586.
- (35) Zhang, S.S. Role of LiNO₃ in Rechargeable Lithium/Sulfur Battery. *Electrochim. Acta*, **2012**, *70*, 344-348.
- (36) Zhang, S.S. A New Finding on the Role of LiNO₃ in Lithium-Sulfur Battery. *J. Power Sources*, **2016**, *322*, 99-105.

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