Reaction between Lithium Anode and Polysulfide Ions in a Lithium-Sulfur Battery

Dong Zheng, Xiao-Qing Yang, and Deyang Qu

Submitted to CHEMSUSCHEM

September 2016

Chemistry Department

Brookhaven National Laboratory

U.S. Department of Energy
USDOE Office of Science (SC),
Basic Energy Sciences (BES) (SC-22)

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE- SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party’s use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
Reaction between Lithium Anode and Polysulfide Ions in a Lithium-Sulphur Battery

Dong Zheng,[a] Xiao-Qing Yang,[b] and Deyang Qu*[a]

Abstract: The reaction between polysulfides and a lithium anode in a Li-S battery was examined by HPLC method. The results demonstrated that the polysulfide species with six sulfur atoms or more were reactive with lithium metal. Although the reaction can be greatly inhibited by the addition of LiNO3 in the electrolyte, LiNO3 cannot form a stable protection layer on Li anode to prevent the reaction during storage.

It’s well known that polysulfide species (Li₂Sn, n≥2) are the important products in a Li-S battery during charge and discharge. The polysulfide species (with n≥3) can be dissolved in organic electrolytes, especially in the ether-based electrolytes.1-3 The soluble polysulfide species play important roles in the redox reaction of sulfur.2 However, the migration of the soluble polysulfide species to the Li anode and subsequent reactions have been the major problem of Li-S batteries. Consequently, the reaction (1) was thought to be responsible for the high self-discharge, low columbic efficiency and poor cycleability for a Li-S battery.2,3

To alleviate the problems associated with the dissolution of polysulfide ions, efforts were made to restrain the soluble polysulfide ions within the porous electrode matrix.4-6 For example, the cathode with sulphur localized in carbon nanotubes demonstrated good cycle life.5 Additives which can form a stable solid electrolyte interface (SEI) layer were also explored to prevent the reaction between dissolved polysulfide ions with Li anode.5,13 Among those additives LiNO3 was found to greatly improve the charge and discharge efficiency (columbic efficiency) for a rechargeable Li-S battery. It is debatable whether LiNO3 can sustain protecting Li anode during a length storage since large amount (e.g. 0.1 M) of LiNO3 was needed. Thus a direct chemical analysis is not only complementary but also necessary to demonstrate that indeed the LiNO3 additive can suppress reaction 1.

\[
S_n^{2-} + 2Li \rightarrow S_{(n-1)}^{2-} + Li_2S \quad (1)
\]

The dissolved polysulfide ions couldn’t be quantitatively or qualitatively analysed until recently when a high performance liquid chromatography (HPLC) – mass spectroscopy (MS) method was successfully introduced into the analysis of polysulfide and elemental sulphur in electrolytes of Li-S batteries.16-19. As shown in reaction 2, the polysulfide anions were first derivatized, and the derivatized mixtures were separated by a HPLC, the sulphur chain length of the derivatized polysulfide species was determined by the mass/charge ratio with a MS. Correspondingly, the distribution of different polysulfide species in the electrolyte could be qualitatively obtained through the chromatographic result of the derivatized species.

\[
S_n^{2-} + 2CF_3SO_3CH_3 \rightarrow (CH_3)_2S_n + 2CF_3SO_3 \quad (2)
\]

The inhibition effect of a LiNO3 additive in the electrolyte of Li-S battery was studied directly and unambiguously in this report. To our knowledge this is the first direct analytical work to investigate the LiNO3 additive in the electrolyte in a Li-S cell. The polysulfide distribution in this polysulfide mixture was determined by the HPLC after derivatization with methyl triflate. The chromatogram of the original polysulfide mixture was shown in Figure 1 line (A). Clearly the concentration of the methylated polysulfide ions and elemental sulfur, which is proportional to the intensities chromatographic peaks, decreased in the following order: \((CH_3)_2S_3\geq(CH_3)_2S_2\geq(CH_3)_2S_1\geq(CH_3)\geqS_0\geq\text{elemental sulfur}\geq(CH_3)_2S_2\). The assignment of each methylated polysulfide species and elemental sulfur were determined by mass-spectroscopy as described in reference 18. Correspondingly, the distribution of all polysulfide anions (S_3^{2-}, S_2^{2-}, S_0^{2-}, S_2^{2-}, and S_7^{2-}) in the original polysulfide mixture was determined.

Figure 1. Chromatograms of derivatized polysulfide mixtures: original polysulfide mixture (A), polysulfide mixture with Li metal for 1hour (B), polysulfide mixture with Li metal for 4hours (C), polysulfide mixture with Li metal for 24hours (D), polysulfide mixture with Li metal for 96hours (E).

A lithium metal disk (about 30mg, 1cm diameter) was then added into the 1.5ml polysulfide mixture solution. The polysulfide solution was measured after being in contact with Li disk for 1 hour, 4 hours, 24 hours and 96 hours along with the original stock solution, the results are summarized in Figure 1 (B) to (E), respectively. By comparing Fig. 1(B) with Fig. 1(A), the distribution of the polysulfide anions substantially changed after being in contact with Li metal, it became evident that polysulfide anions in electrolyte react with lithium metal as expected.1-3,9-15 The dramatically decreased peak intensities for \((CH_3)_2S_3\) and \((CH_3)_2S_2\) indicated the consumption of \(S_3^{2-}\), and \(S_2^{2-}\) in the

[a] Department of Mechanical Engineering, College of Engineering and Applied Science, University of Wisconsin Milwaukee, Milwaukee, WI 53211, USA
E-mail:qud@uwm.edu
[b] Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA
mixture by lithium metal. The chromatograms for shorter contact times were summarized in Fig. S-1 in the supplementary information. Moreover, from Fig. 1 it can also be found that the $S_n^{2-}$ species with $n \geq 6$ are more reactive (or less stable) to lithium metal than that of the $S_n^{2-}$ species with $n \leq 5$. As the polysulfide mixture was contacted with lithium metal for 1 hour, the peak intensities of $(CH_3)_2S_6$ and $(CH_3)_2S_7$ decrease greatly in Fig. 1(B) compared to the corresponding peak intensities in Fig. 1(A), while the peak intensity of $(CH_3)_2S_5$ just slightly decreases and the peak intensity of $(CH_3)_2S_4$ greatly increases in Fig. 1(B) compared to the corresponding peak intensities in Fig. 1(A). The unexpected increase of the intensity of $(CH_3)_2S_5$ in Fig. 1(B) to Fig. 1(E) clearly indicates that the $S_n^{2-}$ species is stable against lithium metal. A similar observation has been reported by Mikhaylik and Akridge, in which the rapid capacity fade at 2.2 to 2.3 V for Li-S battery was attributed to the higher reactivity of longer polysulfide species and the low capacity fade at 2.0 to 2.1 V for Li-S battery was attributed to the higher stability of shorter polysulfide species against lithium metal.15 Interestingly, the peak intensity for $(CH_3)_2S_3$ in all chromatograms of Fig. 1 is pretty low, it may indicate that the solubility of $S_3^{2-}$ in ether-based electrolyte probably is lower than the polysulfide species with a longer S chain.

In order to investigate the influence of LiNO$_3$ additive on stabilizing the Li metal in polysulfide electrolyte, LiNO$_3$ powder was dissolved in the stock polysulfide solution and the concentration of LiNO$_3$ in the polysulfide solution was about 0.1M. After adding LiNO$_3$ for two days, the polysulfide mixture with LiNO$_3$ was derivatized and analyzed by HPLC to examine the chemical stability of polysulfide anion with LiNO$_3$. Fig. 2(A) shows the chromatogram of the polysulfide distribution after mixing with for two days. By comparing the chromatogram in Fig. 1(A) (without LiNO$_3$) with the chromatogram in Fig. 2(A), there is no noticeable change in polysulfide distribution between the polysulfide mixture with LiNO$_3$ and without LiNO$_3$ which indicated the chemical compatibility of polysulfide and LiNO$_3$ additive. A similar Li metal disk was added into the polysulfide mixture with the LiNO$_3$ additive. The polysulfide solution was analyzed in the interval of storage in contact with Li metal as that without LiNO$_3$ additive. The chromatographic results are summarized in Fig. 2(B) to Fig. 2(E). There is little changes in the polysulfide distribution in contact with Li metal over four hours with the existence of LiNO$_3$. Obviously, the reaction between Li metal and polysulfide species was inhibited. The observation was consistent that the LiNO$_3$ in mixture can form a SEI layer on the Li metal surface, which prevented the reaction between Li and polysulfide anions.10,13 Unfortunately, the SEI layer formed on the Li surface with LiNO$_3$ is not stable enough to totally inhibit the reaction with polysulfide ions. Evidently, after being in contact with Li for 24 hours, the distribution of polysulfide starts to change. As shown in figure 2(D), a slight increase of peak intensity for $(CH_3)_2S_4$ can be observed. After being in contact for 96 hours (figure 2E), momentous changes of the polysulfide distribution can be seen with the increase of peak intensity for $(CH_3)_2S_4$ and the decrease of the $(CH_3)_2S_3$ and $(CH_3)_2S_5$ peak intensities. It is worth pointing out that interaction between Li and polysulfide ions with the existence of LiNO$_3$ was trivial in comparison to those without LiNO$_3$.

To investigate the matter further, a Li disk was first put into the electrolyte (0.1M LITFS/DME) with 0.1 M LiNO$_3$ but without polysulfide. After being in contact for two days, the Li metal disk was transferred into a polysulfide mixture without LiNO$_3$. Apparently, the reaction between the Li and the polysulfide ions was slowed down initially as shown in figure S-2 in supplementary materials, but a noticeable change of the polysulfide distribution can be observed after only one hour and the change accelerated after that. The observation of the instability of the SEI layer and irreversible consumption of LiNO$_3$ during the storage of Li-S cell was consistent with other publications10,13. That is the reason high concentration of LiNO$_3$ e.g. 0.1 M was used in Li-S studies. Evidently, LiNO$_3$ of high concentration can provide long protection for a Li anode, if the concentration of the polysulfide ion remains low. It’s also worth pointing out that the LiNO$_3$ additive can prevent the reaction between the dissolved elemental sulfur and Li as well. In Figure 1, the chromatographic peak of S disappeared after being in contact with the lithium metal for just one hour, while in figure 2 the chromatographic peak of S was still noticeable after being in contact with the Li metal for 96 hours. Besides forming a SEI layer on the Li anode, it should be noted that the nitrate anion (NO$_3^-$) was reported to catalyze the conversion of polysulfide to elemental sulfur during the recharge of a Li-S cell.22 In conclusion, through the direct analytical evidence, one can conclude that both dissolved S and polysulfide ions can chemically react with Li metal in a Li-S cell during storage. LiNO$_3$ additive can form a SEI layer on the Li electrode to prevent such reaction. However, the SEI layer was not stable enough for long term storage and needed to be maintained with the continuous consumption of LiNO$_3$. Longer chain polysulfide ions ($S_n^{2-}$ with...
A Shimadzu LC-20AD quaternary pump with a Shimadzu SIL-20A autosampler was used to deliver a methanol/water mobile phase through a Agilent Zorbax C18 column (from Agilent, C18, 4.6*50mm, 5um) at a flow rate of 0.70mL/min. The injection volume was 10μL. A binary gradient of mobile phases were used to elute the injected sample out with the following condition: at 0 min 75% methanol (75% water); at 10 min 25% methanol; at 25 min 50% methanol; at 30 min 100% methanol. All flow from the HPLC was introduced into the Shimadzu SPD-M20A detector, full wavelength range from 190nm to 800nm was recorded by Shimadzu LabSolutions Lite software, and the chromatograms discussed in this work were replotted from data at 230nm.

Acknowledgements

The authors from UWM and BNL are indebted to the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, under the program of Vehicle Technology Program, under Contract Number DE-SC0012704.

Keywords: Solid Electrolyte Interface • Lithium-sulfur battery • Additive • HPLC

References:

The reaction between polysulfides and a lithium anode in a Li-S battery was examined by HPLC method. The results demonstrated that the polysulfide species with six sulfur atoms or more were reasonably reactive with lithium metal and the reaction can be greatly inhibited by the addition of LiNO₃ in the electrolyte.