

# Reaction between Lithium Anode and Polysulfide Ions in a Lithium–Sulfur Battery

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The reaction between polysulfides and a lithium anode in a Li–S battery was examined using HPLC. The results demonstrated that the polysulfide species with six sulfur atoms or more were reactive with regard to lithium metal. Although the reaction can be greatly inhibited by the addition of  $\text{LiNO}_3$  in the electrolyte,  $\text{LiNO}_3$  cannot form a stable protection layer on the Li anode to prevent the reaction during storage.

It is well known that polysulfide species ( $\text{Li}_2\text{S}_n$ ,  $n \geq 2$ ) are the important products in a Li–S battery during charge and discharge. The polysulfide species (with  $n \geq 3$ ) can be dissolved in organic electrolytes, especially in ether-based electrolytes.<sup>[1–3]</sup> The soluble polysulfide species play important roles in the redox reaction of sulfur.<sup>[2]</sup> 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, Reaction (1) was thought to be responsible for the high self-discharge, low columbic efficiency, and poor cyclability for a Li–S battery.<sup>[2,3]</sup>

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.<sup>[4–8]</sup> For example, the cathode with sulfur localized in carbon nanotubes demonstrated good cycle life.<sup>[5]</sup> Additives that can form a stable solid–electrolyte interphase (SEI) layer were also explored to prevent the reaction between dissolved polysulfide ions with the Li anode.<sup>[9–13]</sup> Among those additives,  $\text{LiNO}_3$  was found to greatly improve the charge and discharge efficiency (columbic efficiency) for a rechargeable Li–S battery. It is debatable whether  $\text{LiNO}_3$  can sustain protection of the Li anode during long storage as a large amount (e.g., 0.1 M) of  $\text{LiNO}_3$  was needed. Thus, a direct chemical analysis is not only complementary but also necessary to demonstrate whether indeed the  $\text{LiNO}_3$  additive can suppress Reaction (1).

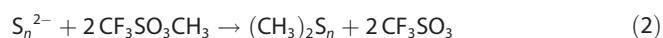


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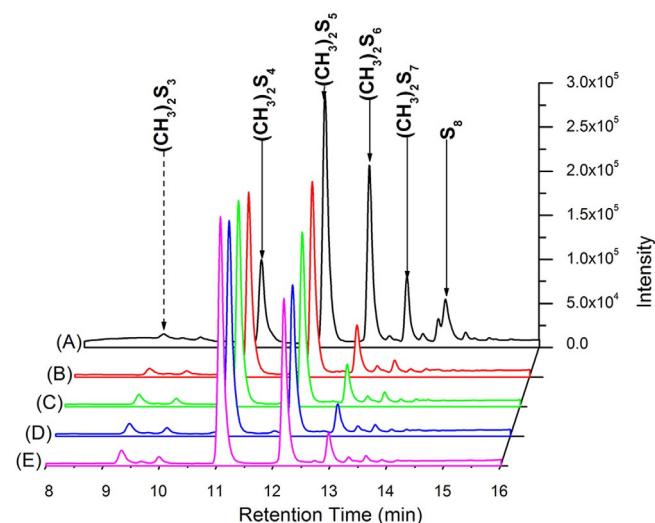
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The dissolved polysulfide ions could not be quantitatively or qualitatively analyzed until recently, when a high-performance liquid chromatography (HPLC)– mass spectroscopy (MS) method was successfully introduced for the analysis of polysulfide and elemental sulfur in electrolytes of Li–S batteries.<sup>[14–17]</sup> The polysulfide anions were first derivatized according to Reaction (2), the derivatized mixtures were separated by a HPLC, and the sulfur 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.



The inhibition effect of  $\text{LiNO}_3$  as additive in the electrolyte of a Li–S battery was studied directly and unambiguously in this report. To our knowledge this is the first direct analytical work to investigate the  $\text{LiNO}_3$  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 is shown in Figure 1, line A. Clearly, the concentration of the methylated polysulfide ions and elemental sulfur, which is proportional to the intensities of the chromatographic peaks, decreased in the following order:  $(\text{CH}_3)_2\text{S}_5 > (\text{CH}_3)_2\text{S}_6 > (\text{CH}_3)_2\text{S}_4 >$



**Figure 1.** Chromatograms of derivatized polysulfide mixtures: original polysulfide mixture (A), polysulfide mixture in contact with Li metal after 1 (B), 4 (C), 24 (D), and 96 h (E).

$(CH_3)_2S_7 >$  elemental sulfur  $> (CH_3)_2S_3$ . The assignment of each methylated polysulfide species and elemental sulfur were determined by MS as described in Ref. [18]. Correspondingly, the distribution of all polysulfide anions ( $S_3^{2-}$ ,  $S_4^{2-}$ ,  $S_5^{2-}$ ,  $S_6^{2-}$ , and  $S_7^{2-}$ ) in the original polysulfide mixture was determined.

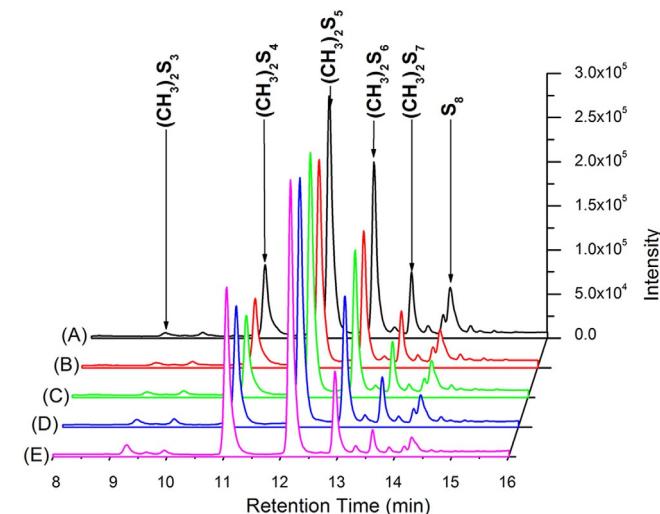
A lithium metal disk (about 30 mg, 1 cm diameter) was then added to the 1.5 mL polysulfide mixture solution. The solution was measured after being in contact with the Li disk for 1, 4, 24, and 96 h along with the original stock solution; the results are summarized in Figure 1B–E, respectively. By comparing Figure 1B with 1A, the distribution of the polysulfide anions substantially changed after contact with Li metal; evidently, the polysulfide anions in the electrolyte react with lithium metal as expected.<sup>[1–3, 9–13, 18, 19]</sup> The dramatically decreased peak intensities for  $(CH_3)_2S_6$  and  $(CH_3)_2S_7$  indicated consumption of  $S_6^{2-}$  and  $S_7^{2-}$  in the mixture by the lithium metal. The chromatograms for shorter contact times are summarized in Figure S-1 in the Supporting Information.

Moreover, based on Figure 1, the  $S_n^{2-}$  species with  $n \geq 6$  are more reactive (or less stable) with regard to lithium metal than the  $S_n^{2-}$  species with  $n \leq 5$ . After the polysulfide mixture was in contact with lithium metal for 1 h, the peak intensities of  $(CH_3)_2S_6$  and  $(CH_3)_2S_7$  decreased greatly (Figure 1B) compared to the corresponding peak intensities in Figure 1A whereas the peak intensity of  $(CH_3)_2S_5$  just slightly decreased and the peak intensity of  $(CH_3)_2S_4$  greatly increased in Figure 1B compared to the corresponding peak intensities in Figure 1A. The unexpected increase of the intensity of  $(CH_3)_2S_4$  in Figure 1B–E clearly indicates that the  $S_4^{2-}$  species is stable against lithium metal. A similar observation has been reported by Mikhaylik and Akridge, who attributed the rapid capacity fade at 2.2 to 2.3 V in a Li–S battery to the higher reactivity of longer polysulfide species and the slow capacity fade at 2.0 to 2.1 V for Li–S battery to the higher stability of shorter polysulfide species against lithium metal.<sup>[19]</sup>

Interestingly, the peak intensity for  $(CH_3)_2S_3$  in all chromatograms shown in Figure 1 is pretty low; this might indicate that the solubility of  $S_3^{2-}$  in an ether-based electrolyte probably is lower than that of polysulfide species with a longer S chain.

To investigate the influence of LiNO<sub>3</sub> additive on stabilizing the Li metal in polysulfide electrolyte, LiNO<sub>3</sub> powder was dissolved in the stock polysulfide solution at a concentration of about 0.1 M. After adding LiNO<sub>3</sub> for two days, the polysulfide mixture with LiNO<sub>3</sub> was derivatized and analyzed by HPLC to examine the chemical stability of polysulfide anion in the presence of LiNO<sub>3</sub>. Figure 2A shows the chromatogram of the polysulfide distribution after mixing for two days. By comparing the chromatogram in Figure 1A (without LiNO<sub>3</sub>) with the chromatogram in Figure 2A, there is no noticeable change in polysulfide distribution between the polysulfide mixture with and without LiNO<sub>3</sub>, which indicate a chemical compatibility of polysulfide and LiNO<sub>3</sub> additive.

A similar Li metal disk was added into the polysulfide mixture with LiNO<sub>3</sub> as additive. The polysulfide solution was analyzed using the same storage intervals in contact with Li metal as that without LiNO<sub>3</sub>. The chromatographic results are summarized in Figure 2–E. There are little changes in the polysul-



**Figure 2.** Chromatograms of derivatized polysulfide mixtures: original polysulfide and LiNO<sub>3</sub> mixture (A), polysulfide and LiNO<sub>3</sub> mixture in contact with Li metal after 1 (B), 4 (C), 24 (D), and 96 h (E).

fide distribution in contact with Li metal over 4 h in the presence of LiNO<sub>3</sub>. Clearly, the reaction between Li metal and polysulfide species was inhibited. The observation is consistent with the fact that LiNO<sub>3</sub> present in the mixture can form a SEI layer on the Li metal surface, which prevented the reaction between Li and polysulfide anions.<sup>[10, 13]</sup> Unfortunately, the SEI layer formed on the Li surface with LiNO<sub>3</sub> is not stable enough to completely inhibit the reaction with polysulfide ions. Evidently, after being in contact with Li for 24 h, the distribution of polysulfide starts to change. As shown in Figure 2D, a slight increase of peak intensity for  $(CH_3)_2S_4$  can be observed. After being in contact for 96 h (Figure 2E), significant changes of the polysulfide distribution can be seen with regard to the increase of peak intensity for  $(CH_3)_2S_4$  and the decrease of the  $(CH_3)_2S_6$  and  $(CH_3)_2S_7$  peak intensities. It is worth pointing out that interaction between Li and polysulfide ions in the presence of LiNO<sub>3</sub> was insignificant in comparison to those without LiNO<sub>3</sub>.

To investigate the matter further, a Li disk was first put into an electrolyte [0.1 M lithium trifluoromethanesulfonate/dimethylmethoxyethane (LiTFS/DME)] containing 0.1 M LiNO<sub>3</sub> but no polysulfides. After being in contact for two days, the Li metal disk was transferred into a polysulfide mixture without LiNO<sub>3</sub>. Apparently, the reaction between the Li and the polysulfide ions was slowed down initially as shown in Figure S-2 in the Supporting Information, but a noticeable change of the polysulfide distribution can be observed after only 1 h and the change accelerated after that. The observation of the instability of the SEI layer and irreversible consumption of LiNO<sub>3</sub> during the storage of Li–S cell was consistent with other publications.<sup>[10, 13]</sup> This is the reason why a high concentration of LiNO<sub>3</sub> for example, 0.1 M, was usually used in Li–S studies. Evidently, LiNO<sub>3</sub> at a high concentration can provide long protection for a Li anode if the concentration of the polysulfide ion remains low.

It is also worth pointing out that the LiNO<sub>3</sub> 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 1 h whereas in Figure 2 the chromatographic peak of S was still noticeable after being in contact with the Li metal for 96 h.

Besides forming a SEI layer on the Li anode, it should be noted that the nitrate anion ( $\text{NO}_3^-$ ) was reported to catalyze the conversion of polysulfide to elemental sulfur during the recharge of a Li–S cell.<sup>[21]</sup>

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.  $\text{LiNO}_3$  additive can form a solid–electrolyte interphase (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 because of continuous consumption of  $\text{LiNO}_3$ . Long-chain polysulfide ions ( $\text{S}_n^{2-}$  with  $n \geq 6$ ) were more reactive with Li than those with shorter chains ( $\text{S}_n^{2-}$  with  $n \leq 5$ ).

## Experimental Section

Sulfur, Li metal, lithium sulfide (99.98%), lithium nitrate (99.99%, anhydrous), HPLC-grade methanol, HPLC-grade water, methyl triflate (from Sigma Aldrich), dimethoxyethane (DME), and lithium trifluoromethanesulfonate (LiTFS) (battery grade from FERRO) were purchased and used without further treatment. A polysulfide mixture was made by mixing  $\text{Li}_2\text{S}$  (0.066 g) with elemental sulfur (0.046 g) in 90 mL 0.1 M lithium trifluoromethanesulfonate/dimethoxyethane (LiTFS/DME) electrolyte for two days, and used as stock solution after.<sup>[20]</sup> Then, the polysulfide mixture containing 0.1 M  $\text{LiNO}_3$  was made by dissolving  $\text{LiNO}_3$  (0.276 g) in 40 mL above stock solution for two days. The lithium disks (1 cm diameter and about 30 mg for each lithium disk) were added to the polysulfide mixtures (1.5 mL for each mixture) with and without  $\text{LiNO}_3$ . After specific reaction time, the polysulfide mixtures were derivatized by the following procedure: DME (450  $\mu\text{L}$ ) containing methyl triflate (0.22 mmol, 25  $\mu\text{L}$ ) was added into a 1.5 mL HPLC vial and vortexed for 1 min; 150  $\mu\text{L}$  of the electrolyte from the used Li–S cell was then added to the DME solution with methyl triflate, and immediately the HPLC vial with the mixture was capped using an air-tight cap and vortexed for 5 min. The derivatized polysulfide samples in the air-tight HPLC vials were taken out of the glove-box for HPLC analysis. All of the above preparations were performed in an Ar-filled glove-box, in which the oxygen and moisture levels were less than 0.1 ppm.

A Shimadzu LC-20AD quaternary pump with a Shimadzu SIL-20A autosampler was used to deliver a methanol/water mobile phase through an Agilent Zobrax C<sub>18</sub> column (from Agilent, C<sub>18</sub>, 4.6 mm × 50 mm, 5  $\mu\text{m}$ ) at a flow rate of 0.70 mL min<sup>-1</sup>. The injection volume was 10  $\mu\text{L}$ . A binary gradient of mobile phases were used to elute the injected sample using the following conditions: at 0 min 25 vol% methanol (75 vol% 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, the spectra at full wavelength range were recorded from 190–800 nm using a Shimadzu LabSolutions Lite software, and the chromatograms discussed in this work were replotted from data at 230 nm.

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