In Situ NMR Observation of the Temporal Speciation of Lithium Sulfur Batteries during Electrochemical Cycling

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ABSTRACT: The understanding of the reaction mechanism and temporal speciation of the lithium–sulfur batteries is challenged by complex polysulfide disproportionation chemistry coupled with the precipitation and dissolution of species. In this report, for the first time, we present a comprehensive method to investigate lithium sulfur electrochemistry using in situ $^7$Li NMR spectroscopy, a technique that is capable of quantitatively capturing the evolution of the soluble and precipitated lithium (poly)sulfides during electrochemical cycling. Through deconvolution and quantification, every lithium-bearing species was closely tracked and four-step soluble lithium polysulfide-mediated lithium sulfur electrochemistry was demonstrated in never before seen detail. Significant irreversible accumulation of Li$_2$S is observed on the Li metal anode after four cycles because of sulfur shuttling. The application of the method presented here to study electrolyte/additive development and lithium protection research can be readily envisaged.

1. INTRODUCTION

Since their introduction in the 1990s, lithium ion batteries (LIBs) have dominated the portable electronic energy storage market.¹ Decades later, LIBs still play a critical role in the portable energy storage market, as well as the nascent but expanding transportation and stationary storage applications. The lithium–sulfur (Li–S) battery is one potential alternative to LIBs with the promise of achieving high specific energy on the pack level with attractive cost.² High energy density and low cost at the pack level are also possible if low excesses of lithium metal and electrolyte are utilized while extending the lifetimes to those required by consumers.²⁻⁴ The attractive system-level promise is built upon the foundation of the low equivalent weight (i.e., 1675 mAh/g) and low cost of sulfur.

However, Li–S batteries suffer from a number of drawbacks that limit their development and commercialization.⁵⁻⁷ The low conductivity of sulfur requires a relatively large amount of conducting agent in the electrode, such as carbon black, and, more importantly, a large excess of electrolyte to dissolve the polysulfide intermediate, which limits the volumetric/areal capacity of Li–S batteries. It has been reported that a dual-layer lithium polysulfide cathode was used to enhance the sulfur utilization and carbon nanoframework to increase the conductivity.⁵⁻¹⁰ However, electrolyte to sulfur ratios of less than 4 mL/g are not reported in the literature.³ Values of 1 mL/g are required to supersede LIBs on an energy density basis.² Perhaps, more importantly, the capacity fade of Li–S batteries was observed in nearly all Li–S batteries. This fade is attributed to the consumption of electrolyte and the shuttle effect: long-chain lithium polysulfides were shuttled from the cathode to the anode, forming an inactive Li$_x$S solid species on the anode.¹¹,¹² The shuttle effect is the main reason that causes Li–S batteries to have capacity fade but has been mitigated to some extent through the use of LiNO$_3$.⁵ Researchers have been investigating novel methods of inhibiting the shuttle effect, but a complete understanding of the mechanism of the shuttle effect is clearly missing.¹³⁻¹⁷ In particular, a quantitative study of the evolution of solid species formation and lithium polysulfide mediation is lacking in the literature. In order for Li–S battery technology to succeed and gain more commercial attention, it is crucial to have a thorough understanding of how a Li–S battery works and a clear explanation of its failure mechanism, i.e., the formation of solid species that leads to capacity fade and cell failure.

A number of characterization techniques have been used to investigate the mechanism of Li–S batteries. Canas et al. and others used in situ X-ray diffraction (XRD) to investigate this lithium–sulfur chemistry and found that Li$_x$S formation starts in the second discharge plateau at 1.8 V and during charging Li$_2$S reacts entirely and sulfur recrystallizes to a different...
structure and particle size.18–20 Nelson et al. discovered that the recrystallization of sulfur occurs only on the sulfur cathode, and their transmission X-ray microscopy (TXM) results showed that lithium polysulfide can be successfully restrained on the cathode.21 Barchasz et al. reported that via UV–vis spectroscopy and HPLC data there is a three-step reaction: (1) long-chain lithium polysulfide (S82− and S62−) formation during the first reduction step (2.4–2.2 V); (2) medium-chain polysulfide (S42−) formation during the second reduction step (2.15–2.1 V); and (3) short-chain polysulfide (S32−, S22−, and S2−) formation at the end of discharge.22 Zou et al. reported their findings on the speciation intermediate with operando UV–vis spectroscopy.23 Cuisinier et al. employed operando X-ray absorption spectroscopy (XANES) to study the speciation process, and they have shown that the first discharge plateau is governed by the formation of long-chain lithium polysulfide (Li2S8, Li2S6, and Li2S4) and the second plateau is governed by the formation of the short-chain polysulfide (Li2S).21 Long-chain lithium polysulfide species (Li2S8, Li2S6, and Li2S4) dissolve in the most commonly used solvent whereas the solid species (Li2S) does not.

Even though many characterization techniques were applied to study Li–S batteries, most approaches are capable only of monitoring either solution or crystalline species but not both. Clearly, a method that can track and quantify the evolution of the entire electrochemical speciation process would be very informative. NMR spectroscopy serves as a useful tool in studying reaction mechanisms. With in situ NMR spectroscopy, See et al. showed Li2S formation presumably on the cathode and proposed an electrolyte as the third phase in the reaction mechanism. However, only the first discharge was reported in this study, and the electrochemical profile showed a nontypical discharge profile (one slope throughout the entire discharge process rather than two discharge plateaus: 2.3 and 2.1 V). It is believed that the cell suffered from a cycling issue, and the short cycling life and the convoluted electrochemistry profile cast much doubt on the conclusions drawn from this study. Notably, the authors claimed that the solid species formation started at the beginning of the first discharge plateau.24 Xiao et al. also reported their findings with NMR spectroscopy.25 However, the observation of a solid species in the pristine state carries significant concerns about the cell design and the spectroscopic resolution. In a pristine Li–S battery, the observation of a solid species other than lithium metal and sulfur should never be expected, and the authors fail to give a reasonable explanation of the appearance of the solid species in their pristine Li–S battery and the basis of their peak assignments.

Though they attempted to employ in situ NMR spectroscopy to study Li–S batteries, neither See et al. nor Xiao et al. reported a convincing method to study the entire chemistry of Li–S batteries. Here, contrary to the undesired electrochemical performance and peak assignment, we present a comprehensive method that can quantitatively monitor the changes of all species in lithium–sulfur batteries during electrochemical cycling. Through quantification of the solid and soluble species, the correlation between the formation of the soluble and solid species is revealed in this study, where a clear four-step soluble-species-mediated electrochemical process is observed and described. Finally, the NMR spectroscopy method presented.
in this report toward researching the Li–S battery speciation process opens up the opportunity to study the Li–S battery speciation process with novel electrolyte/additive systems and will provide tremendous assistance to electrolyte development, sulfur cathode research, and lithium metal protection schemes.

2. EXPERIMENT

2.1. Cathode Preparation. Sulfur-loaded (70% sulfur) porous carbon nanospheres (PCNS) were used as previously reported. Strips of carbon-coated aluminum current collectors were weighed before and after loading any cathode material to determine the cathode loading amount. A recipe of PCNS/Timcal 45 carbon/PVDF (6:2:2 by weight) was used to prepare the slurry. NMP was used to dissolve the binder for a homogeneous mix. The slurry was then brushed onto the carbon-coated aluminum current collectors and dried at 50 °C under vacuum overnight. The effective sulfur loading is 42 wt %.

2.2. Electrolyte Preparation. The electrolyte consisted of 1.0 M lithium bis(trifluoromethane sulfonimide) (LiTFSI, 99.95%, Aldrich) in a binary mixture of 1:1 (v/v) DOL/DME (anhydrous, 99.5%, Aldrich) with 2 wt % lithium nitrate (>99.0%, Aldrich) as the additive was prepared. LiTFSI and LiNO3 were dried in a vacuum oven at 150 °C over night. The as-prepared electrolyte was then stirred for over 12 h before use. All experiments were performed in an argon atmosphere glovebox with H2O and O2 levels of less than 1 ppm.

2.3. Cell Fabrication and Testing. The plastic pouch cells were assembled in an argon atmosphere glovebox (O2/H2O < 1 ppm) of a Li–S battery. The overlap of the in situ NMR spectra with the lithium polysulfide species coexist (Li2S8, Li2S6, and Li2S4) together with the electrolyte (LiTFSI) and additive (LiNO3). The shifts of these Li-bearing species overlap with each other in the 7Li NMR spectra.

The overlap and similarity between these species make it difficult to separate individual peaks in NMR spectra. Attempts have been made to deconvolute the spectra with multiple peaks (more than three) in the diamagnetic region; however, the results do not follow any logical explanation. It is believed that more than three peaks will cause a misinterpretation of the electrolyte/additive resonance with the lithium polysulfide species, making it difficult to track the changes. Therefore, an approximation is used during deconvolution as previously employed in See’s work. Soluble species are grouped in high-frequency and low-frequency features. In Figure 1b, three Li environments were used to deconvolute the spectrum in the 0 ppm region. These three environments are one at around −0.06 ppm, which is ascribed to the solid species formed during the electrochemical cycling process, and two sharp features at around 3.67 and −0.16 ppm, which are ascribed to the soluble lithium-bearing species. Each soluble species NMR feature represents a group of lithium environments that contain lithium-bearing soluble species that resonate at a very similar frequency. Figure 1c shows a closer view of how these two soluble species peaks are assigned.

In Figure 1d, two features were used to deconvolute the spectrum in this region at around 250 ppm: lithium metal at around 247 ppm and dendritic/mossy lithium at around 257 ppm. Because of the bulk magnetic susceptibility difference between these two sites, the dendritic/mossy lithium signal appears at a slightly different chemical shift, enabling the separation from the bulk lithium metal signal.

3. RESULTS AND DISCUSSION

3.1. Peak Deconvolution. A representative spectrum (1.7 V) of a Li–S battery is shown in Figure 1a, where two groups of peaks were used to deconvolute the spectrum: three peaks at around 0 ppm and two peaks at around 250 ppm. Features at around 0 ppm (Figure 1b,c) are ascribed to the soluble species and the solid species that are formed during the electrochemical process. Features at around 250 ppm are ascribed to the metallic lithium, and the large shift is due to the Knight shift.

In a functional Li–S battery, soluble lithium polysulfide species coexist (Li2S8, Li2S6, and Li2S4) together with the electrolyte (LiTFSI) and additive (LiNO3). The shifts of these Li-bearing species overlap with each other in the 7Li NMR spectra. The overlap and similarity between these species make it difficult to separate individual peaks in NMR spectra. Attempts have been made to deconvolute the spectra with multiple peaks (more than three) in the diamagnetic region; however, the results do not follow any logical explanation. It is believed that more than three peaks will cause a misinterpretation of the electrolyte/additive resonance with the lithium polysulfide species, making it difficult to track the changes. Therefore, an approximation is used during deconvolution as previously employed in See’s work. Soluble species are grouped in high-frequency and low-frequency features. In Figure 1b, three Li environments were used to deconvolute the spectrum in the 0 ppm region. These three environments are one at around −0.06 ppm, which is ascribed to the solid species formed during the electrochemical cycling process, and two sharp features at around 3.67 and −0.16 ppm, which are ascribed to the soluble lithium-bearing species. Each soluble species NMR feature represents a group of lithium environments that contain lithium-bearing soluble species that resonate at a very similar frequency. Figure 1c shows a closer view of how these two soluble species peaks are assigned.

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3.2. Cell Performance Improvement. A cell with 1 M LiTFSI in DOL/DME with 2 wt % LiNO3 was employed as a model system. The cell was flooded with electrolyte (E/S > 15 μL/mg), and the electrochemical profile of the in situ NMR cells is consistent with conventional Li–S cells. The cell configuration and testing parameters can be found in the Experiment section. The first multicycle pouch cell was tested, and the electrochemical cycling profile is shown in Figure 2. Significant improvement has been made in the electrochemical cycling performance compared to the cell employed by See et

Figure 2. Electrochemical cycling profile and the discharge/charge capacity of the cell with LiNO3 and four full cycles are shown.
al, where the cell died after the first discharge. The insertion of the multilayer separators is believed to be a contributor to the performance improvement. In addition to the application of the multilayer separator, pressure was applied to the pouch cell so that the contact between the cathode and the anode can be well maintained during data acquisition. We have found that the amount of electrolyte between the cathode and the anode plays a critical role, and the increased distance between the cathode and the anode allows more solvent readily available to dissolve lithium polysulfides.

3.3. Solid/Soluble Species Evolution. A total of 164 NMR spectra were acquired during electrochemical cycling and carefully deconvoluted with the method described in the Experiment section. The integral area of each deconvoluted feature was recorded and plotted together with the electrochemical profile as shown in Figure 3. Figure 3a shows the evolution of the solid species during the electrochemical cycling of the cell, and Figure 3b shows the evolution of the soluble species (−0.16 ppm resonance). During the entire first discharge plateau of the first discharge, no solid species formation was observed (region I in Figure 3a with blue highlighting), and a large increase in the soluble species intensity was noticed (region I in Figure 3b with blue highlighting). These observations suggest that during the first discharge plateau at 2.3 V, elemental sulfur (S₈) dissolves in the solvent and reacts with lithium metal, forming long-chain soluble lithium polysulfides such as Li₂S₈, Li₂S₆, and Li₂S₄. In the following discharge plateau (2.1 V), the solid species (short-chain lithium polysulfide, e.g., Li₂S) was observed to have formed (region II in Figure 3a with yellow highlighting) and the long-chain lithium polysulfides were observed to be consumed and their intensity continued to decrease until the end of the first discharge (Figure 3b region II with yellow highlighting). Once the current was reversed and the charging process began, two charge plateaus were observed: 2.3 and 2.45 V. The intensity of the solid species decreases continuously throughout the entire charge process (region III in Figure 3a with green highlighting). However, the soluble species intensity recovered during the first charge plateau (2.3 V, region III in Figure 3b with red highlighting) and decreased during the second discharge plateau (2.45 V, region IV in Figure 3b with red highlighting). It is believed that, upon charge, the lithium–sulfur chemistry was reversed, where short-chain lithium polysulfide became long-chain lithium polysulfide during the first charge plateau. At the end of the first charge plateau, elemental lithium sulfur started to form until the end of the entire charge process accompanied by the decreased intensity of the soluble long-chain lithium polysulfide. The percentage of the reversible solid species was calculated to be 52% during the first cycle. In subsequent cycles, the solid species formation and consumption repeated themselves upon charge and discharge. However, the irreversible solid species accumulated because of the lithium–sulfur chemistry cannot be completely reversed during the charging process. At the end of the fourth cycle, the solid species intensity increased by 8-fold. To summarize, the soluble species shown in Figure 3b undergoes a four-step evolution in a complete electrochemical cycle: (I) formation from reaction between elemental sulfur and lithium; (II) consumption due to solid species formation; (III) formation through solid species decomposition; and (IV) consumption due to elemental sulfur formation. These four stages repeated themselves in each of the four cycles. Soluble species-mediated lithium–sulfur chemistry is clearly demonstrated in Figure 3a,b, and the soluble long-chain lithium polysulfide plays a significant role in lithium–sulfur chemistry.

In addition, the capacity fade was clearly observed (Figure 2) whereas irreversible Li₂S continues to accumulate as the cell is cycled. The accumulation of the Li₂S solid species is the main contributor of the capacity fade, and the Li₂S solid species is stranded in the cell and loses contact with the electrochemical reaction. Moreover, the slow cycling rate (C/30) utilized in this study also facilitates the shuttling effect accelerating the accumulation of the Li₂S solid species.

For a better visualization of the process, all 164 spectra were stacked and plotted (Figure 4). In this figure, the formation of the solid species (green/yellow intensity) and its evolution can be clearly seen, where the solid species gains intensity on discharging and loses intensity on charging (the appearance and disappearance of the green/yellow feature).

3.4. Lithium Metal/Dendritic Lithium Evolution. Lithium metal and the dendritic/mossy lithium NMR feature were also deconvoluted and shown in Figure 5. The bulk magnetic susceptibility enables peak separation between the two species: the lithium metal signal appears at around 247 ppm, and the dendritic/mossy lithium signal appears at around 259 ppm.

In Figure 5a, an increase in lithium metal intensity during the first discharge process and a continuous decrease in the subsequent cycles were observed. The increase in lithium metal density during the first discharge process is attributed to the skin depth effect, where a radio frequency can penetrate only...
tens of micrometers of the metal chunk. Therefore, the intensity of the lithium metal signal is proportional to the surface area of the lithium metal anode. During discharging, lithium consumption is not evenly distributed on the lithium metal surface, thus causing a coarsening process of the lithium anode. Upon charging, the lithium metal intensity started to decrease as a result of the formation of dendritic/mossy lithium on the surface of the lithium metal anode. Because the density of the dendritic/mossy lithium differs from the lithium metal, the accumulated dendritic/mossy lithium compromises the ability of the radio frequency to penetrate the lithium metal anode as a result of the dendritic/mossy lithium on the surface. In the following cycles, the lithium metal anode intensity continued to decrease as a result of the continuous formation of inactive dendritic/mossy lithium. In Figure 5b, the dendritic/mossy lithium did not form until the beginning of the first charge process and continued to grow through the charging process. During the second discharge, interestingly, the signal intensity did not decrease but plateaued upon discharge and kept increasing in the following discharge process. In the third and fourth cycles, dendritic/mossy lithium formation slowed down during charging and was observed to be reversible during the discharge process. A continuous formation of dendritic/mossy lithium on the surface of the lithium metal and the consumption of lithium metal are observed. The fast accumulation of the dendritic/mossy lithium is ascribed to the quick formation in the first two cycles until a thick layer of dendritic/mossy lithium was formed on the surface of the lithium metal anode. The slowed down formation process during the third and the fourth cycles can be explained by the dendritic/mossy lithium’s participation in the electrochemical process after the lithium metal surface was completely covered with a thick layer of dendritic/mossy lithium.

3.5. Ex Situ NMR Spectroscopy. After in situ NMR spectroscopy data acquisition, the cell was discharged to 1.7 V and disassembled. The cathode and the anode were sealed separately in plastic pouches. The normalized ex situ NMR spectra of the cathode and the anode are shown in Figure 6, which decoupled the cathode reaction and the anode reaction. In this figure, the formation of a solid species was clearly seen on both the cathode and the anode. However, a surprisingly small amount of the solid species is observed on the cathode whereas significant solid species accumulation is observed on the anode. This solid species on the anode is ascribed to the lithium sulfide (Li2S) formed via the sulfur shuttled to the anode and reacted with the lithium metal. The observation is
consistent with the continuous solid species intensity increase as a function of cycle number in Figure 3a and highlights the sulfur shuttling to the anode. This phenomenon is occurring despite the presence of LiNO₃ additive and is more pronounced in a cell without LiNO₃ (suggesting that the majority of the signal in the Figure 6 anode is due to Li₂S, not LiNO₃ decomposition, see Supporting Information), where the overall reversibility of the cell reaction is poor.

3.6. Mechanism Revelation. Via the detailed in situ NMR characterization and the quantitative analysis of solid/soluble species evolution, we report the four-step reaction mechanism of a Li–S battery in never before seen detail as summarized in Figure 7: (I) formation from the reduction of elemental sulfur; (II) consumption due to solid species formation; (III) formation through solid species decomposition; and (IV) consumption owing to the conversion to elemental sulfur. It is clear that the soluble species in the electrolyte plays a critically important part in this chemistry. On the anode side, the evolution of the lithium metal can be accurately correlated with the electrochemical process, where significant irreversible Li₂S formation is also observed in in situ cells, highlighting the magnitude of sulfur shuttling and side reactions in Li–S batteries with conventional electrolytes.

4. CONCLUSIONS

A comprehensive and highly quantitative in situ NMR method is presented in this report to monitor the electrochemical process in Li–S batteries, and this method is a vital complementary tool to other in situ techniques. The intensities of the soluble species and the solid species were carefully deconvoluted, and the evolution is correlated with the electrochemical process nicely (via four-step soluble lithium polysulfide-mediated Li–S electrochemistry). More importantly, simultaneous quantitative detection of both the solid and the soluble species in real time is critical in understanding the lithium–sulfur battery electrochemistry processes and side reactions such as the shuttle effect. The most important outcome of this study is that this method can be readily employed to study a variety of novel Li–S battery electrolytes, assist sulfur cathode design, and guide lithium metal protection research via quantitative real-time monitoring of the changes in the speciation process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b01922.

Species evolution of a lithium–sulfur battery without the LiNO₃ additive (PDF)

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The authors declare no competing financial interest.

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REFERENCES


Figure 7: Demonstration of the four-step soluble species-based Li–S electrochemistry.


