**Thiol-Based Electrolyte Additives for High-Performance Lithium-Sulfur
Batteries**

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Abstract:

The discharge and charge mechanisms of the Li-S battery involve the formation of soluble lithium polysulfide species that can diffuse through the battery and cause issues related to capacity fade and poor Coulombic efficiency. In order to control the behavior of the lithium polysulfides, thiol-based electrolyte additives such as biphenyl-4,4'-dithiol (BPD) were used to enhance capacity retention in lithium-sulfur batteries by controlling polysulfide dissolution. *In situ* Raman spectroscopy, *in situ* UV-vis spectroscopy, and electrospray ionization mass spectrometry show that an additional sulfur reduction process observed at ~ 2.1 V vs Li/Li⁺ as a result of BPD addition is associated with the formation of BPD-short chain polysulfide complexes such as BPD-S_n anion ($1 \leq n \leq 4$). The interaction between BPD and short chain polysulfide postpones formation of soluble short chain polysulfides and alters the kinetics of the dissolution process. A smooth SEI/Li entangled phase is found on the Li anode with BPD addition. The BPD additive increases the capacity retention of lithium-sulfur batteries, mainly due to the formation of various BPD-polysulfide complexes which prevents polysulfide dissolution. Comparison with other thiol-based additives shows that the optimal additive balances solubility and polysulfide-additive stabilization.

Introduction:

The ever-increasing demand for portable energy has prompted a renewed interest in batteries and other energy storage devices.[1] While Li-ion batteries still dominate portable applications, other chemistries have attracted recent attention because they promise increased gravimetric or volumetric capacities over those available from Li-ion chemistries. One of these emerging chemistries is the lithium-sulfur (Li-S) batteries.[2-8] The theoretical capacity of the S cathode is 1672 mAh g^{-1} which is over 5 times higher than the theoretical capacity of the LiCoO_2 cathode ($\sim 272 \text{ mAh g}^{-1}$) in conventional Li ion batteries.[3, 5, 6] In addition to the increased energy density, elemental sulfur is readily available, environmentally friendly, naturally abundant, and cheap.

Many problems associated with battery performance still attend the practical application of Li-S batteries. These problems include the stability of the cathode material,[9, 10] the dissolution of intermediate species from the cathode,[6, 7] dendrite formation at the Li anode, and the high reactivity of the Li metal anode which degrades the electrolyte.[4, 11]

Many of these issues are caused by the formation of soluble polysulfide intermediates during the reduction process. The electrochemical reduction of sulfur

leads to the formation of various polysulfide intermediates such as soluble long chain polysulfides and less-soluble short chain polysulfides through a multistep process.[12-15] While the final product at the end of discharge is the insoluble lithium sulfide, the intermediate polysulfides are soluble in the solvents typically utilized for the Li-S battery.[16, 17] The soluble polysulfide intermediates dissolve into electrolyte upon cycling, leading to capacity fade. Additionally, the polysulfide anions can freely migrate between the cathode and anode, causing a so-called shuttle effect that results in low Coulombic efficiency and rapid capacity fade.[18]

To address issues associated with polysulfide dissolution, both cell-level and electrode level modifications to the Li-S battery have been pursued.[4-7, 19] At the cell level, interlayers and porous current collectors are used to enhance the capacity retention.[6] In another implementation, highly cross-linked polymers with various functional groups prepared *via* thiol–ene chemistry were coated on the cathode surface to increase the battery performance.[20] At the electrode level, different types of S-composites have been examined including various carbon materials,[5, 6, 19, 21-24] cathode additives,[25-28] and functional polymers based on inverse vulcanization and other schemes.[6, 29-31] However, these methodologies require very specialized composites, the scaling of which for practical batteries is complicated. The energy density of the cathode also decreases with incorporation of inactive

materials to the composite electrode.

Another method to retain Li-S battery capacity involves the use of solvent, supporting electrolyte salt, and electrolyte additives. [4, 7, 8, 32, 33] The addition of co-solvents and functional molecules to the electrolyte solution can enhance battery performance [4, 7, 8] Co-solvents such as ionic liquids and fluorinated ethers were used to improve the Coulombic efficiency and prevent self-discharge in Li-S batteries.[34, 35] The use of a polysulfide additive as the functional molecules creates a concentration gradient of polysulfide species at the cathode/electrolyte interface and alleviates some polysulfide dissolution.[36, 37] LiNO_3 is another well-known electrolyte additive that limits the shuttle effect by forming a passivation layer on the Li anode.[38, 39] Benefits of a protective layer on the Li anode have been demonstrated using other electrolyte additives such as P_2S_5 and LiI . [40, 41] However, in most cases the interaction between electrolyte, additive, and electrodes is uncertain.

In this work, we examine thiol-based electrolyte additives such as biphenyl-4,4'-dithiol (BPD) to improve the performance of Li-S batteries. In addition to reporting enhanced capacity retention as a result of BPD addition to the electrolyte solution, we also provide a comprehensive understanding of the origin of capacity retention observed with these additives at both the sulfur-carbon cathode and the Li-metal anode.

2. Experimental Section:

Electrolyte preparation:

The basic electrolyte was 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in 1:1 (v/v) solution of tetraethylene glycol dimethyl ether (TEGDME, $\geq 99\%$, Sigma-Aldrich) and 1,3-dioxolane (DOL, anhydrous, Sigma-Aldrich). The thiophenol ($\geq 99\%$), benzene-1,4-dithiol (99%, GC), biphenyl-4,4'-dithiol (95%), 1,4-bis(4-mercaptophenyl)benzene (96%) and pentaerythritol tetrakis(3-mercaptopropionate) ($\geq 95\%$) were purchased from Sigma-Aldrich and used without further purification. The additives were dissolved in the basic electrolyte solution described above at various concentrations.

Sulfur-carbon slurry and two-electrode Swagelok-cell preparation:

The cathodes were cast from a slurry consisting of 60 wt% sulfur (99.98%, Sigma-Aldrich), 30 wt% carbon black (Super-P Li, Timcal Inc.), and 10 wt% polyvinylidene fluoride (PVDF, Kynar 2801) binder mixed with anhydrous N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) and stirred overnight. Preparation of the sulfur-carbon cathode was described previously.[12] The sulfur loading was 0.7-1.2 mg-sulfur/cm².

Electrochemical measurement:

Cyclic voltammetry (CV) of the sulfur-carbon cathode were obtained by using a 760C or 760D CH Instruments potentiostat at scan rates of 0.1 mV/s in the two-electrode Swagelok cell and the 0.5 mV/s in the *in situ* Raman cell between 3.2 V and 1.5 V (vs. Li/Li⁺), respectively. The current density was estimated by using the geometric area of the Al disk.

Charge and discharge processes in the Swagelok cell (nylon, 1" inner diameter, Chicago Fluid System Technologies) were carried out at the rate of 0.1 C (calculated using the weight of sulfur-carbon cathode) between 3.2 V and 1.8 V by using an Arbin Battery Tester (Model BT 2043, Arbin Instruments Corp., USA). The counter/reference in the two-electrode Swagelok cell was Li metal, and potentials are given with respect to Li/Li⁺.

Electrochemical Impedance Spectroscopy measurements:

The electrochemical impedance spectroscopy (EIS) were performed in the lithium metal symmetric Swagelok cell using a Bio-Logic Variable Multichannel Potentiostat (SP-150, Science Instruments, France) The frequency range is in a 1000 kHz to 10 mHz range with an amplitude of 100 mV.

In situ Raman Spectroscopy measurements:

In situ Raman spectroscopy experiments were performed using a home-built glass cell described previously.[12] Fig. S1 shows the cell design for the *in situ* Raman

spectroscopy experiments. The working electrode was a sulfur-carbon cathode (~0.01g) supported on an Al disk (3/8 inch in diameter, 99.99%, Alfa Aesar). Li metal was used as the reference and counter electrode (99.9 %, Alfa Aesar). The typical acquisition time was 120s per spectrum. In order to reach electrochemical equilibrium, the potential was held at each 100 mV step at least 10 min before collecting the spectrum. The band intensities used for the data analysis in this study were baseline corrected.[12]

In-situ UV-Vis absorption spectroscopy measurements:

The in-situ UV-Vis measurements (Varian model Cary 500 Scan UV-Vis-NIR spectrophotometer) were carried out in an air-tight 10 mm path length quartz cell (Starna, USA) with a cycling region between 3.2 V and 1.5 V and a scan rate of 0.5 mV/s. The electrolyte volume is 3.5 mL. The working electrode is the sulfur-carbon cathode (~0.6 mg sulfur) on an Al plate. The reference and counter electrodes were Li metal. In order to reach electrochemical equilibrium and avoid a concentration gradient of dissolved polysulfides in the electrolyte, the potential was held at each 200 mV step at least 30 min before collecting the spectrum.

Electrospray Ionization Mass Spectrometry (ESI-MS) measurements:

The electrolyte was a mixture of 5mM polysulfides such as Li_2S_4 and 5mM thiol-based molecule in a 1:1 (v/v) solution of TEGDME and DOL. The polysulfide

solutions were prepared from stoichiometric mixtures of S_8 and Li_2S . Prior to measurement, the electrolyte was diluted 1000-fold with ethanol. The microdroplets entering the mass spectrometer undergo desolvation at a capillary temperature of 275 °C in an LTQ-Orbitrap XL mass spectrometer. (Thermo Fisher Scientific, San Jose, CA, USA) The Orbitrap MS was typically operated using the following parameters: single-stage m/z range = m/z 60-500, m/z resolution setting = 100,000 at m/z 400, mass accuracy = 2-5 ppm, microscans = 1, ion injection time = 500 ms, tube lens voltage = 110 V, spray voltage = 5 kV

SEM measurements:

The surface morphology of the Li anode before and after battery cycling was analyzed using SEM (JEOL, JSM-7000F). The Li-S batteries were cycled in the cycle region between 3.2 V and 1.5 V and emerged at 3.2 V. These Li anodes were then dried in an Ar-filled glove box overnight and put into a well-sealed container to transfer to the SEM instrument. However, brief (<10 s) exposure to air was unavoidable during loading of the sample into the SEM.

3. Results and Discussion:

3.1 Biphenyl-4,4'-dithiol (BPD) as an electrolyte additive in Li-S batteries

Figure 1. (A) CV profile of the sulfur-carbon cathodes in the basic electrolyte (black line) and the basic electrolyte with 25mM biphenyl-4,4'-dithiol (BPD) electrolyte additive (red line). Blue line shows the CV profile of sulfur free cathode with 25mM BPD additive. Black and red arrows show the reduction peaks of sulfur-carbon cathode without and with BPD additive. The dashed arrows indicate the scan direction (B) Discharge and charge curves of sulfur-carbon cathode with 25mM BPD in different cycles. (C) The cycling performance and (D) resulting Coulombic efficiency of the sulfur-carbon cathode at the rate of 0.1 C (based on the weight of sulfur-carbon cathode) with the basic electrolyte and with the addition of BPD at 25 mM and 50 mM.

Fig. 1A shows the cyclic voltammetry (CV) of the as-prepared cathodes obtained in two-electrode Swagelok cells at a scan rate of 0.1 mV/s from 3.2 V to 1.5 V vs. Li/Li^+ with and without BPD as an additive in a basic electrolyte (1 M LiTFSI DOL/TEGDME). All further voltages are referenced to Li/Li^+ . The dashed arrows indicate the scan direction. The negative scan of the sulfur-carbon cathode with the basic electrolyte shows the typical cathodic peaks at ~ 2.4 V and ~ 1.95 V associated

with the conventional step-wise sulfur reduction.[12-14] These reduction processes are commonly associated with the formation of long chain polysulfides (~ 2.4 V) and short chain polysulfides (~ 1.95 V, black arrow). [12-14] In the oxidative scan, there are two oxidation peaks at ~ 2.35 V and 2.55 V which are associated with the oxidation of sulfide to elemental sulfur.[12, 14, 16, 17]

The red line in Fig. 1A shows the CV of sulfur-carbon cathode obtained in the basic electrolyte with addition of 25mM biphenyl-4,4'-dithiol (BPD). In addition to the two redox pairs associated with the sulfur reduction and polysulfide oxidation, the addition of BPD to the electrolyte results in the appearance of a new reduction peak at ~ 2.05 V, highlighted by a red arrow in Fig. 1A. There are now three reduction peaks in the voltammetry, rather than the two found with the S-C cathode alone. Further, the ionic conductivity of the basic electrolyte obtained from a symmetric lithium cell by using impedance spectroscopy is 0.5 mS/cm which is similar with a previous report,[42] while the conductivity of the basic electrolyte with 25 mM BPD is 0.4 mS/cm. Thus changes in peak potentials and electrochemistry are not due to changes in ionic conductivity as a result of BPD addition.

To determine if the new peak is due to redox chemistry associated with BPD itself, we obtained the CV of a sulfur free cathode consisting of carbon black and PVDF with the BPD added to the basic electrolyte (blue line). This CV shows redox

waves of BPD alone at ~2.0 V and ~2.5 V for reduction and oxidation respectively.

Fig. S2 shows that the current density of BPD redox peaks decreases slightly in 10 cycles. These redox waves are attributed to the formation/decomposition of an intramolecular S-S bond between BPD molecules.[43]

Although the BPD additive is electrochemically active in the potential window of interest for Li-S chemistry, the small current density ($\sim 20 \mu\text{A}/\text{cm}^2$) found from BPD alone suggests that additional processes occur when S is present in the cathode at the additional reduction peak marked with the red arrow in Fig. 1A. Thus, compared to the basic electrolyte, addition of 25 mM BPD results in a lower current density of the reduction peak at 1.95 V (black arrow) and higher current density of the peak at 2.05 V is likely due to a reaction involving both S and BPD.

Fig. 1B shows discharge and charge curves obtained from the sulfur-carbon cathode in the basic electrolyte following 25 mM BPD addition cycled at a C/10 rate between 3.2 V and 1.8 V in representative cycles. The discharge profile of Li-S battery with the BPD additive can be divided into three regions (labeled 1-3) consistent with the existence of three reduction peaks in the CV. Plateaus 1 and 3 are associated with the typical sulfur reduction found in a Li-S battery in a 1M LiTFSI TEGDME/DOL electrolyte.[12, 13] BPD addition results in the formation of the new discharge plateau at ~2.05 V labeled as region 2. The charge profile shows two

plateaus at ~ 2.35 V and ~ 2.53 V which are associated with the oxidation peaks in the CV profile.

Fig. 1C-D shows the cycling performance of our Li-S battery with and without BPD addition. All cells were cycled at a C/10 rate between 3.2 V-1.8 V. The Li-S batteries in the basic electrolyte exhibit an initial capacity of ~ 900 mAh/g-sulfur. However, this capacity fades in the following cycles to ~ 300 mAh/g-sulfur after 100 cycles in a good agreement with previous studies.[44] The Coulombic efficiency of each cell is $89 \pm 3\%$, consistent with Li-S battery behavior absent nitrate addition.[36] The Li-S batteries with the BPD additive exhibit similar initial capacities (~ 900 mAh/g-sulfur) as compared with the cells in the basic electrolyte. However, the addition of BPD results in substantially better capacity retention relative to the basic electrolyte with a capacity of ~ 600 mAh/g with 25mM BPD and ~ 650 mAh/g with 50mM BPD after 100 cycles. The Coulombic efficiency upon addition of BPD is $93 \pm 3\%$ at both additive concentrations.

3.2 In situ Raman Spectra of the Sulfur-Carbon Cathode with BPD additive

Figure 2. (A) CV profile of the sulfur-carbon cathode obtained in an electrolyte solution of 1M LiTFSI and TEGDME/DOL with 5mM BPD at a scan rate of 0.5 mV/s. The cycle region is 3.2V to 1.5 V in the *in situ* Raman cell. (B-C) *in situ* Raman spectra of the sulfur-carbon cathode at representative potentials with and without 5mM BPD additive.

To understand the interaction between BPD and polysulfides during charge and discharge, we used *in situ* Raman spectroscopy to investigate the potential dependence of these polysulfide species with and without BPD in the electrolyte. Fig. 2A shows the CV profile of the sulfur-carbon cathode obtained at a scan rate of 0.5 mV/s in the basic electrolyte with 5mM BPD. The second reductive peak (~2.15 V) marked with black arrow in the *in situ* Raman cell is slightly different relative to that obtained in a Swagelok cell with a scan rate of 0.1 mV/s (~1.95 V), as shown in Fig. 1A. The more anodic potential may be due to the higher electrolyte volume in the Raman cell.[12] The broad reduction peak at ~2.15 V is attributed to the overlap of the reduction peaks at 2.05 V and 1.95 V shown in Fig.1A.

Fig. 2B-C show *in situ* Raman spectra obtained from the sulfur-carbon cathode at representative potentials with and without 5mM BPD addition during the discharge process. The *in situ* Raman spectra obtained in the TEGDME/DOL electrolyte was studied in previous studies,[12] however, to facilitate direct comparison, we will discuss the relevant features in the *in situ* Raman spectra that change as a result of BPD addition. The peaks of interest are marked with letters a-f, and are assigned in Table 1.[12, 45-51]

Peak label	Peak position (cm^{-1})	Assignments	References
a	217	S_8 and S_8^{2-} (Bending mode)	12, 45, 46
b	234	S_4^{2-} (Bending mode)	12, 47, 48
c	228	(BPD) S_4^{2-}	present study
d	518	S_4^-	12, 50, 51
e	526	(BPD) S_3^-	present study
f	534	$\text{S}_3^{\bullet-}$ (Stretching mode)	12, 45, 46, 49

Table 1. Experimental Vibrational Frequencies and Assignments for Sulfur Species.

Fig. 2B shows the *in situ* Raman spectra of the sulfur-carbon cathode in the region between 190 cm^{-1} and 250 cm^{-1} during the discharge process. Peak a at 217 cm^{-1} found at 3.2 V prior to discharge in the basic electrolyte is associated with the S-S bending mode of the S_8 ring. Other species, however also exhibit a similar Raman shift. In particular, calculations suggest that species such as mono- and dianions like S_5^- (217 cm^{-1}), S_8^- (216 cm^{-1}), S_5^{2-} (214 cm^{-1}), and S_8^{2-} (214 cm^{-1}) have Raman modes at similar vibrational energies.[46] Indeed, S_8^{2-} and S_6^{2-} formation in this

potential region has been suggested by using other techniques.[13, 14] Peak a disappears during discharge and reforms during charge.[12] Peak b at 234 cm^{-1} assigned to S_4^{2-} forms at the second reduction peak and disappears at 1.5 V in the basic electrolyte.[12]

Upon addition of BPD, the Raman spectrum at 3.2 V exhibits similarities with that absent BPD. However, the FWHM of the peak a at 3.2 V in the presence of BPD is wider than in the basic electrolyte. (22 cm^{-1} vs. 14 cm^{-1}), suggesting that other species such as those mentioned above might be present. The intensity of peak a decreases after the first reduction peak ($\sim 2.4\text{ V}$) and decreases further at 2.2 V but does not completely diminished as is found absent BPD addition. Peak b at 234 cm^{-1} -- assigned to S_4^{2-} -- is observed at 2.2 V consistent with the potential dependence of peak b absent BPD. Interestingly, addition of BPD results in the presence of a new peak c at 228 cm^{-1} associated with the second reduction peak in the voltammetry. The persistence of peak a and appearance of peak c could be due to the presence mono- and dianionic polysulfide species. Alternatively, peak c could be assigned to the formation of a complex formed by reaction of BPD with polysulfide species. Indeed, peak c is red shifted relative to the region in which S_4^{2-} is found (228 cm^{-1} vs. 234 cm^{-1}) which would be expect upon formation of BPDS_4^{2-} due to the delocalization of the S-S bond through the phenyl group.

Fig. 2C shows in situ Raman spectra obtained from the sulfur-carbon cathode in the region between 500 cm^{-1} and 600 cm^{-1} . In the basic electrolyte, peak d at 518 cm^{-1} and peak f at 534 cm^{-1} obtained at 2.2 V are associated with S_4^{2-} and S_3^{2-} , respectively.[12] In contrast, sulfur reduction following addition of 5 mM BPD does not yield evidence for S_4^{2-} formation since peak d is absent. A new peak e at 526 cm^{-1} appears at 2.2 V in the presence of 5mM BPD.

We next discuss the possible assignment of peak e. Fig. S3 shows that the intensity of peak e increases with higher BPD concentration, however, BPD itself does not exhibit any Raman modes in this region suggesting that peak e is associated with the formation of a BPD-polysulfide complex. Additionally, we find that as the intensity of peak e increases with high BPD concentration, the intensity of peak f decreases commensurately indicating the consumption of S_3^{2-} . Therefore, we can reasonably suggest that peak e corresponds to the formation of BPD-S_3^{2-} . In order to further support evidence for BPD-S_3^{2-} formation, Fig. S4 shows the Raman spectrum of the “ Li_2S_4 ” reference solution in the basic electrolyte with and without BPD. The Raman spectrum of a nominally “ Li_2S_4 ” reference solution in the basic electrolyte exhibits a very strong mode at 534 cm^{-1} (peak f) likely due to the formation of S_3^{2-} as a result of disproportionation reactions, however, upon addition of BPD to the reference solution, the polysulfide-associated peak in the region of 230~240 nm

marked with yellow band has red shifted in the presence of BPD. BPD addition also results in the formation of a new peak at $\sim 520\text{ cm}^{-1}$ in the Raman spectrum.

We performed calculations examining the Raman modes of $\text{S}_3^{\bullet-}$ and BPD-S_3^- to determine if the observed Raman peak could be due to the formation of the BPD-S_3^- complex. Table S1 shows calculated Raman modes obtained by using the Spartan program. Here the S-S stretching mode of BPD-S_3^- exhibits a red shift ($\sim 26\text{ cm}^{-1}$) relative to the equivalent mode in $\text{S}_3^{\bullet-}$, consistent with the experimental result. On the other hand, the phenyl group of BPD-S_3^- can delocalize the electron of S-S bond in $\text{S}_3^{\bullet-}$ and causes the Raman red shift. Finally, we used electron spin resonance (ESR) spectroscopy to identity the formation of radical species and further support the existence of an interaction between BPD and $\text{S}_3^{\bullet-}$. Fig. S5 shows the ESR spectra of 0.1 M Li_2S_4 in a TEGDME/DOL solution with and without 25mM BPD at 100 K. ESR from the 0.1 M Li_2S_4 solution shows a signature characteristic of $\text{S}_3^{\bullet-}$. In particular, the observed g-factors are consistent with a previous report.[13, 52, 53] The ESR signal disappears in a solution containing 0.1 M Li_2S_4 with 25mM BPD, suggesting that the $\text{S}_3^{\bullet-}$ is quenched by the BPD additive. On the basis of the discussion above, the peak e is assigned to the formation of $(\text{BPD})\text{S}_3^-$. The interaction between sulfur and thiol-based compounds is reported in previous studies.[20, 29, 54]

Figure 3 CV of the as-prepared sulfur-carbon cathode and potential dependence of the Raman peak at 217, 228, 234, 526 and 534 cm^{-1} obtained in the basic electrolyte with 5 mM BPD addition during (A) discharge and (B) charge process.

Figure 3 shows the CV of the sulfur-carbon cathode and the potential dependence of the peak intensity at 217, 228, 234, 526 and 534 cm^{-1} taken from the discharge and charge process with 5 mM BPD addition. All peak intensities were normalized to the intense 526 cm^{-1} peak at 2.1 V. Fig. 3A shows that the $\text{S}_8/\text{S}_8^{2-}$ -associated peak decreases during the first reduction peak at ~2.4 V and drops to zero at 2.1 V. Peaks associated with the short chain polysulfides such as BPDS_4^{2-} , S_4^{2-} , S_3^{2-} , and BPDS_3^{2-} form at 2.3 V and grow to a maximum at ~2.1 V. The Raman result clearly shows that the BPD-polysulfides species form at 2.3 V and decompose into other species again at 1.8 V. Li_2S and Li_2S_2 could be the final product at the end of the discharge process. However, the solid Li_2S peak at 375 cm^{-1} is not observed because solvent modes obscure bands associated with solid Li_2S in the in situ Raman measurement.[55] Fig.3B shows that these short chain polysulfides and BPD-polysulfide species such as BPDS_4^{2-} , S_4^{2-} , S_3^{2-} , and BPDS_3^{2-} reform at 2.0 V and

disappear at 2.7 V during the charge process. The S_8 -associated peak occurs at 2.5 V and reaches a maximum at 2.7 V.

The discharge process as probed by *in situ* Raman is therefore much different relative to that observed in the basic electrolyte. [12, 13, 45] Without BPD addition, *in situ* Raman result shows that the short chain polysulfides such as S_4^{2-} and S_3^{2-} were formed during the discharge process. [12, 13] The *in situ* Raman spectra obtained with BPD addition show that BPD alters the sulfur reaction pathway and forms BPD-short chain polysulfide complexes such as $BPDS_4^{2-}$, and $BPDS_3^{2-}$ in the second reduction peak.

Figure 4. *In situ* Raman spectra of the sulfur-carbon cathode obtained at 3.2 V and after holding the potential at 2.2 V for the indicated times (A) without and (B) with 5mM BPD additive. (C) The normalized intensity of S_3^{2-} and $BPDS_3^{2-}$ plotted as a function of time after switching the potential from 3.2 V to 2.2 V with and without 5mM BPD addition.

We next hold the potential at partial discharge to characterize the effect of the BPD additive on the kinetics of polysulfide formation during the discharge process.

Fig. 4A-B shows in situ Raman spectra of the sulfur-carbon cathode obtained at open circuit potential (OCP, ~3.2 V) and after switching the potential to 2.2 V for the indicated times. Fig. 4A shows that Raman modes associated with short chain polysulfides such as S_4^{2-} and S_3^{2-} grow in as a function of time following the potential step to 2.2 V.[12] Following addition of BPD, Fig. 4B shows that bands associated with both S_3^{2-} and BPD- S_3^{2-} grow with time at 2.2 V and the band associated with S_4^{2-} is not observed. Interestingly, the band associated with BPD- S_3^{2-} appears first at 2.2 V followed by the formation of S_3^{2-} , suggesting fast reaction between BPD and S_3^{2-} .

Fig. 4C shows the normalized intensity of the S_3^{2-} and BPD- S_3^{2-} bands plotted as a function of time after switching the potential from OCP to 2.2 V with and without BPD addition in the electrolyte. In the basic electrolyte, S_3^{2-} grows with time and reaches a maximum at 30 min. Intensity associated with S_3^{2-} is constant for the remaining 10 min of the measurement. As we reported previously, the formation constant of S_3^{2-} can be obtained by a pseudo first order fit to the intensity-time curve.[12]

With addition of 5mM BPD, the band associated with BPD- S_3^{2-} appears 5 min after switching the potential from 3.2 V to 2.2 V, followed by formation of S_3^{2-} . Intensity associated with the S_3^{2-} initially increases according to what could be a pseudo first order fit, but then suddenly increases at $t = 34$ m. This increase suggests

that simple first order kinetics cannot describe the $S_3^{\bullet-}$ behavior. Alternatively, the $BPDS_3^-$ band can be fit with these kinetics. This behavior suggests that BPD addition alters the formation of $S_3^{\bullet-}$.

3.3 *In situ* UV-Vis characterization of the electrolyte with the BPD additive

Figure 5. *In situ* UV-Vis absorption spectra of the (A) basic electrolyte and (B) the basic electrolyte with 0.04 mM BPD addition at representative potentials during the discharge process in. The inserts (A', B') show the absorption band b at 614 nm.

We next use *in situ* UV-Vis spectroscopy to study the effect of BPD on the dissolution of sulfur species in the bulk electrolyte. Fig. 5 shows *in situ* UV-Vis absorption spectra of the electrolyte at representative potentials obtained during the discharge process in the (A) basic electrolyte and (B) the basic electrolyte with 0.04 mM BPD additive. In the UV-Vis experiment, the discharge process is stopped at 2.0 V to avoid cathode instability that occurs with deeper discharge.[9] Furthermore, the concentration of BPD was decreased for the UV-vis measurement relative to the Raman measurements due to the intense BPD-related band at 290 nm, as shown in Fig. S6. The broad absorption band of BPD at 290 nm overlaps with the S_2^{2-} and S_8 band

in the region of 250-300 nm.[13, 56] Thus we focus on the sulfur species in the region of 350-800 nm. Table 2 shows the experimental UV-Vis absorption bands and assignments for the sulfur species. [13, 56-59]

Fig. 5A shows that *in-situ* UV-Vis absorption spectra of the basic electrolyte does not exhibit any absorption bands prior to the discharge process. (~2.7 V) The intensity of absorption band a at 420 nm and band b (shown in the inset) at 614 nm grows at 2.4 V and reach a maximum at 2.2 V, suggesting that more polysulfide species dissolve into the electrolyte from the sulfur-carbon cathode during discharge. Band a is assigned to S_4^{2-} and band b is attributed to $S_3^{\bullet-}$. [13, 56-59]

Fig. 5B shows *in-situ* UV-Vis absorption spectra of electrolyte containing 0.04 mM BPD at representative potentials during the discharge process. The UV-Vis spectrum exhibits similarities with that measured absent BPD before discharge. During the discharge process, the intensities of band associated with polysulfide species such as S_4^{2-} and $S_3^{\bullet-}$ with BPD addition (bands a and b) are much weaker than the corresponding bands in the basic electrolyte, suggesting that the concentration of polysulfide species dissolved into the electrolyte is lower. For example, the intensity of absorption band a associated with S_4^{2-} is 80% weaker than the corresponding band in the basic electrolyte.

Peak label	Peak position (nm)	Assignment	References
a	420	S_4^{2-}	13, 56, 57, 58
b	614	$S_3^{\bullet-}$	13, 56, 59

Table 2. Experimental absorption bands and assignments for sulfur species.

3.4 Mass spectrometry of electrolyte solutions

Figure 6. (A) (-)ESI Mass Spectrum of a solution of 5 mM “Li₂S₄” prepared by reacting 1.875 mM S₈ and 5mM Li₂S in TEGDME/DOL and (B) (-)ESI mass spectrum of the same 5 mM “Li₂S₄” solution with 5 mM BPD. The solution was diluted 1000 times in ethanol before the ESI/MS measurement.

In order to further identify sulfur species present, ESI-MS was used to study the electrolyte with and without BPD addition. ESI-MS can directly observe sulfur species such as S₃⁻.^[60] However, the high concentration of a Li salt such as LiTFSI hinders polysulfide ionization and makes detection of polysulfides complicated.^[60] In

our case formation of TFSI⁻ with m/z ratio of 279.182 dominates the ionization process. Thus we compare electrolyte solutions with and without BPD in the absence of Li salt. Fig. 6 shows the ESI-MS of 5mM Li₂S₄ solution prepared by reacting 1.875 mM S₈ and 5mM Li₂S in TEGDME/DOL (A) without and (B) with 5 mM BPD. Absent BPD (Fig. 6A), the mass spectrum reveals peaks at m/z = 95.915 and 127.887 corresponding to S₃⁻ and S₄⁻, respectively. With BPD addition (Fig. 6B), the spectrum shows ion peaks at m/z = 217.015, 248.987, 280.959, 312.930, and 344.903 along with background peaks marked with a star (*). Peaks at m/z = 95.915 and 127.887 corresponding to the S₃⁻ and S₄⁻ are either not observed, or only observed with very high magnification depending on BPD concentration. The calculated exact m/z values of BPD and BPD-short chain polysulfides correspond within error to peaks found in the mass spectrum. The formation of BPD anion (calc. m/z=217.015), (BPD)S⁻ (m/z=248.986), (BPD)S₂⁻ (m/z=280.959), (BPD)S₃⁻ (m/z=312.930) and (BPD)S₄⁻ (m/z=344.903) suggests that short chain polysulfides form stable complexes with BPD. These stable complexes inhibit the appearance of free S₃⁻ or S₄⁻ in the electrolyte solution.

3.5 SEM characterization of the Li anode with the BPD additive

Figure 7. SEM images of the Li anodes cycled in the (A-D) basic electrolyte (1M LiTFSI and TEGDME/DOL) and (E-H) with 25mM BPD after 3, 50, and 100 cycles. The cells were cycled between 3.2 V and 1.5 V at 0.1 C and the Li was extracted after the charge cycle.

Although the BPD additive affects the S reduction process, it could also have an effect on processes at the Li anode that could affect the battery performance. We investigated the surface morphology of the Li anode in the Li-S battery to evaluate the effect of BPD on the Li anode. Fig. 7 shows SEM images obtained from the Li anodes cycled in the (A-D) basic electrolyte and (E-H) the basic electrolyte with 25mM BPD after charge for 3 , 50 , and 100 cycles following cycling between 3.2 V and 1.5 V. After 3 cycles, the image reveals rough features which decorate the smooth Li surface (Fig. 7A). These features are associated with formation of SEI film and dendritic growth of Li following Li stripping and deposition during cycling, as reported previously.[61] Fig. 7B-C shows that the dendritic SEI/Li entangled phase covers the Li surface. Fig. 7D shows the cross section view of Li anode after 100 cycles. The

SEM image reveals that the thickness of the SEI/Li entangled interface is $70\text{ }\mu\text{m} \pm 10\text{ }\mu\text{m}$ which is in good agreement with previous studies.[62]

Fig. 7E shows the Li surface after 3 cycles in the presence of 25mM BPD. The surface is noticeably smoother relative to the corresponding surface formed in the electrolyte without the additive in Fig. 7A. A few pits are decorated with bright areas associated with regions of lower electronic conductivity which are tentatively associated with the resistive SEI film. Fig. 7F-G shows the Li surface presents as a smooth film with cracks. The smooth film is associated with the SEI/Li entangled phase. The cross section view of the Li anode in Fig. 7H shows that the thickness of SEI/Li entangled phase obtained in the presence of BPD additive is $80\text{ }\mu\text{m} \pm 15\text{ }\mu\text{m}$. BPD addition smooths the SEI/Li entangled phases on the Li anode, an effect similar to that found with other electrolyte additives in Li-S batteries.[40, 41, 63]

3.6 The effect of different thiol-based additives on capacity fade

Figure 8. The cycling performance including the (A) discharge capacity and (B) Coulombic efficiency of the sulfur-carbon cathode with different thiol-based additives at the rate of 0.1C (based on the weight of sulfur-carbon cathode). The additives are biphenyl-4,4'-dithiol (BPD), benzene-1,4-dithiol (BD), thiophenol (TP), 1,4-bis(4-mercaptophenyl)benzene (MPB) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP).

We next investigated other thiol-based molecules as additives to evaluate the effect of different functionalities on Li-S battery performance. Fig. 8 shows the battery performance with different thiol-based additives such as thiophenol (TP), benzene-1,4-dithiol (BD), biphenyl-4,4'-dithiol (BPD), 1,4-bis(4-mercaptophenyl)benzene (MPB) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) charged and discharged at a C rate of 0.1 C between 3.2 V and 1.8 V. The capacity of the Li-S battery with the 25 mM BPD addition is ~650 mAh/g after 100 cycles and falls only to ~575 mAh/g after 300 cycles. With the addition of 25 mM TP, 25 mM BD, or 1mM MPB, the Li-S capacity reaches ~500 mAh/g after 100 cycles. The capacity of Li-S battery with 25 mM PETMP addition results in even worse capacity fade during cycling and reaches ~100

mAh/g after 100 cycles.

We next discuss possible reasons for the different behavior of these thiol-based additives. PETMP is known to undergo a polymerization process which apparently leads to irreversibly capacity fade.[64] MPB exhibits low solubility in the TEGDME/DOL electrolyte and its effect is correspondingly small. While TP, BP, and BPD are all soluble in the electrolyte, (-)ESI-MS results summarized in Table 3 show that BPD forms more complexes with short chain polysulfides relative to the other two additives. There are many possible origins of the increased efficacy of BPD relative to these other two additives. First, BPD- S_3^- complex formation might be energetically favored relative to S_3^- complexation with the other additives. However, DFT calculations obtained by using the Spartan program did not show meaningful differences (data not shown). We note that BPD by itself is less soluble in DOL/TEGDME relative to the other two additives, and suggest that the BPD- S_3^- complex might more readily stay associated with the Li-S composite electrode surface relative to TP and BP.

Additives	Complexes
5mM Biphenyl dithiol (BPD)	(BPD)S, (BPD)S ₂ , (BPD)S ₃ , (BPD)S ₄
5mM Benzene dithiol (BD)	(BD)S
5mM Thiophenol (TP)	(TP)S

Table 3. Results from ESI-MS obtained from a mixture containing 5mM thiol-based additives and 5mM Li₂S₄ in TEGDME/DOL. The solution was diluted 1000 times in ethanol.

4. Conclusions:

The use of thiol-based electrolyte additives like BPD enhances the capacity of Li-S batteries. The formation of BPD-short chain polysulfide (S_n^{2-} , $1 \leq n \leq 4$) complexes inhibits the formation of isolated short chain polysulfides such as $S_3^{\cdot -}$ and changes the kinetics of formation of short chain polysulfides. The BPD-polysulfide complexes formed during discharge decreases polysulfide dissolution which in turn yields better capacity retention. Additionally, a smooth SEI/Li entangled phase on the Li anode is found in the presence of BPD after cycling. Other thiols, however, exhibit varying degrees of capacity retention, most likely due to their different solubilities. BPD is found to be the best performing electrolyte additive and the reactivity of the BPD

toward soluble polysulfide intermediates and the resulting change in S reduction kinetics shows that the S reduction process can be tailored to yield beneficial cycling behavior by tailoring reactive electrolyte additives.

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Notes

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