

TUNING ELECTROLYTE COMPOSITION FOR ENHANCED PERFORMANCE OF LITHIUM-SULFUR BATTERIES

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Presented to
The Academic Faculty

by

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Tuning Electrolyte Composition for Enhanced Performance of Lithium-Sulfur Batteries

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To my cat Luna

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LIST OF SYMBOLS AND ABBREVIATIONS

CEI	Cathode Electrolyte Interface
C-RATE	Charge rate
CV	Cyclic Voltammetry
DIOX	1, 3 Dioxolane
DME	1,2 Dimethoxyethane
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
HFE	Highly Fluorinated Ether (1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropylether unless otherwise noted)
KB	Ketjen Black
LiNO ₃	Lithium Nitrate
LiPF ₆	Lithium hexafluorophosphate
Li-S	Lithium-sulfur
LiSBs	Lithium-sulfur batteries
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
PAA	Polyacrylic Acid
PS	Polysulfide(s)
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
SL	Sulfolane
XPS	X-ray Photoelectron Spectroscopy

SUMMARY

As the world faces a growing need to electrify and reduce carbon emissions, batteries offer much needed energy storage for electric cars, mobile devices, and the grid. For transportation and mobile devices, lightweight batteries are key, while non-toxicity is important for low environmental impact. The lithium-sulfur (Li-S) battery combines low weight, non-toxicity, low cost, and high capacity. With one of the highest theoretical capacities (1675 mAh/g-s) of any conversion-type cathode, the pursuit of low cost, long-lasting Li-S batteries is a global research focus. However, it is difficult to achieve the promised high theoretical capacity because of the polysulfide dissolution in the electrolyte and subsequent reaction at the Li anode surface, depleting the active material in the cathode. Current electrolytes are not effective at managing the polysulfide dissolution and have the negative side effects of high viscosity and high cost.

In this work, low concentration electrolytes were investigated as a possible solution to these challenges. Low concentration electrolytes offer low viscosities, which ease access to sulfur in tortuous cathodes. First, the low concentration regime ($<0.2\text{M}$) was applied to traditional electrolyte salts and solvents: LiTFSI, dimethoxyethane and, dioxolane. The low viscosity and enhanced wettability of such an electrolyte system enabled strong cycling performance as well as better access to active sulfur materials in high loading cathodes.

In order to further limit polysulfide dissolution in Li-S cells, an electrolyte solvent with very low polysulfide solubility (1,1,2,2-Tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (HFE)) was explored. Sulfolane was used as a co-solvent to provide Li^+ solvation and the sulfolane/HFE ratio was systematically investigated. By gradually

altering the solvent ratio, we discovered a change in discharge behavior as the proportion of HFE increases. The analysis of experimental data suggests such a system to enable a dramatic suppression of the long-chain polysulfide formation shifting the discharge to a quasi-solid-state mechanism with a major reduction of the cathode dissolution during the first cycle.

This work demonstrates promising performance characteristics of low concentration electrolytes for S cathodes and provides new scientific insights explaining such favorable behavior features, thus showing multiple avenues for future practical applications. When paired with high loading cathodes and polysulfide-suppressing solvents, low concentration electrolytes may enable lightweight batteries with high mass loadings.

CHAPTER 1. INTRODUCTION

1.1 Introduction to Lithium-Sulfur Batteries

The demand for batteries in modern society is growing rapidly.¹ Smartphone ownership in the United States has grown from 35% in 2011 to 81% in 2019.² Similarly, battery electric vehicles have grown to 1.3% of vehicle sales, with signs of increasing demand.³ This demand comes from individual choices and government regulations aiming to decrease fossil fuel consumption and abate the negative effects of climate change. Secondary (rechargeable) battery demand exists primarily in three categories: stationary energy storage, transportation, and consumer electronics. Each category comes with its own technical demands and challenges; however, within transportation there is a very strong need for lower weight, higher energy, and lower cost batteries. While niche applications may require specialty chemistries and designs, those three general requirements can be met by the lithium-sulfur battery.

A Li-S battery (LiSB) is composed of the standard battery components (discussed in detail below): a cathode, anode, electrolyte, and separator. Unlike most commercial intercalation-type Li-ion batteries, Li-S batteries contain a conversion-type cathode. In a conversion type cathode, the active material (S – charged state or Li_2S – discharged state) changes its chemical bonding, physical properties, volume, and crystal structure during the battery charge and discharge.

Intercalation-type Li-ion battery cathodes are most commonly composed of lithium-metal-oxide particles, where the metal is typically cobalt (Co), manganese (Mn), nickel

(Ni), or a combination of the three: lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium nickel manganese oxide (LMO) and lithium nickel cobalt aluminum oxide (NCA).⁴ However, these heavy metals (particularly Co and Ni) are often mined in unsafe and environmentally unfriendly conditions.⁵ This in addition to the weight of the metals themselves being a negative factor in their use in transportation or mobile electronics. In contrast, many conversion-type cathodes are made of more abundant, lower cost, and environmentally friendlier elements, including S.

While there are many other types of conversion cathodes, the sulfur cathode offers the highest theoretical capacity. Figure 1⁴ presents a comparison of the theoretical performance of the S with other chalcogenide-based cathodes. A LiSB can be constructed either in the charged state with a S cathode or in the discharged state with a Li₂S cathode. Based on the weight difference these two starting materials have different theoretical capacities. Eq. 2 gives the calculation of theoretical capacity, where F is Faraday's constant, n is the number of electrons involved in the reaction, 3.6 is a conversion factor, and M is the molecular weight. Eq. 2 evaluates the theoretical capacity for the S cathode.

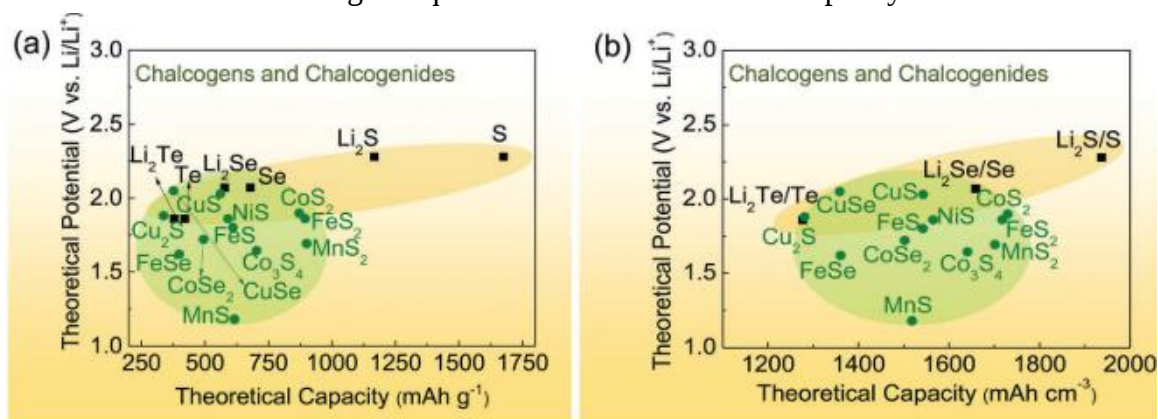


Figure 1. Comparison of theoretical voltage and capacities of conversion-type cathodes: (a) gravimetric (b) volumetric. Reproduced with permission from the Royal Society of Chemistry.

$$\text{Theoretical Capacity of } X = \frac{F * n}{3.6 * M} \quad (1)$$

$$\text{Theoretical Capacity of } S = \frac{96485 * 2}{3.6 * 32.06} = 1675 \text{ mAh/g} \quad (2)$$

Seeing that LiSBs offer such a high theoretical capacity and low weight, they are particularly suited to applications where weight is more important than size, such as electric airplanes, trucks, and busses.⁶ In 2017, our group evaluated the energy density of Li₂S, commercial, and several other conversion-type cathodes. This calculation was versus the anode material (graphite, silicon, and lithium) and was done for a calculating unit of a given thickness of each cell component. As Figure 2⁴ shows, the Li₂S cathode paired with a Li metal anode performs better than the commercial cathodes and better than or on par with the other conversion-type cathodes.

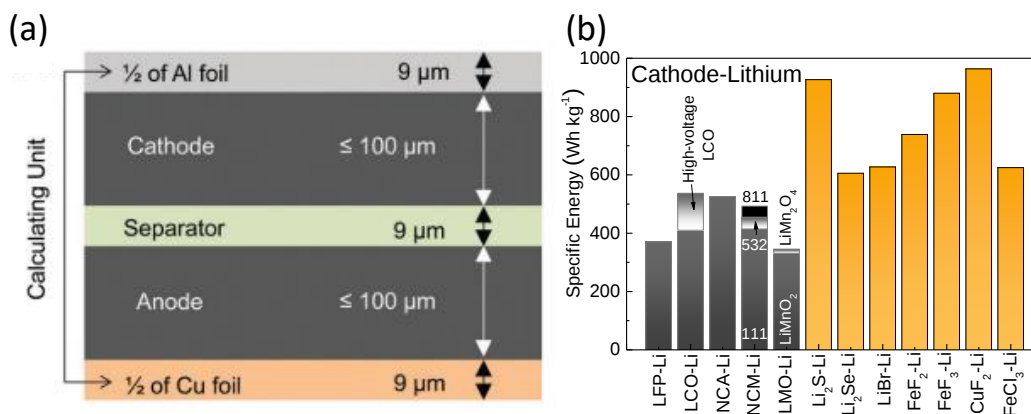


Figure 2. Calculation of the energy densities of various cathode-anode combinations showing: (a) the unit stack used for calculation, (b) cell level energy densities for different cathodes matched with a lithium anode. Reproduced with permission from the Royal Society of Chemistry.

The following sections will describe in more detail the reactions within the LiSB system, the cell components, the cathode microstructure, and the remaining challenges for LiSBs. LiSBs are a promising chemistry; however, there is a considerable amount of

development left within their fundamental operation before they can become commercially viable.

1.1.1 Reaction Mechanism

The LiSB has a complicated reaction mechanism with many intermediate reaction steps. There is also considerable controversy of the specifics of the species produced during discharge and their interactions. Fundamentally, the LiSB discharge follows the overall reaction in Eq. 3. However, there are many intermediate species involved in this reaction in order to transform the S_8 ring into the small Li_2S molecule. These intermediate species are called polysulfides (PS) and they range from Li_2S_8 to Li_2S_2 . The discharge capacity commonly comes from the creation first of long chain polysulfides, then of their reduction to short-chain polysulfides, and finally their reduction to Li_2S . This mechanism is laid out graphically in Figure 3 and in Eqs. 4-8. These PS species are problematic in that they can dissolve into electrolyte and diffuse over to the anode. Once the PS made contact with the Li metal, they are reduced, limiting available active material. This is known as the PS shuttle effect and will be discussed in considerably more detail in a later section.

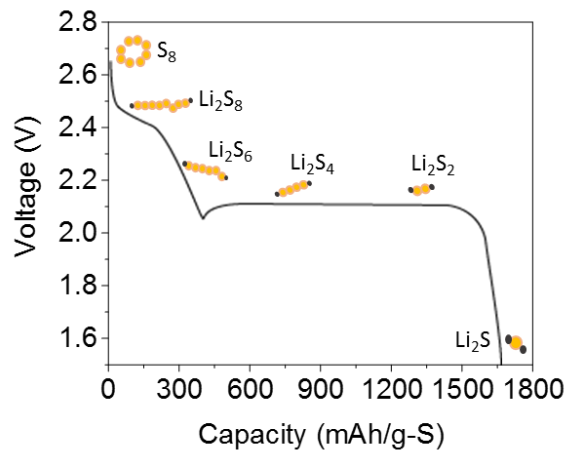
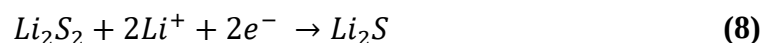
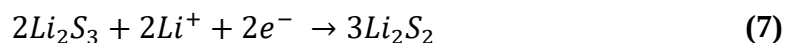
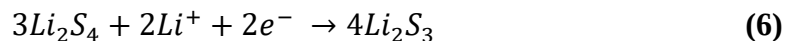
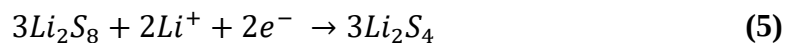


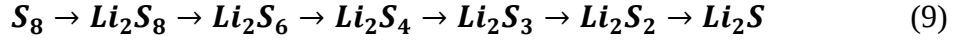
Figure 3. Schematic of discharge behavior of a standard LiSB.



Overall, these reaction steps are separated into a high voltage ($\sim 2.4V$) and low voltage ($\sim 2.1V$) plateau. The reduction of long-chain polysulfides occurs in the upper plateau and the reduction of short chains occurs in the lower plateau. However, the scheme presented above is just one interpretation of the sequence of reaction steps.⁷ In the Li-S electrochemical system, the reactions which occur are a mix of dissolution, dissociation/association, electrochemical, and disproportionation. The stability of the intermediates is dependent on the electrolyte chosen, cycling rate, and cycling history.⁸ The solubility of intermediate species is sensitive to the polarity of the solvent system, the salt concentration, and the donor-ability of the solvents.⁹

Many authors have proposed alternative reaction sequences, varying interpretations on which species are stable at various depths of discharge, and what the true end species is.⁸⁻¹³ The scheme presented above is just one interpretation. For example, Assary et al present a similar reaction sequence, given in Eqn. 9.¹⁰ There is still considerable room for

debate, especially considering the exact reaction intermediates are sensitive to electrolyte and rate design.



Nevertheless, there is relative consensus that reduction of long-chain PS contributes to the capacity of the high voltage plateau and the reduction of short-chain PS contributes to the capacity at the low voltage plateau. The reaction finishes with the deposition of solid and insulating Li_2S on the surface of the cathode, increasing resistance and blocking the interfaces from additional reactants.

1.1.1.1 Quasi-Solid State Mechanism and Non-Traditional Discharge Behavior

The reaction mechanism described above is the traditional discharge reaction sequence for liquid electrolytes. However, there is another reaction mechanism that is prevalent in carbonate-based electrolytes and some ionic liquids. This reaction follows a quasi-solid-state mechanism and exhibits only one discharge plateau (Figure 4). The single

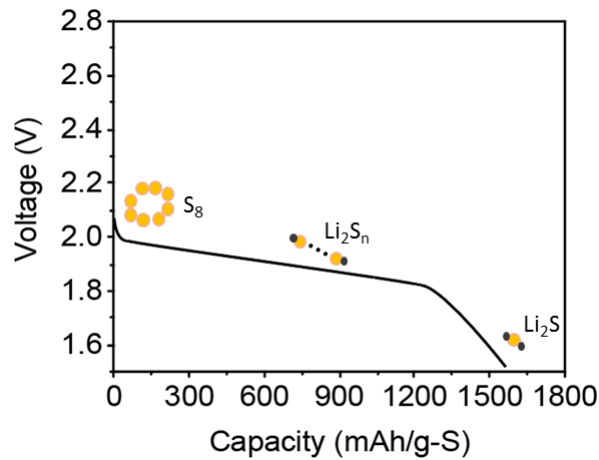


Figure 4. Schematic of quasi-solid state single plateau reaction mechanism.

plateau occurs around 2V and follows a similar curve as in solid-state LiSBs.¹⁴ There have been many explanations for why this single plateau behaviour occurs in liquid-electrolyte LiSBs. The three dominant theories are: (1) confinement of polysulfides in pores so small that they cannot dissolve out, (2) sulfur binding with the carbon additive causing an energy barrier, and (3) the growth of an anode solid electrolyte interphase (SEI) layer and a cathode solid electrolyte interphase (CEI) layer that limits the movement of polysulfides since only Li^+ is able to travel through.¹⁵⁻¹⁸

The quasi-solid-state mechanism is frequently seen in carbonate-based electrolytes. Often the single discharge plateau occurs at or below 2V, which is lower than the 2.1-2.2V range where the low voltage plateau in the two-plateau mechanism typically occurs. Wang et al. theorized that the strong bond S forms with C or O may require additional energy to break, giving an energy barrier that causes polarization and depresses the plateau voltage.¹⁸ Zhang et al. proposed the low voltage comes from the affinity between S and the acetylene black additive causes similarly strong binding and energy barrier.¹⁹ Peng et al. argued for the nano-confinement of sulfur explanation. They used a LiTFSI/DME/DIOX electrolyte and showed evidence of chemical bonding between the carbon and sulfur.²⁰ The carbon used in their study which exhibited the single plateau had micropores that were 5.8-6.8Å in dimension, which they argue is so small as to confine small sulfur molecules.

Some authors disagree with the validity of the micropore and bonding explanations, arguing the effect truly comes from the electrolyte.²¹ Markevich et al strongly argued in favour of the CEI/SEI mechanism, referencing numerous studies where the micropore mechanism was debunked.¹⁴ They also argued that such quasi-solid state reactions have been seen in many systems with varying sulfur infiltration methods, but that

it does only seem to come up in ionic liquids and carbonate-based electrolytes, not the traditional ether-based ones. In the work presented here, the electrode will be held constant, and the electrolyte will be varied to avoid confounding variables.

In one study Markevich et al. took electrodes cycled in an ionic liquid (IL) electrolyte that exhibited a single voltage plateau and cycled them in carbonate-based electrolytes and ether-based electrolytes. In the carbonate case, the single discharge plateau mechanism was maintained. In the DIOX/DME ether-based case, the cell regained its two-plateau discharge characteristic. The authors attributed this to the dissolution of the CEI formed in the IL in the ether-based solvents, although the impact of the bulk electrolyte on the interaction with the S-based cathode cannot be excluded.¹⁶ XPS studies further confirmed that CEI formation induces the quasi-solid state mechanism. For example, Rosenman et al. used a carbonate based electrolyte (LiPF_6 in fluorethylene carbonate and dimethyl carbonate) which induced a quasi-solid state mechanism.²² The study confirmed the presence of LiF and compounds which could be part of polymeric species (C-O, C=O, C-F) produced from the reduction of the solvent. In additional two papers from the Aurbach group, Markevich et al. attributed the single discharge plateau to the CEI formed during the first discharge resulting from the electrolyte composition and low first discharge voltage.^{16, 17} They claimed that the CEI forced S to react with Li in the pores absent from the solvent.

The discussion of this quasi-solid-state mechanism reveals that the electrolyte may have a significant impact on the discharge behavior and the shape of the discharge curve (number of plateaus and reduction voltages). The creation and dissolution of polysulfide intermediates can be suppressed. Based on activation barriers, the voltages at which these

species appear can also be reduced. Choi et al. saw the conventional two plateaus, but with the second plateau at a depressed voltage of 1.9V.²³ In another paper from the same group using the same solvents,²⁴ the authors attributed the suppressed voltage to low electrolyte volume, which could increase polarization.

Interestingly, some groups have observed three or even four plateaus in a Li-S discharge curve as the voltage at which each intermediate reaction occurs shifts differently. For example, Yu et al. demonstrated an all solid state LiSB with three plateau regions and reduction peaks at 2.42, 2.1, and 1.95V.²⁵ They proposed that the low voltage plateau comes from the further reduction of Li_2S_2 to Li_2S , which does not always occur in liquid electrolyte LiSBs. Throughout cycling, the middle voltage plateau shrinks, though the authors do not provide an explanation for this phenomenon. Jeong et al observed four plateaus in a LiSB with a PEO polymer electrolyte.²⁶ They proposed that essentially multiple of the intermediate reaction steps occur at separate plateaus. They attributed this effect to the better ionic conductivity of the PEO electrolyte which allows Li^+ to reach S and LiS_n . In another PEO-based solid polymer electrolyte, Zhang et al. attributed the single plateau observed to reversible reaction intermediates.

In conclusion of the literature review on the LiSB reaction mechanism, the discharge behavior in a LiSB is not along one conclusive path. It is heavily dependent on the electrolyte used and the CEI/SEI formed based on both that electrolyte, type of S-based cathode, and the cycling history. There is the traditional two plateau discharge behavior seen in the standard ether-based electrolytes and a range of numbers of plateaus and plateau voltages seen in alternative electrolytes. The specific requirements for a LiSB electrolyte and a review of LiSB electrolyte literature will elaborate on this point in later sections.

1.2 Background on Li-S Battery Components

This section provides a review of the components within the LiSB, including the anode, cathode, separator, current collector, and coin cell. Figure 5 illustrates the assembly of the coin cell parts and images of their real components. For further information, Urbonaite et al. and Manthiram et al. provide excellent reviews on this subject.^{27, 28} This section acts as a review of the necessary properties of each component and common architectures. The rationale for much of LiSB component design is heavily influenced by efforts to mitigate the PS shuttle. Adaptations to each component for PS shuttle mitigation are discussed in section 1.3.

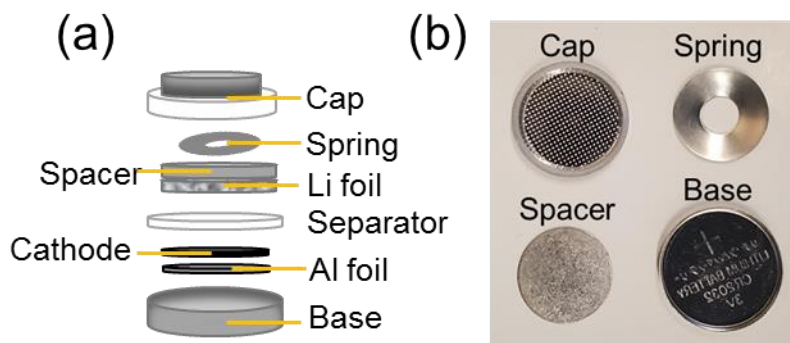


Figure 5. (a) Schematic of a LiSB coin cell construction and (b) images of components.

1.2.1 Li-Metal Anode

Most LiSBs employ a Li-metal anode because it affords high capacity, excess Li, and low weight. Having Li excess is beneficial for isolating the effects of changes made to other cell components since it eliminates issues of insufficient Li. While there are cost and weight limitations to the Li metal anode approach at the commercial level, it is the most

suitable material for the research level. Generally, when studying the anode, the interest lies in the CEI/SEI formed and the surface reactivity with polysulfides. Methods to tailor the CEI will be discussed in the electrolytes section below as the effort largely involves additives to electrolyte or solvent changes, not a modification to the initial anode itself.²⁹ Ultimately, the protection of the Li is vital to limit reduction of PS and runaway of the PS shuttle.

Tao et al. reviewed strategies to improve the LiSB anode and also concluded that the surface stability is key to proper LiSB function.³⁰ However, they also proposed that this could better be achieved through modifications to other cell components (electrolyte, separator, interlayer) rather than to the protection of Li metal anode ex-situ. These improvements will be further reviewed when discussing the PS shuttle in the next section.

1.2.2 Cathode

The LiSB cathode can be based on either S or Li₂S. Sulfur is an advantageous starting material because it is not air sensitive and therefore simplifies processing as cathodes can be produced outside the glovebox. Conversely, Li₂S has a much higher melting point (>900°C vs 116°C for sulfur), opening up high temperature processing routes, such as chemical vapor deposition (CVD) techniques, that can contribute to attaining highly beneficial properties, such as formation of protective surface layers.^{31, 32} S and Li₂S are both insulating, meaning strategies of coatings or conductive additives are necessary to give the cathode adequate electrical conductivity regardless of the starting material. During discharge there is a considerable volume expansion when S is lithiated. When using a Li₂S cathode, that volume expansion is already built in and there is less

mechanical stress on the carbon encapsulation. The focus here will be on S-based cathodes as they are the material used in the experimental section. S-based cathodes were chosen because of their facile processing and ease of reproducibility. Figure 6 illustrates the microstructure within a cathode. The cathode is composed of S, typically encapsulated in a conductive carbon particle, mixed with an additional conductive additive and a polymer binder. As in some other studies, the S is simply mixed in with additional conductive additive and no additional shell is included.³³

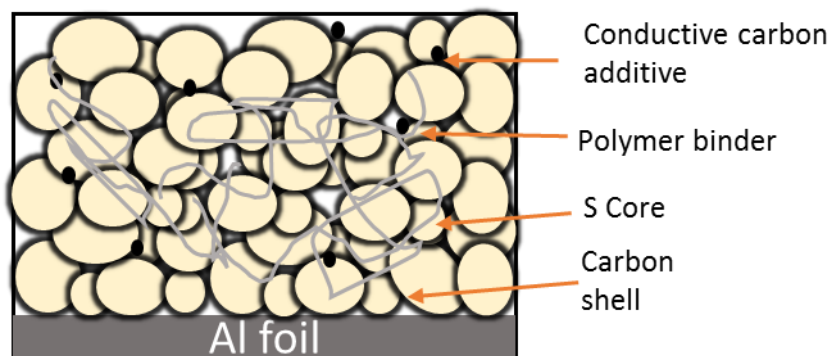


Figure 6. Illustration of cathode components in a S-based cathode.

Typically, S is melt infiltrated into the carbon substrate to a desired S/C ratio. The carbon particles and substrates that have been explored are extensive and include, but are not limited to, acetylene black,¹⁹ Ketjen Black,^{34, 35} carbon nanotubes,³⁶ activated carbon,³⁷ CMK-3,³⁸ carbon cloths,^{39, 40} graphene/reduced graphene oxide,⁴¹ and various other carbon nanoparticles.⁴²⁻⁴⁴ Wang et al.'s review provides excellent depth on this topic.⁴⁵ In melt infiltration, the mixture of S and C sits at 157°C, the lowest viscosity point for S,⁴⁶ for 12 hours followed by a “burn-off” step at 250°C to remove extra S from the outside of the carbon particles and achieve the desired S/C ratio. This process is depicted in Figure 7.

There are alternatives where the S is bonded to or infiltrated in a polymer; however, those cathodes architectures are outside the scope of this work.

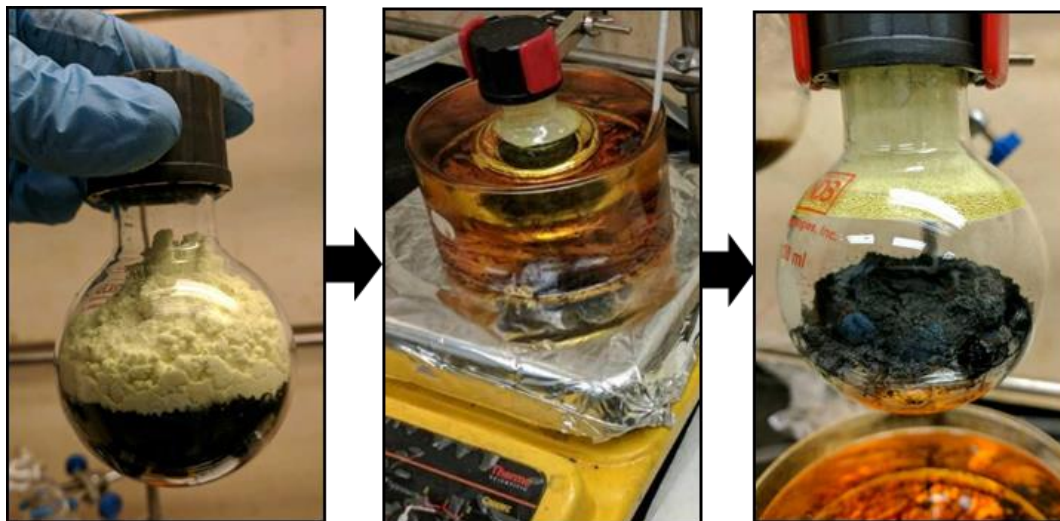


Figure 7. Steps in sulfur infiltration into ketjen black. (left) mix of S and C, (middle) melting at high temperature, and (right) sulfur inside carbon particles.

This initial layer of carbon or carbon inclusion provides conductivity and a physical barrier to PS diffusion but offers no additional functionality. Many authors have built on this core-shell particle approach and have added additional shells to the sulfur or S/C composite.³⁷ Often these shells are metal oxides which help adsorb polysulfides. More details on this topic will be given in a later section on mitigating the PS shuttle.

Once the S is infiltrated into or mixed with the carbon and coatings or other active architectures are added, additional conductive additives are needed to enhance conductivity. Additive options range from conductive carbon nanoparticles to carbon

nanotubes. Zhao et al. compared Super P and carbon nanotubes as additives and found that CNTs gave a higher initial capacity, but decayed more over 20 cycles.³³

In the LiSB cathode, the binder glues the disparate S/C particles and additives together. In order to produce a stable slurry that casts, dries, and punches properly, the molecular weight of the binder should also be considered when optimizing a cathode slurry. Binders typically comprise from 10% up to 20% of the cathode weight. Binders also provide mechanical stability to the cathode as it undergoes volume contraction and expansion throughout charge and discharge. The binder further helps attach the cathode components to the current collector and keeps the cathode particles in close contact, both of which enhance electrical conductivity. While mechanical strength is key, so is stability under severe electrochemical, and also potentially thermal, conditions.^{47, 48}

There are many variations on the polymer binder, some multifunctional, but polyacrylic acid (PAA) and its salts, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polyvinylpyrrolidone (PVP) are some of the more common in literature.⁴⁸ These conventional polymers are what is used if the binder is not the subject of study. Until a few years ago these linear binders were the bulk of binders used in and investigated for LiSBs. These polymers have polar groups which help the various cathode components and current collector adhere together while Van der Waals forces add strength and elasticity.⁴⁷ Nevertheless, these linear binders may be exposed to significant and repeated mechanical stress with the cathode volume changes and may not necessarily be the best solution for all S cathodes, particularly if such volume changes are not compensated at the S-composite particle level.

In the last several years it has become popular to add additional functionality to binders, primarily to help adsorb PS. Schneider et al. compared Nafion, PAN, and PTFE as binders.⁴⁹ While PTFE had the best performance of the three when used as a conventional binder, the authors found that coating an additional Nafion layer on top of the cathode significantly improved performance. Liu recently reviewed functional binders in Li-S batteries.⁵⁰ They emphasized the need for binders to not contribute significantly to the weight, cost, and environmental impact of a LiSB, including the solvent required to solvate the binder and cast the cathode slurry. Binders are not the main focus of this study and an extensive review of them is outside the scope of this work, therefore Liu's review is given as further reference.

The cathode described thus far includes S, a conductive additive, a binder, and possibly additional PS-absorbing or adsorbing additives. However, these cathodes often provide low S loadings. High loading cathodes improve specific energy, pack more active material into a cell, and minimize the number of cells needed in a pack. Unfortunately, the slurry method often results in cracks when it dries if it is cast too thick. In addition, it is difficult to access all the S in a high loading cathode within a tortuous electrode and high loading cathodes can suffer from low capacity.⁵¹ Producing high loading cathodes is very important to the future success of LiSBs. What follows is an overview of strategies to create high-loading cathodes.

The strategy of binder-free, or freestanding cathodes, has become popular enough to merit reviews of their own.^{28, 52} In a freestanding cathode, the S is melt or vapor infiltrated in to a carbon cloth or fabric. This method allows for easy tailoring of the S loading, creation of a high-loading cathode, and the removal of the excess weight of binders

and additives. Elazari et al., Miao et al., and Zhao et al. all employed this method for high capacity, high loading cathodes.^{39, 40, 53} The experimental work presented in later chapters in this thesis build on this method of producing high-loading cathodes. Aerogels are another example of a freestanding 3D cathode architecture.⁵⁴

Other methods of producing high loading cathodes include near-excessive infiltration of S into the carbon host. It is advantageous to leave extra porous space in a hollow carbon particle when infiltrating S to allow space for volume expansion during lithiation. However, higher S loadings can be achieved by fully filling the carbon's pores. Further efforts towards high loading cathodes focus on increasing the complexity of the cathode architecture and adding hierarchy to the composite, which Peng et al. argued is the future of high loading S cathodes.^{52, 37}

Another approach is the assembly of carbon nanoparticles into micron-seized agglomerates. This can be done via emulsion polymerization,⁵⁵ spray drying,⁵⁶ and templating,⁵⁷ though that list is not exhaustive. Spray drying in particular is already an industrial process in other industries; however, it can be a difficult process to optimize with new materials.

1.2.3 Separator

The purpose of the separator is to electrically insulate the anode and cathode from each other. This ensures that the electrons released in the half-cell reactions go out to the external circuit and do not short through the cell. A good separator needs to be thin and lightweight to not add unnecessary bulk to the cell and to ease diffusion across the cell. The separator must have good wettability with the electrolyte and be porous enough to

allow diffusion across it, but not so porous it is no longer a good insulating layer. Lastly, the separator must be mechanically, thermally, and electrochemically stable. It cannot break down during testing, cannot decompose, cannot be punctured by a Li dendrite, and cannot lose mechanical integrity. Typical separators are 25 μ m thick and are made of a polypropylene membrane. Common examples are Celgard 2400 and 2500 (Figure 8⁵⁸) because of their excellent wettability, non-reactivity, and light weight. Glass fiber separators are also used in LiSBs, but they are less common. Modifications to the separator are made to address the PS shuttle and therefore will be discussed in more depth later in that section.

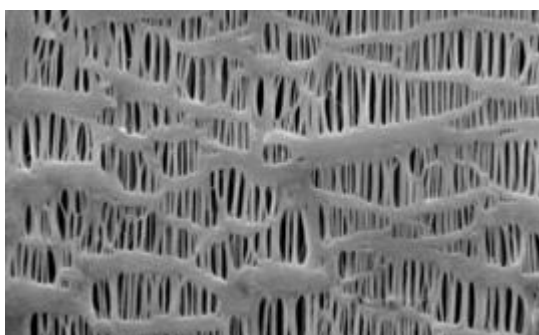


Figure 8. Image of Celgard 2500 microstructure from company data sheet.

1.2.4 Electrolyte

The electrolyte is responsible for transporting species between the anode and cathode, helping form interface layers, and wetting the cathode particles. Ideal electrolytes must balance a relatively low viscosity and a sufficiently high dielectric constant (to dissociate the Li salt) with relatively small Li⁺ solvation energy to enable high Li⁺ ion mobility and conductivity. Additionally, electrolytes should ideally minimize

flammability, offer small solvent vaporization at moderate temperatures and mitigate thermal runaway. For the LiSB in particular, a good electrolyte needs a low donor-ability to limit dissolution of PS, high chemical stability against the PS species, stability with respect to the Li metal so only the desired SEI is formed, and adequate solubility with the salt.⁵⁹ The electrolyte ideally needs to only dissolve the Li salt, while not promoting the PS dissolution. In addition, all of the electrolyte components must be stable in the voltage window for testing. Therefore, a discussion of the electrolyte is by necessity a discussion of its components: the solvent(s), the salt, and the additive(s). Each component impacts the interface layers formed on the anode and cathode. As this discussion overlaps considerably with the next section on the PS shuttle and mitigation efforts, an overview of common components and properties will be given here and a deeper discussion of their impact on the PS shuttle will be given in section 1.3.

1.2.4.1 Solvent

The electrolyte solvent exists to conduct Li^+ across the separator to the cathode while having limited solubility for PS. Part of the function of the solvent is to partially decompose on the anode and cathode, forming an SEI and CEI, respectively. These layers offer protection from the PS shuttle, Li dendrite formation, and loss of active material. Such solvent decomposition is not only a factor of the solvent itself, but also of cycling history, viscosity, and salt interaction.⁶⁰ The solvents can decompose and effectively polymerize on the interface, contributing to mechanical stability.⁶¹

While carbonate-based solvents are the most common in Li-ion batteries, they are generally not compatible with most sulfur cathodes.⁶² Therefore, the majority of solvents

used for LiSBs are ether-based. In particular, the dimethoxyethane (DME) and dioxolane (DIOX) blend is especially prevalent. DME has low viscosity (0.455 mPa*s at 25°C⁶³), a high donor number (20 kcal/mol⁶³), and a moderate dielectric constant (7.2⁶⁴). This means that DME has sufficiently solvates Li⁺ and most Li-salts.⁶⁵ DIOX has a similar dielectric constant of 7.1⁶⁶ and low viscosity of 0.6 mPa*s at 25°C⁶⁷. The reaction of DIOX and Li on the anode surface helps form an SEI.^{68, 69} The DME/DIOX blend offers good kinetics and high S utilization, though often at the cost of the PS shuttle, and low viscosity when mixed with salts in high concentration.⁷⁰ However, the DME/DIOX blend does not limit the PS shuttle on its own and replacement solvents have been investigated for this purpose.

Variations on this system include tetraethylene glycol dimethyl ether (TEGDME) and TEGDME/DIOX blends. Barchasz et al. evaluated TEGDME/DIOX ratios and found that a 25:75 TEGDME:DIOX ratio gives the highest ionic conductivity.⁷¹ Kim et al similarly concluded a ~1:3 ratio gives the highest ionic conductivity.⁷² Nevertheless, there are studies which make use of many other DME/DIOX and TEGDME/DIOX ratios.⁶⁸ Carbone et al. compared DME, DME/DIOX, TEGDME, diethylene glycol dimethyl ether (DEGDME), and polyethylene glycol (PEG) for their physical properties and electrochemical results. DME/DIOX and TEGDME have the lowest interface resistance and DME/DIOX has one of the highest conductivities; however, DME and DME/DIOX show a more significant PS shuttle than the longer-chain ethers.⁷³

A promising new category of solvents that have minimal solubility for PS are fluorinated ethers. Fluorinated ethers have low solubility for Li⁺, minimizing PS solubility and elongating cycle life.⁷⁴ The mechanism and properties with respect to the PS shuttle

will be discussed further in section 1.3.3. ILs and polymer electrolytes are also important areas of research, but are outside the scope of this work.

1.2.4.2 Salt

The electrolyte salt adds ionic conductivity to the electrolyte. The salt must be soluble in the chosen solvents and sufficiently stable in the voltage window desired for testing or use. If the salt is designed to contribute to the SEI and CEI, it should dissociate and decompose a desired amount for effective interfaces, but not so much as to deplete the electrolyte and grow excessively thick SEI and CEI layers.

Han et al. compared anion options for Li^+ including TFO^- , FSI^- , TFSI^- , and TDI^- in 1:1 DME:DIOX.⁷⁵ They showed that DME plays a bigger role than DIOX in solvating the Li^+ , but has a moderate strength of interaction with the anion. TFSI^- has the largest ionic radius and second highest ionic conductivity. The anion also has an effect on the solvate structure formed. They show that TFSI^- participates along with the solvent in the solvate structure of Li^+ , whereas FSI^- ions are less bound. They concluded that weaker interactions with the cations and solvent may yield a thicker SEI, whereas stronger interactions (particularly with PS) may contribute to PS shuttling. Therefore, TFSI^- sits nicely in the middle as a balance of properties. Kim et al. performed a study in TEGDME/DIOX and found that regardless of solvent ratio, the LiTFSI salt had a higher ionic conductivity than LiTF or LiClO_4 .⁷² Binary salt mixtures of $\text{LiTFSI}/\text{LiFSI}$ have also been investigated.⁷⁶ Hu et al. borrowed LiFSI from carbonate-based electrolytes and applied it to the LiSB system. They found that the composite had higher capacity over its cycle life than the salts on their own.

When considering salt concentration for LiSBs, most work has focused on high concentration electrolytes.⁶⁸ Suo et al. showed that highly concentrated electrolytes enable high capacity and long cycle life.⁷⁷ Wu et al showed that increasing salt concentration leads to less degradation during extended cycling.⁷⁸ Han et al showed that at 3M, the clustering of Li is because of a lack of solvent molecules to solvate all ions individually and solvent spheres overlap.⁷⁵ When the solvent is occupied solvating the Li^+ , there is less free solvent to solvate the PS and their dissolution decreasing. However, this comes at the detriment of conductivity, weight and cost. Conversely, Hwang et al. studied the moderately low concentration of 0.5M LiTFSI and showed that the lowered viscosity led to better wettability and higher capacity than the 1M LiTFSI electrolyte.⁷⁹ Wu et al further showed the strong performance of low concentration electrolytes from lower viscosity and reduced solubility for short chain PS.⁸⁰

1.2.4.3 Additives

Additives are important for stabilizing the electrode surfaces, improving electrolyte safety, and minimizing current collector corrosion.⁸¹ The most prevalent, and nearly default, electrolyte additive for LiSBs using ether-based electrolytes is lithium nitrate (LiNO_3). Lithium nitrate is very effective at forming an SEI on the Li anode and therefore minimizing the PS that can come into contact with the Li metal and be reduced.⁸² The addition of LiNO_3 creates a surface film composed of Li_xNO_y and Li_xSO_y which passivates the Li metal.⁸³ Lithium nitrate does not impact the PS dissolution itself, the PS still dissolve into the electrolyte and diffuse over to the anode, but the LiNO_3 provides the surface protection that greatly minimizes PS reduction on the Li anode and thus improves cycling efficiency and stability.⁸⁴ Ebadi et al. modelled the interface of the Li anode when LiNO_3

is added.⁸⁵ They found a complicated series of potentially stable compounds. However, the small voltage window in which LiNO_3 is stable is a drawback on its use. Below 1.6V, lithium nitrate undergoes an irreversible reaction, limiting its effectiveness in long term cycling.⁸⁴ Additionally, the SEI growth depends on the decomposition of LiNO_3 on the anode into the protective layer. Overtime, the LiNO_3 is consumed and cell capacity decreases. The lifetime of a LiSB is heavily dependent on the amount of LiNO_3 added to the electrolyte. Kim et al. found an optimum of 0.2M LiNO_3 in a DOL/TEGDME electrolyte⁷² and 0.1-0.2M are the most common concentrations used in literature.

Wu et al., from our group, proposed LiI as a substitute for LiNO_3 .⁸⁶ LiI helps protect the cathode particles and limits PS dissolution. They proposed several mechanisms through which LiI improves performance: LiI operates as a redox mediator, helping with electron transfer between the electrolyte and electrode, LiI forms an SEI on the Li, which aids ionic conductivity, and LiI helps catalyse the electrochemical reaction.

1.2.5 *Current Collector*

A LiSB current collector must be highly electrically conductive, have good adhesion with the cathode particles, and not be prone to corrosion in the given electrochemical system and voltage range. As mentioned in the discussion of freestanding cathodes, some cell designs do not include an external current collector and it is implicit to the conductive carbon substrate. In conventional cell designs, aluminium (Al) foil is the most common current collector, distantly followed by nickel (Ni). Both exist as foils and foams, which provide higher interfacial area, but foils are overwhelmingly more common because of ease of production and use. Al is inexpensive, easy to work with, has good

adhesion with most sulfur-based slurries, and does not induce side reaction.⁸⁷ The surface is modifiable with various coatings if this is not the case. However, Al foil current collectors can corrode when the common LiTFSI salt is used, though coatings and electrolyte additives can help mitigate this.⁸⁷

1.3 Polysulfide Shuttle and Mitigation Methods

The previous discussion concerned what reaction intermediates are present, at what voltages, and what may induce the existence of some and absence of others. The concept of polysulfides (PS) was introduced and the shuttle was briefly mentioned for introduction. However, PS play a considerably bigger role in LiSBs than simply as reaction intermediates. The PS shuttle is the fundamental problem plaguing LiSBs, limiting their cycle life, and driving new designs. Figure 9 shows the steps of the polysulfide shuttle mechanism schematically. In the first step, S is present in the cathode and the electrolyte is clear. The yellow S is embedded in a black carbon matrix. These cell components will be discussed further in the next section. In step II, current is applied and discharge begins. Sulfur is initially reduced to long-chain PS and these PS start to dissolve out of the cathode as they are soluble in the electrolyte. Step III shows more PS have diffused out into the electrolyte and have started to turn the electrolyte yellow. The PS are free to diffuse unimpeded to the Li metal anode. Step IV shows the shuttle in full effect. The PS that have diffused over to the Li and are reduced. The PS can either be fully reduced to Li_2S , where they deposit as an insulating layer that increases cell resistance, or they can be partially reduced to $\text{Li}_2\text{S}_{n-2}$ and diffuse back towards the cathode.⁸⁸ In the latter case, the PS can continuously shuttle back and forth from cathode, being reduced until they deposit as Li_2S on one of the electrodes. When S and PS are reduced on the cathode, the electrons flow to

the appropriate current collector and contribute to cell capacity.^{13, 89} However, when the reduction occurs on the Li, that active material is essentially lost. Figure 10a shows what charge-discharge behavior looks like when the PS shuttle is active. As the sulfur loading increases, so does the PS shuttle as PS dissolution increases.

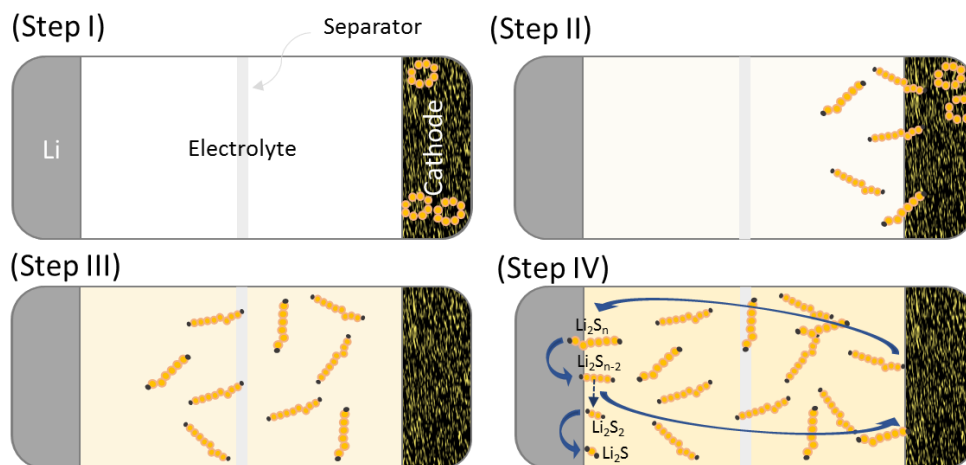


Figure 9. Schematic of the process of the polysulfide shuttle. Step I: cell as constructed, Step II: S is reduced to long-chain PS, Step III: PS diffuse across the separator towards the Li anode, Step IV: PS reduce on the Li and diffuse back towards the cathode.

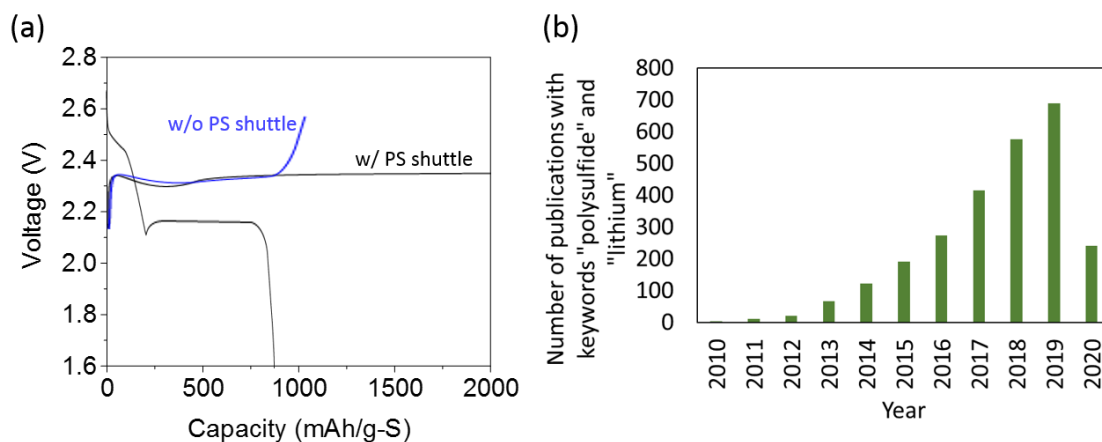


Figure 10. (a) Illustration of charge-discharge behavior with (black) and without PS shuttle effect (blue) and (b) number of publications via Web of Science with keywords “polysulfide” and “lithium” – accessed May 8th, 2020.

Mitigating the PS shuttle has been a major thrust of LiSB research as show in Figure 10b.⁹⁰ Researchers have pursued a plethora of solutions to the PS shuttle problem. These include, but are not limited to:

- Electrolyte additives (salts & solvents)
- Separator coatings
- Cathode coatings
- Metal oxide additions (dispersion & coating)
- Cathode/separator interlayers
- Carbon doping

Each of these strategies will be briefly reviewed and evaluated here. Overall, PS mitigation comes in the form of chemical or physical confinement, or some combination. In chemical confinement, the PS bind or are attracted to an additive. Usually the additive is polar and therefore attracts the PS. In physical confinement, the PS are prevented from diffusing out of the cathode by entrapment inside pores or other physical features. Extensive review papers on this topic, and some specific ones on each strategy, are available elsewhere.^{88, 91-93} The discussion here will centre on topics relevant to the research subjects to follow.

1.3.1 Cathode Modifications

Cathode modifications to chemically and physically trap PS primarily follow the strategies of coatings, additives, and dopants. The most popular sulfur coating is a carbon particle, which may be additionally coated or doped. Carbon particles provide needed electronic conductivity as discussed previously. Dopants and additives are mostly based on the inclusion of polar species to attract the PS.

A large portion of the additions and coatings in literature are metal oxides. They are either added as particles mixed into the slurry or coated onto the individual S or S/C particles. Many studies have demonstrated their benefits across oxide chemistry and morphology.⁹⁴⁻¹⁰⁰ Silica, alumina, and manganese, titanium, and vanadium oxides are common choices. MnO₂ has been used as nanoflakes, nanowires, and nanoparticles, all of which provide PS adsorption and enhance performance.^{94, 96, 101-104}

Other authors have tried alternatives metal oxides by coating the S/C particles with a functional polymer. Mukkabl et al. used a PEDOP coating which facilitated better capacity retention than the uncoated cathode.¹⁰⁵ They attributed the improved performance to the interaction of the O in the polymer and the sulfur, trapping the PS. Zhou et al. used a complex core-shell structure of a nitrogen-doped carbon shell for the sulfur with an additional polydopamine coating.¹⁰⁶ This carefully constructed architecture employed the N-doped carbon to provide conductivity and a polar site for the PS to be attracted to. The polymer coating helped retain the S inside the shell instead of redepositing on the outside of the shell. Zheng et al. applied a amphiphilic polymer to the carbon nanotubes which house the S, providing a polar species to attract the PS.¹⁰⁷ This coating helped prevent the detachment of the L₂S from the carbon during cycling.

1.3.2 Separator Modifications & Interlayers

Separator modifications and interlayers are often a combined chemical and physical confinement approach. The separator can be doped or coated. A similarly active interlayer can be added as a physical barrier and dopants can provide additional chemical confinement.

Bauer et al. used a Nafion-coated Celgard separator and achieved high capacities, claiming PS dissolution mitigation.¹⁰⁸ Wei et al. coated their separator with PVDF and carbon using a phase-inversion process.¹⁰⁹ Their CV results indicate PS suppression, but their explanation of the mechanism is not thorough. In multiple studies, Chung et al. took a similar approach of carbon coating their separator.^{110, 111} The carbon layer is a physical barrier for polysulfides. Su et al.'s interlayer approach is one step further, leaving the separator alone and inserting a MWCNT interlayer for the same effect.¹¹² The improved electrical conductivity and physical barrier to PS diffusion improve performance.

Chang et al. used a nitrogen-doped interlayer to help chemically trap PS.¹¹³ Nitrogen doping provides a polar site that can adsorb PS and minimize the shuttle effect while the carbon interlayer is additional physical blocking. They showed long cycle life and improved discharge capacity in their study. Numerous other studies recount the chemical and physical trapping properties of interlayers and separators with dopants and other additives.¹¹⁴⁻¹¹⁶

1.3.3 *Electrolyte Modifications*

Electrolyte modifications fall into two categories: additives and changes to solvent composition. The goals of electrolyte modifications are (1) to build protective CEI or SEI which limit reaction of the PS with the Li anode and (2) reduce solubility/diffusivity of the PS in the electrolyte. These effects are produced in-situ as salts and solvents decompose or interact with the PS, producing the desired effect. Additives will be discussed first.

One approach focuses on mitigating PS dissolution over CEI/SEI formation is the addition of PS themselves. Agostini et al. dissolved PS of various lengths into glyme-based

electrolytes and found that the added PS limit their dissolution out of the cathode.¹¹⁷ They also found that the added PS impact the SEI composition depending on the chain length added with the long-chain PS being the most favourable. Chen et al. added long-chain PS to the electrolyte in order to negate the loss in active material; however, they found the PS addition had more of a beneficial effect on Li_2S formation.¹¹⁸ Their addition of PS increased cell capacity and cycle life. Lee et al. showed that the Li_2S_8 addition to the electrolyte follows Le Chatlier's principle and mitigates the dissolution of PS from the cathode if there is already PS in the electrolyte.¹¹⁹ They claim this aids the long-term stability of their cells, which do in fact reach a very high capacity, but only for 50 cycles.

Pan et al investigated ammonium salts to intentionally help dissolve Li_2S .¹²⁰ Such enhanced dissolution promotes reaction kinetics, likely because there is less deposition of insulating Li_2S on the electrode surface. However, the authors did not provide EIS data and focused on the dissolved species in the electrolyte. By a similar theory, Lin et al. proposed a P_2S_5 additive to improve dissolution of Li_2S and produce an SEI on the Li anode.¹²¹ The P_2S_5 forms a complex with the low solubility PS to aid their solubility while also forming a Li_3PS_4 layer on the anode that limits contact of PS and the Li metal. Such combined effects produced a cell with a higher capacity.

Secondly, changing solvents or adding co-solvents can help limit the PS shuttle effect. Solvents which limit PS dissolution are typically based on non-solvent approaches. Solvents which cannot solvate Li^+ commonly have a very low solubility for PS.⁹³ These solvents with low donor-ability typically fall into the categories of ILs, fully fluorinated solvents (mostly fluorinated ethers), or their mixtures.^{70, 122, 123} As previously noted Suo et al. also demonstrated that high electrolyte concentrations can suppress the PS shuttle.⁷⁷

Their solvent-in-salt method limited free molecules available to further solvate the PS species.

The fluorinated ether approach is particularly relevant to this work and therefore will be discussed in greater depth. In highly fluorinated ethers, the F additions provides steric hindrance for the O, lowering its ability to act as a donor and solvate Li^+ .¹²⁴ Fluorinated ethers have low flammability and high oxidation potential, making them good candidates for electrolyte solvents.¹²⁵ Gu et al. balanced this lower solubility for PS with DME/DIOX co-solvents to provide adequate solubility for the salt and saw a suppressed PS effect.¹²⁶ Cuisinier et al. suggest that the PS are formed, but their solubility is so low that they have low mobility and side reactions are suppressed.⁷⁰ Chen et al. used PS solubility tests to prove their low solubility.¹²⁷ In several key works, Azimi et al. have made significant contributions to the subject of highly fluorinated ethers for LiSBs.^{74, 128, 129} They evaluated blends with DIOX and DME and saw higher capacity, coulombic efficiency (CE), and cycle life. The high CE in particular indicates small PS loss. They showed that the decomposition of the fluorinated ethers on the Li metal forms LiF, which produced a strong SEI. The fluorinated ethers decreased the redox shuttle and limited self-discharge. Many other authors have investigated highly fluorinated ethers for LiSBs and found a similar pattern of low solvation for Li^+ , depression of the PS shuttle, and production of a protective SEI.¹³⁰⁻¹³² Wang et al. offer an instructive review on the subject.⁶⁹

However, fluorinated ethers generally require a cosolvent since they have such low Li^+ solubility that they often cannot even dissolve the conductive electrolyte salt.¹³³ DME, DIOX, and DME/DIOX mixtures are prevalent¹³⁴ since they are the common solvents for LiSBs as discussed previously. Lu et al. used this method with a DIOX co-solvent and

found the fluorinated ether helped limit PS dissolution, but the DIOX helped provide adequate solubility for high capacity.¹²³ Highly fluorinated ethers can contribute to SEI formation even without the LiNO_3 additive, further protecting the Li metal anode from the PS.¹³⁵

1.4 Other Loss Mechanisms

While the PS shuttle is the primary cause of degradation in the LiSB system, it is not the only process through which capacity can fade or be limited. First, upon lithiation, the S experiences significant volume expansion. If not properly accounted for, generally via entrapment in a porous carbon matrix, such volume expansion can cause mechanical damage to the cathode structure.⁹ Second, through CEI and SEI formation, electrolyte salt and solvents can decompose, depleting the electrolyte. When the Li metal reacts with the electrolyte, an unstable SEI may be formed. Nanda et al additionally proposed that dead Li can be trapped under the growing SEI layer, causing degradation.¹³⁶ Lastly, LiSBs are subject to self-discharge, particularly because of the instability of the Li metal with the electrolyte.¹³⁷

While electrolyte degradation and self-discharge contribute to capacity fade, they are also merely an extension of the necessary process of SEI formation that protects and stabilizes the Li metal anode. SEI formation comes from the decomposition of electrolyte salts and solvents on the Li. Aurbach et al describe the variety of mechanisms and pathways for surface species formation in an electrolyte made of LiTFSI, LiNO₃, and DOL.⁸³ Figure 11 demonstrates the possible species that could be produced from this simple salt solvent system. Since similar species can be produced from multiple pathways, it is often difficult to assign a degradation or SEI-building mechanism to one particular salt or solvent.

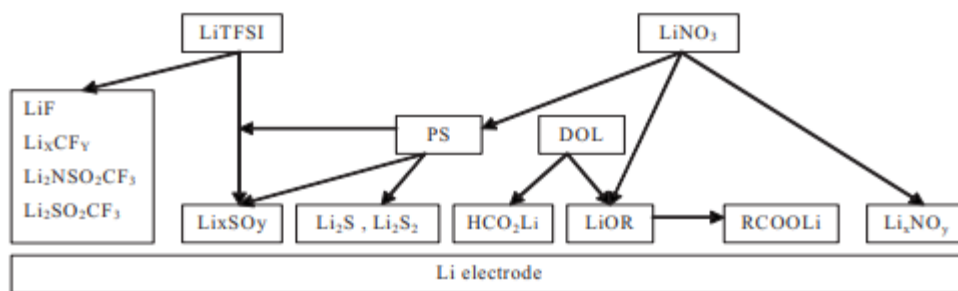


Figure 11. Schematic of possible pathways of electrolyte decomposition on Li metal anode. Reproduced with permission from the Journal of the Electrochemical Society.

1.5 Summary of Challenges in Li-S Battery Development

The LiSB system suffers from many challenges. Table 1 summarizes the challenges and common solutions. This list is by no means exhaustive, but rather reflects the challenges that are the most important and the most relevant to the work discussed in the following chapters.

Table 1 Summary of challenges in the LiSB system and some of their solutions.

Challenges	Solutions
Insulating nature of S and Li_2S	Mix or encapsulate active material in conductive additive (carbon etc.)
Air sensitivity of Li_2S	Process the cathode in the charged state (sulfur)
PS shuttle	• Chemical confinement (polar dopants, metal oxide coatings, functional binders and separators, electrolyte additives/solvent changes, etc.) • Physical confinement (interlayers, coatings)
Production of high loading cathodes	Freestanding cathode architecture, micron-sized particles, stronger binders

CHAPTER 2. EXPERIMENTAL DESIGN

2.1 Research Objectives

The lower density, cost, and viscosity of low-concentration electrolytes may offer practical benefits to the battery industry, if comparable or better cell performance can be attained. The primary goal of this work is to gain deeper fundamental understanding of the interactions of S cathodes with low concentration electrolytes and explore the potential of such electrolytes for LiSBs. High concentration electrolytes have been thoroughly studied, but there is a lack of research on the opposite end of the concentration spectrum. Additionally, while other works have focused on cathode modifications to build high loading cathodes, there has been less focus on electrolyte access to this active material. This work seeks to fill those gaps while building scientific understanding of the impact of low salt concentration on battery performance.

Within this broad goal, this work has four Research Objectives:

1. Evaluate the feasibility of using low concentration electrolytes in practical LiSBs

High concentration electrolytes have high conductivity, and it is unclear whether ultra-low concentration (0.1M) electrolytes have enough conductivity and are capable of establishing the stable interphases (SEI/CEI) to support stable cell cycling. Therefore, the first objective of this work is to evaluate conductivity and other physical properties of low concentration electrolytes and subsequently investigate their behavior in battery cells to establish whether these are suitable electrolytes for basic battery operation.

2. Investigate behavior of high mass loading cathodes with low concentration electrolytes

Once objective 1 is met, a proof of concept is needed to understand if low concentration electrolytes may be more effective than high concentration electrolytes when tested with high loading cathodes. The goal is to understand the impact of electrolyte salt concentration on performance of such cells, not to evaluate best practices for producing high loading cathodes.

3. Explore the impacts of alternative salts and solvents for low concentration electrolytes

After initial evaluation low concentration electrolytes, the next objective is to explore the opportunities to gain additional performance benefits in that concentration regime. The low salt concentration investigated here may allow the use of salts that do not conventionally dissolve in ether-based electrolytes, but may at such a low concentration. Additionally, new classes of electrolyte solvents explored at 1M and above have not been investigated at low concentration. It is the third objective of this work to study the behavior of the most promising salt and solvent candidates at low concentration, namely LiPF_6 and sulfolane/highly fluorinated ether systems.

4. Examine the impact of low concentration electrolytes on discharge behavior

The final objective of this work is to understand any impact operating in the low concentration regime has on the LiSB discharge mechanism. The LiSB chemistry has two unique discharge plateaus corresponding to the multistep conversion reaction. Altering the

electrolyte concentration and composition has the potential to alter the discharge characteristics. It is the final objective of this work to understand the relationship among salt concentration, electrolyte composition, and discharge mechanism.

2.2 Hypotheses

Since low concentration electrolytes are relatively unexplored, it is useful to put forward several hypotheses on their performance.

1. Low concentration electrolytes may interact with S cathodes differently, have a different propensity for the PS formation and exhibit a different solubility of PS, thus affecting initially accessible capacity in S cathodes,
2. Low concentration electrolytes may induce different CEI on the cathode and different SEI on the anode, thus affecting cell rate and cell stability,
3. Low concentration electrolytes may likely have a lower viscosity, which may enable better access to S in the cathode and prevent formation of a blocking layer on the S cathode, thus further maximizing capacity utilization and minimizing resistance build-up, particularly for high loading cathodes,
4. LiPF_6 may become a viable salt for LiSBs at low concentration,
5. The use of highly fluorinated ether-based electrolytes at low concentration combined with a diluent solvent may suppress PS formation and dissolution, while providing sufficient Li salt solubility and electrolyte conductivity for cell operation.

Throughout the following sections, these hypotheses will be evaluated and an understanding of the performance of LiSBs with low concentration electrolytes will be offered.

2.3 Experimental Approaches

In order to complete the research objectives and evaluate the hypothesis laid out above, various experimental tools and techniques are required. The following sections describe the equipment and experimental methods used in this work, including purpose of analysis, experimental set up, and desired results. These methods are general tools used across the studies in this work. Sample preparation specific to each chapter topic is described in detail in those sections.

The experimental methods used in this work fall into three categories: electrochemical tests, characterization of physical properties, and tools for analysis following electrochemical testing (post-mortem analysis).

2.3.1 *Electrochemical Tests*

2.3.1.1 Charge-Discharge (C/D)

The goal of charge/discharge testing is to characterize the charge and discharge capacities of a battery, discharge behavior, rate capability, and cycle life. A constant current is applied (negative for discharge, positive for charge) until the cell reaches the pre-determined charge or discharge voltage. For the purposes of the experiments discussed in the following chapters, cells were cycled between 1.6 and 2.8V. LiNO_3 , a common electrolyte additive discussed above, decomposes below 1.5 V, limiting the voltage range for cycling. During cycling, voltage and capacity were measured. In this experiment, the metrics of interest are discharge capacity and discharge plateau shape, where the shape corresponds to the discharge mechanism.

The current applied determines the cycling rate (C-rate) of the battery. In rate capability tests, cells were cycled across a range of C-rates to understand the effect of rate on capacity. In cycle life testing, cells were discharged at a slow rate once to aid SEI formation and then cycled at a faster rate for many cycles, in order to explore capacity decay and cell stability. In long term testing, the coulombic efficiency (CE) were also measured. CE is the percentage of charge capacity maintained by the subsequent discharge and demonstrates active material loss.

Coin cell components and construction were described above. In this work, 2032 coin cells are used for all electrochemical testing. A S cathode, Celgard 2500 separator, Li metal anode, and 30 μ L of electrolyte are used unless otherwise noted. Cells are constructed in an Ar-filled glovebox with water below 0.1ppm. In this study, an Arbin system is used for rate and long term testing.

2.3.1.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) involves applying a sinusoidal voltage and measuring the resulting sinusoidal current and phase shift between them. The applied AC voltage and resulting current are given by Equations 10 and 11, where ω is the frequency and ϕ is the phase shift. Impedance is the complex version of resistance and is the ratio of voltage and current (Equation 12). By measuring the impedance across a broad frequency range (0.01 – 10⁶ Hz), electrochemical processes which occur at specific frequencies can be probed. The experimental set up is shown in Figure 12.

$$V_t = V_0 \sin(\omega t) \quad (10) \text{Error! Reference source not found.}$$

$$I_t = I_0 \sin(\omega t + \phi) \quad (11)$$

$$Z = \frac{V_t}{I_t} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (12)$$

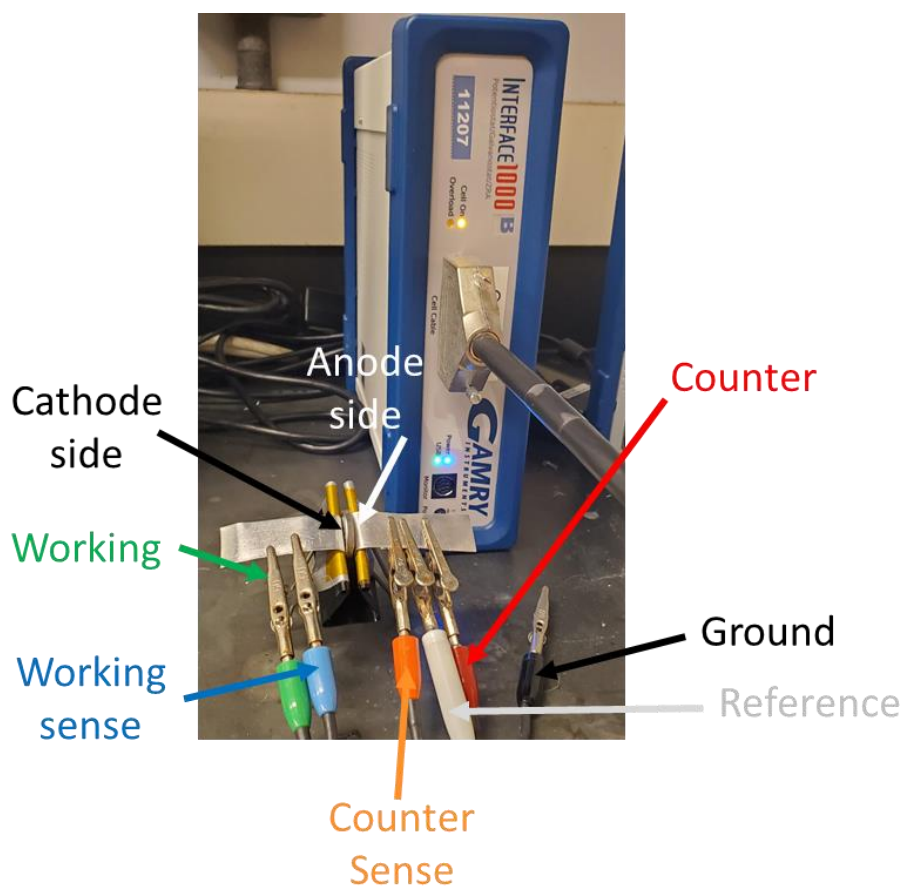


Figure 12. Experimental set up for electrochemical impedance spectroscopy (EIS).

In analyzing impedance across a battery coin cell, a Nyquist plot is the most useful. A Nyquist plot (Figure 13), or a plot of the imaginary component of impedance versus the real component of impedance, gives information on a cell's Ohmic resistance and the

dominant processes contributing to cell resistance. While a thorough discussion of EIS theory is beyond the scope of this work, there are several key components of a Nyquist plot that will be used later in this work to compare cell attributes. First, where the plot crosses the x-axis is the Ohmic resistance. This is effectively the resistance across the liquid

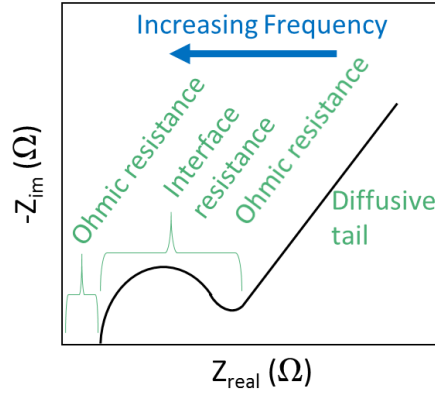


Figure 13. Nyquist plot schematic.

electrolyte. In Li/Li symmetric cells, the Ohmic resistance can also be used to roughly calculate electrolyte conductivity through Equation 13, where R is the Ohmic resistance, t is the distance (the thickness of the separator in this case), and A is the electrode area.

$$\sigma = \frac{t}{R * A} \quad (13)$$

Second, the arc in a Nyquist plot can be modelled as a RC circuit element and represents the resistance across the electrode/electrolyte interface. The length of the arc along the x-axis is the charge transfer resistance. Lastly, many batteries display a long tail in the low frequency regime. This feature comes from the slow diffusion processes occurring in the battery.

In this work, EIS was used to calculate and compare conductivities of symmetric cells with different electrolytes, characterize the change in interfacial resistance over long term testing, and qualitatively compare cell processes. Specific details are given in the appropriate chapters. A Gamry system is used as the potentiostat in this work.

2.3.1.3 Cyclic Voltammetry (CV)

In CV, a constant current is applied and the corresponding voltage is measured. As opposed to rate testing, in the case of CV, the plot of current versus voltage is of interest. CV gives specific information on the voltage a reaction occurs at and how this evolves with cycle number or rate. In this study, CV was used to track the change in reaction voltage over dozens of cycles to understand changes in discharge mechanism. For CV, coin cells were made in the same way as for rate-testing and the experimental set up is the same as for EIS.

2.3.2 *Characterization of Physical Properties*

2.3.2.1 Viscosity Testing

Understanding electrolyte viscosity is critical to understanding wettability. Viscosity measurements were taken with a RheoSense μ Viscometer. Samples were stored in septum-capped vials and only momentarily exposed to air before testing.

2.3.2.2 Polysulfide Solubility (PS) Test

Polysulfide dissolution is one of the main challenges in LiSBs. It is vital to understand the polysulfide solubility in alternative electrolytes and aim for electrolytes that

help suppress polysulfide solubility and diffusion. In order to make PS solutions, stoichiometric ratios of S and Li_2S were mixed in the electrolyte, stirred at 40°C for five days, and then mixed at room temperature for another 5 days. Depending on the PS chain length and concentration, the solution presents as a range of colors from green to red. Due to this color change, UV-vis spectrometry can be used to characterize the produced PS solutions.

However, the PS solubility question is further complicated by the fact that PS species have a tendency to disproportionate in solution. The PS made via stoichiometric addition of S and Li_2S does not guarantee only the desired PS chain length is produced. More likely, a range of PS species are created.⁸ Furthermore, PS peaks in tests like Raman, FTIR, and NMR overlap and are difficult to deconvolute. Therefore, without in situ methods, the PS solubility test discussed here is more effective as a qualitative comparison of PS color and concentration among different electrolytes.

Additionally, for electrolytes that have extremely low PS solubility, determining the PS solubility limit requires an infeasible volume of solvent. Therefore, PS characterization in this work compares concentration based on visual data.

2.3.2.3 Butler-Emmet-Teller (BET) Isotherm

BET Isotherms allow characterization of a material's pore volume and size. Such characterization is very important in this work to understand the microstructure of the sulfur/carbon cathode being used. Carbons are analyzed as received and sulfur carbon composites are analyzed after melt infiltration.

2.3.2.4 Raman Spectroscopy

In Raman spectroscopy, a laser of a specific wavelength interacts with a sample and the inelastic scattering signal is collected. This corresponding Raman shift, plotted as wavenumbers, is indicative of specific vibrations in a molecule and therefore can be used to identify species in a sample. For this study, Raman spectroscopy helps elucidate the components of the electrolyte.

To complete the experiment, electrolytes were sealed in septum-capped vials and a high magnification lens were used to focus on the liquid sample through the glass vial. Appropriate care was taken with focusing to eliminate the glass signal from data collection.

2.3.2.5 Nuclear Magnetic Resonance (NMR) Spectroscopy

In NMR, a sample is exposed to an extremely high magnetic field. As certain atoms are exposed to this field, they undergo a characteristic spin in response.¹³⁸ NMR is useful to calculate the diffusion coefficients of species in an electrolyte and the electrolyte's transference number (the ratio of current carried by the anion vs the cation). Here, liquid samples were placed in standard NMR tubes and sealed with Kapton tape to ensure the samples were kept air-free.

2.3.3 *Post Mortem Analysis*

The purpose of post mortem analysis is to understand the difference in surface morphology and composition before and after rate or long term testing. This involves a visual analysis of cell components after disassembly, microscopy to determine if the cathode or anode surface microstructure changed, and spectroscopy to identify any changes

in surface and bulk composition. The four primary tools in post mortem analysis were: visual analysis, Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS).

2.3.3.1 Visual Analysis

After cells were disassembled, each cell component was inspected. The cathode and anode were inspected for surface layers and structural integrity (i.e. any flaking off the current collector or delamination of the SEI layer). The separator was inspected for its color. A yellowed separator indicates high polysulfide dissolution, whereas a separator that is still its original white color indicates fewer polysulfides in the electrolyte. The electrolytes start clear and the PS species have a yellow to red color, lending to a simple visual identification of their existence in solution. Lastly, the cells were characterized by how wet or dry the components are. A wet cell indicates remaining electrolyte, whereas a dryer cell indicates the degree of electrolyte consumption. This visual analysis is not conclusive proof of cell mechanisms, degradation pathways, or performance; however, it is a useful method to compare cell to cell.

2.3.3.2 Scanning Electron Microscopy

In SEM, a sample is hit with a focused electron beam at a specific voltage and current. When the beam interacts with a sample, several different types of signals are produced, including: backscattered, secondary, and Auger electrons and characteristic x-rays. Each signal gives unique information about the sample surface and composition. In particular, secondary electrons yield topographic information and thus are used to form an image of the sample at very high magnification.

For this study, SEM was used to analyze surface morphology before and after electrochemical testing. Information about SEI formation and degradation mechanisms can be obtained by identifying changes in surface features due to electrochemical testing.

Samples were prepared by taking apart the coin cell as described above, washing the cell components in DME to remove residual salt, and drying off the solvent. In this work, a glove-bag is used to keep air-sensitive samples in an inert N₂ environment while transferring them to the SEM.

2.3.3.3 Energy Dispersive Spectroscopy (EDS)

EDS is a tool to identify the chemical composition of a sample. EDS is produced during SEM operation; however, in the case of EDS the characteristic X-rays are detected. The energy of a characteristic X-ray is directly related to elemental composition. In this study, EDS was used to determine the chemical makeup of the anode and cathode after long term electrochemical testing.

2.3.3.4 X-ray Photoelectron Spectroscopy (XPS)

In XPS, a sample is subjected to a beam of X-rays and the energy of the electrons emitted from the surface are measured (Figure 14). In XPS, an incoming photon directly knocks an electron out of the core level and the electron energy is measured directly. The kinetic energy is directly related to the binding energy of the electron and thus the element and chemical state it originated in. Equation 14 describes the governing principle of XPS, where ϕ is the work function. A shift in energy is related to a shift in oxidation state of the species the electron is emitted from and can therefore be used to identify bonding

information. Since there is a significant chance of the electron scattering on the way out of the material, XPS is a highly surface sensitive technique.

$$E_{BE} = E_{source} - (E_{KE} + \phi) \quad (14)$$

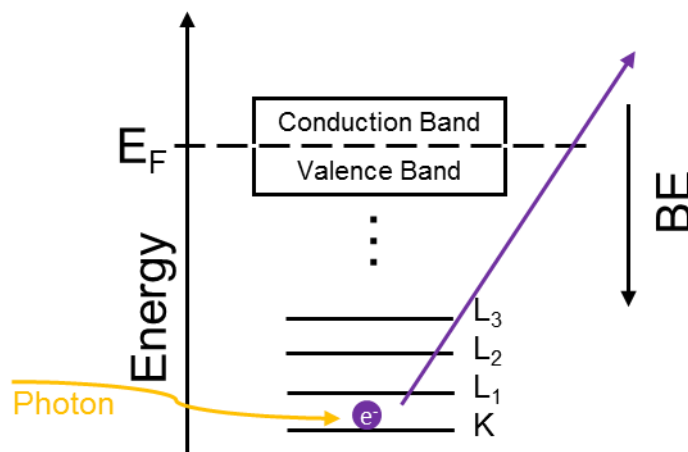


Figure 14. Schematic of mechanism of X-ray photoelectron spectroscopy.

XPS is extremely important in this work to characterize the composition of the SEI. While EDS gives bulk elemental composition, XPS gives bonding information, from which surface species can be deduced. The surface species help indicate which electrolyte components decomposed to form the SEI and can help inform understanding of cell degradation. XPS samples were prepared by the same washing and drying method as described for SEM. For this work, an air-free sample holder was used to transfer air-sensitive samples from the glovebox to the XPS.

CHAPTER 3. EVALUATION OF LOW CONCENTRATION LITFSI- AND LIPF₆-BASED ELECTROLYTES FOR LI-S BATTERIES

The following is reproduced and reformatted from the author's publication in the Journal of the Electrochemical Society, which allows re-publishing for the purpose of use in a dissertation. The publication is entitled "Tuning Low Concentration Electrolytes for High Rate Performance in Lithium-Sulfur Batteries" and its authors include: Rebecca Glaser, Feixiang Wu, Emily Register, Mara Tolksdorf, Billy Johnson, Jud Ready, Mohan Sanghadasa, and Gleb Yushin. This work was supported by US Army CCDC AvMC under contract numbers W31P4Q18D0002-W31P4Q18F0133.

3.1 Introduction

With the increasing adoption of electric vehicles, the desire for drones and electric planes to travel longer distances, and the need for cheap, grid-scale energy storage, the demands for improved battery performance and reduced battery weight and cost will grow rapidly. While commercial Li-ion batteries have been very successful so far, they are still too heavy, too costly, and are made of too many toxic materials to be the future of energy storage long-term.^{139,140} Lithium-sulfur (Li-S) batteries provide a promising alternative in that the cathodes are made of non-toxic, earth-abundant materials, which are both inexpensive and lightweight. Li-S batteries not only satisfy these supply-chain requirements, but also provide the highest theoretical gravimetric capacity (and the second highest gravimetric energy density) of conversion-type cathodes, far exceeding those of

commercial cathode materials.^{4, 27, 37,42, 141,142} With a theoretical capacity of 1,675 mAh/Sulfur, S-based cathodes raise the bar of the achievable capacity for rechargeable batteries.⁴

Unfortunately, corrosion of the aluminum foil current collector by the LiTFSI salt,¹⁴³ high cost of the electrolyte salts,¹⁴⁴ and polysulfide dissolution into the electrolyte⁸⁹ ultimately limit attainable Li-S battery capacity, rate performance and cell stability. Our group⁴² and others⁷⁷ demonstrated that high-concentration electrolytes may suppress lithium polysulfide dissolution due to the common ion effect and overall smaller fraction of the solvent molecules that induce formation and dissolution of polysulfides. With certain salts or salt additives, they may additionally form a favorable cathode solid electrolyte interphase (CEI)^{145,146,147,86} that protects the S cathode against such dissolutions. However, high concentration electrolytes suffer from high viscosity¹⁴⁸ and typically decreased ionic mobility,¹⁴⁹ limiting active material utilization at high loadings and high rates. High electrolyte viscosity also requires longer wetting (electrode stack infiltration) time, which undesirably increases cell fabrication time and cost. Finally, high concentration electrolytes also use large amounts of relatively expensive and heavy salt(s), which reduce the specific energy of the cell and increase cell cost. Low concentration electrolytes, in contrast, received very little attention with the expectation that they would offer substantially inferior performance for Li-S cells as they may enhance polysulfide dissolution. Interestingly, a recent comparison of the Li-S performance in 1M and 0.5M LiTFSI electrolytes showed the improved performance of the lower concentration solution, possibly due to the lower viscosity.⁷⁹ Sun et al also showed a lowered concentration improves sulfur utilization.¹⁵⁰ Here we were interested to explore even lower molarity

electrolytes with different salt and salt mixtures and investigate how their physical properties (e.g., viscosity and internal resistance) may impact Li-S cell performance (capacity, internal resistance, and long-term stability). By limiting our salt concentrations to those below 0.1M per salt (and below 0.3M for the salt mixtures), we could explore the impacts of salts which do not traditionally dissolve in ether-based electrolytes, such as LiPF₆.

3.2 Methods

3.2.1 S/KB Cathodes Preparation

As we wanted to highlight the impact of electrolytes, we purposely selected S-based cathodes without any protective shells⁹⁶ or oxide additives¹⁰¹ that may improve cathode stability. As such, we selected standard and easy-to-reproduce procedure: S/nanocarbon electrodes are prepared by melt infiltration of S (99.5%, Sigma-Aldrich, USA) into Ketjen Black® (Lion Specialty Chemicals Co. LTD) at 157°C for 12 h, thus making S/KB composites. The specific surface area of the KB and sulfur-infiltrated KB were analyzed with the Brauner-Emmett-Teller (BET) isotherm method. The excess S was evaporated at 250°C until the desired S:C ratio (~50 wt.% S) was achieved. The S/KB particles were then mixed with a polyacrylic acid (PAA) binder (450,000 MW, Aldrich, USA) and pure black (Superior Graphite, USA) conductive additives in a 70:20:10 S/KB:PAA:CB weight ratio. To prepare electrodes, the solids were mixed with a solvent (ethanol:water = 1:1 by volume), sonicated for 30 minutes and stirred in a vial over-night. The produced slurry was then cast on aluminum (Al) foil (MTI) and left to dry in air at room temperature. The active material loading was approximately 0.45 mg.s/cm². The dried electrodes were then

punched into ½ inch diameter disks, dried in a vacuum oven at 60°C for 12 h and then assembled into 2032 coin cells with a Celgard 2500 separator, a 0.75mm thick Li foil anode (99.9%, Alfa Aesar) and 30μL of the prepared electrolyte.

3.2.2 Electrolyte Preparation & Characterization

All the electrolytes used in this study employed various combinations of LiTFSI (Sigma-Aldrich, USA), LiPF₆ (Aldrich, battery grade), LiNO₃ (Alfa Aesar, 99%) salts in identical (commonly used) ether-based solvent mixture: a 1:1 ratio by volume of dimethoxyethane (DME, 99%, Sigma-Aldrich): dioxolane (DIOX, 99%, Sigma-Aldrich). 1 M LiTFSI + 0.1M LiNO₃ and 3 M LiTFSI + 0.1M LiNO₃ electrolytes were used as references for standard and high-concentration electrolyte compositions. All the individual salt components were kept at a concentration at or below 0.1M.

Table 2 shows the list of the experimental electrolytes investigated here.

Table 2. Experimental electrolyte compositions.

Sample	[LiTFSI]	[LiPF ₆]	[LiNO ₃]
A	0.1M	-	0.1M
B	0.05M	0.05M	0.1M
C	-	0.1M	0.1M
D	1M	-	0.1M
E	3M	-	0.1M

Once the electrolytes were prepared, their resistances and viscosities were tested. Resistance measurements were done by taking an EIS spectrum (Gamry Interface 1000, USA) in Li/Li symmetric coin cells. Viscosity measurements were taken with a RheoSense μ Viscometer (RheoSense, USA) Contact angle measurements were done by taking a video with a goniometer (Ramé-hart Instrument co., USA) and processing the frames with ImageJ processing software to determine the contact angle and the time until the electrolyte was fully wetted and soaked into the electrode substrate.

3.2.3 *Electrochemical Measurements*

All electrochemical experiments were done using an Arbin system (model BT2X43, USA). For galvanostatic charge-discharge testing, cells were cycled between 1.5 and 2.8 V for two cycles at C/20, followed by one cycle each at C/10, C/5, C/2, 1 C, and 2C rates. For long term tests cells were discharged at C/20 then charged and discharged at C/5 rate for 200 cycles. Each cell was characterized with EIS (Gamry Interface 1000, USA) in the frequency range 1 MHz – 0.01 Hz before testing and after long term testing to investigate the change in impedance after cycling.

3.2.4 *Post-Mortem Analysis*

After testing, the coin cells were disassembled and inspected. The electrodes, separators, and Li foil anodes were visually examined for their color changes and any surface deposits. The color of the remaining electrolyte was also examined as a qualitative indication of the concentration of the polysulfides in the electrolyte. The electrodes were

rinsed in DME before analysis with scanning electron microscopy (SEM) using Hitachi 8030 (Japan) and X-ray photoelectron spectroscopy (XPS) using Thermo K-alpha (USA) to investigate their microstructural changes and the CEI composition. The Li foil was washed in DME before SEM and energy dispersive spectroscopy (EDS) analyses on the Hitachi 8230.

3.3 Results & Discussion

3.3.1 Physical Properties

For the electrolytes tested, the viscosities expectedly increase with increasing salt concentration. All the low concentration electrolytes have a 0.2M of total salt concentration and show similar viscosities of ~ 0.5 mPa·s, regardless of their salt composition (Figure 15a). Increasing LiTFSI salt concentration to 1M tripled the viscosity to ~ 1.5 mPa·s and 3M LiTFSI showed the most dramatic increase to 42.5 mPa·s. This increase in viscosity is enough to impact wetting of the separator during coin cell preparation. Figure 15b shows that while the use of higher concentration of 1M gives a slightly lower ohmic cell resistance than the low concentration electrolytes, the overall interfacial resistance with the Li foil was noticeably higher. While low electrolyte resistance is important, low resistance and fast kinetics at the Li anode interface could be more impactful to the overall cell behavior. The 3M LiTFSI gives a higher ohmic resistance (Figure 15c), but lower interfacial resistance than many other LiTFSI-based electrolytes, while the 0.1M LiPF₆ electrolyte gives the lowest interfacial resistance (Figure 15d).

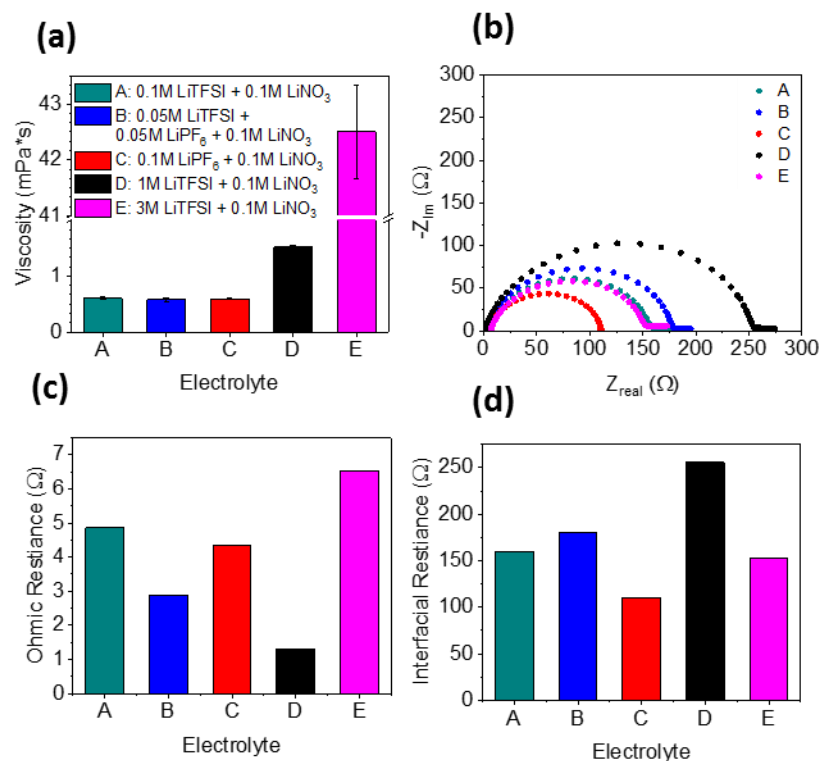


Figure 15. Physical properties of electrolytes (a) viscosity, (b) EIS from Li/Li symmetric cells, (c) ohmic resistance, (d) Li interfacial resistance. All electrolyte concentrations in 1:1 (v:v) DME:DIOX.

Contact angle measurements (Figure 15) showed results for 0.1M LiTFSI, 1M LiTFSI, and 3M LiTFSI samples (A, D, and E). The remaining electrolytes (samples B and C) were too volatile to form a drop. While the higher angle 1M LiTFSI was only slightly higher than the 0.1M LiTFSI, the 3M LiTFSI was more than double the contact angle of both. Samples A, D, and E took 1.5, 3, and 10 respectively to soak into the electrodes, matching with the viscosity data. The lower contact angle and faster time to absorb make these low concentration electrolytes more attractive than their high concentration counterparts from the cell fabrication point of view.

The sorption isotherms and the pore size distribution are given in Figure 16 and clearly indicate that sulfur is filling the pores in the KB samples. The BET specific surface area of the KB is 1303 m²/g and the surface area of the sulfur- carbon composite is 227 m²/g.

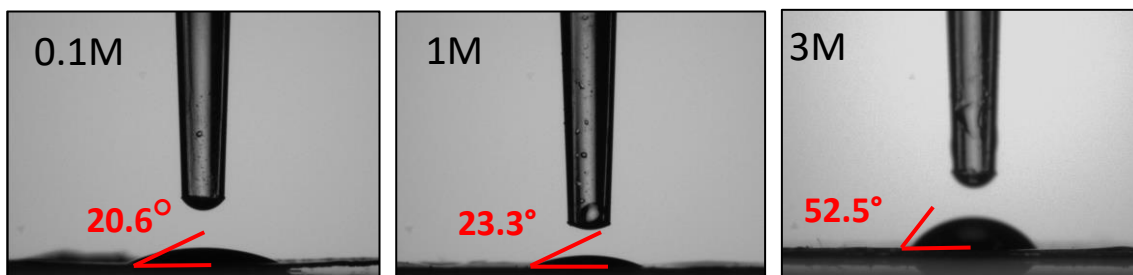


Figure 16. Contact angle measurements revealing wetting of 0.1M, 1M and 3M LiTFSI electrolytes (all with 0.1M LiNO₃) on the identically produced electrodes.

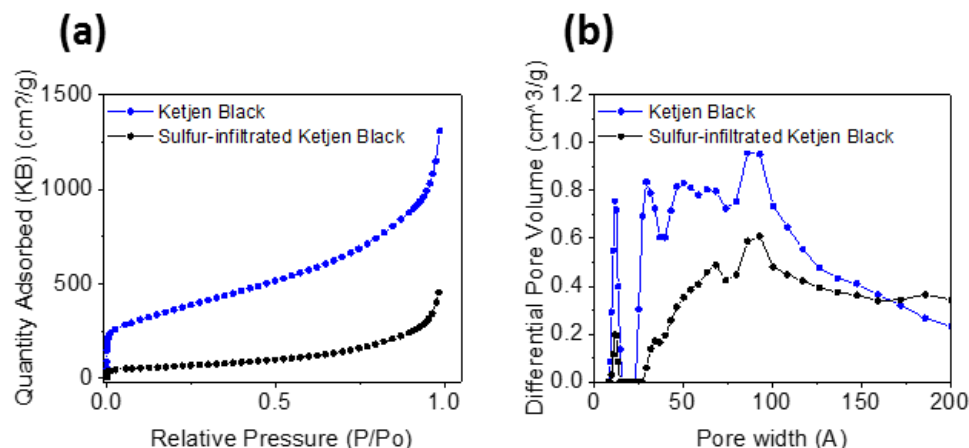


Figure 17. Characterization of pristine Ketjen Black and sulfur-infiltrated Ketjen Black with N₂ sorption: (a) isotherms, (b) pore size distributions.

3.3.2 Electrochemical Testing

Figure 18 shows the electrochemical performance of the low concentration electrolytes. Of the low concentration electrolytes and 1M LiTFSI, the performance of the low concentration electrolytes across C-rates is similar, with the 0.1M LiTFSI electrolyte

on average performing the worst. Figure 18b displays the C/10 charge/discharge cycle for each electrolyte. All low concentration electrolytes exhibit flat plateaus, low hysteresis, and low polarization. Similarly, at 2C (Figure 18c), the reaction still proceeds along the correct pathway, with higher hysteresis, but no evidence of significant kinetic limitations.

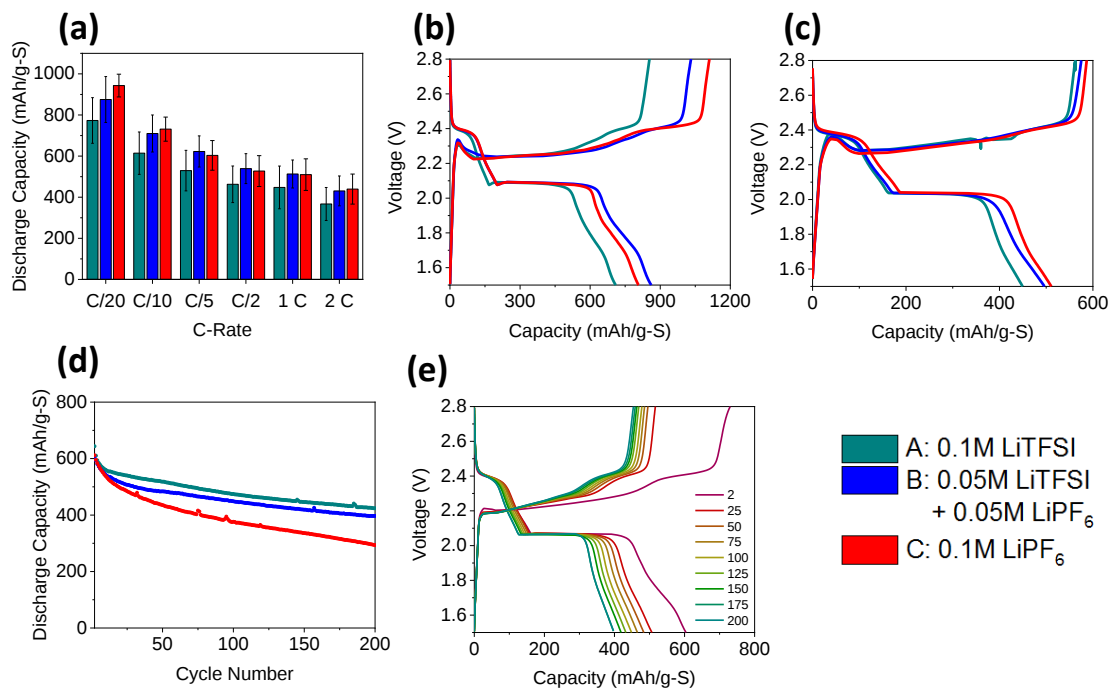


Figure 18. Electrochemical results for low concentration electrolytes (a) c-rate testing, (b) charge-discharge at C/10, (c) charge-discharge at 2C, (d) cycle stability at C/5, (e) Charge-discharge change through long term test with 0.05M LiTFSI + 0.05M LiPF₆ electrolyte. All with 0.1M LiNO₃ in 1:1 DME:Diox.

A comparison of long-term testing (Figure 18d) shows the lowest decay in capacity for the mixed LiTFSI/LiPF₆ electrolyte. The 0.1M LiTFSI electrolyte has a higher initial capacity, but is less stable, as is the 0.1M LiPF₆, the combination proves the most stable at this rate.

Low concentration electrolyte samples A, B, and C show similar capacity and hysteresis to the 1M LiTFSI electrolyte, indicating that the salt concentration above 0.1-0.2M (to around 1M) may be unnecessary additions to the electrolyte weight and cost. Sample B performs comparably or better than sample D across C-rates (Figure 19a-c).

Within error, the difference between 1M and the low concentration electrolytes is not significant and thus the lighter, cheaper low-concentration electrolytes can likely replace the 1M LiTFSI standard without sacrificing performance. Even for the relatively thin electrodes tested here, the highly concentrated electrolyte (3M LiTFSI – sample E) enables the highest capacity, it does so with higher polarization, higher resistance, and an

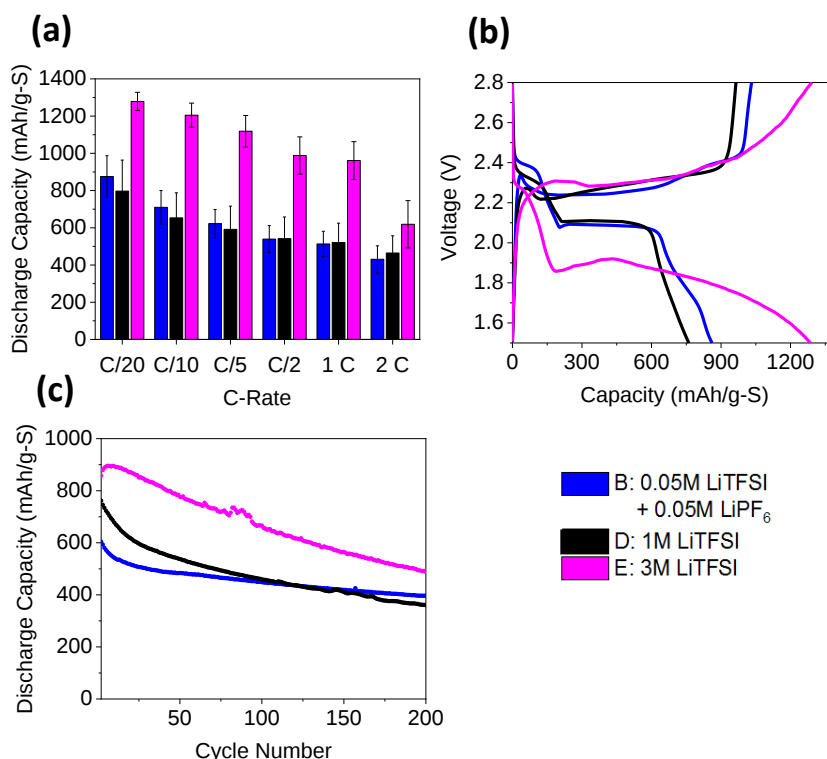


Figure 19. Comparison of electrochemical results for best low concentration electrolyte and high concentration electrolytes (a) c-rate testing, (b) charge-discharge at C/10, (c) cycle stability at C/5. All electrolytes with 0.1M LiNO₃ in 1:1 DME:DIOX.

inefficient conversion reaction illustrated by the curved plateau. And, as previously discussed, it suffers from undesirably high viscosity and increased cost. In contrast, cheaper and less viscous electrolytes A-C offer much flatter plateaus, significantly lower hysteresis, and capacity similar to or better than the conventional 1M LiTFSI (sample D).

Comparing EIS results from before and after long-term testing (Figure 20) reveals the reduction in impedance for the 0.1M electrolyte to be the greatest. Note that for all the

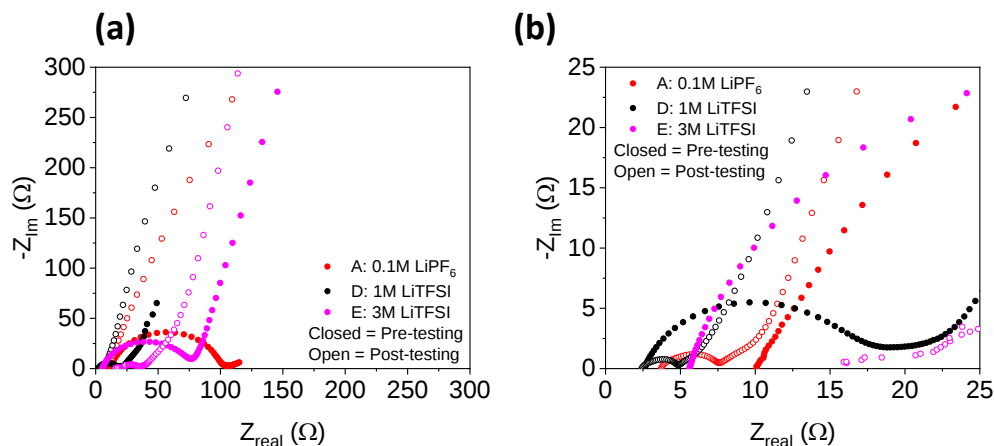


Figure 20. (a) Comparison of EIS results for 0.05M LiTFSI + 0.05M LiPF_6 electrolyte with 1M and 3M LiTFSI electrolytes (all with 0.1M LiNO_3 in 1:1 DME:DIOX); (b) zoom into a high-frequency region.

electrolytes shown, the major arc decreased in size during testing, indicating a lower interfacial resistances. Yet, the concentrated 3M electrolyte exhibits the largest impedance and the largest interfacial resistance after cycling.

3.3.3 Post Mortem SEM/EDS Results

Post-mortem SEM analysis of the tested S-KB cathodes shows very small changes in the microstructures for all samples (Figure 21). Individual carbon particles are visible without a change in morphology and no thick surface layer (e.g., CEI or re-deposited (poly)sulfides or S), likely related to the very high external surface area of the porous KB particles and relatively small electrode loadings (Figure 21). This may be beneficial as it should allow conductive carbon of KB to remain being available for charge transfer, but may also explain small differences in the electrochemical performance between cells (Figure 18). The Li anode (Figure 22a, b, c), on the other hand, showed significant changes

after cycling. We can observe distinct new features that exhibit four additional elements segregated together: S, C, F and O. All Li foil samples were mostly bare Li in the center, with the intensity and size of features increasing towards the edge. Figure 22d, e show EDS results from the Li foil at the end of a 2C discharge. The 1M electrolyte produced the greatest (normalized) intensity of N, F, and S, as compared with both the low concentration and high concentration electrolytes, indicating the largest S dissolution and the thickest SEI formation. The LiTFSI, LiPF₆ mixed electrolytes has a greater F intensity than the 0.1M LiTFSI electrolyte, which follows from the additional F available from the decomposition of the LiPF₆. Mapping of the mixed low concentration LiTFSI, LiPF₆ electrolyte shows that the features are mostly composed of O, S, and F, with C being more uniform across the surface.

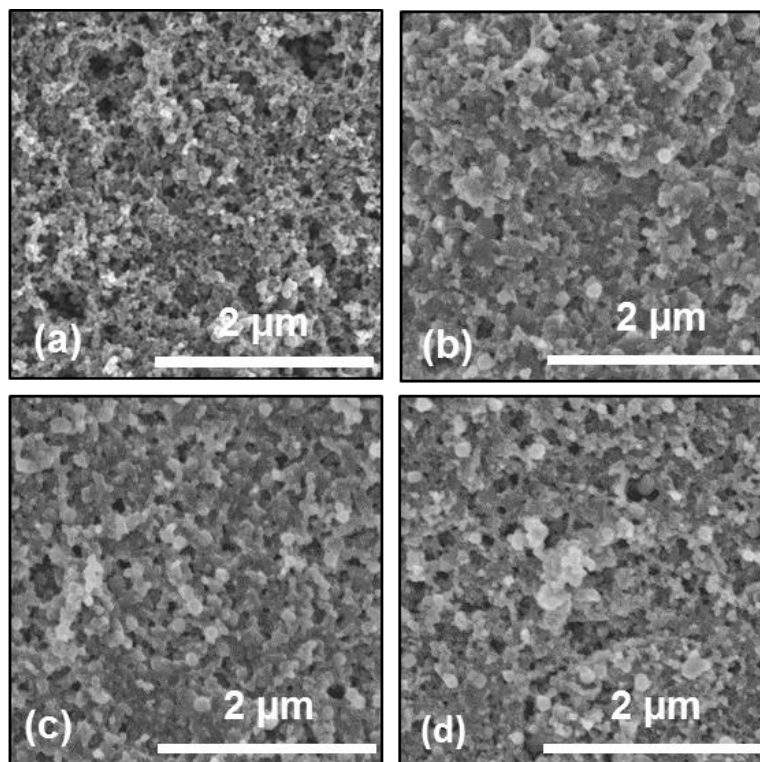


Figure 21. (a) Pristine cathode and post-mortem SEM of cathode after C-rate testing of (b) 0.1M LiTFSI (c) Li foil, 0.05M LiTFSI + 0.05M LiPF₆, (d) 1M LiTFSI

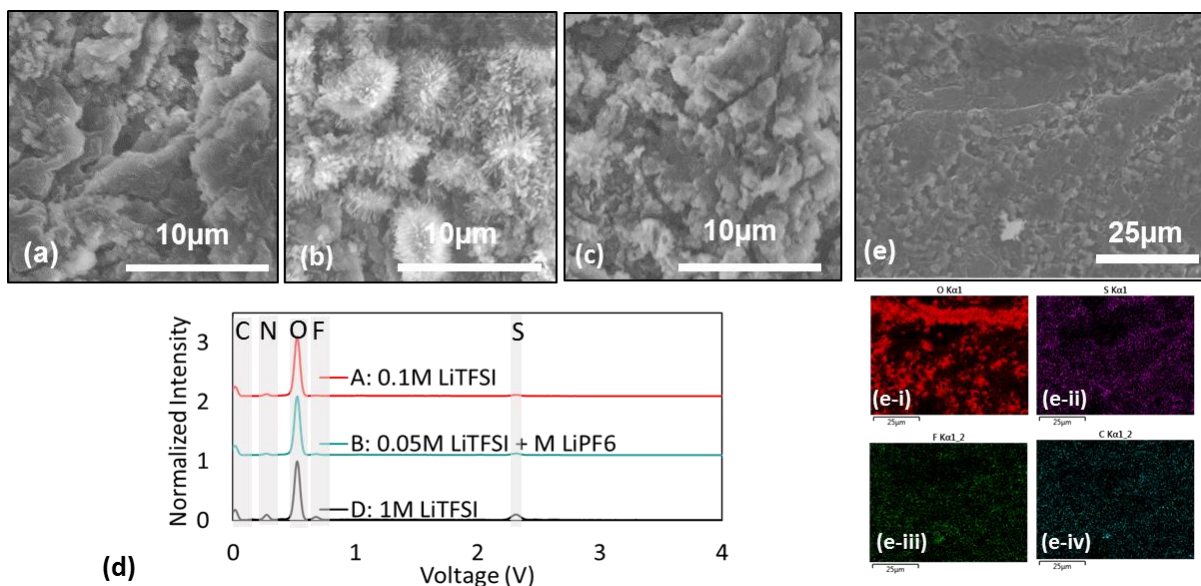


Figure 22. Post-mortem SEM of Li foil after C-rate testing of (a) 0.1M LiTFSI, (b) 0.05M LiTFSI + 0.05M LiPF₆, (c) 1M LiTFSI cells, (d) EDS spectra on Li foil, (e) EDS mapping on Li foil tested with 0.05M LiTFSI + 0.05M LiPF₆ (i- O, ii-S, iii-F, iv-C).

3.3.4 XPS Results

Post-mortem XPS analysis of thin tested cathodes (Figure 23 and Figure 24) indicates decomposition of the LiTFSI salt and electrolyte solvents with the formation of slightly different CEI in the case of all electrolyte compositions.^{151,152,153,117} For the low concentration electrolytes, CEI species mostly include: CF_n, LiF, N-containing compounds, sulfites, and sulfates. Overall, even 1/10-1/3 salt concentration in the electrolyte may apparently be enough to reproduce the composition of the protective CEI formed in 1M and 3M electrolyte compositions. Electrolytes containing 0.05-0.1M LiPF₆ show lower intensities of CF₂ than the majority-LiTFSI electrolytes while having a higher ratio of LiF to CF_n. Since LiF can be created by the decomposition of both LiTFSI and LiPF₆¹⁵⁴, the multiple pathways to LiF make it the more dominant F-containing compound on the surface. Interestingly, only the electrolyte comprised of 0.05M LiPF₆ and 0.05M

LiTFSI contains the most noticeable amount of Li_3N , a compound very important for favorable electrode protection.¹⁵⁵ The low concentration electrolytes have more N-O containing compounds than N-containing organic compounds, relatively, as compared to the 1 and 3M electrolytes. This is likely due to the higher relative proportion of LiNO_3 in the low M electrolytes since all five electrolytes comprised 0.1M LiNO_3 . Perhaps with less LiTFSI to break down, there are more N-O containing species leftover to deposit and favorably protect the cathode. Only 0.1M LiTFSI exhibits both CF_2 and CF_3 bonds, while all electrolytes show C-C, C-H, C-O, and C=O bonds consistent with the decomposition and polymerization of the dioxolane solvent.¹⁵⁶ Another interesting observation – electrodes from the 1M LiTFSI, 3M LiTFSI and 0.1M LiPF_6 electrolyte cells did not show any Li_2S on the surface, suggesting the incomplete reduction of polysulfides (the electrodes were examined at the end of discharge, thus mostly comprising Li_2S in the bulk). The low concentration LiTFSI samples A and B cells showed mostly colorless electrolytes during the post-mortem analysis, further supporting the minimum content of polysulfides remaining in the bulk of the electrolyte. The lack of yellowing of the low concentration electrolyte also goes against the theory that high concentration electrolytes are necessary to minimize polysulfide dissolution. Low concentrations of LiTFSI showed higher surface intensities of sulfites over sulfates, with the opposite true for high concentrations of LiTFSI. This may indicate a less thorough oxidation of S after the decomposition of the LiTFSI. While increasing electrolyte concentration undesirably increases cell polymerization,¹⁵⁴ the low concentration electrolytes are clearly adequate to achieve

similar or better rate performance (Figure 18, Figure 19) and may have more favorable CEI protection.

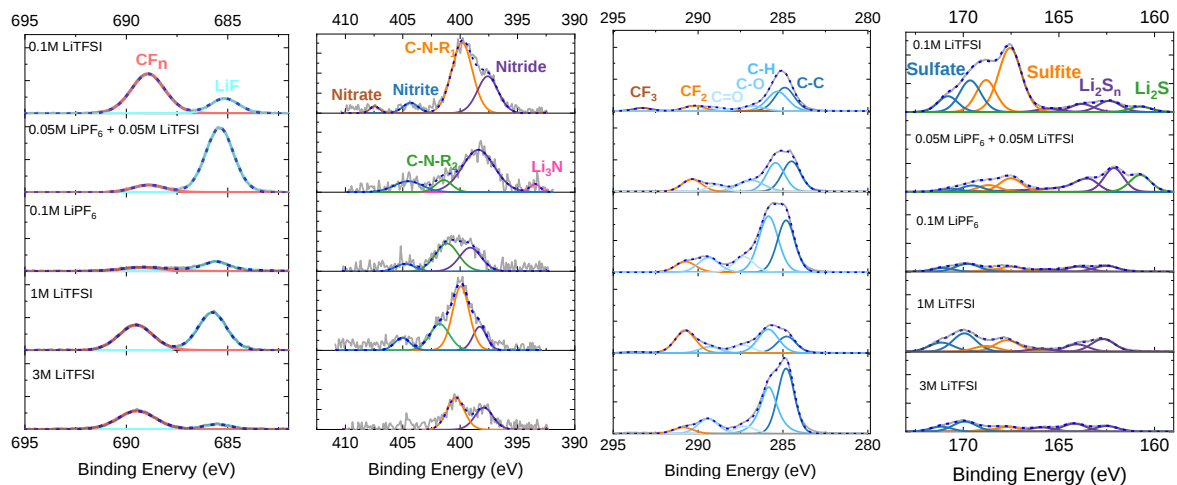


Figure 23. XPS results and peak deconvolution of S cathodes for all electrolytes (all with 0.1M LiNO₃ in 1:1 DME:DIOX): (a) F, (b), N, (c) C, (d) S spectra.

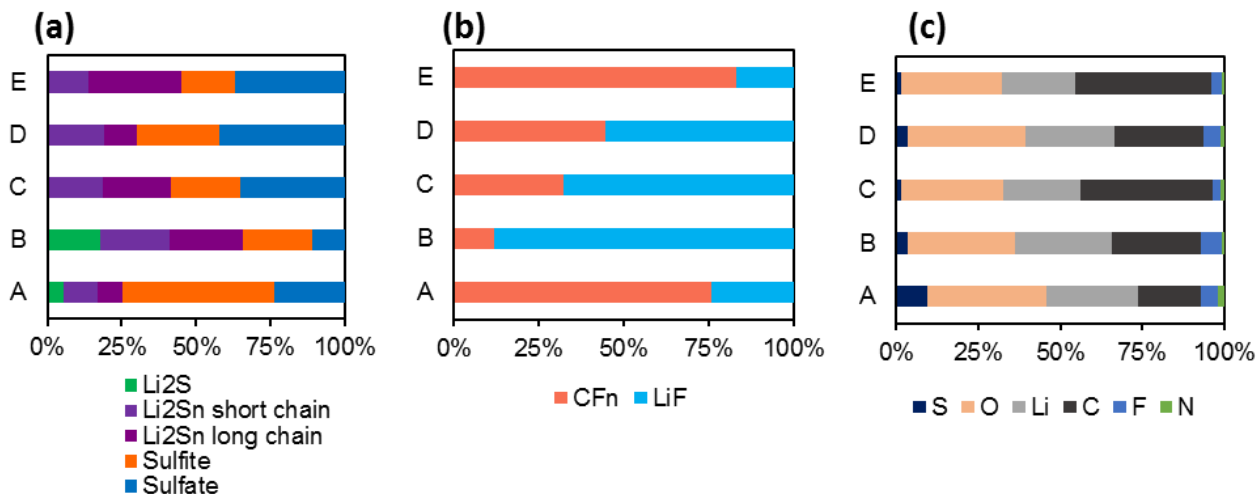


Figure 24. Quantification of XPS peaks of post mortem S cathodes with electrolytes A (0.1M LiTFSI), B (0.05M LiTFSI + 0.05M LiPF₆), C (0.1M LiPF₆), D (1M LiTFSI), and E (3M LiTFSI) for (a) S compounds, (b), F compounds, (c) by element. All electrolytes have 0.1M LiNO₃ and are in 1:1 (v:v) DME:DIOX.

3.4 Conclusion

This work reports on the first exploration of extremely low ($<0.3\text{M}$) salt concentrations in Li-S batteries. This study combined two common electrolyte salts, LiTFSI, and LiPF_6 , at low concentration and showed that their combination produced capacities comparable to the conventional 1M LiTFSI electrolyte. In contrast to our initial expectations, reducing electrolyte concentration from 1M to 0.2M did not increase PS dissolution and Li_2S precipitation on the Li anode. In fact, both the C-rate and long-term cycling tests reveal low concentration electrolytes perform similarly or better than the standard 1M electrolyte. Post-mortem SEM and XPS analysis illustrate that the low salt concentrations maintain the same cathode microstructure after cycling with no re-precipitated active material visible, while the Li anode showed smaller S content than 1M electrolyte. Low concentration electrolytes enable lightweight batteries at lower cost while offering similar or better rate performance and better stability to than the more traditionally used 1M LiTFSI or 3M LiTFSI electrolytes. Based on such promising results, our future studies on low concentrated electrolytes will be focused on increasing mass loadings, conducting tests in pouch cells (thus with minimum content of electrolyte excess) and using more advanced surface-protected S cathodes that exhibit substantially reduced PS formation and dissolution.

CHAPTER 4. APPLICATION OF LOW CONCENTRATION ELECTROLYTES TO HIGH-LOADING CATHODES

4.1 Introduction

As previously discussed, the Li-S battery is commonly composed of a S-composite cathode, a liquid organic electrolyte, a polymer separator, and a Li metal anode. Carbon is the most common inactive material in the S-composite cathode as it offsets the insulating nature of S. Significant progress on the carbon host has been made in recent years, allowing increasing amounts of sulfur loading,^{34, 38, 52} excellent conductivity, facile processability³⁷, and high capacity³⁶. However, processing such nanoparticles into high loadings cathodes ($>5\text{mg-s/cm}^2$) and providing electrolyte access to all the active material are still significant challenges. Sun et al. and many others demonstrated that increasing the mass loading leads to lower performance. They attribute this too poor ionic transport in thick electrodes,⁵¹ particularly if the re-deposited Li_2S blocks access to the cathode or anode. Therefore, there are two main challenges: (1) producing cathodes with adequately high loadings and (2) finding appropriate electrolytes that can access all the active material.

Some work has been performed on using carbon cloths to produce high loading cathodes via melt or vapor infiltration.^{39, 40, 157} Miao et al. infiltrated carbon fiber up to 8 mg-S/cm^2 with an optimal loading of 6.7 mg-S/cm^2 .⁴⁰ Such methods allow facile infiltration of S up to extremely high mass loadings in an electrode free of binder or conductive additive. However, most studies just consider one type of carbon cloth and little comparative work has been done among different types of carbon cloths.

To address the challenge of tortuosity, our group has recently proposed low concentration electrolytes as a solution to poor access to active material, demonstrated in the previous chapter.¹⁵⁸ Sun et al. also showed that lower concentration electrolytes can give high capacity while having low viscosity.¹⁵⁰ Hwang et al. also showed that low concentration electrolytes in Li-S batteries have better wettability than their high concentration counterparts.⁷⁹ As the previous chapter showed, low concentration electrolytes have strong performance and low viscosity.

In this study, we investigate the application of low concentration electrolytes to high-loading cathodes made of S-infiltrated carbon fabrics. The effects of electrolyte concentration, S infiltration method, and carbon fabric type were evaluated.

4.2 Experimental Details

4.2.1 Carbon substrates and infiltration

In this study, three carbon fabric materials were screened as sulfur substrates: Carbon felt (ACF 1600, CeraMateials), AvCarb fabric (Plain Carbon Cloth 1071, Fuel Cell Store), and Flexorb fabric (FM30K, Chemviron). Industrial carbon fabrics are more commonly used in fuel cell or filtration applications; however, here they are repurposed as sulfur hosts. Figure 25 shows SEM images of all the fabrics as received and characterization of fiber widths. These activated carbon fabrics represent a range of weave types and fiber sizes, which may affect their ability to absorb sulfur.

Three types of S infiltration were attempted on these fabrics: (i) melt, (ii) vapor in a furnace, and (iii) vapor in a desiccator. Procedures for each infiltration method were as follows:

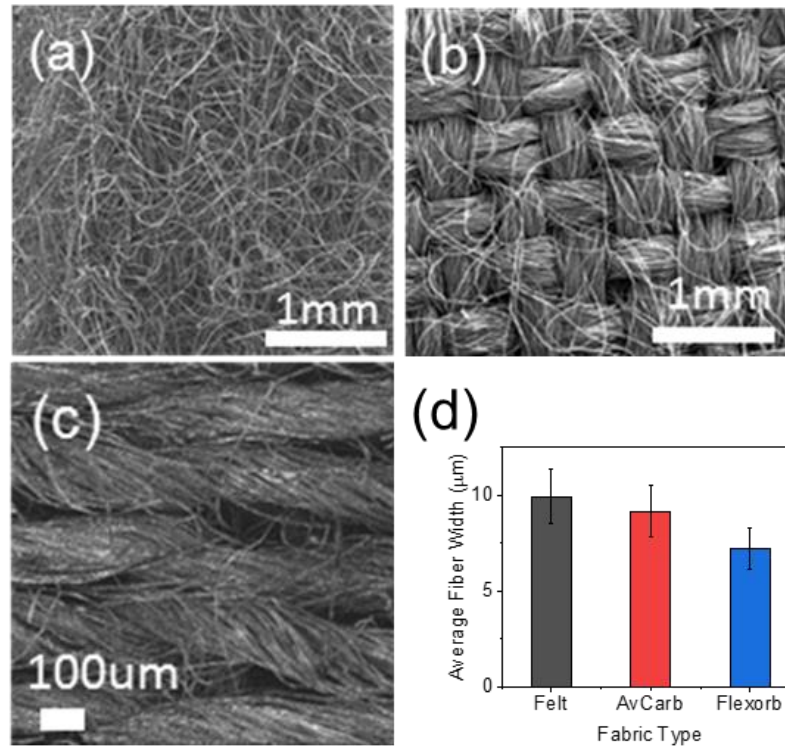


Figure 25. SEM images of (a) felt, (b) AvCarb, and (c) Flexorb as-received; (d) average fiber width for each sample.

Melt: Carbon was buried under a bed of sulfur powder, placed in a box furnace, and heated at 157°C for 12 hours (Figure 26). This allows the S to melt into the fabric.

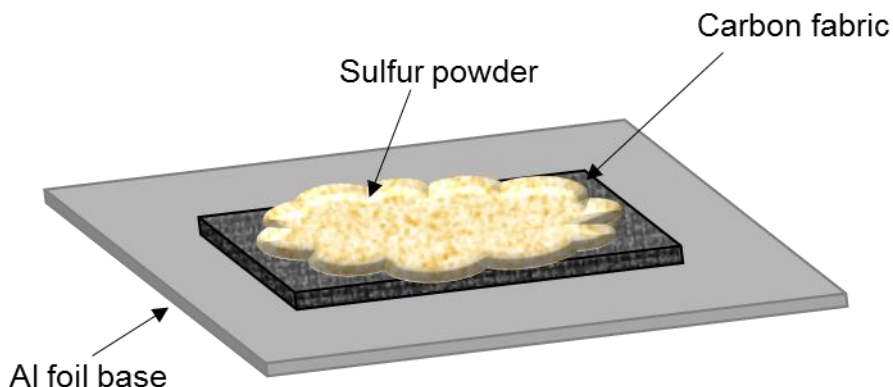


Figure 26. Schematic of melt infiltration of sulfur into carbon fabric.

Vapor (furnace): A bed of S was made on top of a sheet of Al foil. A table made of stainless-steel mesh was placed on the S powder and the carbon fabric was placed on the stainless steel. This mesh allows the carbon fabric to be suspended approximately 1mm above the S powder. The assembly was then placed in a box furnace and heated at 157°C for up to 12 hours. The infiltration time was lowered to achieve lower S loadings. In this case, the slight vapor pressure of S at its melting point allows S to evaporate and then condense onto the outside of the carbon fibers. This setup is shown schematically in Figure 27.

Vapor (desiccator): This procedure was the same as the vapor (furnace) method; however, instead of placing the S/steel mesh/carbon assembly in a box furnace, it was placed in a desiccator. The desiccator was then placed on a hotplate and heated until the base of the desiccator reaches 157°C. The set-up was left to heat and infiltrate for up to 12 hours, depending on the desired sulfur loading.

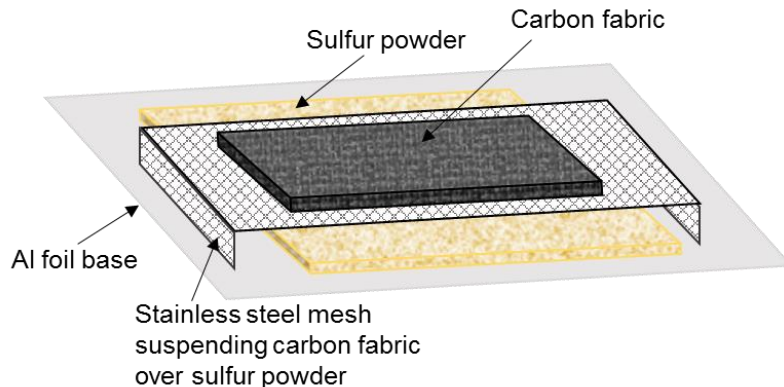


Figure 27. Schematic of set up for vapor infiltration of carbon fabrics.

4.2.2 Electrolytes

In this study, 0.1, 1, and 3M LiTFSI (Sigma-Aldrich, USA)) were mixed in 0.1M LiNO_3 + 1:1 DME:DIOX (DME, 99%, Sigma-Aldrich, dioxolane, 99%, Sigma-Aldrich) in order to assess the impact of electrolyte concentration on S utilization in the high loading electrodes discussed in the previous section.

4.2.3 Cell assembly and testing

Once infiltrated with S, the carbon fabrics were used without further modification. Since the carbon substrate is conductive, the cathode was used as-is without a current collector. 2032-coin cells were assembled with the S-infiltrated carbon cloth, a Celgard 2500 separator, and a Li metal anode. 75 μL of electrolyte was used, 60 μL of which was dropped on the cathode and the remaining 15 μL was dropped on the separator.

4.3 Results and Discussion

4.3.1 Comparison of infiltration methods

In this study, we evaluated melt and vapor infiltration for various carbon fabrics. Table 3 describes the merits and problems with each infiltration type. Melt infiltration provides fairly uniform mass loadings, but the mass loading is difficult to tailor to a given amount. Additionally, the SEM (Figure 28) shows that S does not always coat the fibers but can sit in between them. When S sits between the fibers, it limits the fibers' effectiveness as conductive additive and current collector.

Table 3. Pros and cons of sulfur infiltration methods for carbon fabrics.

Method	Pros	Cons
Melt infiltration	• Easy to tailor sulfur amount • Uniform infiltration	• Sulfur site in chunks between fibers • Time-intensive process to burn excess sulfur off
Vapor infiltration	• Sulfur coats fibers directly • Produce high loadings ($\sim 10\text{mg}/\text{cm}^2$) • Tailor mass loadings by infiltration time	• Not perfectly uniform mass-loading

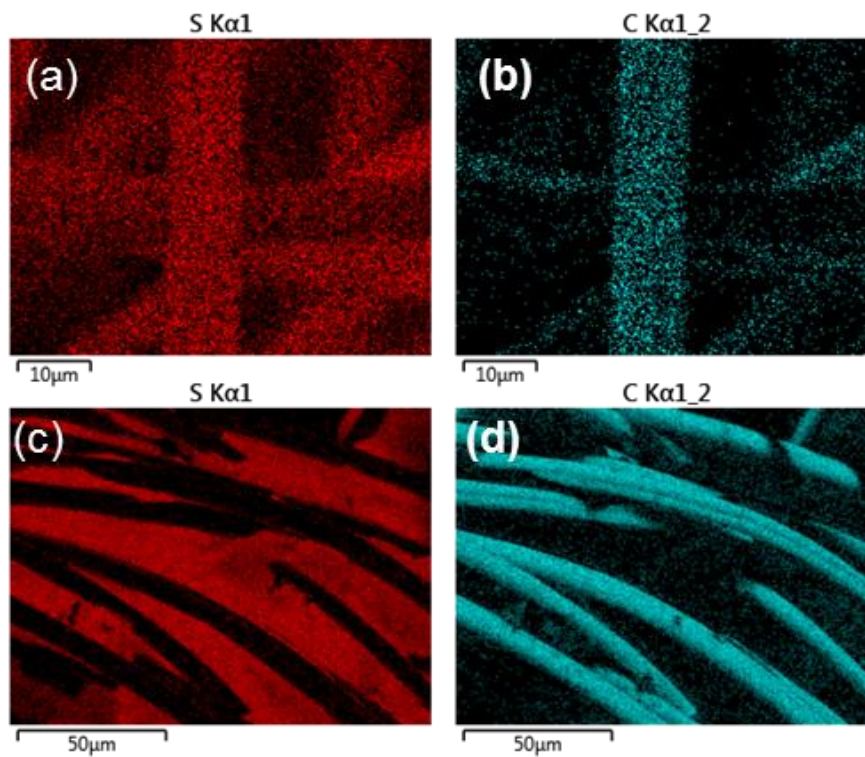


Figure 28. Example SEM images of vapor-infiltrated carbon felt (a - S, b - C) and melt-infiltrated AvCarb cloth (c - S, d - C).

Sulfur coats the fibers more evenly in vapor infiltration, but the mass loading can be variable across the sample. It is easier to tailor the mass loading based on infiltration time. Varying the heating time from 4 to 12 hours was an effective method to produce a desired range of mass loadings. Vapor infiltration in a desiccator has the same advantages and disadvantages as infiltration in a furnace; however, the furnace is a simpler process.

Additionally, not all fabrics were compatible with all infiltration methods. Vapor infiltrating the AvCarb fabric did not result in any significant sulfur loading. Melt infiltration of the carbon felt sticks to the substrate when burning off excess sulfur to achieve the desired loading.

4.3.2 *Electrochemical Testing*

Given the variety of infiltration methods and fabric types, not all combinations performed equally in testing. In order to investigate the impact of mass loading and electrolyte concentration on performance, the carbon fabric and infiltration method that offers the best performance and mass loading tailorability was needed. The AvCarb was not a candidate because the S did not attach to it in vapor infiltration. Melt infiltration does not give the range of necessary mass loadings. The Flexorb fabric infiltrated well under all methods; however, initial electrochemical tests revealed poor capacity from the material. Therefore, the vapor-infiltrated (in a furnace) carbon felt was chosen for further tests.

Figure 29 demonstrates the proof of concept that low concentration electrolytes may yield superior performance with low concentration electrolytes. The lower viscosity, as shown in the previous chapter improves wetting and permeation through the dense, tortuous cathode, allowing access to more of the active material. This effect is particularly pronounced in high loading cathodes, particularly those made of dense fibers. In the previous chapter, low concentration electrolytes were shown to perform well, but the low loading, low density cathodes were thin enough for the high viscosity 3M electrolyte to

still wet. However, in the more practical and commercial case of high loading cathodes, this effect disappears and the benefits of the low concentration electrolyte are clear.

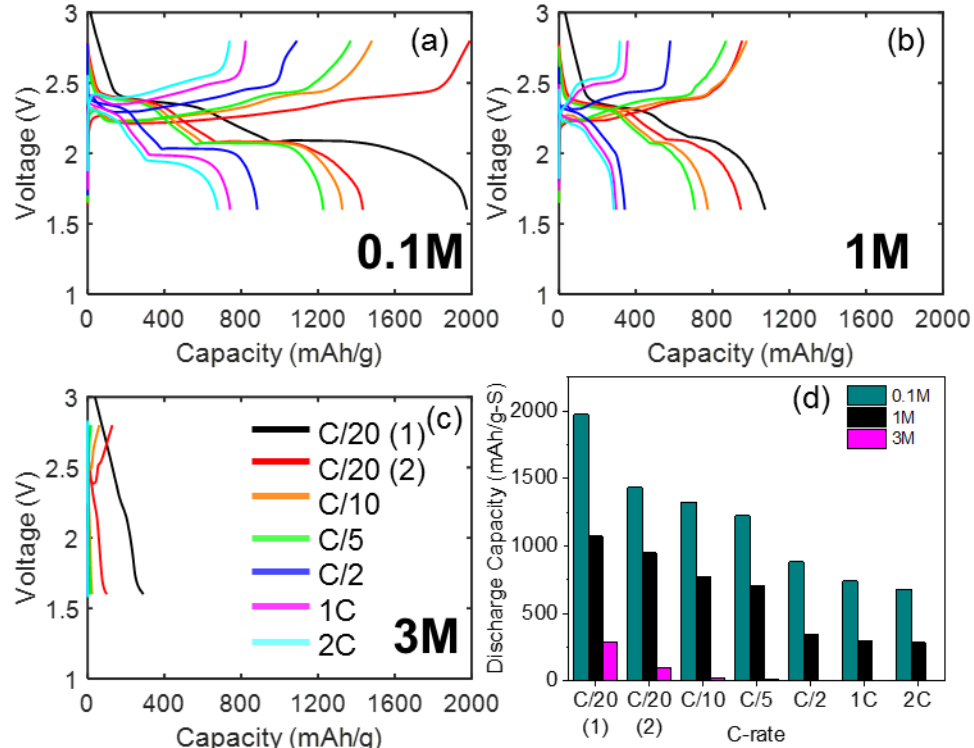


Figure 29. Charge/discharge results of carbon felt cells with $\sim 2.5\text{mg-S/electrode}$ tested with (a) 0.1M, (b) 1M, and (c) 3M LiTFSI in 1:1 DME:DIOX electrolyte, (d) comparison of discharge capacities.

4.4 Conclusion

In this study we evaluated several carbon fabrics and S infiltration methods for their merits at producing high-capacity high mass loading cathodes. The carbon felt proved to be the most effective substrate in terms of ease of sulfur infiltration to various loadings and electrochemical performance. The vapor infiltration method proved to be the most versatile in terms of tailoring sulfur loading based on infiltration time. In the case of high loading cathodes, the low concentration electrolyte strongly outperformed the standard 1M and high concentration 3M.

CHAPTER 5. PERFORMANCE OF LI-S BATTERIES WITH LOW CONCENTRATION, FLUORINATED ETHER-BASED SOLVENTS

The following is reproduced and reformatted from the author's submission to the Journal of Materials Chemistry A. The manuscript is entitled "Minimizing Long-Chain Polysulfide Formation in Li-S Batteries by Using Localized Low Concentration Highly Fluorinated Electrolytes" and its authors include: Rebecca Glaser, Oleg Borodin, Johnson, Samik Jhulk, and Gleb Yushin. Small changes between this chapter and the published paper may exist as this thesis was submitted before adjustments to reviewer comments were made. Differences between the manuscript and this chapter include inclusion of the supplemental information directly in the main text. Computational work was performed by our collaborator Dr. Oleg Borodin at the U.S. Army Research Laboratory.

5.1 Introduction

For the last few decades, the Li-S chemistry has promised lightweight and high energy density batteries for lower-cost electric transportation.^{140, 159, 160} Li-S batteries have the potential to help electrify bus fleets, trucks, drones, airplanes and other electric vehicles, an important step to lowering CO₂ emissions and combatting climate change. However, Li-S batteries face several significant challenges: formation and high solubility of intermediate polysulfide species in traditional ether-based electrolytes and the resulting difficulty in producing high-loading cathodes.¹⁶⁰ The polysulfide dissolution causes the

shuttle effect, loss of active material in the cathode, low cycle life, loss of cell capacity, and an increase in anode resistance from the deposition of insulating Li_2S on the surface. Long-chain polysulfides are particularly soluble in ether-based electrolyte solutions.^{160, 161} The use of solid electrolytes may overcome some of such challenges, but at the expense of poor low temperature performance, increased electrolyte weight and more elaborate and expensive cell fabrication procedures.¹⁶² Developing lightweight liquid electrolytes that may dramatically reduce long-chain polysulfide formation and cathode dissolution is thus critically important for practical applications of Li-S cell chemistry.^{163, 164} Such electrolytes may complement significant efforts in the development of advanced S-based cathodes, where S is encapsulated within carbon^{36, 38, 42, 44, 45, 165, 106} or metal oxides^{23, 95, 96, 101, 104, 166, 167} in order to physically or chemically trap polysulfides.

DME/DIOX blends are traditionally used as electrolyte solvents for Li-S cells due to their good solvation of Li^+ , favorable SEI formation,⁷⁰ and low viscosity. However, these solvents induce formation and rapid dissolution of polysulfides. Two other solvents for Li-S battery electrolytes have recently been explored: highly fluorinated ethers and sulfones. Highly fluorinated ethers have emerged as a new class of electrolytes that have limited solubility for polysulfides, thus limiting their dissolution and reducing the shuttle effect.^{124-126, 153, 168} Fluorinated electrolytes have poor donor-ability^{59, 126, 133} which minimizes their ability to dissolve Li^+ and polysulfides, making them promising for Li-S batteries but often at the expense of reduced rate capability.¹⁶⁹ Several studies have shown that fluorinated ether co-solvents are beneficial at limiting self-discharge.^{127, 129, 168, 170, 171} Azimi et al. have made significant contributions toward the study of fluorinated ethers in the Li-S system. Fluorinated ethers also have lower viscosities and melting points than traditional ether-

based solvents.¹²⁵ At the same time, highly fluorinated ethers also have low solubility for Li salts and thus require co-solvents in the electrolyte systems. Conversely, sulfones, and sulfolane (SL) in particular, have been predominantly investigated as a high voltage Li-ion battery electrolyte because of their high oxidative stability, high dielectric constant and high Li transference number.¹⁷²⁻¹⁷⁸ For Li-S batteries, SL was recently evaluated as a co-solvent with the traditional DIOX and DME ethers to enhance cell rate performance.^{65, 179-181} Interestingly, the addition of highly fluorinated ethers to highly concentrated SL-based electrolytes was also found to improve their rate performance by decreasing polysulfide solubility.^{182, 183} Such electrolytes are often termed “localized” since Li salts are localized at the non-fluorinated co-solvent.^{184, 185} Most commonly, the local concentration of Li at such co-solvent(s) is very high and thus electrolytes are called “localized high concentration electrolytes (LHCE)”.¹⁸⁶ These LHCEs maintain the high capacity from a high concentration electrolyte while preserving low viscosity and cost.

An additional challenge to the commercialization of Li-S batteries is the difficulty accessing material in high loading cathodes.⁵¹ Our group previously reported a new class of low concentration electrolytes (0.1M) with a significantly lower viscosity that could enable fuller access to active material within the sulfur cathode.¹⁵⁸ In this study, we systematically investigate the discharge behavior as we combine the approaches of fluorinated electrolytes and low concentration electrolytes. We explore the ratio between 1,1,2,2-Tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (HFE) and the sulfolane (SL) co-solvent, evaluate the discharge reaction mechanism, and analyze the SEI formation. Based on the previously used notation, we call such electrolytes localized low concentration electrolytes (LLCE). LLCE may offer unique behavior – suppression of the formation and

dissolution of the long-chain polysulfides, thus dramatically enhancing accessible S capacity.

5.2 Experimental Details

5.2.1 S/C Cathode and Coin Cell Preparation

The S-based cathodes are composed of bulk S (99.5%, Sigma-Aldrich, USA) and Ketjen Black® (Lion Specialty Chemicals Co. LTD, Japan). The S was melt-infiltrated into the Ketjen Black (KB) at 157°C for 12h then the excess S was burned off at 250°C to create a sulfur:KB composite with approximately 50 wt.% S. The S/KB composite was mixed with polyacrylic acid (PAA) (450,000 MW, Aldrich, USA) and PureBlack® (Superior Graphite, USA) as binder and conductive additive, respectively. The components are mixed in a 70:20:10 S/KB:PAA:PB weight ratio. A 1:1 ethanol:water mixture was used as the slurry's solvent. The mixture was sonicated and then stirred overnight to produce a viscous slurry. The slurry was cast on aluminum (Al) foil (MTI, USA), dried in air, punched into disks, and then dried in a vacuum oven at 60°C for 12 h. The electrodes produced had a sulfur loading of approximately 0.5 mg.S/cm². The S/KB electrodes were assembled into 2032 coin cells using a Celgard 2500 separator, Li foil (0.75mm thick, 99.9%, Alfa Aesar), and 30μL of electrolyte.

5.2.2 Electrolytes

Electrolytes consisting of 0.1M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich, USA), sulfolane (SL, >99% purity, Sigma-Aldrich), and 1,1,2,2-Tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (HFE, >95% purity, TCI Chemicals) were

mixed with SL:HFE molar ratios of 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, and 1:10. The comparison 0.1M LiTFSI + 0.1M LiNO₃ in 1:1 1,2 DME:1,3 DIOX (DME - 99.5%, Sigma Aldrich, DIOX – 99.8%, Sigma Aldrich) electrolytes were also prepared. An additional 1M LiTFSI in 1:2 SL:HFE was also made for comparison. Unless otherwise noted, all data shown are for 0.1M electrolytes. For characterization measurements (viscosity, conductivity, polysulfide tests), sulfolane was used as received. For electrochemical tests, sulfolane was further purified via vacuum sublimation followed by 3A molecular sieves.

The chemical structure and simplified schematics of the solvents used in this work and the LLCE system are given in Figure 30. A RheoSense μ Viscometer (RheoSense, USA) was used for viscosity measurements. Ionic conductivity measurements were done using electrochemical impedance spectroscopy (EIS, Gamry Interface 1000, USA) on Li/Li symmetric cells. The ohmic resistance and the cell dimensions were used to calculate the ionic conductivity. Raman spectra of all electrolytes were taken with a Renishaw Raman Spectrometer (Vis / near-IR, USA) using a 785nm laser. Samples were sealed in air-tight septum vials for analysis. For the pulsed-field gradient (PFG) NMR measurements all samples were prepared in standard 5 mm (o.d.) NMR tubes inside an Ar-filled glovebox and sealed with Teflon tape. All samples were allowed to equilibrate for 30 min inside the spectrometer before analysis to minimize the effects of convection in the diffusion measurements. A Bruker Avance III NMR spectrometer equipped with a Diff-50 diffusion accessory was used to measure self-diffusion coefficients of each component across a range of compositions: SL/TFE (¹H, 399.9 MHz), TFE/TFSI (¹⁹F, 376.3 MHz), and Li⁺ (⁷Li, 155.4 MHz). A stimulated echo sequence (Bruker “diffSte”) was used to collect the NMR data and the diffusion coefficients were computed with the T1/T2 relaxation module of

Bruker's TopSpin software package. A gradient pulse length δ of 1 ms was used for all experiments. The gradient strength g was varied between 200-400 G·cm⁻¹ and the diffusion time Δ varied between 20-100 ms depending on the nuclei being measured.

Polysulfide stability in each electrolyte composition was analyzed by mixing stoichiometric amounts of S and Li₂S in 0.1M LiTFSI, 1:y SL:HFE for y = 1, 2, 3, 4, 5, 6, and 10 to create 0.01M polysulfide solutions. LiTFSI was first dissolved in the SL. Then the S and Li₂S were dissolved in the solution to ensure the reaction to form polysulfides. Lastly, the HFE was added to produce the desired solvent ratio. Solutions were then stirred at 40°C for 5 days and at room temperature for another 5 days to ensure the reaction went to completion. Solutions of Li₂S₂, Li₂S₄, Li₂S₆, Li₂S₈, were made for each SL:HFE ratio, centrifuged to separate precipitates, and analyzed with UV-Vis (Avantes, AvaSpec-ULS2048CL-EVO-RS, Netherlands). Reference samples were also made with 0.1M LiTFSI + 0.1M LiNO₃ in 1:1 DME:DIOX. Analysis of solution color was used to qualitatively compare polysulfide concentration in solution.

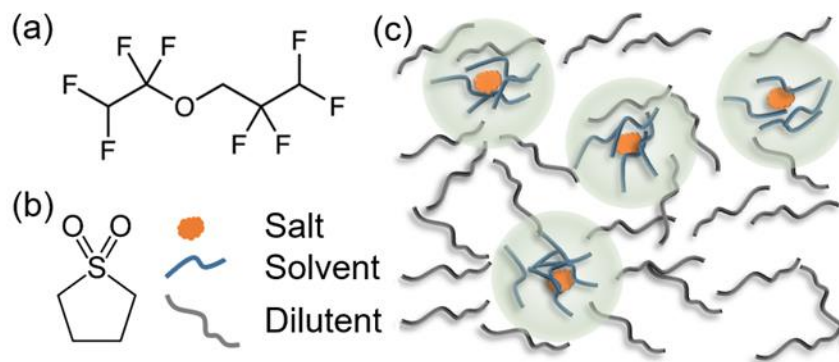


Figure 30. Chemical structures of (a) 1,1,2,2-Tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (HFE) (b) sulfolane, and (c) localized low concentration electrolyte (LLCE), where green circles indicate localized salt/solvent regions, SL is the solvent, and HFE is the diluent.

5.2.3 Electrochemical Testing

Charge-discharge testing was done on an Arbin system (BT2X43, USA). Samples were cycled between 1.6 and 2.8V vs. Li/Li⁺. All samples underwent a first discharge at C/20. In rate testing, this was followed by charge-discharge cycles at C/20, C/10, C/5, and 1C. For long term tests, cells were discharged at C/50, then cycled at C/5 for 200 cycles. EIS spectra were taken in the frequency range 1 MHz – 0.01 Hz before and after testing. For the 1:2 SL:HFE ratio, cyclic voltammetry (CV) testing was done for 100 cycles at a rate of 0.1mV/s. EIS was done before testing and every 25 cycles during cycling.

5.2.4 *Post-Mortem Analysis*

After testing, cells cycled for 200 cycles were disassembled, washed with dimethoxyethane (DME), and dried in a desiccator under vacuum for 12 hours to remove residual solvent. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to analyze surface features of the S/KB cathodes and Li anodes. A Hitachi 8200 SEM microscope (Japan) was used in this study. X-ray photoelectron spectroscopy (Thermo-K Alpha, USA) was used to evaluate surface species for the tested cathode and Li SEI.

5.2.5 *Molecular Dynamics Simulations*

Molecular dynamics (MD) simulations were performed on the ~0.1M LiTFSI SL-HFE electrolytes at SL:HFE ratios of 2 and 5 with Li₂S₄ and 1M LiTFSI SL-2HFE doped with 0.37M Li₂S₄ added to examine the influence of electrolyte composition of the polysulfide aggregation. Compositions of MD simulation cells are given in Table S1. A many-body polarizable force field (APPLE&P) was used for simulations with the SL, LiTFSI and Li₂S₄ parameters taken from previous work,^{177, 187, 188} while HFE force field

was derived for this work. Partial charges were determined by fitting electrostatic potential on a grid of points around the molecule for multiple conformers from MP2/aug-cc-pvTz calculations. Torsional parameters were fit to MP2/aug-cc-pvTz energies at wB97XD/6-311+G(2df,p) geometries. MD simulation methodology is given in Supporting Information. In order to speedup ion transport and aggregation, MD simulations were performed at 363 K with first 40 ns discarded as equilibration. Statistics was collected over the last 17 ns of simulations.

The Ewald summation method was used for the electrostatic interactions between permanent charges with permanent charges and permanent charges with induced dipole moments with $k = 63$ vectors. Multiple timestep integration was employed with an inner timestep of 0.5 fs (bonded interactions); a central time step of 1.5 fs for all nonbonded interactions within a truncation distance of 7.0-8.0 Å and an outer timestep of 3.0 fs for all nonbonded interactions between 7.0 Å and the nonbonded truncation distance of the smaller of 11 Å. The reciprocal part of Ewald was updated only at the largest of the multiple time steps. A Nose-Hoover thermostat and a barostat were used to control the temperature and pressure with the associated frequencies of 10^{-2} and 0.1×10^{-4} fs. The atomic coordinates were saved every 2 ps for post-analysis.

Solvent and ion self-diffusion coefficients and conductivity extracted from MD simulations are given in Table 4. They show that increasing fraction of HFE increases dynamics of all species but conductivity decreases due to increased salt aggregation and localization of the SL-LiTFSI-rich domains as shown in Figure 30(a-b).

Table 4 Solvent and ion self-diffusion coefficients (D) in (10-10 m2 s-1) and ion conductivity from MD simulations at 363 K.

	HFE:SL=2	HFE:SL=5	HFE:SL=2
c(M) LiTFSI	0.09	0.12	1.0
Number of SL	390	182	80
Number of HFE	780	912	160
Number of LiTFSI	16	16	42
Number of Li ₂ S ₄	8	8	16
D(SL)	14.5	17.1	1.8
D(HFE)	17.7	24.1	9.3
D(TFSI)	7.4	6.1	0.68
D(S ₄)	2.3	5.2	0.54
D(Li)	3.6	5.3	0.57
conductivity (mS cm ⁻¹)	0.98	0.52	1.1
Ionicity	0.18	0.07	0.15

5.3 Results and Discussion

5.3.1 Computational Results

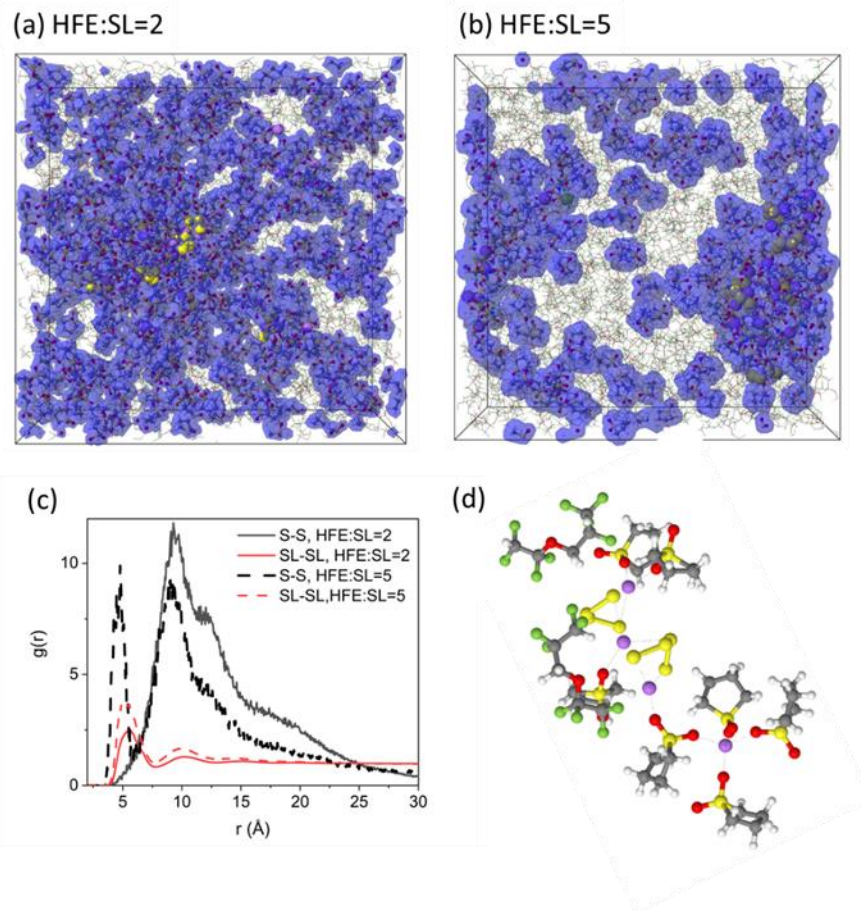


Figure 31. (a-b) MD simulation boxes of SL-LiTFSI-Li₂S₄ electrolytes for HFE:Li=2 (a) and HFE:Li=5 (b) with HFE shown as wireframe the SL-LiTFSI-Li₂S₄ are highlighted by purple isosurface; (c) radial distribution functions of the terminal sulfur of S₄⁻ (S-S) and SL for electrolytes shown in (a) and (b), (d) a representative cluster.

Snapshots of MD simulations cells are shown in Figure 31a,b for two compositions HFE:SL ratios 2 and 5, they confirm that HFE behaves as antisolvent with the Li⁺ and anions being localized in the SL-rich domains. Purple regions represent SL-LiTFSI-Li₂S₄ domains. Figure 32 shows that Li⁺ has the highest probability of being coordinated by anions following by oxygens of SL, while no oxygens of HFE contribute to the Li⁺ first coordination shell. Increasing the ratio of HFE to SL from 2 to 5 decreases available SL for solvating Li⁺ resulting in higher salt aggregation as reflected by higher Li-O(TFSI) and

Li-S⁺(S₄) peaks shown Figure 32. Importantly, the nanodomain structure of SL solvents modulates a dramatic increase of S₄²⁻ localization and aggregation in SL-5HFE electrolyte compared to SL-2HFE electrolyte as shown in Figure 31(c-d). Such location is consistent with the reduced solubility of Li₂S₄ in SL-5HFE electrolyte and is expected to facilitate conversion of longer polysulfides into shorter sulfides.

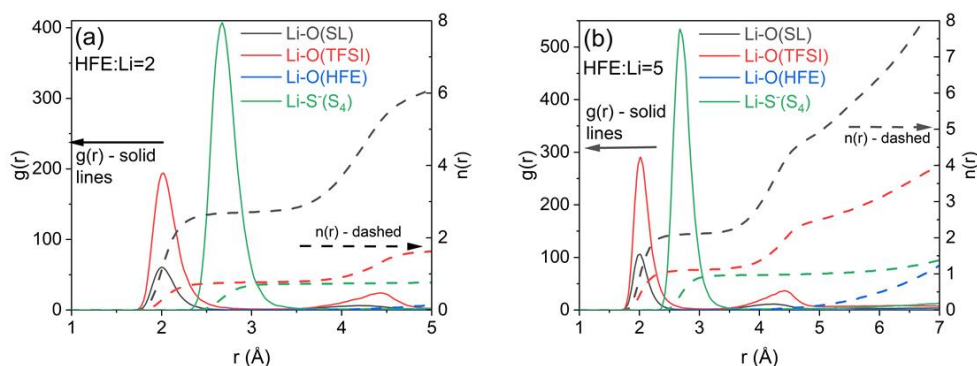


Figure 32. Radial distribution functions $g(r)$ and running coordination numbers $n(r)$ from MD simulations of SL- x HFE ($x=2,5$) electrolytes doped with LiTFSI and Li₂S₄.

5.3.2 Electrolyte Characterization

The viscosity, conductivity, and component diffusivities of all the electrolytes considered are compared in **Error! Reference source not found..** Since SL is more viscous than HFE, as the HFE content increases, the viscosity decreases. All the SL:HFE electrolytes are more viscous than the low concentration DME/DIOX electrolyte. Conductivity, calculated from the ohmic resistance of a Li/Li symmetric cell after EIS, similarly shows decreasing conductivity as HFE content increases. HFE has much lower solubility for Li⁺ than SL, explaining the decrease in conductivity with the decrease in SL content. All SL:HFE electrolytes have lower conductivity than the DME/DIOX electrolyte.¹⁸⁸ For testing, the DME/DIOX electrolyte required additional 0.1M LiNO₃ to produce high capacity at low concentration, whereas the SL/HFE electrolytes did not. The

higher concentration and the higher solubility for Li^+ in the DME/DIOX electrolyte may account for the difference in conductivities. The transference number also increases with HFE content. Diffusion coefficients, from NMR, (Table 1) of Li^+ and TFSI^- both increase with HFE content. Raman spectra (Figure 34) of pure solvents and electrolytes shows a clear transition between SL and HFE as the ratios change with no visible additional peaks attributable to LiTFSI due to the low concentration.

Ionicity (Figure 33d) is calculated by taking the ratio of the molar conductivity calculated from NMR results to the molar conductivity calculated from symmetric cell EIS. Ionicity clearly decreases with increasing HFE content and values are in line with the

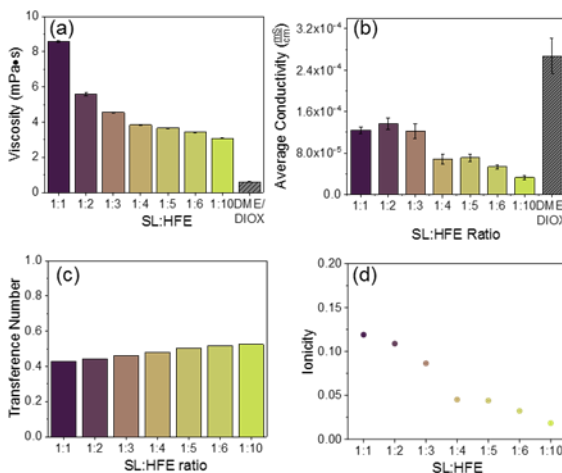


Figure 33. (a) Viscosities, (b) conductivities, (c) and transference numbers of electrolytes at 0.1M LiTFSI in given ratios of SL:HFE (+0.1M LiNO_3 for DME/DIOX), (d) Ionicity - ratio of molar conductivity calculated from NMR to molar conductivity calculated from symmetric cell EIS.

computational results above. The decrease in ionicity with increasing HFE further confirms higher ionic aggregation with higher HFE content. The lower ionicity at high SL:HFE ratios also explains the decreasing conductivity, as fewer species are participating in conductivity when there is higher aggregation. Significant deviation from ideal in the Walden plot (Figure 35) also indicates a high degree of ion aggregation.

Table 5 Diffusion coefficients of electrolyte components.

SL:HFE	D- Li	D - SL	D - TFSI- m ² /S (x10 ⁻¹⁰)	D - HFE 19F	D - HFE 1H
1:1	1.2	2.5	2.5	1.6	2.4
1:2	1.5	3.1	3.4	1.9	3.3
1:3	1.7	3.8	4.3	2.0	4.2
1:4	2.0	4.1	4.9	2.1	4.7
1:5	2.2	4.4	5.3	2.1	5.1
1:6	2.3	4.5	5.6	2.1	5.3
1:10	2.5	4.6	6.4	2.3	6.1

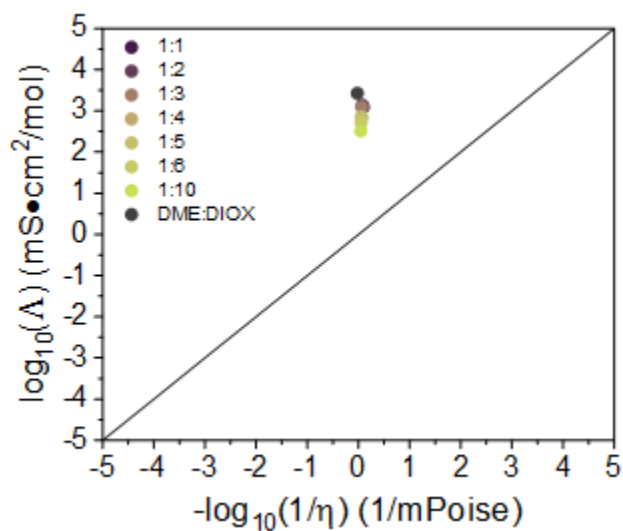


Figure 35. Walden plot of molar conductivity vs. inverse viscosity for all electrolyte solutions.

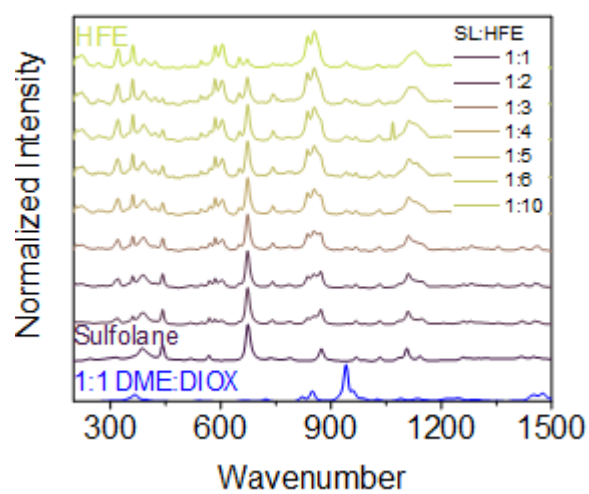


Figure 34. (a) Raman spectra of all electrolyte solutions.

5.3.3 Electrochemical Testing

Electrochemical performance of 0.1M LiTFSI + 0.1M LiNO₃ in DME/DIOX was compared with that of 0.1M LiTFSI in SL:HFE ratios of 1:1-1:10. Figure 36a shows the comparison of 1:2 and 1:5 ratios by rate (additional results of the other ratios are given in Figure 37). The SL/HFE-based electrolyte consistently produces higher capacity than the DME/DIOX electrolyte across all SL:HFE ratios, suggesting reduced dissolution of the active material. The DME/DIOX electrolyte shows the conventional two plateau discharge behavior – the first plateau at ~2.4 V vs. Li/Li⁺ corresponding to the formation of long-chain polysulfides and the second one at ~2.1 V vs. Li/Li⁺ corresponding to the lithiation of long-chain polysulfides and their transformation to shorter chained polysulfides, and

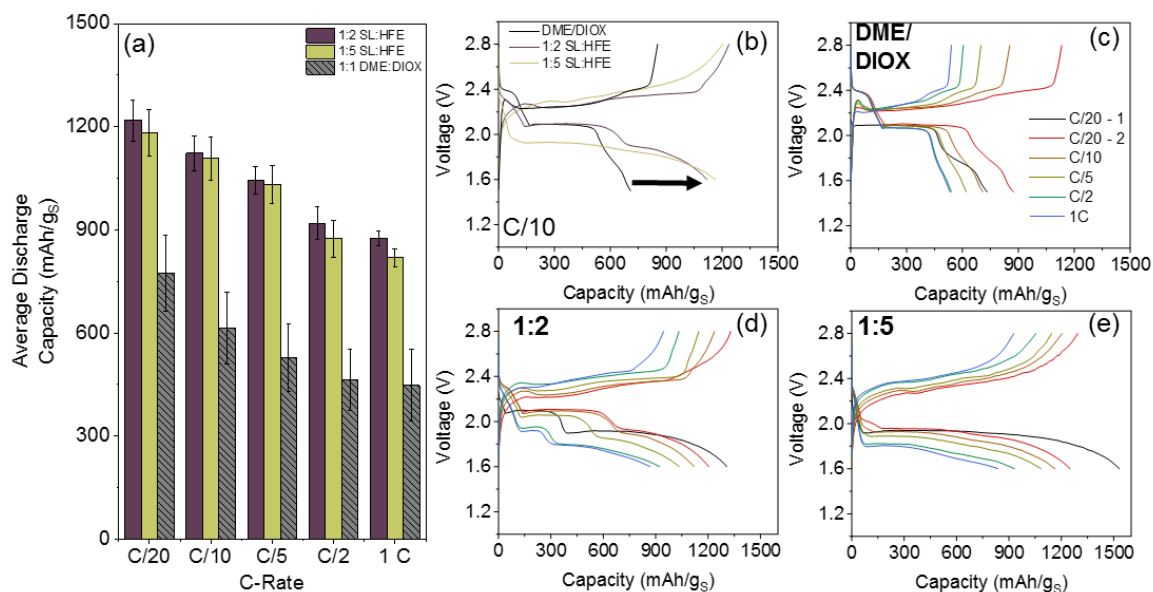


Figure 36. Electrochemical results showing (a) comparison of rate performance of 0.1M LiTFSI in DME/DIOX and all fluorinated electrolytes, (b) discharge curves at C/10 representative discharge curves by rate for 0.1M LiTFSI in (c) DME/DIOX, (d) 1:2 SL:HFE, (e) 1: 5 SL:HFE.

eventually Li₂S.⁹ Interestingly, in the SL/HFE electrolytes, a third lower voltage appears

at ~ 1.9 V vs. Li/Li^+ , which we assign to a higher overpotential direct transformation of S to short chain polysulfides and Li_2S , as often observed in quasi-solid state reactions.¹⁴ As the proportion of HFE increases, the cells discharge behavior changes between 1:3 and 1:4 SL:HFE (Figure 38b, Figure 37), where the second plateau nearly completely disappears. Figure 36d-e compare the shape of the discharge profiles for (1:2) and (1:5) ratios. The change in the discharge behavior can be seen particularly clear in Figure 36b, where we

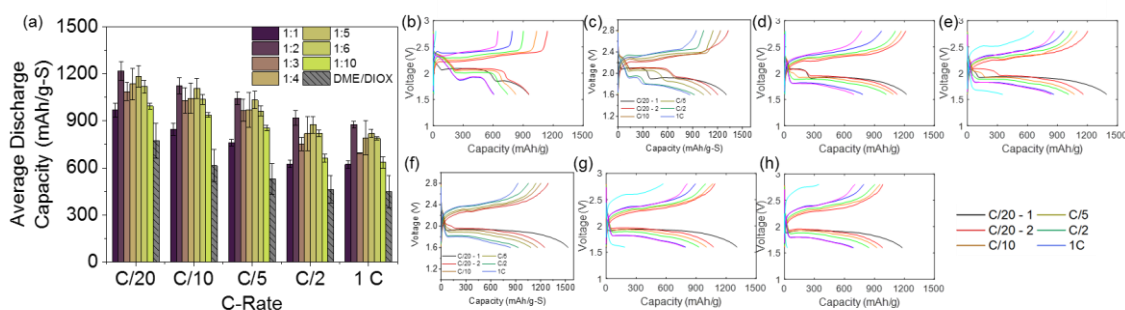


Figure 37. (a) Full charge and discharge capacity across C-rates for all SL:HFE ratios evaluated, charge/discharge curves for (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4, (f) 1:5, (g) 1:6, and (h) 1:10 showing the evolution in discharge behavior.

compare both charge and discharge curves at C/10 in these two electrolytes with that of conventional DME/DIOX mixture.

The change in reduction mechanism has two components: (1) the appearance of a 3rd low voltage plateau and (2) the shrinkage and near disappearance of the 2nd plateau as the HFE proportion increases. Increasing the HFE content clearly increases the fraction of capacity that is borne by the third plateau (Figure 38). This is consistent across all C-rates for the solvent compositions where the 3rd plateau appears (Figure 38c-d). We propose that as the proportion of HFE increases, the ability to form long-chain polysulfides from S in such an electrolyte system noticeably decreases. As a positive outcome, the dissolution of the polysulfides is reduced significantly, leading to higher capacity (Figure 36a). Effectively, at SL:HFE > 1:4 we observe a shift of the reaction pathway into a quasi-solid-state reaction largely reducing S to Li₂S₂ and eventually to Li₂S on the cathode (Figure 38). This leads to an experimentally observed higher overpotential. We also cannot exclude a

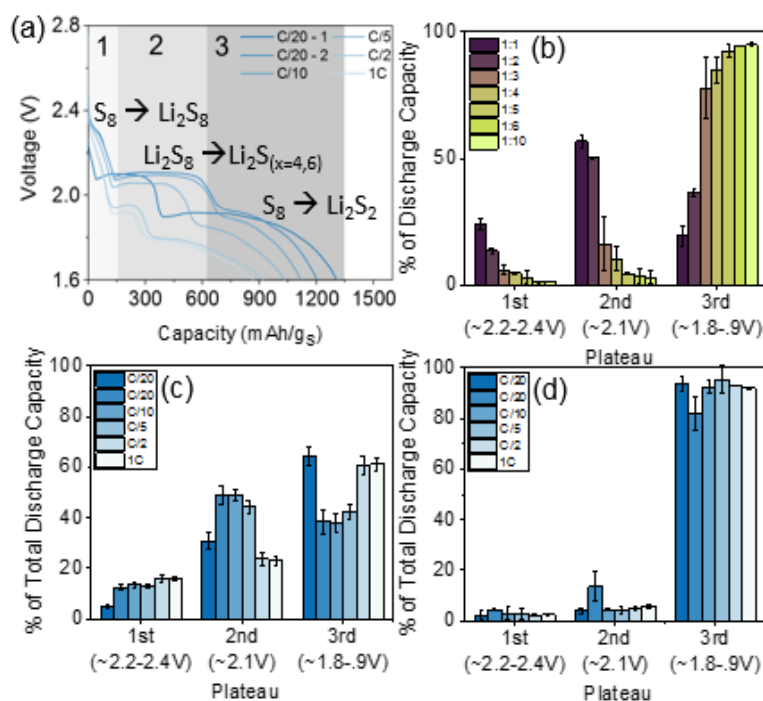


Figure 38. (a) Discharge curves for 1:2 SL:HFE showing three distinct plateaus; breakdowns of percent of capacity per plateau (b) for all SL/HFE electrolytes at C/10, (c) for SL:HFE = 1:2 for all rates, (d) for SL:HFE = 1:5 for all rates.

possibility of developing anode SEI resistance, which may further lower the plateau voltage.

Figure 38c,d breaks this down by rate for 1:2 and 1:5 SL:HFE electrolyte compositions and show the stark difference in proportion of capacity coming from the 1st and 2nd plateaus for a high and low SL:HFE ratio. Importantly for the 1:5 SL:HFE case, the capacity in the first and second plateau is relatively constant as the rate increases; however, the total capacity decreases, making their proportion increase (Figure 37). This means that the capacity loss is coming off the 3rd plateau most likely as the kinetics of the quasi-solid-state reaction is the slowest. Other contributions to the reduced rate may include a buildup of polysulfides on the separator¹⁸⁹ and the growing, resistive SEI on the anode.

5.3.4 Polysulfide Solubility Tests

To explain the surprising discharge behavior, solutions of Li₂S₂, Li₂S₄, Li₂S₆, and Li₂S₈ for each SL:HFE ratio were made (Figure 39a). As the Li₂S_x chain length increases, the solution color lightens, indicating a lower concentration of polysulfides and a decreased solubility. Similarly, as the HFE content increases, the polysulfide solubility also decreases. Additionally, the Li₂S₂ in the 1:1 SL:HFE solution was the only solution where the polysulfides fully dissolved; all other polysulfide solutions formed precipitates upon addition of the HFE and throughout the several days of heating and stirring. UV-vis (Figure 39b-f) demonstrates the decreased intensity with increased amount of HFE. 1:1 and 1:2 SL:HFE show a broader color spectrum, whereas higher SL:HFE ratios show one narrower peak that decreases in intensity with more HFE. Figure 39f compares the different chain

lengths for 1:2 SL:HFE. There is a decrease in intensity and loss of the higher wavelength peak with the increasing polysulfide chain length. While stoichiometric solutions of Li_2S and S are intended to yield specific polysulfide chain lengths in solution, realistically, disproportionation reactions occur and a range of polysulfide chain lengths emerge, which UV-vis cannot separate out. However, the lightening color is an indication of change in overall concentration.

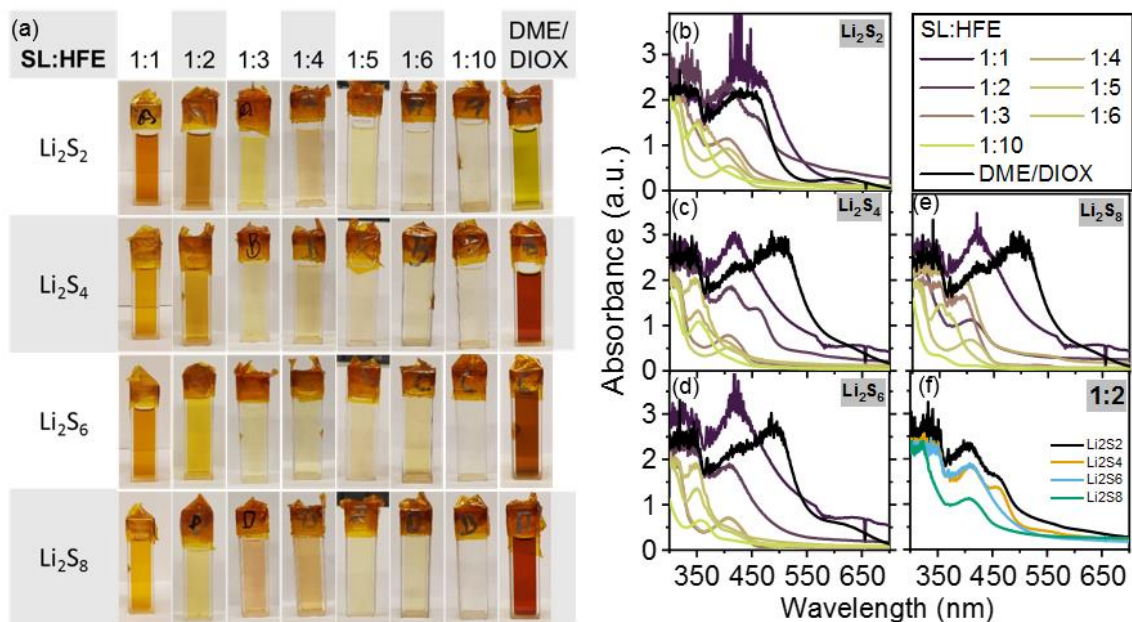


Figure 39. (a) Optical images of supernatant of polysulfide solutions (0.01M Li_2S_x in 0.1M LiTFSI, given SL:HFE) after preparation and centrifugation; (b-f) UV-Vis of polysulfide solutions for (b) Li_2S_2 , (c) Li_2S_4 , (d) Li_2S_6 , and (e) Li_2S_8 for all SL:HFE ratios, and (f) all Li_2S_x chain lengths for the 1:2 SL:HFE ratio.

Raman and FTIR spectra of the polysulfide solutions (Figure 40) do not show any additional polysulfide peaks, likely due to the extremely low concentration. The polysulfide tests show that shorter polysulfide chain lengths are more soluble in the SL/HFE-based electrolytes and that polysulfides are not stable in these electrolytes at high concentration. 10x dilution with the given ratio of SL:HFE to determine the solubility limit of each polysulfide did not dissolve the precipitates, indicating an extremely low polysulfide solubility.

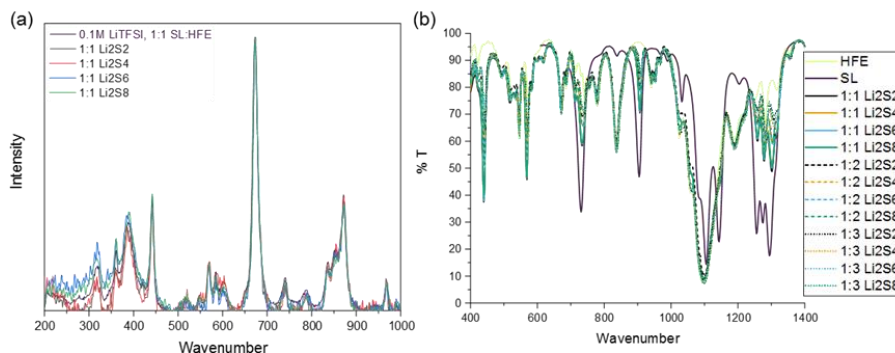


Figure 40. (a) Raman spectra of polysulfide solutions of all chain lengths for the 1:1 solvent ratio, (b) FTIR spectra of polysulfide solutions of all chain lengths for the 1:1-1:3 solvent ratios.

5.3.5 Comparison to 1M

In order to more deeply understand the impact of solvent ratio and salt concentration on electrochemical performance, 1:2 SL:HFE was evaluated at 1M (Figure 41). As Figure 41a shows, the discharge capacities across C-rates for the 1M 1:2 electrolyte is very similar to the 0.1M 1:2 electrolyte; however, there are some noticeable differences. Primarily, in the 1M case, the 2.1V discharge plateau is missing and the reaction largely follows the single low voltage plateau. Figure 41b offers some insight into this difference. Since the LiTFSI is solvated by the SL and the HFE largely acts as a non-solvent, it is useful to calculate the concentration of LiTFSI in just the SL and not the whole electrolyte. This indicates that the 0.1M LiTFSI in 1:2 SL:HFE is closer to 0.5M in the concentrated regions and the 1M is closer to 4M. At such high concentration, more SL molecules are used to solvate the LiTFSI and fewer remain to solvate the PS, pushing the reaction into the quasi-solid-state regime formerly only seen at the higher SL:HFE ratios. MD simulations confirm that Li_2S_4 are localized only in the highly concentrated 4M LiTFSI SL nanodomain as shown in Figure 41c. Most of SL molecules (80%) are bound to one or two Li^+ as expected for the localized salt-in-solvent electrolyte. Previous MD simulations of

electric double layer for salt-in-solvent electrolytes showed that anions preferentially adsorb on the positive electrode pushing the solvent complexed to Li^+ into the outer part of Helmholtz layer.¹⁹⁰ We expect similar behavior for the localized salt-in-solvent electrolyte where the majority of Li_2S_4 will be partitioned to the inner part of the Helmholtz layer at the positive electrode making it readily available for redox reactions.

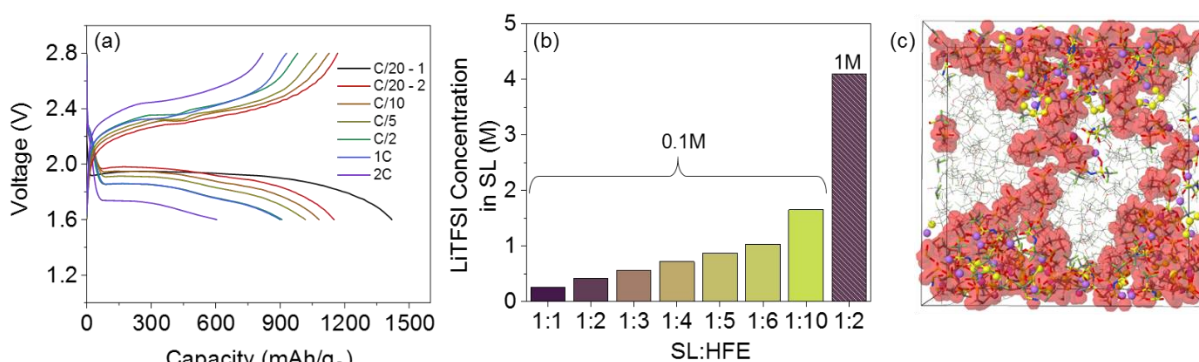


Figure 41. (a) Rate testing results for 1M LiTFSI in 1:2 SL:HFE, (b) concentration of LiTFSI in just SL for each SL:HFE ratio, (c) MD simulation box for 1M LiTFSI in SL:HFE=1:2 with 0.37Li₂S₄, van der Waals surface around SL molecules is shown in red, HFE are shown as wireframe.

5.3.6 Long Term Testing

The electrochemical stability of S cathodes in 1:2 and 1:5 SL:HFE electrolytes was evaluated for 200 cycles at the C/5 rate after an initial discharge at C/50 (Figure 42). The coulombic efficiency (CE) of the 1:5 electrolyte is higher than that of the 1:2 as the higher HFE content leads to stronger suppression of the formation of long-chain polysulfides and leads to reduced cathode capacity losses from their dissolution (Figure 42a), side reactions, and the shuttle effect. The SL/HFE electrolytes show substantially superior capacity to the DME/DIOX electrolyte, as might be expected from high solubility of polysulfides in

DME/DIOX (Figure 42a). Somewhat to our initial surprise, despite suppressing polysulfide dissolution the SL/HFE electrolytes suffered from faster degradation over the course of 200 cycles. The capacity losses correlated with steadily rising polarization and resistance in such cells (Figure 42). The diffusion-controlled tail in EIS also becomes dominant, indicating the difficulty of transporting Li^+ . Additionally, the mid-voltage plateau in 1:2 electrolyte shrinks as the cycle number increases and the discharge profile becomes similar to that of the 1:5 electrolyte (compare Figure 42c and d). This may potentially indicate a reduction in the SL:HFE ratio as a result of SL consumption to side reactions, such as solid electrolyte interphase (SEI) formation, or a from the resistive layer on the Li increasing cell resistance and suppressing the plateau voltage.

Cyclic-voltammetry (CV) of the 1:2 SL:HFE cell demonstrates the shift in discharge plateaus with increasing cycle number (Figure 42). EIS, taken every 25 cycles, also shows a clear increase in resistance throughout the course of the test, after initial equilibration with the first cycle. The increase in resistance may come from the SEI layer as it grows on the Li metal throughout cycling.

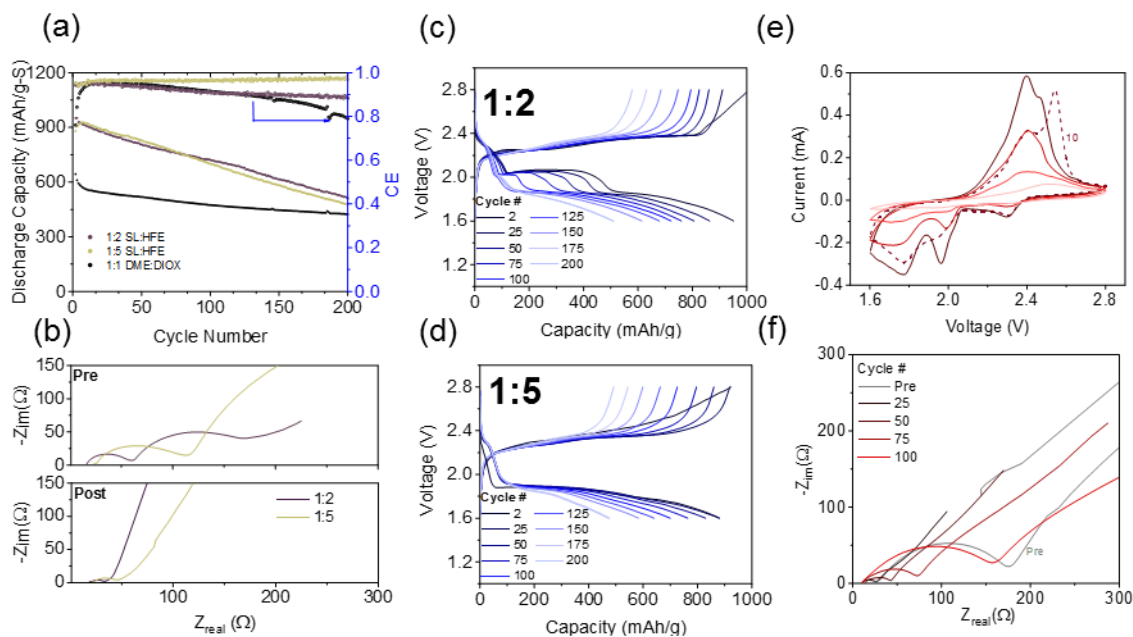


Figure 42. (a) Long-term cycling of all electrolytes, (b) EIS before (top) and after (bottom) long term cycling, (c-d) charge/discharge curves during long term cycling for (c) 1:2 and (d) 1:5 SL:HFE electrolytes. (e) EIS at 10 cycles and every 25 cycles throughout CV cycling and (f) CV scan at 0.1mV/S.

5.4 Post-Mortem Analysis

In order to gain insights into a possible degradation mechanism, we conducted post-mortem analyses following long-term testing on both sulfur cathodes and Li foil anodes (Figure 43). The separator in the 1:2 SL:HFE cell was more yellow than for the cell tested with 1:5. This indicates polysulfide suppression was greater with the higher HFE content, consistent with previous measurements (Figure 39). The most important result that explained the observed lack of cycling stability (Figure 42) was the formation of a very thick and brittle SEI layer on the Li anode foil in cells with 1:2 SL:HFE (Figure 43). This effect has also been seen in high concentration electrolytes with similar solvents.¹⁸⁶ EDS

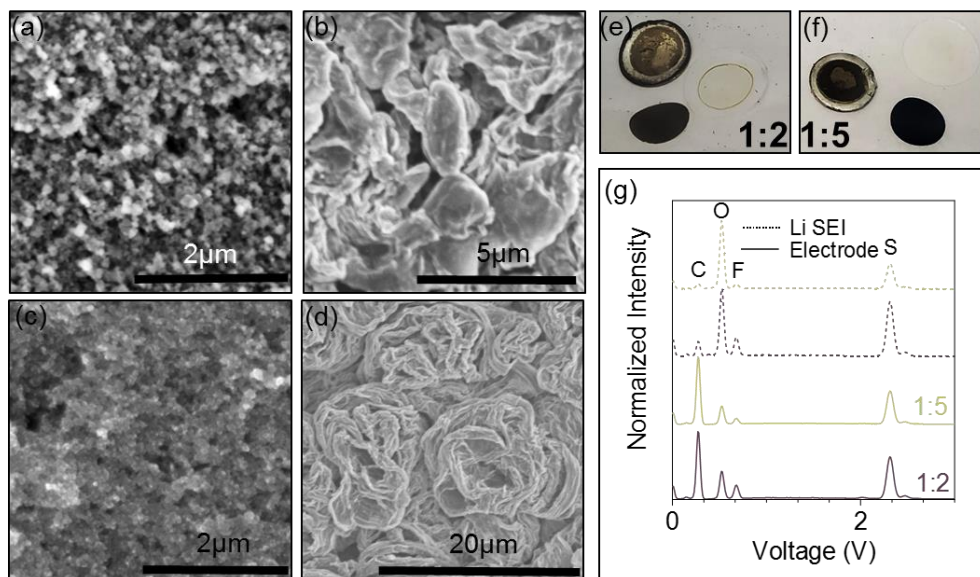


Figure 43. Post mortem of cells tested for 200 cycles with 0.1M LiTFSI in 1:2 and 1:5 SL:HFE electrolytes. Disassembled cell components for (a-b, e) 1:2 and (c-d, f) 1:5. SEM images of 1:2 (a) cathode and (b) anode, 1:5 (c) cathode and (d) anode. (g) EDS comparison of electrode and Li for 1:2 and 1:5 electrolytes.

indicates this SEI layer is primarily composed of oxygen (O), with S, C, and F also being present. Though the component species forming the SEI are similar to the DME/DIOX electrolyte, the effect on degradation is more extreme. The increase in resistance throughout testing, as shown with the CV experiment, combined with the visible SEI layer, support the theory of the thick SEI limiting access to the active material of the underlying

Li metal electrode and trapping species at the surface. Such a thick layer may explain much faster capacity loss in the SL-based electrolyte. Although small (Figure 39) such a gradual dissolution of the short chain polysulfides into electrolyte and their subsequent precipitation on the anode would contribute to SEI buildup and some loss of active material from the cathode. A thick SEI would limit Li^+ diffusion to the metal surface, deplete the electrolyte, and cover the Li metal available to react. Clearly, eliminating long-chain polysulfide formation in Li-S cells is important, but not sufficient to eliminate cell degradation. The formation of stable SEI is equally important. SL in particular is especially prone to dissociation on the Li metal anode.^{186, 191}

Nevertheless, no observable changes to the cathode morphology or structure were observed, compared to the DME/DIOX case (Figure 44). According to EDS measurements on the cathode, O and F, common cathode electrolyte interphase (CEI) components, accompany the expected S and C peaks (Figure 43). The surface composition was also investigated further with X-ray photoelectron spectroscopy (XPS) (Figure 46). On the cathode side (Figure 46a-d), the two electrolytes show similar surface species. The 1:2 case shows slightly more polysulfide species and Li_2S on the surface than the 1:5 case. A blend of carbon species is present on the electrodes tested with both electrolytes. Notably C-F and many C-O species are identifiable. These species are produced via electrolyte decomposition. Interestingly, no significant N peak was visible in EDS or the XPS survey scan, indicating a preferential decomposition of SL over TFSI⁻.

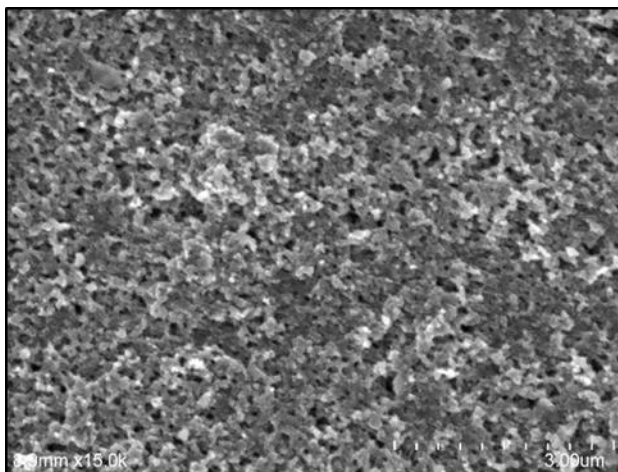


Figure 44. SEM of cathode tested with 0.1M LiTFSI + 0.1M LiNO₃, 1:1 DME:DIOX for 200 cycles.

On the anode side, SEM reveals dense surface features of varying structure (Figure 45). The thick SEI layer on the anode may contribute to the capacity decay throughout long term testing and the high surface area features provide a large area for further SEI-building reactions.¹⁸⁶ EDS indicates this layer is primarily composed of O, with S, C, and F also being present. From XPS (Figure 46e-h), sulfites and sulfate are present in the 1:2 and 1:5 cases as reaction products of electrolyte decomposition. The cell tested with the 1:5 electrolyte shows less intensity of Li₂S and sulfur atoms in a central position in a polysulfide chain. Sulfur in terminal positions shows a similar intensity to the 1:2 cell. This may mean there are more short chain polysulfide species on the anode side in the 1:5 case, either from fewer species dissolving and diffusing to the anode or from more complete reduction. LiF (Figure 45, Figure 47) is also an important component of the anode SEI. The carbon species on the anode are varied in both the 1:2 and 1:5 electrolyte cases, though similar species are seen on the anode as on the cathode. C-O features indicate decomposition of the HFE or a more complicated decomposition of SL or LiTFSI. S-O

species may come from decomposition of SL or LiTFSI and Li-F and C-F species may come from HFE or LiTFSI.

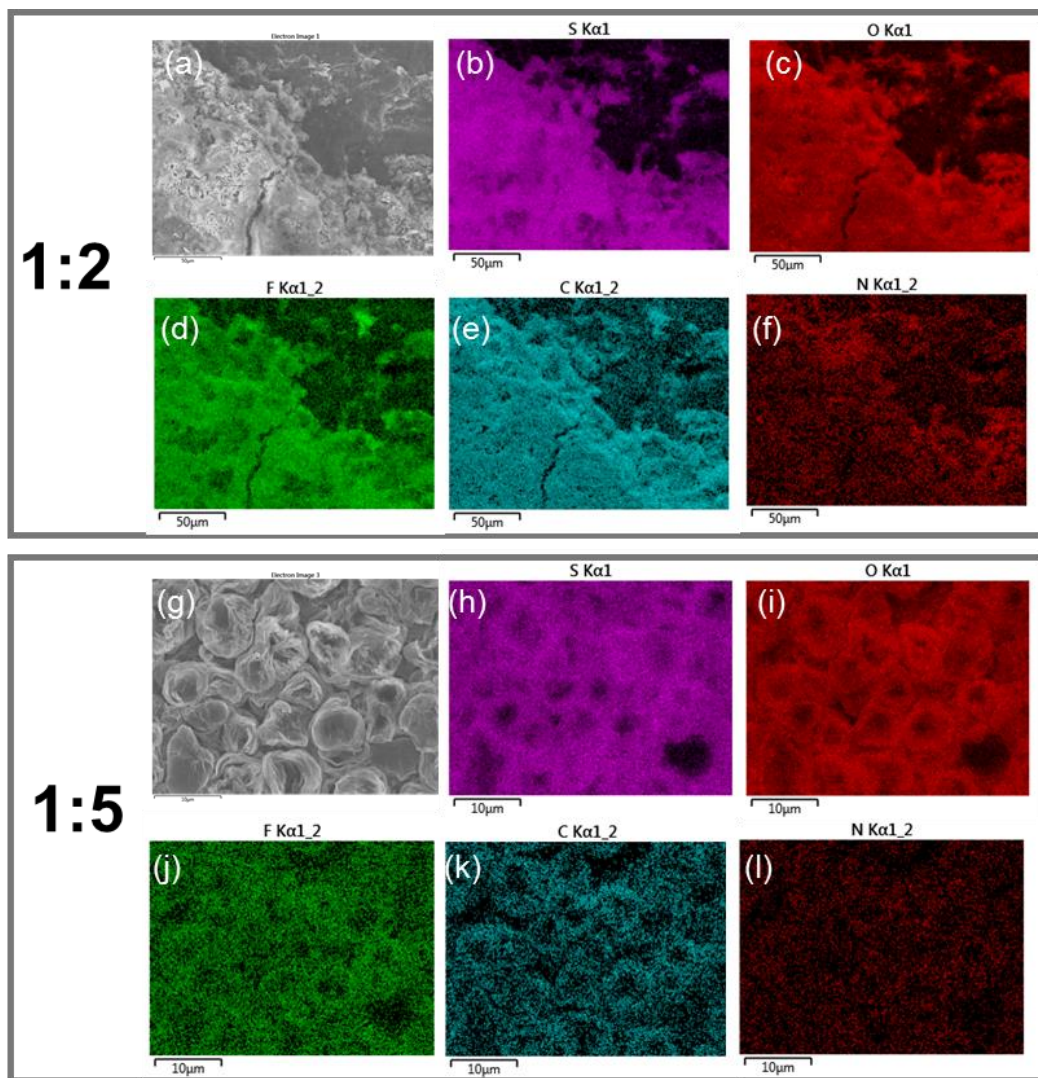


Figure 45. EDS results (S, O, F, C, N) for Li anode for (a-f) 1:2 and (g-l) 1:5 SL:HFE.

Figure 46 displays the relative proportion of elements on the cathode and anode surface for the 1:2 and 1:5 electrolytes. For the cathode, there is less O and S and more C and F in the 1:2 than the 1:5. For the anode SEI, the 1:2 electrolyte has more O, slightly more S than the 1:5 electrolyte, potentially indicating higher SL reduction in the 1:2 case.

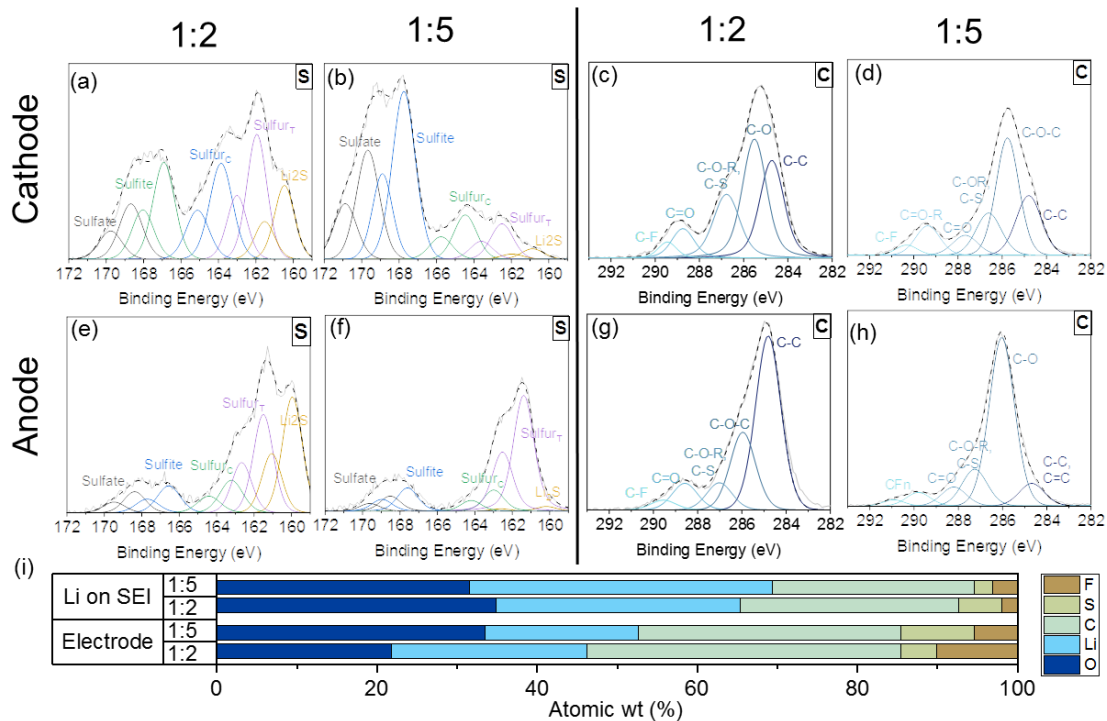


Figure 46. S and C XPS spectra of cathode (a-d) and Li (e-h) surfaces after long term testing. (i) Quantitative breakdown in elements on SEI and cathode surface. Li, O, and F spectra given in supplemental information.

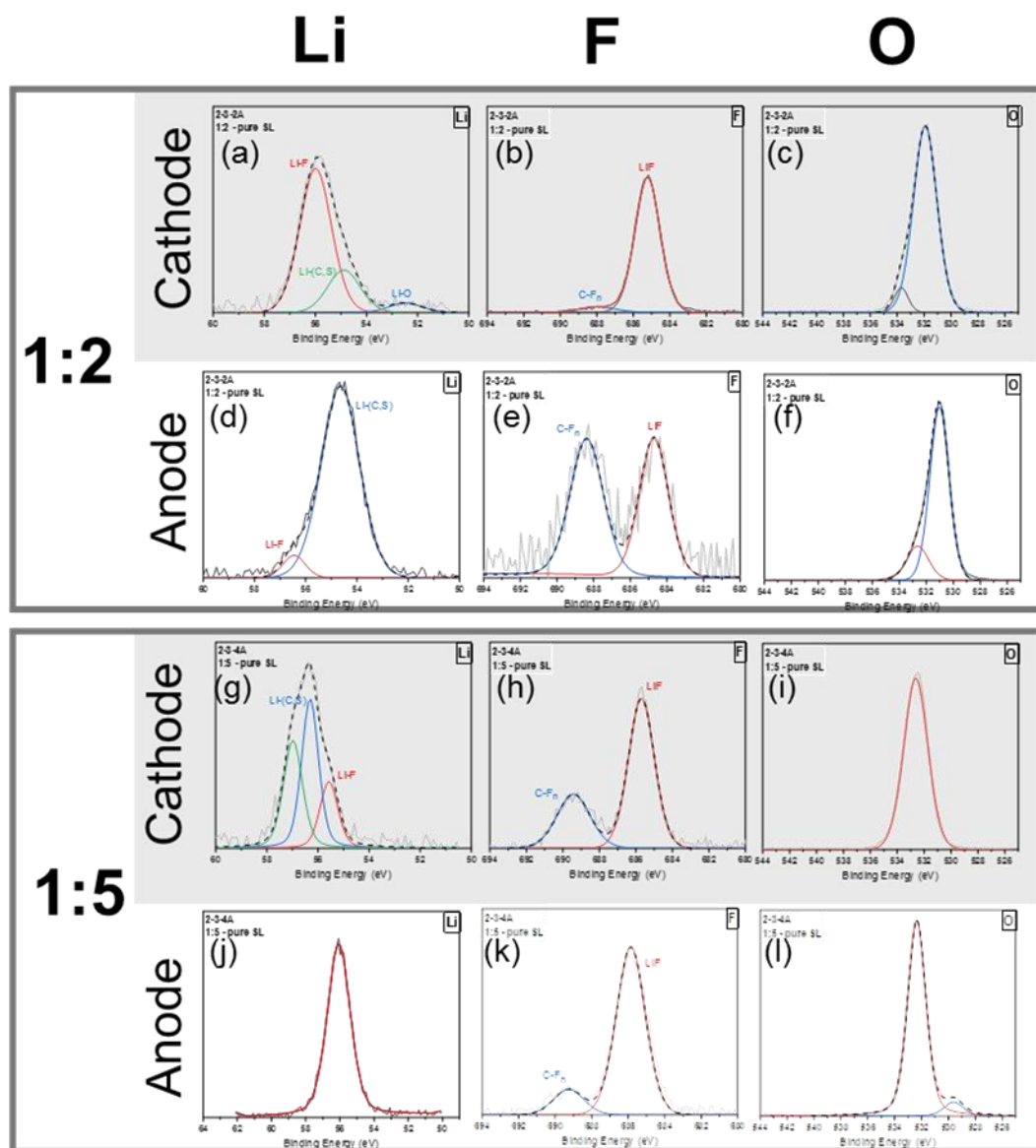


Figure 47. XPS spectra of the cathode and anode for Li, F, and O after testing for 200 cycles at C/5 with the (a-f) 1:2 and (g-l) 1:5 SL:HFE electrolytes.

5.5 Purification of Sulfolane

Sulfolane as-received contains a small percentage of impurities. While a small amount of impurities is expected in a commercial solvent, in sulfolane-based electrolytes they can have a particularly deleterious effect. This section focuses on a brief discussion of the effect of sulfolane purification on performance.

Sulfolane was purified by vacuum sublimation and 3A molecular sieves. As received sulfolane appears anywhere between clear and slightly yellow. Upon purification, the sulfolane appeared clear and a slight yellow residue was left behind in the remaining unpurified solvent. The previous section discussed the strong results of a SL/HFE-based electrolyte; however, an unpurified solvent negatively impacts capacity and stability. All previous electrochemical results utilized purified SL, what follows is a discussion of the rationale for the extra purification step.

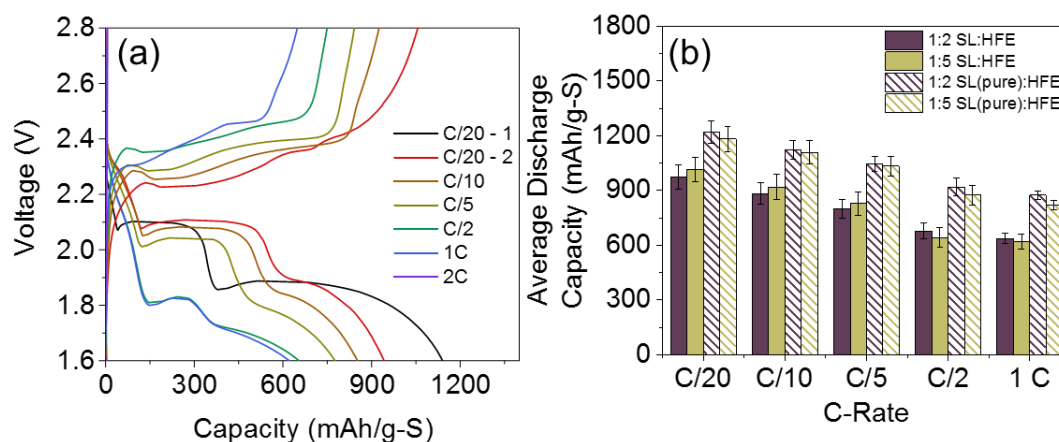


Figure 48. (a) discharge capacity of 1:2 SL:HFE cell using as-received SL, (b) Comparison of discharge capacities of cells tested with SL as received (solid columns) vs purified SL (dashed columns).

Purified and as-received SL-based electrolytes display the same discharge behavior across SL:HFE ratios. The change in discharge curve shape and transition in shape as the proportion of HFE increases is consistent between the purified and as-received SL. However, the discharge capacity is significantly lower in the case of the as-received SL (Figure 48). In long term testing, while both SL-based electrolytes decay and have similar CE, the overall capacity of the purified- SL is higher (Figure 49). Based on these electrochemical results, the purification of SL is shown to be extremely important in achieving high capacity, but is not the deciding factor in discharge mechanism.

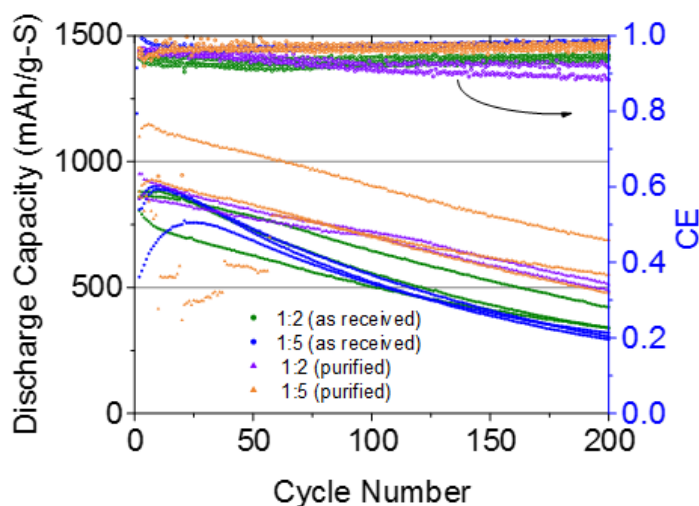


Figure 49. Comparison of long term cycling of cells with as-received and purified SL. Three example cells per SL:HFE ratio.

5.6 Conclusion

In this study we investigated the application of localized low concentration electrolytes (LLCE, $\sim 0.1\text{M}$) in lithium-sulfur (Li-S) batteries. In particular, we explored the effect of SL:HFE electrolyte solvent ratios on attainable Li-S battery capacity operating

in the low concentration electrolyte regime. These studied LLCEs enabled dramatically higher capacity than the DME/DIOX electrolyte for all SL:HFE ratios. This is due to the polysulfide suppression of the HFE and a decreased loss of active material during the first cycle with the greatly reduced formation of long-chain polysulfides and the accompanied shrinkage of the 2.1V discharge plateau with higher HFE content, as in quasi-solid-state reactions.¹⁷¹ Despite suppression of the polysulfide shuttle, gradual increase in the anode SEI thickness and continuous electrolyte and polysulfide consumption on the anode was causing increasing resistance and capacity decay during cycling. While further tuning LLCE is needed to attain the desired anode SEI stability, the low concentration SL/HFE electrolyte system shows great promise for the combination of polysulfide suppression, low electrolyte viscosity, and high capacity in rate testing.

5.7 Acknowledgements

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CHAPTER 6. SCOPE FOR FUTURE WORK

This work has demonstrated the benefits of low concentration electrolytes for lithium sulfur batteries and the effect of solvent composition on performance. However, the study of low concentration electrolytes in LiSBs and sulfolane/fluorinated ether-based electrolytes in particular is far from complete. The work presented here has opportunities for optimization and serves as inspiration for new directions of work. These directions can be summarized in four categories: advancements in high loading cathodes, new directions in highly fluorinated ethers, in situ experiments, and investigation into used Li anodes.

6.1 High Loading Cathodes

The high loading cathodes presented here are carbon cloths, which show the proof of concept of low concentration electrolytes, but do not include the polysulfide trapping and other optimization strategies that are common in low loading cathodes. In particular, employing metal oxide coatings can help trap polysulfides when such a large amount of sulfur is present. Cathodes with advanced nanostructures of precisely formed carbon nanoparticles that are specialties of other research groups could be combined with the electrolytes investigated here to form a more robust system.

6.2 Highly Fluorinated Ether Electrolytes

The highly fluorinated ether electrolyte in this work displayed unique discharge behavior and it is unknown if this discharge behavior across different highly fluorinated ether chemical structures. It would be beneficial to investigate highly fluorinated ethers with different numbers of fluorine atoms as well as structures with the same number of

fluorine atoms but in different positions. Since the polysulfide suppression comes from the presence of many fluorine atoms, altering their number and structure to determine if the discharge behavior seen here is consistent would be an interesting investigation. Further study in this direction would help elucidate the nature of polysulfide/electrolyte interactions and inform strategies for long-term use of lithium-sulfur batteries.

6.3 In Situ Experiments

The study of sulfolane/highly fluorinated ether electrolytes presented here explored their viability in the low concentration regime. Now that their performance in that regime is shown to be strong, there is an opportunity to more deeply explore the underlying mechanism. Ex situ and post mortem measurement, like the polysulfide test and XPS presented here, give useful information on solubility and species present, but do not give real time understanding of cell mechanisms. Additionally, given the light-sensitivity of polysulfides, their tendency to disproportionate, and their overlapping peak positions in many spectrometry experiments, measurements like Raman and FTIR are not especially informative. However, in situ Raman and XAS experiments can help track polysulfide species in solution at different depths of discharge. This information would help inform the hypothesis of the discharge mechanism presented in this work.

Further using in situ methods could help track the pace of SEI growth. This information would help in the design of surface improvements to the Li metal anode that would minimize long term capacity degradation.

6.4 Investigations into Lithium Anode

As shown in Chapter 5, the anode grows a thick SEI during testing with low concentration SL/HFE-based electrolytes. This SEI contributes to cell degradation and loss of capacity. To separate the effects of SEI growth and electrolyte consumption, it would be useful to cycle a cell (0.1M LiTFSI in SL/HFE) for 100 cycles, then disassemble the cell and perform the following experiments:

1. Take the used Li foil and make a fresh cell with a new cathode, separator, and electrolyte
2. Replace the used Li foil in the tested cell with a fresh Li anode and reassemble

After these two cells are assembled, they could be cycled another 50-100 cycles. In (1), if the cell starts at a low capacity and continues to degrade, the SEI will be responsible for the initially low capacity. In (2), the negative electrolyte consumption would be shown if the cell does not recover capacity or continues to degrade at the same rate. Full post mortem analysis on these samples would also be necessary.

LIST OF PUBLICATIONS (2016-2021)

Glaser, R.; Wu, F.; Register, E.; Tolksdorf, M.; Johnson, B.; Ready, J.; Sanghadasa, M.; Yushin, G., Tuning Low Concentration Electrolytes for High Rate Performance in Lithium-Sulfur Batteries. *Journal of The Electrochemical Society* 2020, 167 (10).

Glaser, R.; Borodin, O.; Johnson, B.; Jhulki, S.; Yushin, G. Minimizing Long-Chain Polysulfide Formation in Li-S Batteries by Using Low Concentration Highly Fluorinated Electrolytes. *Submitted to Journal of Materials Chemistry A April X, 2021.* (to be submitted after submission of this draft, but before completion of final dissertation)

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