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Journal

APL Materials, 7(8)

ISSN

2166-532X

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et al.

Publication Date

2019-08-01

DOI

10.1063/1.5110525

Peer reviewed

Recent Advances in Polysulfide Mediation of Lithium-Sulfur Batteries via Facile Cathode and Electrolyte Modification

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ABSTRACT

Lithium–sulfur (Li-S) batteries have garnered immense interest due to their potential to surpass the energy densities of state-of-the-art lithium-ion batteries. However, severe technical problems of polysulfide dissolution and shuttle effect still prohibit the commercialization of Li-S batteries. This review focuses on the recent advances of polysulfide mediation in conventional Li-S batteries with liquid electrolytes. Simple yet effective solutions to control polysulfide dissolution and shuttling via facile modification of the cathode and the electrolyte are highlighted. The rational design of cathode composition, the use of polysulfide barrier layers, and the selection of electrolyte components are discussed. These strategies offer significant promise to address the challenges and increase the viability of the large-scale application of Li-S batteries.

I. INTRODUCTION

There has been a global transition over the past few decades from fossil-fuel to renewable energy sources driven by a multitude of economic and environmental considerations. However,

this development is gated by the intermittent nature of renewable resources such as solar and wind powers that requires low-cost energy storage systems with high energy density.^{1,2} Lithium-ion batteries (LIBs) have long been the frontrunner for energy storage devices but the price-performance ratio of LIBs is still insufficient to satisfy the rapidly growing demands of the energy market.^{3,4}

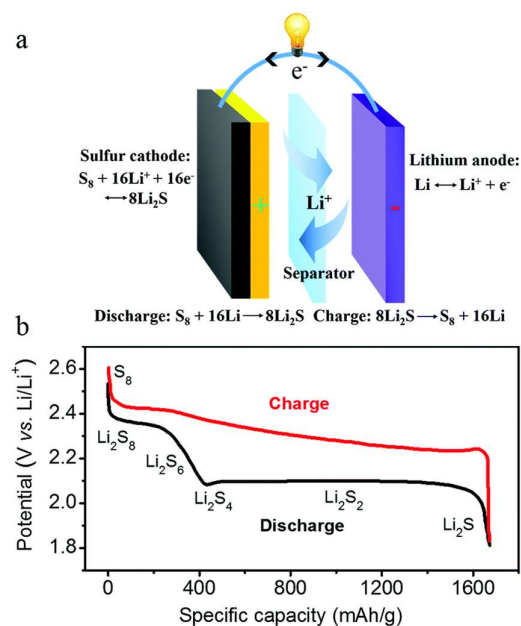


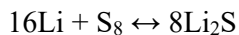
FIG. 1. a) Schematic of a typical Li-S battery and the corresponding electrochemical reactions. b) Typical charge/discharge voltage profile of Li-S batteries with ether electrolytes. Reproduced with permission from Seh *et al.*, Chem. Soc. Rev. 45, 5605 (2016). Copyright 2016 Royal Society of Chemistry.

As a promising candidate for the next-generation energy storage system, lithium-sulfur (Li-S) batteries have attracted significant research interest in recent years because of the high theoretical specific capacity of sulfur (1675 mAh g^{-1}).⁵ Moreover, sulfur is low-cost, non-toxic, and abundant in nature, and offers a more environment-friendly option for large-scale energy storage applications.⁶ Despite the low physical density and redox potential of sulfur, Li-S

batteries offer a promising path for achieving higher gravimetric and volumetric energy densities than other lithium-ion and lithium battery chemistries.⁷

A typical Li-S battery is composed of a lithium metal anode, a sulfur-based cathode, and a separator (Fig. 1a).^{2,6} Lithium-ion transport between the two electrodes is facilitated through the use of a non-aqueous liquid electrolyte (typically an ether-based solvent) that contains a lithium salt. The use of lithium metal anode may lead to a series of issues including dendrites formation, electrically isolated ‘dead’ lithium and poor coulombic efficiency,³ which have been the subject of a few recent reviews.^{2,6,8}

Several technical challenges particular to the Li-S chemistry exist in polysulfide dissolution and shuttling.⁹ The overall lithium-sulfur reaction is shown below:



As shown in Fig 1b, during the discharge process of Li-S battery, solid S_8 reduces into a series of readily soluble lithium polysulfide intermediates (Li_2S_x , $4 \leq x \leq 8$) before further reduction to solid Li_2S_2 and Li_2S products, which re-precipitate on the electrode.² This multi-stage reaction mechanism results in two plateaus in the discharge curve, where the first plateau (2.3 V versus Li/Li^+ , corresponding to $\text{S}_8 \rightarrow \text{Li}_2\text{S}_4$) contributes a quarter of the theoretical capacity and the second plateau (2.1 V versus Li/Li^+ , corresponding $\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}$) contributes the rest of the capacity. The dissolved long-chain polysulfide intermediates may be reduced directly by the lithium metal anode, resulting in severe loss of active cathode materials, self-discharge, and low coulombic efficiency.¹⁰ In addition, polysulfide intermediates in the electrolyte phase can migrate back and forth between the cathode and the anode and undergo undesired redox reactions.¹⁰ This phenomenon is known as the polysulfide shuttle effect.

The disproportionation of polysulfides is a complicated process that may involve key intermediates other than those shown in Fig. 1b (e.g. S_3^{2-} and S_3 radical anion), and these proposed reaction pathways have been reviewed elsewhere.¹¹ Although a detailed, mechanistic understanding of polysulfide reactions including kinetics and thermodynamics is still the subject of investigation, effective strategies for preventing the dissolution and shuttling of polysulfide species have been developed and preliminarily demonstrated. This review summarizes recent efforts that address these issues through facile modifications of sulfur cathodes and electrolytes. Porous electrodes and functional binders may help to reduce polysulfide dissolution upon their formation at the cathode. Interlayers and electrode coatings may also prevent the diffusion of polysulfides to the lithium metal anode. Co-solvents may reduce the solubility of sulfide species in the electrolyte or modify electrochemical reaction pathways of sulfides. Electrolyte additives may also help to passivate the cathode surface or react with soluble lithium polysulfides during electrochemical cycling.

II. CATHODE MODIFICATION

The formation of readily soluble lithium polysulfides is an inevitable electrochemical process for Li-S batteries, and consequently, confinement of polysulfides upon their generation at the electrode has become a common strategy for mitigation of polysulfides.^{2,6,12} The two most promising methods are the rational design of the cathode composite (i.e. internal modification of cathode) and the incorporation of interlayers and coatings for the sulfur cathode (i.e. external modification of cathode).¹³

A. Cathode composite modification

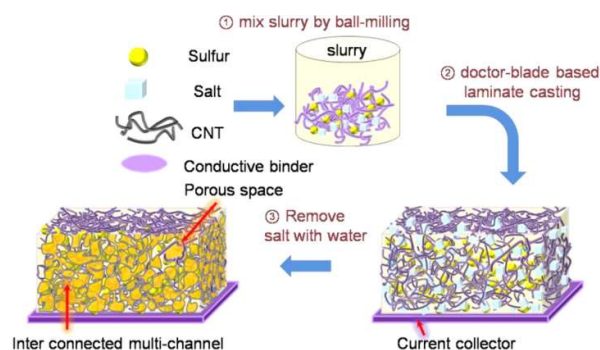


Fig. 2. Schematic of the fabrication process of a porous S-CNT composite electrode using salt as templating agent. Reproduced with permission from Ai *et al.*, Nano Lett. 16, 5365 (2016). Copyright 2016 American Chemical Society.

Porous cathode composite can provide increased adsorptive capacity for polysulfide intermediates,¹⁴ and the use of a templating agent is a convenient method to introduce porosity into a conventional cathode composite.¹⁵ NaCl (table salt) was demonstrated as an effective sacrificial template to create a porous, ant-nest-like sulfur-carbon nanotube (S-CNT) composite electrode (Fig. 2).¹⁶ The use of cheap, benign materials (NaCl and H₂O) makes this strategy a particularly attractive approach for large-scale production. The interconnected structure of the templated cathode composite was shown to facilitate ion transport, assist efficient sulfur precipitation, and contain polysulfide intermediates within the pores to prevent them from diffusing into the bulk electrolyte. These advantages were conferred for electrodes with areal mass loadings up to 3 mg cm⁻² for which discharge capacity of 900 mAh g⁻¹ was observed for the ant-nest cathodes (two times greater than that of the non-ant-nest electrodes).

The use of functional binders that facilitate polysulfide confinement is another promising method for the mediation of these intermediate sulfur species. Binders are typically chemically inert polymeric materials used to mechanically reinforce composite electrodes consisting of active materials and conductive additives.¹⁷ The rich field of organic chemistry offers the

possibility of synthesizing binders that are intentionally designed to interact with and thus confine polysulfide intermediates through chemisorption or chemical reaction.

Binders that possess polar or ionic moieties can suppress the dissolution of lithium polysulfides via strong interactions with the polysulfides molecules.¹⁸ Polar groups present in poly(3,4-ethylenedioxythiophene) (PEDOT)¹⁹ and poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM)²⁰ have demonstrated the ability to minimize polysulfide dissolution as evidenced by both higher capacity and capacity retention of the cells compared to those of polyvinylidene fluoride (PVDF) binder based cells. Stronger interaction between functional binders and polysulfide intermediates can be achieved with cationic binders such as poly[bis(2-chloroethyl) ether-*alt*-1,3-bis[3(dimethylamino) propyl]urea] quaternized (PQ), whereby the negatively charged polysulfides are firmly trapped by the positively charged quaternary ammonium units.²¹ Similar approaches have shown that poly(ethylenimine) (PEI) binder can trap lithium polysulfides through interaction with the abundant amine groups of the polymers,²² and the iodomethane quaternization of PEI (product noted as MPEII) can further enhance the capacity for polysulfide confinement through the introduction of ammonium units.²³ PQ, PEI and MPEII binders delivered higher capacity performance compared to PDVF binders under the same conditions, and their polysulfide confinement ability have been verified by in situ ultraviolet–visible (UV) spectroscopy.

Binders that undergo chemical reactions to immobilize lithium polysulfides through covalent bonding with the polysulfides may also result in the effective confinement of polysulfide. Poly(vinyl sulfate) potassium salt (PVS) and sulfate-rich carrageenan binders can undergo nucleophilic substitution reaction with polysulfide intermediates (Fig. 3a).²⁴ The stronger mechanical properties offered by carrageenan delivered stable cycling performance of a sulfur cathode composite with areal mass loadings $\sim 17 \text{ mg cm}^{-2}$. The initial delithiation capacity was about 1200 mAh/g, which stabilized at 940 mAh/g after cycling at 0.01C. The confinement of

polysulfides by both PVS and carrageenan was visually confirmed through the spontaneous reaction of the binder with polysulfide solution (Fig. 3b). An enhancement of this substitution reaction-based polysulfide confinement mechanism may be accomplished through the incorporation of primary carbon electrophilic sites rather than the secondary carbon sites present in both PVS and carrageenan.²⁵

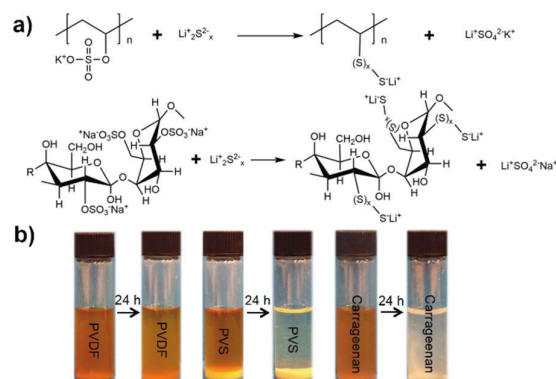


Fig. 3. a) Chemical reactions of soluble polysulfide intermediates with PVS (top) and carrageenan (bottom) binders. b) Polysulfide reactions were visually confirmed through the formation of insoluble products from an orange-yellow polysulfide solution that yielded a colorless solution. Reproduced with permission from Ling *et al.*, Nano Energy 38, 82 (2017). Copyright 2017 Elsevier.

B. Interlayers and coatings for cathodes

A straightforward strategy to mitigate polysulfide dissolution and the shuttle effect is to incorporate an external interlayer that serves as an additional barrier between the cathode and the separator. The typically porous, electronically conductive interlayer allows for the diffusion of lithium ions in the electrolyte while preventing the diffusion and the shuttle effect via electrochemical reduction of the polysulfide species.²⁶ As the interlayer is a discrete part of the Li-S battery, cathode fabrication can remain simple and/or be designed to maximize electrochemical performance. It is worth mentioning that this approach is similar to the

modification of separators with respect to the integration of polysulfide-mitigating components, but the latter offers only passive containment as separators must remain electronically insulating.²⁷ Carbonaceous materials are commonly utilized as interlayer scaffolds due to their high surface area and electronic conductivity.²⁸ However, the difference in polarity between carbon and lithium polysulfides (non-polar and polar, respectively) results in only weak interactions between the two species. Transition metal oxides²⁹ may be incorporated to simultaneously mediate polysulfides through sulfur-metal chemical interactions.³⁰ A porous graphene/TiO₂ interlayer demonstrated the ability to trap polysulfides while contributing only 7.8% mass of the entire cathode (Fig. 4a).³¹ The cells demonstrated excellent cycling stability over 1000 cycles with a capacity decay of only 0.010 and 0.018% per cycle at rates of 2C and 3C (determined by sulfur mass), respectively. At a rate of 0.5C, the cell demonstrated a reversible specific capacity of 1040 mAh g⁻¹ over 300 cycles.

Carbonaceous scaffolds functionalized with organic molecules have also been developed for Li-S battery applications.^{32,33} Dithiothreitol (DTT) demonstrated the ability to cleave the sulfur-sulfur bonds of lithium polysulfide molecules, effectively eliminating the polysulfide shuttle effect.³² The incorporation of DTT into a graphene interlayer in a Li-S battery resulted in a reversible capacity of 301 mAh g⁻¹ at a rate of 5C with 0.036% capacity degradation per cycle over 1100 cycles.

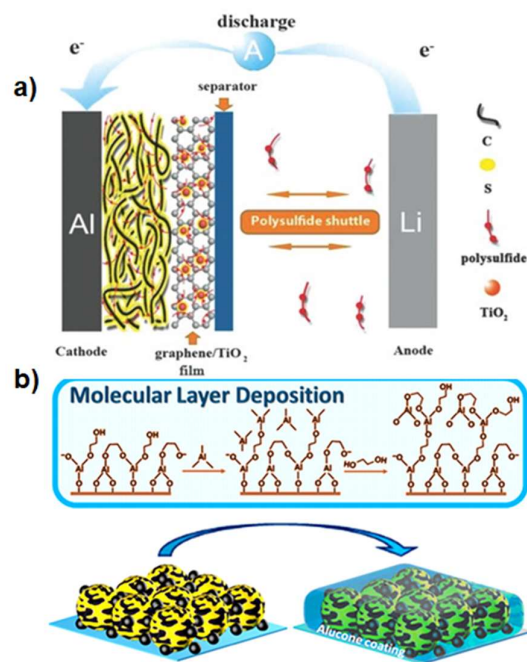


Fig. 4. a) Schematic of the confinement of polysulfide intermediates by a TiO₂/graphene interlayer. Reproduced with permission from Xiao *et al.*, Adv. Mater. 27, 2891 (2015). Copyright 2015 Wiley-VCH. b) Schematic of the synthesis of an alucone coating via molecular layer deposition (MLD). Adapted with permission from Li *et al.*, Nano Lett. 16, 3545 (2016). Copyright 2016 Royal Society of Chemistry.

Coatings on cathodes can have similar benefits with respect to polysulfide dissolution and shuttle effect.³⁴ Atomic layer deposition (ALD)³⁵ and molecular layer deposition (MLD)^{36,37} have emerged in recent years as promising techniques to synthesize ultrathin coatings for Li-S batteries. ALD and MLD rely on self-terminating half-reactions that offer the control of the deposition to the nanometer level. A 0.5 nm thick Al₂O₃ layer deposited via ALD onto a porous carbon cloth interlayer demonstrated the ability to reactivate dissolved polysulfides. The Li-S cells showed a 25% greater specific discharge capacity on the initial discharge and a 114% greater capacity by the 40th cycle compared to cells without ALD treatment.³⁸ MLD is compatible with the deposition of organic and inorganic–organic hybrid materials. An alucone coating with flexible mechanical properties was deposited directly onto sulfur cathodes via

MLD through the alternating deposition of trimethylaluminum and ethylene glycol precursors (Fig. 4b).³⁷ The coating demonstrated the ability to reduce polysulfide dissolution and the polysulfide shuttle effect. The alucone film was also shown to prevent the side reactions between the polysulfide intermediates and carbonate-based electrolytes even during high-temperature electrochemical cycling of the cells.³⁷

III. Electrolyte Modification

Alternative electrolyte systems that minimize polysulfide dissolution while remaining ionically conductive for lithium ions is also a strategy for improving the electrochemical performance of Li-S batteries. The high solubility of polysulfide intermediates in ether-based solvents may be modulated through the use of a co-solvent with lower solubility for these sulfide phases or that alters the polysulfide reaction pathway. The use of electrolyte additives that form protective surfaces during electrochemical cycling is another promising strategy.

A. Co-solvents

The incorporation of co-solvents may serve as a convenient method to tune the solubility of lithium polysulfides in the electrolyte. Room-temperature ionic liquids (ILs) such as 1-butyl-1-methyl-pyrrolidinium-bis(trifluoromethanesulfonyl)imide³⁹ possess low solubility for polysulfide intermediates (less than 0.06M for 50% IL electrolyte) but the high viscosity and relatively low ionic conductivity require dilution with ether-based solvents. A comparison between 75% IL and 0% IL electrolyte systems in Li-S cells demonstrated that an electrolyte with a high IL content delivered a reduced self-discharge capacity loss (7.4% versus 25.8%) and an improved cycling stability over 50 cycles (stable at 1000 mAh g⁻¹ level compared to a fast decay to 300 mAh g⁻¹ level). On the other hand, low IL ratios are preferred to support the larger current densities required for electrochemical cycling at high rates (>1C) or increased sulfur loading.

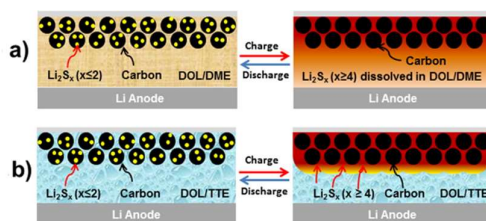


Fig. 5. Schematic of a) dissolution of polysulfide into DOL/DME electrolyte, and b) confinement of polysulfides by DOL/TTE electrolyte. Reproduced with permission from Azimi *et al.*, ACS Appl. Mater. Interfaces 7, 9169 (2015). Copyright 2015 American Chemical Society.

Fluorinated ethers are another class of solvents in which polysulfide intermediates are insoluble.^{40,41} 1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) was explored as co-solvent with 1,3-dioxolane (DOL) for Li-S batteries.⁴⁰ As shown in Fig. 5a, polysulfides can easily dissolve into 1,3-dioxolane (DOL)/dimethoxyethane (DME) electrolyte system during the discharge process. In contrast, DOL/TTE solvent mixture was found to suppress polysulfide dissolution due to TTE's lower solubility for higher-order polysulfides (Fig. 5b). During initial discharge, TTE reductively decomposed on the cathode to form products with rich content of C-F bonds, which resulted in the formation of a protective layer that provides additional ability to mitigate polysulfide dissolution and the polysulfide shuttle effect. It is worth noting that like the aforementioned ionic liquids, the use of fluorinated solvents may provide ancillary benefits such as low flammability,⁵ which can improve the safety of the Li-S batteries.

Reactive co-solvents may alter the electrochemistry pathway and suppress the generation of lithium polysulfide species. Dimethyl disulfide (DMDS) co-solvent has been shown to react with sulfur to yield dimethyl polysulfides and lithium organosulfides in the DMDS-ether electrolyte system.⁴² This new sulfur reduction chemistry circumvented the formation of common lithium polysulfide species. Use of carbon disulfide (CS_2) as co-solvent was also

found to alter the electrochemistry and result in the formation of insoluble complexes, effectively suppressing the polysulfide dissolution and shuttle effect.⁴³ The precise electrochemistry mechanism is not yet understood and further work is required to rationally design co-solvents that alter these electrochemical pathways.⁴³

B. Additives

Additives that protect the electrodes upon electrochemical decomposition can provide another convenient approach for improve the Li-S battery performance without altering the existing battery configuration.⁴⁴ Pyrrole is a small-molecule additive for DOL/DME electrolyte system. Oxidation of the pyrrole monomer during electrochemical cycling resulted in the formation of a polypyrrole layer on the sulfur cathode.⁴⁵ This film was found to effectively prevent polysulfide dissolution from the electrode into the electrolyte. Similarly, triphenylphosphine additive can undergo an *in situ* wrapping process to introduce compact triphenylphosphine sulfide (TPS) layers onto the cathode composite.⁴⁶ This electrolyte system delivered a low decay rate of 0.03% per cycle at a rate of 1C over 1000 cycles. Additives may also directly react with polysulfide intermediates. Biphenyl-4,4'-dithiol (BPD) has been demonstrated to participate in a chemical transformation with short-chain polysulfides to form BDP-S_n complexes ($1 \leq n \leq 4$).⁴⁷ The generation of these less soluble sulfur species may suppress the rapid generation of short-chain lithium polysulfide species and contribute to greater capacity retention (approximately halved capacity degradation after 100 cycles compared to that of non-BDP electrolyte).

IV. CONCLUSION AND PERSPECTIVE

This review briefly investigates recent developments of techniques that address polysulfide dissolution and the polysulfide shuttle effect in Li-S batteries. The strategies are summarized and compared as follows.

I) Cathode composite can be structurally or chemically modified to incorporate porous composite structures or polysulfide absorbing components such as polar/ionic binders, which do not change the classic battery configuration but may lower the gravimetric or volumetric power density;

II) Interlayers and ALD/MLD coatings over the cathode provide additional barriers for polysulfide dissolution and shuttle effect, but interlayers contribute additional mass to the battery while ALD/MLD techniques involves high-cost processes that are less suitable for commercialization;

III) Polysulfide-insoluble cosolvents are efficient for suppression of polysulfide dissolution but they are not entirely compatible with traditional electrolyte systems, and polysulfide-reactive cosolvents can eliminate polysulfide intermediates but their rational design and selection is restricted by the limited understanding of the electrochemical processes involved with the cosolvent molecules;

IV) The employment of additives is the most convenient approach to improve battery performance and additives may either form protective films on the electrodes or alter the polysulfide reaction pathway, but the lack of a detailed mechanistic understanding of the polysulfide chemistry and the electrode passivation process poses significant challenge for the development of additives.

Recent reports addressing polysulfide dissolution and the shuttle effect in Li-S batteries reveal a strong drive to develop technologies that are highly compatible with current Li-S battery fabrication processes and techniques. Future efforts to develop polysulfide confinement methods with low-cost materials and scalable processes are essential for application of Li-S batteries. The improvement of Li-S batteries is hindered by the complex sulfide chemistry, which requires extensive investigation. Future research efforts should be devoted to elucidating

the precise electrochemistry processes and interactions between sulfides, solvents, and cathode materials for rational design of novel Li-S battery technologies.

ACKNOWLEDGMENTS

This work is funded by the Assistant Secretary for Energy Efficiency, Vehicle Technologies Office of the U.S. Department of Energy (U.S. DOE) under the Advanced Battery Materials Research (BMR) program.

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