

Challenges and Prospects of Lithium–Sulfur Batteries

ARUMUGAM MANTHIRAM,* YONGZHU FU, AND YU-SHENG SU

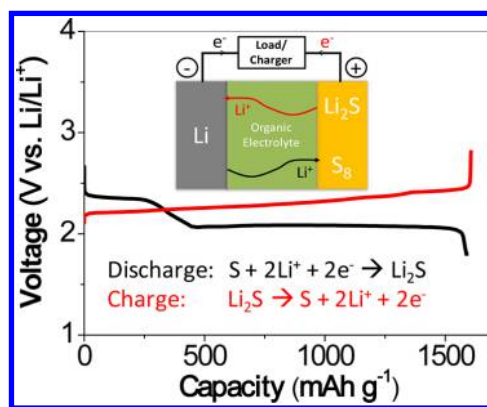
Electrochemical Energy Laboratory & Materials Science and Engineering Program, The University of Texas at Austin, Austin, Texas 78712, United States

RECEIVED ON JUNE 15, 2012

CONSPECTUS

Electrical energy storage is one of the most critical needs of 21st century society. Applications that depend on electrical energy storage include portable electronics, electric vehicles, and devices for renewable energy storage from solar and wind. Lithium-ion (Li-ion) batteries have the highest energy density among the rechargeable battery chemistries. As a result, Li-ion batteries have proven successful in the portable electronics market and will play a significant role in large-scale energy storage. Over the past two decades, Li-ion batteries based on insertion cathodes have reached a cathode capacity of $\sim 250 \text{ mA h g}^{-1}$ and an energy density of $\sim 800 \text{ W h kg}^{-1}$, which do not meet the requirement of $\sim 500 \text{ km}$ between charges for all-electric vehicles. With a goal of increasing energy density, researchers are pursuing alternative cathode materials such as sulfur and O_2 that can offer capacities that exceed those of conventional insertion cathodes, such as LiCoO_2 and LiMn_2O_4 , by an order of magnitude ($>1500 \text{ mA h g}^{-1}$). Sulfur, one of the most abundant elements on earth, is an electrochemically active material that can accept up to two electrons per atom at $\sim 2.1 \text{ V}$ vs Li/Li^+ . As a result, sulfur cathode materials have a high theoretical capacity of 1675 mA h g^{-1} , and lithium–sulfur (Li–S) batteries have a theoretical energy density of $\sim 2600 \text{ W h kg}^{-1}$. Unlike conventional insertion cathode materials, sulfur undergoes a series of compositional and structural changes during cycling, which involve soluble polysulfides and insoluble sulfides. As a result, researchers have struggled with the maintenance of a stable electrode structure, full utilization of the active material, and sufficient cycle life with good system efficiency. Although researchers have made significant progress on rechargeable Li–S batteries in the last decade, these cycle life and efficiency problems prevent their use in commercial cells.

To overcome these persistent problems, researchers will need new sulfur composite cathodes with favorable properties and performance and new Li–S cell configurations. In this Account, we first focus on the development of novel composite cathode materials including sulfur–carbon and sulfur–polymer composites, describing the design principles, structure and properties, and electrochemical performances of these new materials. We then cover new cell configurations with carbon interlayers and Li/dissolved polysulfide cells, emphasizing the potential of these approaches to advance capacity retention and system efficiency. Finally, we provide a brief survey of efficient electrolytes. The Account summarizes improvements that could bring Li–S technology closer to mass commercialization.



1. Introduction

Lithium-ion (Li-ion) batteries have dominated the battery market for portable electronics since their launch in the early 1990s by Sony and are believed to be promising candidates for electric vehicles and grid energy storage due to their higher energy density compared with other battery chemistries.^{1–4} Insertion cathode materials, such as LiCoO_2 , LiMn_2O_4 , and LiFePO_4 , have been well developed in the last 2

decades and are being widely used in current Li-ion batteries.^{2,5} To improve the energy density of Li-ion batteries further to meet the requirement of $\sim 500 \text{ km}$ range between charges for all-electric vehicles and grid energy storage, alternative cathodes with a significant reduction in cost and increase in capacity and energy density are needed.⁶

Sulfur, one of the most abundant elements on earth, is a promising cathode with the highest theoretical capacity of

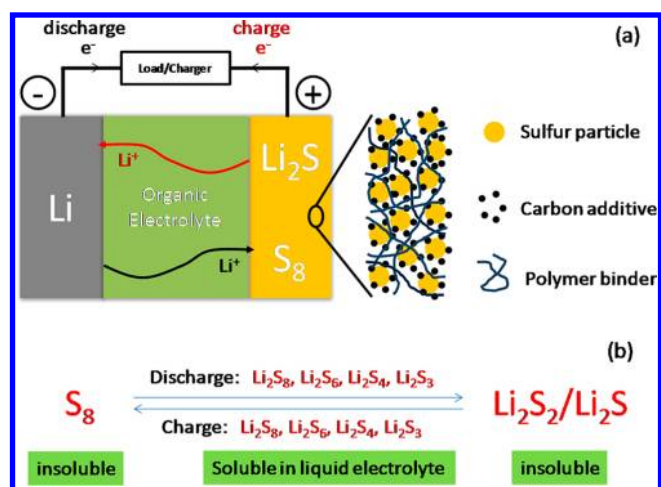


FIGURE 1. (a) Illustration of the charge (red)/discharge (black) process involved in a rechargeable Li–S cell consisting of lithium metal anode, organic electrolyte, and sulfur composite cathode and (b) charge/discharge process involving the formation of soluble lithium polysulfides (Li_2S_8 , Li_2S_6 , Li_2S_4 , and Li_2S_3) and insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$.

1675 mA h g^{-1} among the solid elements. Moving from the traditional insertion cathodes to sulfur has many benefits besides the high capacity, such as the low operating voltage (2.15 V vs Li/Li^+) improving the safety, the low-cost sulfur replacing expensive transition metals like cobalt, and environmentally friendly sulfur compared with certain toxic transition-metal compounds. An order of magnitude higher capacity than that of the conventional insertion compound cathodes can enable packaged lithium–sulfur (Li–S) cells with an energy density of $400\text{--}600 \text{ W h kg}^{-1}$, which is two or three times higher than that of current Li-ion batteries, and it could meet the target for the 500 km range.⁶ The low-cost and high energy density are also appealing for grid energy storage for renewable energies such as solar and wind if long cycle life and high system efficiency can be achieved.

Conventional Li–S cells consist of a lithium metal anode, an organic liquid electrolyte, and a sulfur composite cathode (Figure 1a). There are several major issues facing rechargeable Li–S batteries that impede their practical applications.^{6,7} Sulfur is in the form of polyatomic molecules with different structures, and octasulfur (cyclo- S_8) is the most stable allotrope at room temperature. Cyclo- S_8 undergoes a series of structural and morphological changes during the charge–discharge process involving the formation of soluble lithium polysulfides Li_2S_x ($8 \leq x \leq 3$) and insoluble sulfides $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ in liquid electrolyte (Figure 1b). The high resistances of sulfur and the intermediates formed along with their structural changes result in unstable electrochemical contact within sulfur electrodes. In addition, the dissolved polysulfides

shuttle between the anode and cathode during the charge process involving side reduction reactions with lithium anode and reoxidation reactions at the cathode.⁸ These issues result in a low utilization of active material, poor cycle life, and low system efficiency. Apparently, it is impossible to meet all the requirements with the conventional Li–S battery electrode formula consisting of micrometer-sized active material, carbon, and polymer binder (Figure 1a). A variety of strategies have been developed to form sulfur composites with favorable structures and properties to improve the discharge capacity, cyclability, and Coulombic efficiency.⁶ Other approaches being pursued include novel cell configurations with trapping interlayers, Li/dissolved polysulfide cells, and efficient electrolytes.^{9–12}

2. Sulfur–Carbon Composite Cathodes

2.1. Porous Carbon-Based Composites. The main efforts to improve the electrochemical performances of Li–S batteries have been on the development of carbon-based sulfur composites. Following the report of high-capacity Li–S cells in 2009 with highly ordered mesoporous carbon and sulfur, studies on sulfur–carbon composite cathodes have grown rapidly.¹³ An ideal carbon matrix for sulfur–carbon composites needs to have (i) high electrical conductivity, (ii) electrochemical affinity for sulfur, (iii) small cells (pores) without large outlets to accommodate polysulfides, (iv) accessibility of liquid electrolyte to active material, and (v) stable framework to sustain the strain generated by the volume changes of the active material during cycling.

Recent progress on the sulfur–carbon composites benefits from their hierarchical design (Figure 2). Carbon spheres with micropores can encapsulate sulfur (Figure 2a), but the total pore volume needs to be increased to enhance the sulfur loading.¹⁴ Spherical ordered mesoporous carbon with a large number of inner pores is a superior option to serve as the matrix to accommodate more sulfur without compromising battery performance (Figure 2b).¹⁵ Porous hollow carbon–sulfur composites exhibit impressive cyclability over 100 cycles (Figure 2c).¹⁶ Graphene oxide has also been used (Figure 2d), but the graphene–sulfur composite may need further treatment for immobilizing the intermediate polysulfides.^{17,18} Porous carbon nanofibers and hollow carbon nanofibers or nanotubes are also good substrates to be impregnated with sulfur (Figure 2e,f).^{19–21} Although these carbon-based sulfur composites have shown outstanding progress in Li–S battery performance, high active material loading ($>70 \text{ wt } \%$), high specific capacity ($>1200 \text{ mA h g}^{-1}$), and excellent cycle stability and life

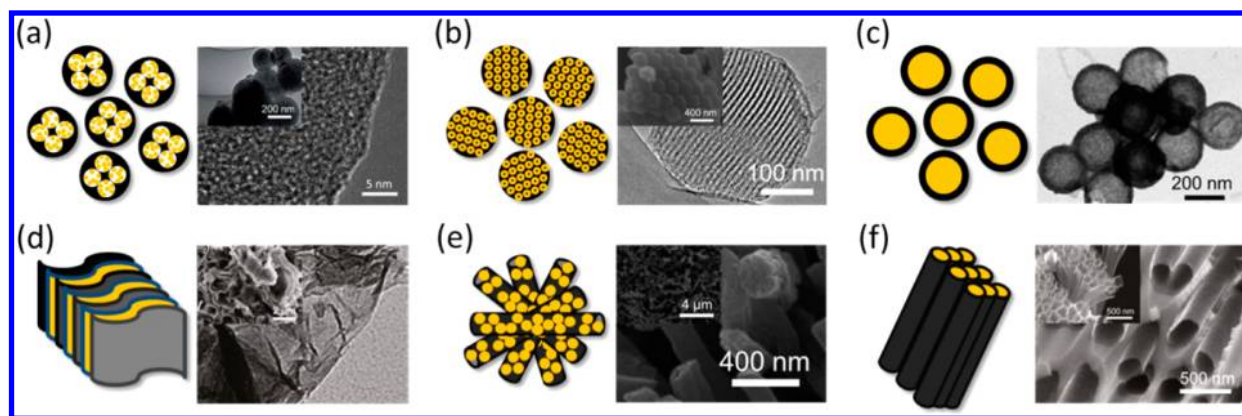


FIGURE 2. Hierarchical designs of carbon-based sulfur composites: (a) microporous carbon spheres, (b) spherical ordered mesoporous carbon nanoparticles, (c) porous hollow carbon, (d) graphene oxide sheets, (e) porous carbon nanofibers, and (f) hollow carbon nanofibers to encapsulate sulfur. Panels a and e were reproduced with permission from refs 14 and 19. Copyright 2010 and 2011 Royal Society of Chemistry. Panels b and c were reproduced with permission from refs 15 and 16. Copyright 2012 and 2011 Wiley. Panels d and f were reprinted with permission from refs 17 and 20. Copyright 2011 American Chemical Society.

TABLE 1. Summary of Representative Synthesis Routes To Make Sulfur–Carbon Composite Cathode Materials

method	description	binding between S and C	feature	ref
mixing	mixing materials by magnetic stirring	weak		24
ball-milling	ball-milling materials with binders	medium	high-energy ball-milling	22
thermal treatment	one step heating: 155 °C	strong	good for mesoporous carbons	13, 27
	two step heating: 150–200 °C; 300–350 °C	strong	superficial sulfur removed by the second step	18, 25, 26
heterogeneous nucleation	sulfur vaporizing	very strong	molecular infiltration	16
	$S_x^{2-} + 2H^+ \rightarrow (x-1)S\downarrow + H_2S$	strong	producing hazardous H_2S gas	19, 28
	$SO_2 + 2S^{2-} + 4H^+ \rightarrow 3S\downarrow + 2H_2O$	strong		29
	$S_2O_3^{2-} + 2H^+ \rightarrow S\downarrow + H_2SO_3$	strong	involving the fewest chemicals	30

(<10% capacity loss over 100 cycles) could not be obtained simultaneously with any single composite material.

2.2. Composites Synthesized by Various Methods. In conventional sulfur electrodes, ball-milling or mixing sulfur powder and carbon materials have been used.^{22–24} The poor contact between sulfur and carbon results in low initial discharge capacities (e.g., 300–500 mA h g⁻¹), so improved processes to prepare sulfur–carbon composites have been developed (Table 1). For example, a two-step sulfur melting route was first reported by Wang et al.,²⁵ involving a thermal treatment at 200 °C to melt sulfur that can diffuse into the pores of active carbon followed by a second firing at 300 °C to vaporize sulfur covering the outer surface of active carbon. A high first discharge capacity of 800 mA h g⁻¹ was achieved with this composite. This heating process has been further used with slightly modified temperature and dwell time and with different carbon materials to obtain high performance sulfur–carbon composites.^{18,26} One-step sulfur melting route was later employed especially with mesoporous carbons, which could effectively absorb fused sulfur into the interconnected pore structure during synthesis without further thermal treatment.^{13,27} Jayaprakash et al.¹⁶

utilized a sulfur vaporizing route to infuse gaseous sulfur into porous hollow carbon and obtained outstanding cyclability as sulfur vapor led to molecular contacts with the carbon framework.

Heterogeneous sulfur nucleation on carbon matrices in an aqueous solution has become a favorable process not only because of the low-cost solution-based reactions but also due to the elimination of toxic solvents. Sulfur nucleates on dispersed carbon substrates after dropping acid into the polysulfide solution prepared by the dissolution of sulfur in a sodium sulfide (Na_2S) solution.^{19,28} Another method involving Na_2SO_3 , Na_2S , and acid has led to a core–shell carbon/sulfur material.²⁹ An *in situ* sulfur deposition route has also been developed to synthesize carbon-wrapped sulfur composites.³⁰ High-purity sulfur heterogeneously nucleates on highly dispersed carbon nanoparticles in an aqueous solution as the thiosulfate ions are reduced or sulfide ions are oxidized to sulfur. These synthesis methods involve a simple water-based reaction to bind sulfur and carbon strongly and are applicable to any carbon substrate.

2.3. Binder-Free Composite Electrodes. Owing to establishing green processes, avoiding toxic chemicals in the

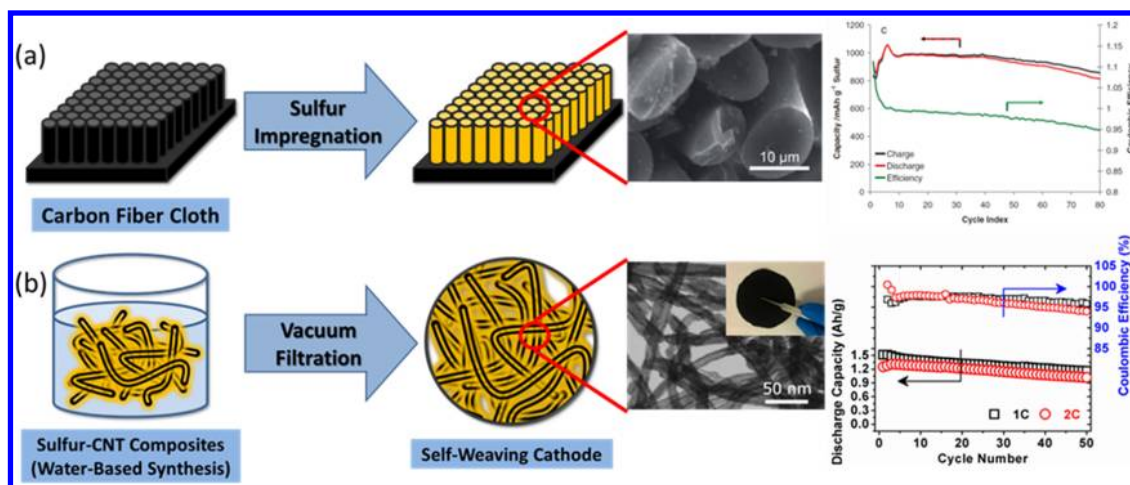


FIGURE 3. Comparison of binder-free cathodes: (a) Carbon substrate-based composite cathode Reproduced with permission from ref 32. Copyright 2011 Wiley. (b) Self-weaving sulfur–CNT composite cathode.

manufacturing of battery electrodes is appealing. *N*-Methyl-2-pyrrolidone (NMP) is a solvent generally used in fabricating Li-ion battery electrodes to disperse the polymer binder and active materials. However, NMP is harmful to human health and the environment.³¹ One possible approach is making binder-free electrodes, which can eliminate the use of NMP. By removing the binder, the active material loading and electrode conductivity can also be increased.

Two methods for preparing binder-free sulfur composite cathodes have been developed (Figure 3). Aurbach et al.³² have fabricated a sulfur-impregnated activated carbon fiber cloth as a binder-free cathode (Figure 3a). They employed a commercial carbon cloth as the substrate, and sulfur was injected into the pores of carbon fibers by cofiring sulfur and the carbon cloth. Vertically aligned carbon nanotubes grown on a metal foil can be used as a binder-free cathode matrix as well, which is then infiltrated with a sulfur solution and melt.³³ Both these binder-free features of the cathodes were inherited from the formed robust substrates. Another approach was depositing sulfur onto multiwalled carbon nanotubes (MWCNT) via an *in situ* sulfur deposition route, and the sulfur–carbon nanotube composite forms a free-standing paper after vacuum filtration without binders (Figure 3b). Curly carbon nanotubes were specifically used to have a self-intertwining behavior.^{34,35} This binder-free sulfur–carbon nanotube composite shows excellent high-rate cycle performance, retaining $>1000 \text{ mA h g}^{-1}$ for 50 cycles even at 2 C rate (Figure 3b).³⁶ The high capacity in the composite at high rates is attributed to the superior electrical properties of MWCNT, resulting in low resistance in the cathode. The tortuous interspaces located in the network of MWCNT offer a stable accommodation of sulfur for rapid redox reactions

TABLE 2. Summary of the Voltage Window and Electrode Performance of Possible Insertion Hosts for Hybrid Sulfur Composite Cathodes

electrode material	reduced product	voltage (V)	capacity (mA h g^{-1})	ref
S_8	Li_2S	3.0–1.5	>1000	
TiS_2	Li_xTiS_2	3.0–1.5	240	39
$\text{VO}_2(\text{B})$	$\text{Li}_{1-x}\text{VO}_2$	3.5–2.0	200	41
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	$\text{Li}_7\text{Ti}_5\text{O}_{12}$	2.0–1.2	150	42
$\text{TiO}_2(\text{B})$	$\text{Li}_{1-x}\text{TiO}_2$	2.5–1.0	200	45
$\text{Li}_2\text{C}_6\text{O}_6$	$\text{Li}_4\text{C}_6\text{O}_6$	2.5–1.5	200	46

and prevent sulfur/ Li_2S from forming extensive agglomerates during cycling, leading to good cyclability. In addition, the composite cathode is also current collector-free, further reducing the net weight of cathodes.

2.4. Hybrid Sulfur Composite Cathodes. Although sulfur–carbon composites have shown good cyclability, about 30–50% of the electrode weight belongs to inactive carbon and binder. To improve the energy density, the active material loading in the cathode must be increased. A prospective strategy is replacing a portion of carbon and binder by a lithium insertion oxide or sulfide. These materials need to work in the voltage range similar to that of sulfur (3–1.5 V) to contribute capacities. Some potential candidates are summarized in Table 2. TiS_2 operates in exactly the same voltage window as sulfur.^{37–39} Nanosized $\text{VO}_2\text{–B}$ with a sloping discharge profile can be partially lithiated by controlling the terminal operating potentials.^{40,41} Nanostructured spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ^{42,43} and $\text{TiO}_2\text{–B}$ ^{44,45} are other possibilities. Furthermore, there is growing interest in organic redox hosts such as $\text{Li}_4\text{C}_6\text{O}_6$,⁴⁶ which is another potential candidate. These lithium insertion hosts could be used as a matrix with reduced amount of carbon to generate sulfur by the sulfur melting route or *in situ* synthesis approach described earlier.

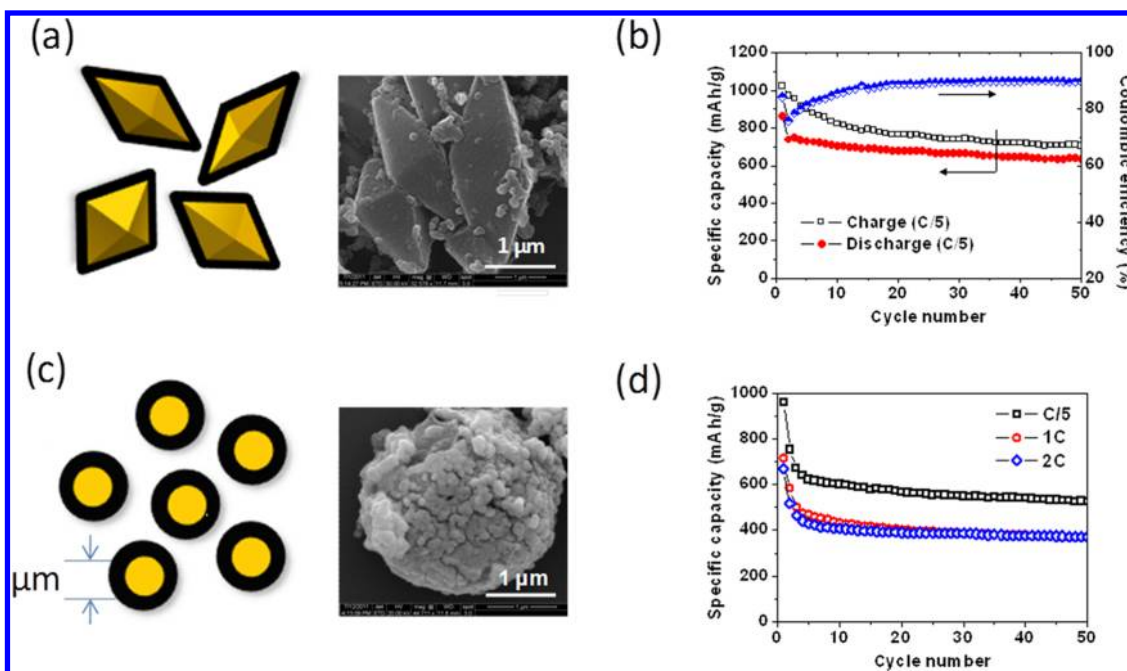


FIGURE 4. (a) Schematic illustration and scanning electron microscopy (SEM) image of bipyramidal sulfur particles coated with a layer of conductive polymer nanospheres. Reprinted from ref 56. Copyright 2012 American Chemical Society. (b) Cyclability of the bipyramidal composite at C/5 rate. Reprinted from ref 56. Copyright 2012 American Chemical Society. (c) Schematic illustration and SEM image of spherical sulfur particles coated with a layer of conductive polymer. Reprinted from ref 57. Copyright 2012 Royal Society of Chemistry. (d) Cyclability of the spherical composite at various rates. Reprinted from ref 57. Copyright 2012 Royal Society of Chemistry.

3. Sulfur–Polymer Hybrid Cathode Materials

Polymers can play a significant role in rechargeable Li–S batteries. For example, the attachment of poly(ethylene glycol) onto sulfur–carbon composites, which provides a chemical gradient that retards diffusion of polysulfides out of the electrodes, has been noticed to improve the electrochemical performance.^{13,47} Yang et al.⁴⁸ have reported that coating of mesoporous carbon/sulfur composites with a conducting polymer poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT:PSS) improves the electrochemical performance. Although conductive polymers are a good choice because they provide a matrix for electron transport, they have much lower electronic conductivity than carbon materials, which prevents them being a sole electron conductor within the sulfur electrode. The diverse synthesis of conductive polymers provides opportunities for morphology control and materials design. We survey below a few strategies exploring conductive polymers as a conductive matrix or barrier for blocking polysulfides that can improve the electrochemical performance of Li–S batteries.

A few sulfur–conductive polymer composites with various structures and morphologies have been developed.^{49–57} For example, granular and tubular polypyrrole have been used as a conductive matrix and sulfur has been introduced by

melting and forming a thin layer (nanoscale) of sulfur on the surface of polypyrrole.^{49,50} This outer coating strategy can improve sulfur utilization due to its nanosized coating, facilitating ion and charge transport. This approach could not reduce the dissolution of polysulfides in liquid electrolyte, but polypyrrole could act as a conductive matrix for sulfur, reducing agglomeration of large solid particles within the composite electrodes. An improved strategy is coating the sulfur particles with a conductive polymer (e.g., polythiophene or polypyrrole), forming a core–shell structure (Figure 4a,c).^{55–57} Sulfur and discharged polysulfides are expected to be confined within the polymer shell, leading to good cyclability, efficiency, and rate capability (Figure 4b,d). This approach utilizes commercial sulfur or sulfur formed in aqueous solution by the thiosulfate reduction reaction with acid and postpolymerization involving self-assembly of these polymers onto the surface of sulfur particles.^{56,57} However, the large (micrometer-sized) sulfur particles lead to low utilization of sulfur. New synthesis methods are needed to form nanosized sulfur particles within the conductive polymer shells that could improve the utilization of active material.

Additional functionalities could be introduced into the conductive polymers to improve the performance further.

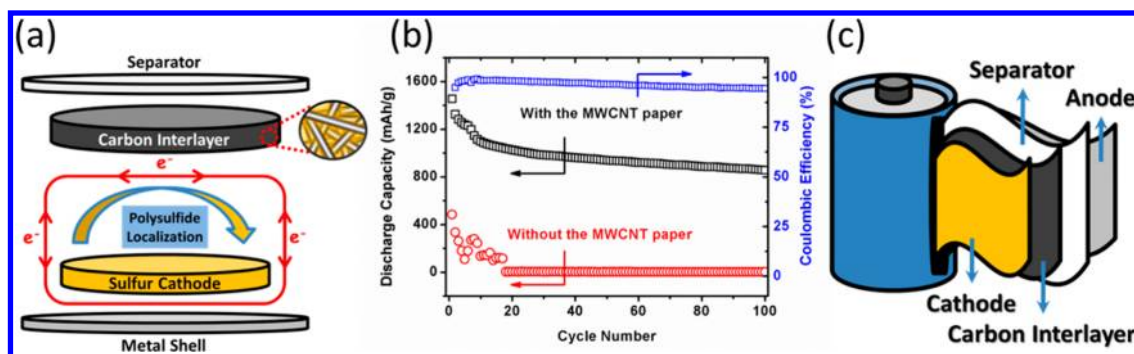


FIGURE 5. (a) Prototype Li–S coin cell configuration with a carbon interlayer in the cathode region. (b) Electrochemical performance of the Li–S cell with a MWCNT interlayer at 0.5 C rate. Reprinted from ref 9. Copyright 2012 Royal Society of Chemistry. (c) New Li–S cell configuration with a carbon interlayer.

For example, a mixed ionic–electronic conductor (MIEC) consisting of electronic and ionic conducting components^{58,59} could improve electron and ion transport, retard polysulfide dissolution, and maintain a robust but porous electrode structure improving the electrochemical performance. Future efforts could focus on multifunctional polymers or inorganic–organic hybrid composites with both ion and electron transport components as additives in the sulfur electrodes.

4. Novel Li–S Cell Configurations

4.1. Conductive and Porous Carbon Interlayers. Recently, a novel Li–S cell configuration has been designed utilizing carbon interlayers between the separator and the regular sulfur electrodes for improving the cyclability of Li–S batteries (Figure 5a).^{9,10} Preliminary data show that a Li–S cell with an inserted conductive MWCNT paper exhibits outstanding cyclability with a capacity of $>800 \text{ mA h g}^{-1}$ over 100 cycles (Figure 5b). The structure of the interlayer has to be porous or should possess many interspaces to accommodate the migrating active material during cycling. The dissolved polysulfides form a stable composite with the interlayer after charging/discharging, leading to excellent cyclability, long cycle life, and high Coulombic efficiency.

Current research spotlights on Li–S batteries are mostly on modifications “inside” sulfur cathodes. Although those approaches aiming at synthesizing composite materials or coating sulfur with protective layers improve the electrochemical performance, cost issues and challenges with large-scale manufacturing still remain as impediments for the commercialization of Li–S batteries. To overcome these problems, innovations “outside” sulfur electrodes could be a promising option, like the carbon interlayer configuration. Thus, conventional sulfur cathodes can be applied with a modification of Li–S cell configuration by inserting a conductive and porous carbon interlayer between the cathode

and separator (Figure 5c). This interlayer works as not only an “upper current collector” to improve the active material utilization but also a “polysulfide stockroom” to maintain the cycle stability and good system efficiency.

4.2. Li/Dissolved Polysulfide Cells. To enhance reaction kinetics in the electrodes, dissolved active material as catholytes are preferred like the electrolyte in conventional redox flow batteries and newly developed cathode-flow Li-ion batteries.^{60,61} Lithium polysulfides are highly soluble in some organic solvents like tetrahydrofuran (THF). Up to 10 M polysulfide in THF can be prepared and a rechargeable lithium/dissolved sulfur battery has been demonstrated in 1979 by Rauh et al.⁶² A capacity of $1,532 \text{ mA h g}^{-1}$ corresponding to 1.83 electrons per sulfur has been achieved in the first discharge, but limited cyclability was achieved with depths of discharge (DoD) as low as 0.5 electron per sulfur corresponding to a capacity of 418 mA h g^{-1} . Such cells show a single voltage plateau at $\sim 2.1 \text{ V}$ (Figure 6a). Recently, Zhang et al.¹¹ have modified the dissolved polysulfide electrolyte with LiNO_3 to promote Li anode passivation and improve Coulombic efficiency. The Li/dissolved polysulfide cells show superior performance to conventional Li–S cells in specific capacity and capacity retention. The predominant issue with these cells is the poor cycle life,^{11,62} which is due to the passivation of lithium metal anode and cathode. Li metal anode needs to be improved by reducing lithium roughness,⁶³ and novel carbon cathode materials with engineered porosity and structure that can provide consistent electron transport while suppressing the passivation are needed to advance this approach to a practical stage.

The Li/dissolved polysulfide cell configuration could be further explored in a half-flow-mode Li–S battery with catholyte circulating at the cathode side like redox flow batteries (Figure 6b). A large amount of polysulfide dissolved in an external tank to the carbon current collector can result

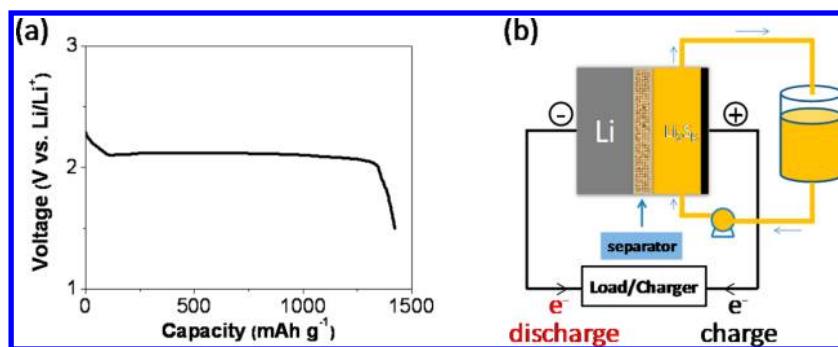


FIGURE 6. (a) First discharge voltage vs specific capacity profile of a Li/dissolved polysulfide cell at 2.8–1.5 V and $C/10$ rate and (b) a schematic of half-flow mode Li/dissolved polysulfide system.

in clogging the pores in the carbon electrodes due to the precipitation of high order polysulfides or sulfides upon cycling. This can be overcome by controlling the charge/discharge cutoff voltages to allow only soluble lithium polysulfides to be present in the catholyte, which would reduce the energy density of the overall systems but could lead to long cycle life. The half-flow mode Li–S batteries could be a promising candidate for large-scale storage for renewable energies.

5. Selection of Electrolyte Materials

Liquid electrolytes containing lithium salts (e.g., LiClO_4 , LiCF_3SO_3 , or $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$) and a mixture of cyclic or linear ethers (e.g., tetrahydrofuran, 1,3-dioxolane, dimethoxyethane, and tetra(ethylene glycol)–dimethyl ether) are commonly used in Li–S batteries.^{63–65} Additives can have significant effect on Li–S performance by reducing the shuttle mechanism arising from the dissolution of polysulfides in the liquid electrolyte. Mikhaylik⁶⁶ discovered that additives with a N–O bond (e.g., LiNO_3) enhance passivation of lithium metal, forming a nonreactive surface exposed to dissolved polysulfides and thereby preventing the shuttle mechanism. This additive has been successfully applied in Li–S cells with almost 100% Coulombic efficiency with various cathode materials and cell configurations.^{9–11,20,36,67,68}

It is favorable to use lithium metal as anode in Li–S batteries since sulfur cathode is lithium-free and lithium has the highest capacity (ca. 3861 mA h g^{-1}). However, there are several problems with using lithium metal such as loss of lithium on each cycle, requiring excess Li that reduces the overall energy density, and reaction with polysulfides, resulting in insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ at the surface of lithium metal.⁶ In addition, the dendrite formation on the surface of lithium metal is a significant safety hazard. Use of a solid-state electrolyte that is impermeable to polysulfides can effectively suppress the formation of dendrites. For example,

Hassoun and Scrosati^{12,69} have developed a solid-state Li–S battery employing a poly(ethylene oxide)-type polymer electrolyte containing finely dispersed nanosized zirconia. High cell performance and Coulombic efficiency were obtained at elevated temperatures. Hayashi et al.⁷⁰ have developed an all solid-state Li–S cell with $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramic electrolytes, which retained a capacity of over 650 mA h g^{-1} for 20 cycles at room temperature. Although high Coulombic efficiency can be achieved and no dendrite with lithium metal is formed with the all solid-state cell configuration, the low ionic conductivity of solid-state electrolyte limits their cell performance. Alternative solid-state electrolytes that can show high ionic conductivity ($\geq 0.5 \times 10^{-3} \text{ S cm}^{-1}$) and be stable with lithium metal are needed to further improve all solid-state Li–S batteries. Promising solid-state electrolytes include silicon-containing polymer electrolytes,^{71,72} garnet-type lithium-ion conducting oxides,^{73–76} and LISICON-type conductors.^{77,78}

6. Conclusions and Outlook

In this Account, we have surveyed recent developments on novel sulfur composite materials, new cell configurations, and electrolytes for rechargeable Li–S batteries. New nanostructured composites, facilitating rapid ion/electron transport while trapping polysulfides, have been largely developed. Sulfur–carbon nanocomposites have shown promising performances in terms of capacity and rate capability. Sulfur–polymer composites are also promising, and multifunctional polymers like MIEC could further improve the cell performance. Li–S cells with novel configurations like a carbon interlayer show impressive performance improvement. Li/dissolved polysulfide cells, an “old” configuration, hold the promise to regain renaissance if good improved lithium metal anodes and carbon cathodes can be developed. Flow mode Li/dissolved polysulfide cells are promising for grid energy storage applications. Electrolyte is equally important

for solving the problems with Li–S batteries. The use of LiNO_3 additive solves the low-Coulombic-efficiency problem. New solid electrolytes with high ionic conductivity and stability with lithium metal anode are needed to make further advances.

In summary, significant improvements have been realized in the past decade with Li–S batteries, but challenges still remain. Development of novel nanocomposite materials with smart engineering design combined with new cell configurations will have a significant impact in the field. In addition, development of advanced materials and electrode characterization tools and methodologies can help enhance the fundamental understanding of the chemical and physical processes occurring.^{79,80} The key issue with Li–S batteries to become a commercially viable technology is the poor reversibility of lithium anode in presence of the polysulfides dissolved in the electrolyte; this could become the limiting factor for Li–S cells over prolonged cycles, ca. 1000 cycles. Development of a selective coating layer on the lithium metal anode or a solid-state electrolyte, which allow only lithium-ion transport, could be an effective strategy to solve this problem. Li–S and Li–O₂ batteries are both appealing in terms of energy density, but the Li–O₂ system faces many more challenges. The poor cyclability and efficiency of Li–O₂ cells along with the engineering challenges to keep the electrolyte and lithium metal free from contamination by ambient air make them far behind the Li–S batteries to become a practical technology. Rechargeable Li–S batteries are the most promising high energy density (>600 W h kg⁻¹) batteries for transportation and large-scale grid energy storage applications in the near future.

Financial support by the Welch Foundation Grant F-1254 and Seven One Limited is gratefully acknowledged.

BIOGRAPHICAL INFORMATION

A. Manthiram is the Joe C. Walter Chair in Engineering and the Director of the Materials Science and Engineering Program and Texas Materials Institute at the University of Texas at Austin. His research interests are in the area of materials for rechargeable batteries, fuel cells, and solar cells, including novel synthesis approaches for nanomaterials. He has authored 450 publications including more than 370 journal articles. See www.me.utexas.edu/~manthiram for further details.

Y.-Z. Fu obtained his B.E. (2000) and M.S. (2003) in Chemical Engineering from Tsinghua University and Dalian Institute of Chemical Physics, respectively, in China, and Ph.D. in Materials Science and Engineering from the University of Texas at Austin in

2007. He was a Chemist Postdoctoral Fellow at Lawrence Berkeley National Laboratory and Research Scientist at Lynntech, Inc., before joining the University of Texas at Austin as a Research Associate. His current research is focused on new materials for Li-ion batteries and fuel cells.

Y.-S. Su obtained his B.S. (2005) and M.S. (2007) degrees from Department of Materials Science and Engineering of National Tsing Hua University in Taiwan. He is currently a Ph.D. candidate in Materials Science and Engineering Graduate Program at The University of Texas at Austin. His research is focused on advanced materials for Li–S batteries.

FOOTNOTES

*Corresponding author. Tel: +1-512-471-1791. Fax: +1-512-471-7681. E-mail address: rmanth@mail.utexas.edu. The authors declare no competing financial interest.

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