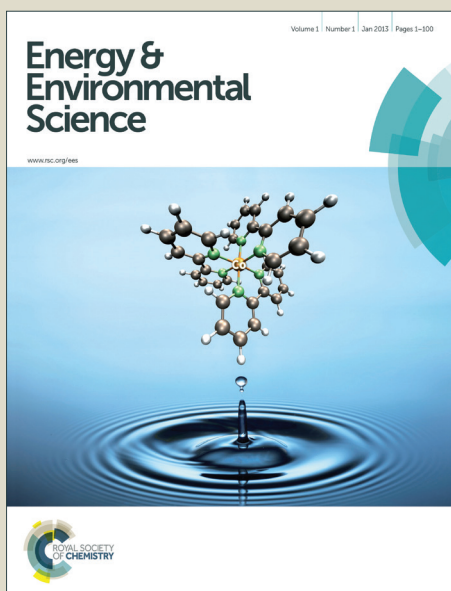


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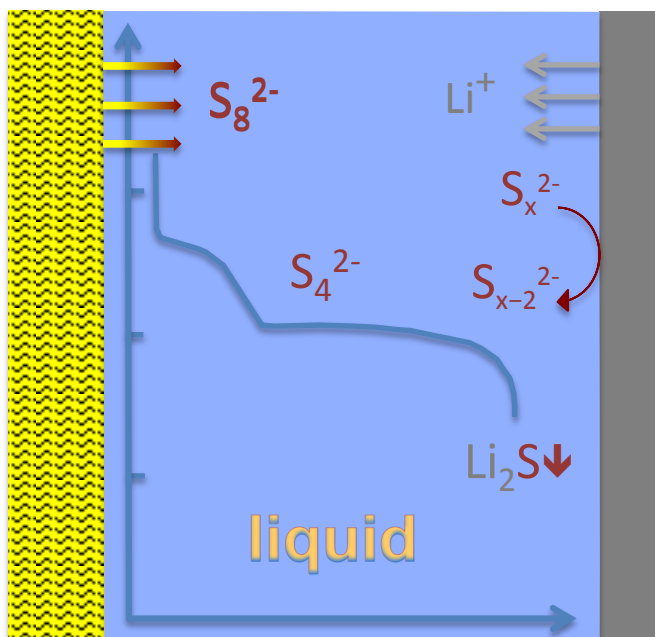
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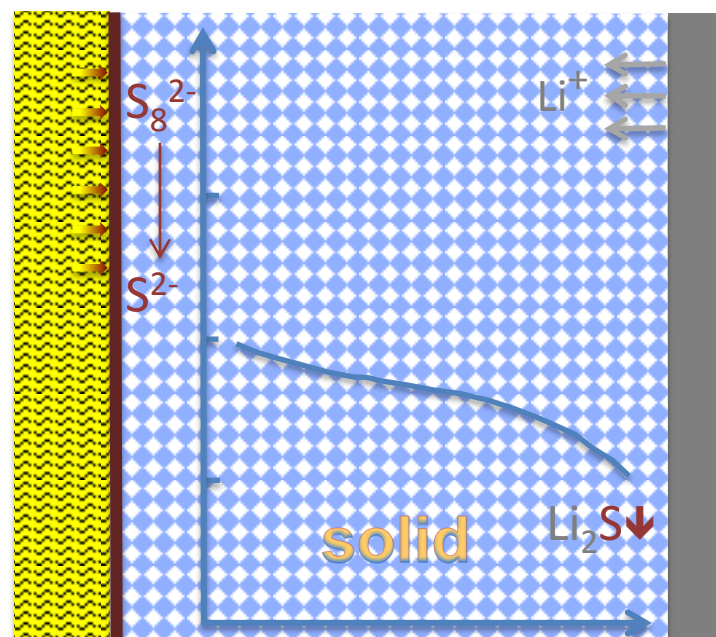
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- High rate capability ✓
- Polysulfide shuttle ✗



- No polysulfide shuttle ✓
- High resistance ✗



Whether lithium-sulfur batteries succeed hinges largely on taming sulfur's complex electrochemistry, over which choice of electrolyte exerts an equally complex influence.

Lithium-Sulfur Batteries — the solution is in the electrolyte, but is the electrolyte a solution?

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At first glance, the combination of the lightest, most electropositive metal (lithium) with a safe, abundant (and reasonably light) non-metal (sulfur) makes good sense as a prospective battery. However, while the lithium-sulfur battery offers a very high theoretical specific energy ($\sim 2600 \text{ Wh kg}^{-1}$) the actual performance delivered is proving to be severely limited — in many cases, this is directly related to the role of the electrolyte. The fundamental issue is that the reduction of sulfur proceeds through a series of polysulfide species, which are for the most part soluble in common organic solvents, including those employed in battery electrolyte solutions. So, despite the fact that the ultimate product (Li_2S) is essentially insoluble, the intermediate stages of discharge see a migration of redox-active species out of the cathode, from where they can react with the lithium anode, which sets in train a series of equilibria that cause both a loss of charging efficiency and a gradual loss of discharge capacity. In the last decade, a major stream of the research to overcome this complex situation has focused on minimizing the solubility of polysulfides. From this we now have a range of media in which the lithium-sulfur system can operate with much improved charge–discharge characteristics: ionic liquids (and blends with organic media); super-saturated salt-solvent mixtures; polymer-gelled organic media; solid polymers; solid inorganic glasses. Underlining the multi-faceted nature of interactions within the lithium-sulfur cell, though, none of these improved electrolytes has been able to bring the performance of this system up to the levels of reliability and capacity maintenance (without sacrificing high specific energy) that are benchmarks in energy storage applications. Our survey indicates that only by combining particular electrolytes with cathode materials that are designed to actively retain sulfur and its reduction products, have a relatively few studies been able to obtain the desired levels of performance. Ultimately the successful development of the lithium-sulfur battery requires careful coordination of the choice of modified electrolyte with the specific nature of the cathode material, underpinned by the assumption that the resulting electrolyte composition will meet established criteria for compatibility with the lithium anode.

1. The Case for Better Batteries

The demand for energy storage systems that are compact, lightweight, and powerful continues to grow, mainly due to the worldwide proliferation of portable electronic devices. A second factor is the need to develop improved batteries for an expanding fleet of electric vehicles (EVs), and related variants (hybrid electric vehicles - HEVs, plug-in hybrid electric vehicles - PHEVs).¹⁻⁹ This will become increasingly important as gasoline prices continue to rise, and environmental regulations on vehicle emissions become more stringent. On an even bigger scale, improved technologies for energy storage will also enable the incorporation of more renewable energy resources into the main (grid-based) energy supply.

Arguably the greatest challenge for battery technology is meeting the demand for huge increases in specific energy. For electric vehicles to achieve driving ranges exceeding 300 miles (500 km), cell specific energy of $\sim 500 \text{ Whkg}^{-1}$ is required.¹⁰⁻¹⁸ By contrast, the rate of increase in specific energy for

contemporary lithium-ion battery technology is slowing, with the result that reliable battery performance at levels beyond 200 Whkg^{-1} is still some way off.¹⁰⁻¹⁵ Thus, present day lithium-ion battery technology is effectively limiting the growth of the EV, and to some extent the PHEV market.^{11,13} Quite clearly, an increase in energy density from present day values (150 to 200 Whkg^{-1}) to the targets of 500 to 700 Whkg^{-1} , requires a major breakthrough in battery materials. In this context, lithium-sulfur batteries attract immediate attention. With elemental sulfur as the positive electrode, the theoretical specific capacity is 1672 mAhg^{-1} . Assuming an equivalent amount of lithium for the negative electrode, complete reaction of Li and S to form Li_2S , and an average discharge potential of 2.2 V per cell, the electrode specific energy for Li-S is 2600 Whkg^{-1} .^{11,16-34} Fully packaged, it is expected that Li-S batteries will operate at close to 500 Whkg^{-1} . While this level of performance places lithium-sulfur well clear of existing battery systems, the significance of this technology will ultimately depend on whether it can be made into a durable and safe device. Much of

the research effort in the last decade has been devoted to the retention of sulfur and its reduction products and this has produced some marked improvements in cathode durability.^{16-18,20-22} In terms of safety, most research to date has employed flammable organic electrolyte materials, and lithium metal anodes are widely used, despite the general lack of acceptance by the battery industry. Both of these issues underline the importance of developing new electrolyte media which, together with the large body of research available on new cathode materials, has inspired this review into the key role played by the electrolyte solution/medium. In this regard, we note the recent appearance of a review of lithium-sulfur electrolytes by Scheers et al.³⁵ and have aimed to provide an analysis that complements this and other similar works.

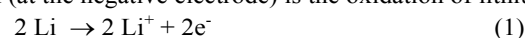
2. Li-S battery: Origins and Principles

The high specific energy of the Li-S system is the direct result of combining two relatively light elements as the primary active materials: a lithium metal anode and an elemental sulfur cathode. Sulfur, however, has very low conductivity (5×10^{-30} S.cm⁻¹ at 25°C), as is also the case with Li₂S. With both the reactant and ultimate product being close-to-insulating, establishing effective charge transfer and material utilization requires that the reactant (sulfur) and all reaction products remain integrated with, and confined within, the current collector. This role is now typically filled by one of a range of mesoporous carbon-based composites.²⁰⁻³⁴ The lithium anode works reasonably well in the short term, but suffers from well-known forms of degradation: (i) loss of lithium due to dendritic growth on charging (ultimately leading to cell short circuits and failure); (ii) corrosion of lithium through direct reaction with polysulfides in solution (also leading to passivation of the anode by deposited lower order lithium sulfides). As we will show in the course of this review, the performance of both electrodes is a complex function of the components of the electrolyte solution, where beneficial effects at one electrode are often established at the expense of other characteristics.

The first developments of the lithium-sulfur battery were, not surprisingly, aimed at accessing the maximum available energy dividend through complete utilization (two-electron reduction) of sulfur.³⁶⁻³⁸ Difficulties with the incorporation of the insulating cathode material into a suitable host, together with the recognition that the initial reduction products are freely soluble in most organic electrolyte solutions, showed that this new system would require significant development before realizing its promised levels of performance. Recognizing that the early problems with Li-S were largely associated with the dissolution of the initial products of discharging (long-chain polysulfides), Rauh et al.²⁷ produced a landmark study in which they proposed a positive electrode comprising an inert current collector (carbon) immersed in a solution of higher-order polysulfides (i.e., a catholyte). In solvents like dimethyl sulfoxide or ethers like tetrahydrofuran, the concentration of dissolved polysulfides (as Li₂S_x) can exceed 10 M.^{21,27,30} This

approach led to the demonstration of an impressive capability for high rates and a wide range of operating temperatures as well as obviating the problems associated with solid sulfur, but was also disadvantaged by the concomitant loss of a portion of the available specific energy, with only around 300 Whkg⁻¹ being the practical achievable value.²⁷ The significance of this work, and hence its prominence in the literature, is that it unravelled some of the mysteries of polysulfide solution behaviour and showed that the obvious complexities did not preclude operation of a rechargeable battery. Since then, most research effort has focused on trying to control the behaviour of sulfur species in solution. In the last decade, as a counterpoint to work with liquid electrolyte solutions, several groups have shown that solid electrolyte media can also be used to produce a viable Li-S battery. Before exploring these two approaches in more detail, it is useful to review the basic characteristics of lithium-sulfur electrochemical cells.

During discharging of the lithium-sulfur cell, the anodic reaction (at the negative electrode) is the oxidation of lithium:



while the cathodic reaction (at the positive electrode) is the reduction of sulfur:



The overall cell reaction is



However, elemental sulfur exists as octasulfur (S₈) rings, which adopt a stable orthorhombic crystal structure, so that equation (3) is modified to;



The electrochemical reduction of sulfur in lithium-sulfur cells occurs through the formation of a series of intermediate lithium polysulfides with a general formula Li₂S_x ($8 \geq x \geq 2$) followed by the final reduction product, Li₂S.^{15,23,24} However, the exact number of stable intermediate sulfide ions during the discharge of a lithium-sulfur cell has not yet been identified beyond doubt. During discharge, it is assumed that the elemental sulfur in the solid phase S₈(s) is firstly dissolved in the electrolyte as S₈(solvated), which is then gradually reduced to lithium polysulfide. Intermediate products of high order lithium polysulfide (Li₂S_x, $4 \leq x \leq 8$) are soluble in most of the commonly used organic solvents, but the lower order lithium sulfides (Li₂S₂ and Li₂S) are insoluble.²²⁻²⁶ During cell discharge, the polysulfide chain length is shortened as the sulfur is further reduced until the final product, lithium sulfide (Li₂S) is formed at the end of discharge. The following chemical species, polysulfide anions or radicals, have been identified during the reduction of sulfur in organic solution: S₈²⁻, S₇²⁻, S₆²⁻, S₅²⁻, S₄²⁻, S₃²⁻, S₂²⁻, S²⁻, S₃⁻·, S₂⁻·, S⁻·.²⁵

It is well known that the polysulfides undergo a variety of disproportionation and exchange reactions in solution, to form species of varying chain length. Moreover, due to the complexity and solvent-dependence of these reactions, the discharge profile of a sulfur electrode can show significant variance with the choice of electrolyte solution.^{28,33} In general though, the reduction of sulfur is mainly defined by the stepwise formation of four intermediate polysulfides, Li₂S₈,

Li_2S_6 , Li_2S_4 , Li_2S_2 , followed by the final reduction process that yields Li_2S .²⁰ Solubility increases with the length of the sulfide chain – lithium sulfide is essentially insoluble in common organic solvents. The involvement of several chemically distinct species leads to a complicated voltage-time profile during discharging which, for the purposes of description, can be divided into four regions, as shown in Fig. 1.³⁹ The first region (I), where voltage falls only slightly (2.4–2.2 V vs Li^+/Li), is associated with the reduction ($\frac{1}{4}$ e per S atom) of S_8 to S_8^{2-} , which is soluble in most electrolyte media. Region II is characterised by a sharp fall in voltage as a further $\frac{1}{4}$ e per S

atom reduction takes place along with the complex series of reactions and equilibria that result in the polysulfide chain length being reduced to four sulfur atoms (Li_2S_4). From there, region III consists of a relatively stable voltage plateau (~ 2.1 V vs Li^+/Li) which is associated with the $\frac{1}{2}$ e reduction of the tetrasulfide to the disulfide (Li_2S_2) as well as the deeper (1e) reduction to Li_2S . The final stages of discharging occur in region IV where the fully reduced sulfide is formed. Both the disulfide and sulfide are insoluble in most electrolyte media.^{26–28}

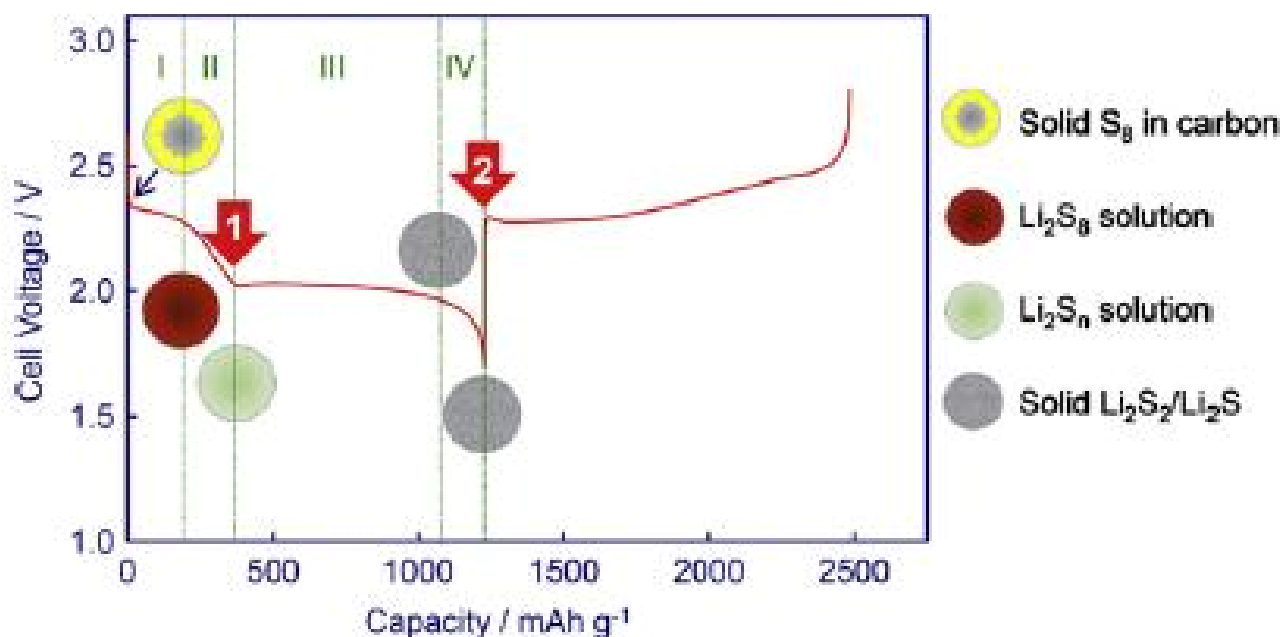
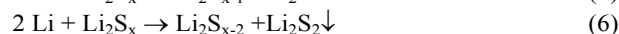
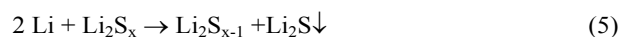


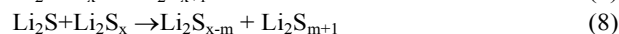
Fig. 1. Typical discharge-charge curve for a lithium-sulfur cell (reproduced with permission from Ref. 39).

3. Solubility of Species and Electrochemistry

As mentioned earlier, and unlike virtually all other batteries, the reduction of the sulfur cathode proceeds through several distinct steps, with each intermediate product having a defined stability and solubility that is a function of the medium (identity of solutes and solvent) in which it is formed. Any soluble sulfur-based species can diffuse out of the electrode, through the separator, to the lithium negative electrode. During charging, or simply from direct chemical reaction with lithium, these soluble sulfur-containing species will be reduced and ultimately deposited as insoluble Li_2S or Li_2S_2 (equations 5 and 6). The process by which this occurs is essentially a form of self-discharge and, more seriously than self-discharge in other systems, it results in a permanent loss of active material. This process accounts for the dramatic loss of discharge capacity with repetitive cycling that was a feature of many early studies into the lithium-sulfur system.^{30,31,36}



Migration of sulfide species has further effects as the highly reduced species, Li_2S and Li_2S_2 , react with the S_x^{2-} from the electrolyte to form lower order polysulfides (S_{x-n}^{2-}) (equations 7 and 8). On diffusing back to the positive electrode, these species are then re-oxidized into S_x^{2-} . The resultant internal “redox shuttle” lowers both the available discharge capacity and the efficiency of recharging. The shuttle mechanism generally becomes active at around 2.4 V and, if the concentrations of participating species are appreciable, it will support a significant parasitic current.



Unless a larger current is imposed by the charging system, the cell voltage will remain stable at ~ 2.4 V and the state-of-charge

of the cell will remain well below 100%. While the redox shuttle established by polysulfide interconversion does, in theory, offer a measure of protection against overcharging, it does so by imposing a constant cost on the energetics of the lithium–sulfur system. Unlike in classic overcharge protection mechanisms (e.g., water electrolysis in aqueous battery systems) where the overcharge reaction is largely dormant at normal operating potentials, the dissolution and subsequent reactions of sulfide species proceed throughout all phases of service. As a result, it is a major goal of researchers to find ways of limiting the liberation of polysulfides and their subsequent transport through the cell. As contended at the outset, the selection and formulation of electrolyte solutions are crucial in deciding how migration of electrode products can influence the electrochemical performance of Li-S cells.

4. Liquid electrolyte solutions

Generally, lithium battery electrolytes are based on solvents from two groups: (i) organic carbonates, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC); (ii) ethers, such as 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME) and tetra(ethylene glycol) dimethyl ether (TEGDME), tri(ethylene glycol) dimethyl ether (triglyme), diglyme, etc. Electrolyte solutions for battery applications invariably consist of mixtures of these solvents so as to allow optimization against a range of key parameters (volatility, viscosity, conductivity, etc.). Early on, it became clear that carbonate solvents underwent a variety of reactions with reduced sulfur species. These were later characterized by XAS analysis, with the result that this class of solvents is no longer considered for use in Li-S batteries.⁴⁰ Chang et al.⁴¹ presented an early study into the optimization of the ratio of TEGDME and DOL on the basis of solvent properties (especially with respect to the polysulfides) and showed that a 1:2 volume ratio of TEGDME:DOL gave the best discharge capacity, although lithium triflate (LiCF_3SO_3) was the only salt employed. Choi et al.⁴² worked at refining the best mixtures of ether solvents by comparing the performance of single and binary solvent based electrolyte with lithium triflate as lithium salt. Their studies on systems with TEGDME, DME/DEGDME (di(ethylene glycol) dimethyl ether) and DOL/TEGDME revealed the beneficial effect of DOL, which is attributed to the lowering of viscosity and improved compatibility with lithium. They also demonstrated that, in addition to the electrolyte composition, the volume of electrolyte solution was also shown to influence the first discharge capacity and cycling stability of the Li-S cells. This idea was developed in greater detail later by Zhang.⁴³

Ryu et al.⁴⁴ investigated discharge characteristics of Li-TEGDME-S cells at low temperatures and found that performance is improved by adding DOL and methyl acetate (MA) to TEGDME solutions. The optimum composition of this mixed electrolyte is MA/DOL/TEGDME (5:47.5:47.5, v/v). The Li-S cell using the optimum electrolyte gave a first

discharge capacity of 994 and 1342 mAh/g-S at -10 and 20 °C, respectively. However, while the addition of MA improved the initial cell performance, capacity fading was higher after about 20 cycles. Of the other organic additives that were evaluated, toluene added to 1 M lithium triflate in TEGDME electrolyte was found to improve the initial discharge capacity, but only from a very low base, and as with MA, long-term performance was unclear. Finally, the addition of γ -butyrolactone (GBL) (2.5 vol.%) which has a relatively high dielectric constant, was shown to adversely affect the cycle performance.⁴²

The composition of the electrolyte solution used by most Li-S research groups is up to 1 M of either lithium triflate or lithium bis(trifluoromethanesulfonyl)imide (LiTFSI , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$) in a 1:1 mixture of TEGDME and DOL.⁴⁵ While as noted earlier, the ether solvents are chosen because they are generally stable in the presence of lithium, it has been shown that dioxolane is susceptible to cleavage and formation of alkoxy lithium fragments.^{46–48} Similarly, while lithium perchlorate has been used by some groups^{45,49}, the performance is inferior, presumably due to the inability to form a stable SEI (solid electrolyte interphase) on the lithium anode. The perfluoroalkylsulfonate electrolyte salts are not completely stable under strongly reducing conditions, but they are known to form a stable interphase layer on a lithium electrode surface.^{50–53} It is apparent, however, that this does not create sufficient long-term stability in a Li-S cell, which has led recently to two more changes to the composition of the liquid electrolyte.

At Sion Power, Mikhaylik⁵⁴ patented the incorporation of 0.2 to 0.4 M LiNO_3 in the electrolyte solution. The presence of this compound was linked to the limitation of the effects of the polysulfide shuttle. However, it was not until a study by Aurbach et al.⁵⁵ detailed the differences in surface chemistry of the lithium anode in the presence and absence of nitrate, that some understanding of the mechanism of action became possible. When nitrate is present, the main differences in lithium surface composition are the higher abundance of oxy-sulfur and oxy-nitrogen species. The direct implication of these findings was that their presence made the SEI much less permeable to polysulfide species, and thereby greatly limited the reactions between these compounds and the lithium electrode. Recently, more details of the effects of nitrate on the morphology of the lithium electrode have been provided by Xiong et al.⁵⁶ With scanning probe microscopy (SPM) combined with XPS, they demonstrated the formation of a smooth and compact film on the lithium surface — such film properties (cf. porous, open morphology) would be expected in a surface layer that limited access by bulky (e.g., polysulfide) ionic species. Kim et al.⁵⁷ have also recently provided new detail on the reactivity of nitrate with lithium sulfide, through a study that involved infrared spectroscopy and electrochemical impedance spectroscopy.

Interestingly, the electrolyte solution promoted by Sion Power also included an appreciable concentration of lithium hexasulfide (Li_2S_6)⁵⁴. In broad chemical terms, this additive will shift the equilibria that involve the higher polysulfides, thereby altering the concentration of a number of other species

in solution. It will also increase the viscosity of the electrolyte solution as, for the same concentrations, the viscosity of Li_2S_x solutions (e.g., in sulfolane) is significantly higher than that of corresponding electrolyte solutions made with LiClO_4 or LiCF_3SO_3 .⁵⁸ This is most likely due to the strong self-association of lithium polysulfides in solutions. Whatever the benefits of setting solution concentrations of polysulfide species at high levels, they will ultimately be limited by the point at which high viscosity slows ion movement, particularly in the mesoporous cathodes. Adding another aspect to this discussion, Xiong et al.⁵⁹ very recently provided evidence that links the presence in solution of hexasulfide with the formation of a protective 'under-layer' of lithium sulfide on the lithium electrode surface. They in effect propose that the SEI on lithium in Li-S cells develops a bilayer morphology in which the outer oxy-sulfur layer (promoted by the presence of nitrate) is supported in its protective role by the formation of more reduced forms of sulfur close to the electrode. In a parallel study, this group showed that LiNO_3 could also have undesirable effects, such as contributing to the (largely irreversible) oxidation of sulfur to oxy-sulfur species that deposit in the cathode and constitute lost active materials.⁶⁰

In recent years, one of the strongest and most prolific research groups advocating the further development of liquid electrolyte solutions for Li-S batteries has been that of Zhang at the US Army Research Laboratories. In a recent review of the liquid electrolyte Li-S battery, they discuss in detail all the issues that are currently hampering commercialization of the technology, with particular attention paid to the problems created by the polysulfide shuttle. After considering a wide variety of strategies for dealing with the effects of this phenomenon, Zhang concludes in favour of promoting the dissolution of polysulfide species and then managing the interaction of these species with cell components, especially the electrodes.^{61,62} In support, they cite earlier work by the group, which has greatly improved our understanding of the mechanism of action of LiNO_3 .^{63,64} While the presence of

nitrate is clearly beneficial to the extended cycling of the lithium anode, Zhang shows that there are adverse effects at the cathode that can offset the benefit. From extensive voltammetric studies, it is seen that discharging the sulfur cathode to low values (below a critical value of 1.7 V vs $\text{Li}|\text{Li}^+$) causes irreversible reduction of lithium nitrate and also renders the ultimate discharge product (Li_2S) even more difficult to recharge.⁶³ The magnitude of these effects, in terms of electrode impedance, is also quantified by means of impedance spectroscopy. Overall, it is concluded that liquid electrolyte Li-S cells must be provided with what amounts to a reserve of LiNO_3 so as to account for the quantities that are inevitably lost to: (i) formation of the SEI on the lithium electrode; (ii) trace consumption each cycle at the cathode due to the difficulty of completely separating sulfur-based reduction from nitrate reduction.⁶⁴

A second contribution to our understanding of the influence of electrolyte properties on the Li-S system concerns the role of average concentration of polysulfide species during operation of the cell. Here the USARL group⁴³ has shown that by adjusting the ratio of electrolyte solution volume to cathode sulfur loading (E/S), they create a trade-off between good initial capacity performance that rapidly decreases (high E/S makes recharging difficult) and low capacity performance that remains steady with cycling (low E/S leads to highly viscous solutions that impede diffusion but limit loss of polysulfides). This suggests that earlier research on the effects of dissolved higher polysulfides on the properties of lithium anodes should now be qualified, or even re-evaluated, by an analysis of the electrolyte composition in terms of E/S. As with the discussion of the role of LiNO_3 , and also now with regard to dissolved polysulfide species, no aspect of the Li-S battery can ever be treated in simple terms. A summary of the main performance characteristics for solvent-based liquid electrolytes is included in Table 1.

Table 1. Summary of Main Characteristics of Electrolytes and Corresponding Performance in Lithium-Sulfur Cells.

Electrolyte Type and Composition		Additive	Indicative Conductivity (S cm ⁻¹) / T °C	Initial Discharge Capacity (mAhg ⁻¹) / Current density / T (°C)	Residual Discharge Capacity (mAhg ⁻¹) / Cycles	Comments	Ref.	
IL: P14- Based	P14-TFSI: TEGDME (1/1, w/w)	0.2 mol/kg LiTFSI	$6.3 \times 10^{-4} / 17$	887/ 0.054 mAcm ⁻² / RT	420/20	Amount of organic directly affects conductivity and causes 5% weight loss at >140 °C	65	
	P14-TFSI: TEGDME (1/2, w/w)	0.2 mol/kg LiTFSI	$8.6 \times 10^{-4} / 17$	-	-		65	
	P14-TFSI: PEGDME (1/2, w/w)	0.5M LiTFSI	$4.2 \times 10^{-3} / 29$	450/ 0.054 mAcm ⁻² / 40	250/100	Adding a proper amount of organic modifier to the pure IL leads to higher and more stable capacity due to higher conductivity. Added organic introduces volatility, up to a worst case of ~5% weight loss at 140 °C (TGA). Organic free electrolyte has <1% weight loss at 300 °C	66	
	P14-TFSI: PEGDME (1/1.5, w/w)	0.5M LiTFSI	$3.5 \times 10^{-3} / 29$	500/ 0.054 mAcm ⁻² / 40	180/100		66	
	P14-TFSI: PEGDME (1/1, w/w)	0.5M LiTFSI	$3.8 \times 10^{-3} / 29$	320/ 0.054 mAcm ⁻² / 40	100/80		66	
	P14-TFSI: PEGDME (1/0.1, w/w)	0.5M LiTFSI	$2.9 \times 10^{-3} / 29$	-	-		66	
	P14-TFSI	0.5M LiTFSI	$1.7 \times 10^{-3} / 30$	120/ 0.054 mAcm ⁻² / 40	20/50		66	
	P14-TFSA	0.5 mol/kg LiTFSA	$1.4 \times 10^{-3} / 30$	720/ 139 mA g ⁻¹ /30	550/50		Different performances are due to the fact of PS solubility dependence on the anionic structure (subsequently donor ability) of IL.	67
	P14-OTf	0.5 mol/kg LiTFSA	$1.1 \times 10^{-3} / 30$	650/ 139 mA g ⁻¹ / 30	190/50			67
P13-TFSA	0.5 mol/kg LiTFSA	$2 \times 10^{-3} / 30$	800/ 139 mA g ⁻¹ / 30	700/50	67			
IL: P13- Based	P13-BETI	0.5 mol/kg LiTFSA	$0.47 \times 10^{-3} / 30$	620/ 139 mA g ⁻¹ / 30	200/50		67	
	P13-FSI	0.5 mol/kg LiTFSA	$6.4 \times 10^{-3} / 30$	1000/ 139 mA g ⁻¹ / 30	50/50		67	
	IL: C ₂ mim- Based	C ₂ mim-TFSI	1M LiTFSI	-	1300 / 50 mA g ⁻¹	500/40		68
IL: PP13 – Based	PP13-TFSA	0.5 mol/kg LiTFSA	$0.78 \times 10^{-3} / 30$	600 / 139 mA g ⁻¹ / 30	520/50	Organic modifier increases capacity by improving electrolyte conductivity.	67	
	PP13-TFSI / DME (2/1, v/v)	1M LiTFSI		1000 / 0.2 C	900/50		69	
	PP13-TFSI	1M LiTFSI		405 / 0.1C	320/10		69	
IL: DEME- Based	DEME-BF ₄	0.5 mol/kg LiTFSA	$1.4 \times 10^{-3} / 30$	900/ 139 mA g ⁻¹ /30	50/50	The capacity of the battery with the BF ₄ anion electrolyte declines in the first cycles due to irreversible reaction between this anion and PSs.	67	
	DEME-TFSA	0.5 mol/kg LiTFSA	$1.4 \times 10^{-3} / 30$	780/ 139 mA g ⁻¹ /30	650/50		67	
	DEME-TFSA	0.64 M LiTFSA	$1.30 \times 10^{-3} / 30$	800 / 139 mA g ⁻¹ / 30	580/100		70	
	DEME-TFSA	-	$3.44 \times 10^{-3} / 30$	-	-		70	
IL: P2225- Based	P2225-TFSA	0.5 mol/kg LiTFSA	$0.92 \times 10^{-3} / 30$	700/ 139 mA g ⁻¹ /30	500/50	Cations of IL can affect the battery performance as a result of difference in viscosity and Li ion transportation.	67	
IL: C ₄ dmim- Based	C ₄ dmim-TFSA	0.5 mol/kg LiTFSA	$1.4 \times 10^{-3} / 30$	750/ 139 mA g ⁻¹ /30	580/50		67	
Solvate IL	Li(G4)-TFSI		$1 \times 10^{-3} / RT$	1100/139 mA g ⁻¹ / RT	700/50	Solvate IL suppresses PSs solubility which gives a battery with stable capacity.	71	
	Li(G3) ₁ -TFSI		$1 \times 10^{-3} / 30$	1100 / 0.083 C / 30	700/400		72	
	Li(G3) ₄ -TFSI		-	800 / 0.083 C / 30	500/35		72	
	Li(G4) ₁ -TFSI/HFE (1/1/4)		$5.2 \times 10^{-3} / 30$	1000 / 0.083 C / 30	750/50		72	
	[Li(G4) ₁][TFSI]		$1 \times 10^{-3} / 30$	900/0.083 C/30	600/50		72	
	Li(G3) ₁ -OTf		$0.3 \times 10^{-3} / 30$	280/139 mA g ⁻¹ / 30	150/100		73	

	Li(G ₃)-NO ₃		$0.31 \times 10^{-3} / 30$	380/139 mA g ⁻¹ / 30	30/100		73
	Li(G ₄)-BETI		$0.91 \times 10^{-3} / 30$	700/139 mA g ⁻¹ / 30	550/100		73
	Li(G ₄)-BF ₄		$0.5 \times 10^{-3} / 30$	400/139 mA g ⁻¹ / 30	100/100		73
Solid Electrolyte	80Li2S-20P2S5 (mol%)		$1 \times 10^{-3} / RT$	1200 / 0.64 mA cm ⁻² / RT	996/200	Battery operates between -20 to 80 °C. The capacity decreases at higher temperature.	74, 75
	80Li2S-20P2S5 (mol%)		$10^{-4} - 1 \times 10^{-3} / 0 - 80 \text{ } ^\circ\text{C}$	400 / C/20 / 80 °C	400/20		76
Polymer Electrolyte	PVDF activated in 1M LiOTf in TEGDME		$0.7 \times 10^{-3} / RT$	860/0.167C / RT	311/50	The composition of the organic solvent affects the polymer electrolyte performance; here the more DOL content leads to the faster capacity decline.	42
	PVDF activated in 1M LiOTf in TEGDME:DOL (2/1, v/v)		$0.7 \times 10^{-3} / RT$	1056/0.167C / RT	210/50		42
	PVDF activated in 1M LiOTf in TEGDME:DOL (1/1, v/v)		$0.7 \times 10^{-3} / RT$	1000/0.167C / RT	220/50		42
	PVDF activated in 1M LiOTf in TEGDME:DOL (1/2, v/v)		$0.7 \times 10^{-3} / RT$	860/0.167C / RT	270/50		42
	PVDF-TEGDME-LiOTf	M.P. = 100 °C T _g = -117 °C	$3.28 \times 10^{-4} / 30$	1200/0.14 mAcm ⁻² / RT	400/10	The composition of the organic solvent affects the polymer electrolyte performance; here LiPF ₆ shows the best result due to higher conductivity.	77
	PVDF-TEGDME-LiBF ₄	M.P. = 98 °C T _g = -99 °C	$6.22 \times 10^{-4} / 30$	1500/0.14 mAcm ⁻² / RT	400/10		77
	PVDF-TEGDME-LiPF ₆	M.P. = 103 °C T _g = -97 °C	$1.88 \times 10^{-3} / 30$	1500/0.14 mAcm ⁻² / RT	500/10		77
	PEO:LiTFSI (mass ratio 49/1)		$4.9 \times 10^{-4} / 90$	700/0.1 mAcm ⁻² / 104°	270/10		78
	PEMO: LiTFSI (20/1)		$4.9 \times 10^{-5} / 23, 1.2 \times 10^{-4} / 60$	220/0.025 mAcm ⁻² / 60°	30/10		78
	PEO - LiOTf :10 mass% ZrO ₂		$\sim 1 \times 10^{-4} / \sim 70$	180/ C/20 /70	200/25		79
	PVDF/HFP		$1.2 \times 10^{-3} / -$	440 / 0.3mAcm ⁻² /RT	360/25		80
Organic Electrolyte	PEGDME 500	1M LiTFSI	-	1200/50 mA g ⁻¹	400/40	Both conductivity and capacity increase in the present of higher percentage of DOL. Also using modified amount additives (LiNO ₃ and MA) improves capacity.	68
	TEGDME	0.5M LiTFSI	$8.1 \times 10^{-5} / -10$	330/10mA g ⁻¹ / -10			44
	TEGDME:DOL (1:1 v/v)	0.5M LiTFSI	$9.6 \times 10^{-5} / -10^\circ$	760/10mA g ⁻¹ / -10			44
	TEGDME:DOL (1/1 v/v)	1 M LiTFSI	$7 \times 10^{-3} / RT$	720/0.1C / -	460/20		45
	TEGDME/DOL (33/67, v/v)	1 M LiTFSI + 0.2 M LiNO ₃	$8 \times 10^{-3} / -$	900/0.1 C / -	600/20		57
	TEGDME:DOL (1/1 v/v) + 5% v MA	0.5M LiTFSI	$1.2 \times 10^{-4} / -10^\circ$	900/10mA g ⁻¹ / -10			44
	TEGDME:DOL (1/1 v/v) + 10% v MA	0.5M LiTFSI	$1.4 \times 10^{-4} / -10$	600/10mA g ⁻¹ / -10			44
	TEGDME	1 M LiOTf	-	400/0.063C/RT	390/50	The result is a proof for the positive effect of adding DOL to this electrolyte.	42
	TEGDME:DOL (1/1, v/v)	1 M LiOTf	-	500/0.063C/RT	500/50		42
	TEGDME:DOL (30/70, v/v)	0.5 M LiOTf	$15 \times 10^{-3} / -$				41
	TEGDME:DOL (70/30, v/v)	0.5 M LiOTf	$1 \times 10^{-3} / -$				41
	TEGDME:DOL (100/00, v/v)	0.5 M LiOTf	$0.5 \times 10^{-3} / -$				41
	TEGDME:DOL (00:100, v/v)	0.5 M LiOTf	$1 \times 10^{-4} / -$				41
TEGDME:DOL (50/50, v:v)	-	$12 \times 10^{-3} / -$			41		
TEGDME:DOL (1:1 v/v)	1 M LiClO ₄	$5 \times 10^{-3} / RT$	1000/0.1C	310/20	Appreciable effect on cell performance from choice of	45	

	TEGDME:DOL (1:1 v/v)	1 M LiOTf	1.5×10^{-3} / RT	750/0.1C	450/20	lithium salt anion.	45
	TEGDME	0.98 M LiTFSI	3.2×10^{-3} / 30	950 /139 mA g^{-1} /30	500/60		70
	DOL	0.5M LiTFSI	9.8×10^{-5} / -10 ⁰	550/10mA g^{-1} /-10			44
	DOL:DME (4/1, v/v)	1 M LiClO ₄		900/0.4 mA cm ⁻² /RT	320/20	Modified proportion of DOL/DME improves the battery performance, DOL can improve electrode/electrolyte interfacial properties and DME modifies PS solubility.	49
	DOL:DME (2/1, v/v)	1 M LiClO ₄		1200/0.4 mA cm ⁻² /RT	750/20		49
	DOL:DME (1/1, v/v)	1 M LiClO ₄	7×10^{-3} / RT	1050/0.4 mA cm ⁻² /RT	510/20		45, 49
	DOL:DME (1/2, v/v)	1 M LiClO ₄		1000/0.4 mA cm ⁻² /RT	500/20		49
	DOL:DME (2/1, v/v)	1 M LiClO ₄		950/0.4 mA cm ⁻² /RT	260/20		49
	DOL:DME (1/1, v/v)	1 M LiClO ₄	7×10^{-3} / RT	750/0.1C	500/20		Battery with LiClO ₄ shows lower capacity.
	DOL:DME (1/1, v/v)	1 M LiTFSI	11×10^{-3} / RT	1000/0.1C	520/20	45	
	DOL:DME (1/1, v/v)	1 M LiOTf	2×10^{-3} / RT	900/0.1C	550/20	45	
	DOL:DME (1/1, v/v)	1M LiTFSI	13×10^{-3} / RT	1200/0.1C / RT	450/120	81	
	DOL:DME (1/1, v/v)	0.25 mol/ kg LiTFSI+ 0.25 mol/ kg P14TFSI		1000 /0.2 mA cm ⁻²	450/200	Adding LiNO ₃ is effective in forming a stable SEI layer on Li anode.	
	DOL:DME (1/1, v/v)	0.25 mol/kg LiNO ₃ + 0.25 mol/ kg P14TFSI		1100 /0.2 mA cm ⁻²	500/200		62
	DOL:DME (1/1, v/v)	0.25 mol/kg LiNO ₃ +0.25 mol/kg TBAOTf		1200 /0.2 mA cm ⁻²	500/120		62
	DME:DEGDM E (1/1,v/v)	1 M LiOTf	0.65×10^{-3} / RT	944/0.063C/RT	350/50		42

5. Modified liquid electrolyte solutions

5.1 Variation in electrolyte salt concentration

First consideration is given to the recent work of Shin et al.⁸² who have taken a similar approach to Zhang⁴³ in looking at solubility effects, but have used lithium ion concentration as the principal variable. They reason that increasing the concentration of the primary lithium salt (LiTFSI in their case) will likely suppress the solubility of lithium polysulfides. Having shown that this indeed is the case, they also suggest that the high viscosity of the electrolyte solutions containing >4 M LiTFSI impedes the diffusion of polysulfides to such a degree that the efficiency of charging is greatly improved. The results presented by Shin et al.⁸² are certainly impressive, with initial discharge capacities holding at around 1000 mAhg⁻¹ for around 50 cycles.

More recently, the idea of pushing salt concentration to even higher values has been presented by Suo et al.⁸³ on what they term 'solvent-in-salt' systems. Here the authors have

extended the concentration range of typical battery electrolyte solutions from around one mole of solute per litre of solvent up to seven mole per litre. In the latter region, they show that LiTFSI – (DOL-DME) solutions certainly become more viscous (>60 cP for the 7:1 solution), but at the same time some important characteristics appear. Of particular relevance to Li-S batteries, there is a large increase in transference number for the lithium ion ($t_{Li^+} = 0.7$) and an appreciable decrease in the solubility of polysulfide species. XPS data suggest that the SEI on lithium is thicker than usual, and this appears to be consistent with the overall lower voltages recorded during discharge (i.e., there is significantly more cell internal resistance for the highest salt concentration.) Nevertheless, the cells with 7:1 electrolyte solutions yielded discharge capacity that remained above 800 mAhg⁻¹ (based on sulfur) for 100 cycles, at close to 100% coulombic efficiency. These results, together with those of Shin et al.⁸², are good grounds for further investigation of these 'solutions' with extremely limited liquid component.

5.2 Mixed organic – ionic liquid electrolyte solutions

The possible effects of high concentrations of TFSI are also critical to a consideration of research conducted on a range of mixed organic – ionic liquid electrolyte media. The commonly used ionic liquids (ILs) are the relatively hydrophobic and electrochemically stable salts of the TFSI anion. This anion is typical of the weakly Lewis basic ionic species that comprise the sub-group of ILs that are used widely in electrochemical applications.^{50,52} Room-temperature ionic liquids (RTILs), also known as organic molten salts, consist only of cations and anions, and exhibit the important properties of good electrochemical stability, low volatility, good thermal and chemical stabilities, and are also environmentally benign. With regard to the Li-S battery, the use of ILs can decrease the solubility of polysulfides, increase the ionic conductivity of the electrolyte, and in some cases lower the viscosity.^{65,66,71,84,85}

In what appears to be the first reported use of an organic-IL mixed electrolyte solution in a Li-S cell, Shin and Cairns^{65,66} investigated the performance of mixtures of poly(ethylene glycol) dimethyl ether (PEGDME) with N-methyl-N-butylpyrrolidinium ($C_4\text{mpyr}$) TFSI and produced an impressive first cycle capacity of around 1300 mAh g^{-1} for the highest ratio of ether to IL (2:1 by mass).⁶⁶ A rapid fall in capacity ensued in all cells though, to around 500 mAh g^{-1} , after approximately 25 cycles. Significantly, the authors recorded voltage-time curves for galvanostatic cycling of Li-Li symmetrical cells and these revealed that impedance steadily grew with cycling, and showed no signs of reaching a plateau. This suggested that further optimization of the proportion of IL in these mixtures was required. As something of a postscript to this work, the Cairns Group⁸⁶ more recently employed the same electrolyte solution with an advanced graphene oxide – sulfur nanocomposite and demonstrated remarkably steady discharge capacity of almost 900 mAh g^{-1} after 50 cycles. Importantly, the same cell in which the electrolyte solution was simply a mixture of 1 M LiTFSI in the same PEGDME, showed substantial capacity loss after less than 20 cycles. This clearly emphasises the role of the ionic liquid with the implication that the likely suppression of solubility of polysulfides on adding the IL is just enough to limit movement of these species to negligible levels.

At around the same time, Kim et al.^{42,84,85} were also investigating ionic liquid – organic solvent mixed electrolyte solutions, but were focused on the imidazolium salts of TFSI. They considered the cations 1-ethyl-3-methyl- (emim), 1-butyl-3-methyl- (bmim), and 1-propyl-2,3-dimethyl-imidazolium (dmpim) with the common anion (TFSI) in mixtures with 0.5 M LiSO_3CF_3 in DME-DOL. The cells which contained emimTFSI and bmimTFSI maintained capacities of 721 and 642 mAh g^{-1} (sulfur), respectively, after 100 cycles. While this compared favourably with the corresponding value of 534 mAh g^{-1} (sulfur), for the IL-free control cells, the latter is unusually low. Arguably of greater interest, in terms of understanding some of the mechanisms that explain capacity loss in Li-S cells, the cell containing dmpimTFSI showed the poorest cycle-life

performance. Well before this study, it had been found by several groups that imidazolium TFSI ionic liquids were not suitable for use in lithium-ion batteries because they were generally not stable under strongly reducing conditions.⁸⁷ The exception sometimes noted was with cations such as dmpim, where the somewhat acidic proton at C2, is replaced by a methyl group, thereby greatly increasing the difficulty of reduction.⁸⁸ In terms of the results of Kim et al.,^{42,84,85} perhaps the greater reactivity of the emim and bmim cations keys in with mitigating the effects of the more reduced forms of sulfur (lower polysulfides) which are reasonably strong reductants. It is also interesting to compare these results with those of Wang et al.⁶⁸ who evaluated the performance of an electrolyte comprised of 1M LiTFSI in pure emimTFSI. They recorded discharge capacity that was initially 1200 mAh g^{-1} and gradually fell to around 600 mAh g^{-1} after 40 cycles. This is clearly inferior to that observed by Kim et al.^{42,84,85} and, allowing for slight differences in electrode behaviour, suggests that reactivity of the imidazolium cation may become difficult when the neat IL is used as the basis for the electrolyte.

Wang and Byon⁶⁹ returned to the first studies of IL electrolytes for Li-S and used a piperidinium TFSI IL, similar to that featured originally by Yuan et al.⁸⁹ In Li-S cells with typical mesoporous sulfur-carbon composite cathodes, Wang and Byon⁶⁹ evaluated the performance of electrolyte solutions that were 1 M in LiTFSI, and different ratios of N-propyl-N-methyl-piperidinium TFSI ($C_3\text{mpipTFSI}$) and DME. The S-C composite cathode was prepared by precipitation of sulfur, from aqueous sodium thiosulfate solution, on to suspended particles of carbon (Ketchen Black). Against lithium metal anodes, these cathodes delivered best performance in a 2:1 (V/V) mixture of ionic liquid and DME. Initial discharge capacity of ~ 1000 mAh g^{-1} fell steadily over 50 cycles to around 850 mAh g^{-1} . Given that cell impedance, as measured by EIS, did not change appreciably during this period of service, the authors attributed the bulk of capacity loss to the effects of the polysulfide shuttle. They did not, though, report any analysis of the electrolyte solution at the completion of charge-discharge service.

In a recent study of Li-S cells with mixed IL-organic electrolyte solutions, Zheng et al.⁸¹ offer some more detailed data that provides an interesting comparison with those of Wang and Byon.⁶⁹ Zheng et al.⁸¹ examined the behaviour of Li-S cells (typical contemporary configuration) in which the electrolyte solution comprised various proportions of ($C_4\text{mpyrTFSI}$) and a 1:1 (V/V) mixture of DOL and DME (all 1 M in LiTFSI). By examining the full range of IL:organic ratios, they were able to show that while the rate of capacity loss falls as the ratio of IL increases, the available discharge capacity also decreases. Thus, while Zheng et al.⁸¹ were able to report 120 charge-discharge cycles with $<6\%$ capacity loss, the value of specific capacity was ~ 700 mAh g^{-1} , significantly less than that reported by Wang and Byon.⁶⁹ In both studies, though, discharge capacity was trending lower at the end of service, which suggests that a similar mechanism of degradation is acting in both cases.

To obtain information on why their cells were losing capacity, Zheng et al.⁸¹ carried out extensive studies on the lithium metal electrodes removed from both Li-S cells and from Li-Li symmetrical cells, all operated with the mixed IL-organic electrolyte solutions. With greater fractions of IL present, the impedance of the lithium electrode increases significantly when the cell is held at open circuit. The magnitude of the increase is however, greatly attenuated in full Li-S cells, presumably due to the influence of the portion of sulfur that dissolves into the electrolyte and then reacts with the lithium anode. SEM images show that the presence of at least 50% IL ensures a much smoother anode surface and corresponding XPS analysis indicates that the SEI formed in the IL-containing electrolyte is rich in oxy-sulfur species and other fragments of the ionic liquid component ions. As noted by the authors, these findings confirm those from the original surface studies of lithium electrodes in ionic liquids in which the compositional markers of a robust SEI were described.^{50,51}

5.3 Ionic liquid electrolyte solutions

The solubility of sulfur in various ionic liquids has been studied by Boros et al.⁹⁰ and a detailed electrochemical and spectroscopic study of sulfur and polysulfides has been reported by Manan et al.⁹¹ The latter shows that while the general features of the voltammetry of sulfur and its reduction products are similar in the commonly used ionic liquids, there are some differences with respect to the relative stabilities of the intermediate species, S_3^{2-} and S_4^{2-} .⁹¹⁻⁹³

Apparently the first report of operation of a Li-S cell with an IL electrolyte was from Yuan et al.⁸⁹ who employed a mixture of 1M LiTFSI and N-methyl-N-butyl-piperidinium (C_4mpip) TFSI. They indicated that the basis for choosing the ionic liquid was to suppress the dissolution of polysulfides, and thereby minimize capacity loss. While they were able to record a reasonable initial discharge capacity (just over 1000 mAh g^{-1} with respect to sulfur), the performance fell away dramatically over ten cycles. In addition, their control cell used a standard lithium-ion electrolyte solution ($LiPF_6$ in EC – DMC) and thus exhibited relatively poor capacity and cycling behaviour. Surprisingly, there was no discussion of the likely protective effects of the IL on the lithium anode.

Yan et al.³⁹ reported the behaviour of a Li-S cell with ionic liquid electrolyte and a lithiated Si-C composite anode (replacing metallic lithium). The IL was a somewhat unusual variant of pyrrolidinium (N-methyl-N-allyl-pyrrolidinium) TFSI and was mixed with LiTFSI (0.5 M) to form the electrolyte solution. These cells typically displayed a high initial discharge capacity (~ 1450 mAh g^{-1}) followed by rapid loss of capacity, to below 800 mAh g^{-1} within 50 cycles. The cell voltage during discharging was also lower than standard Li-S cells. While this was due in most part to the Si-based anode, the shape of the V-t curve during discharging was clearly different to the standard curve, which suggested that the changes in electrode and/or electrolyte had altered the stability

of the polysulfide species that form during discharge. This issue was not taken up by the authors in discussion.

Watanabe and co-workers⁷⁰ have investigated the characteristics of the Li-S system in an 'all-IL' electrolyte, that is comprised of 0.64 M LiTFSI in N,N-dimethyl-N-methyl-N-methoxyethylammonium (DEME) TFSI. This ionic liquid is known to be compatible with reversible operation of the lithium electrode as well as providing for good lithium-ion transport when mixed with LiTFSI. By comparison with an electrolyte solution of 1 M LiTFSI in TEGDME, the solubility of all lithium polysulfides was markedly less in DEMETFSI and, for the higher polysulfides, reduced even further when 0.64 M LiTFSI was mixed with the IL. Electrolyte of the latter composition conferred the best cycling behaviour, with Li-S cells exhibiting an initial capacity of 800 mAh g^{-1} , which decreased to around 600 mAh g^{-1} after 100 cycles. The coulombic efficiency of the charge-discharge cycle was more than 98%, which indicates that this research succeeded in its intention to restrict the dissolution of the lithium polysulfides. Presumably, the substantial loss of capacity was attributable to other aspects of cell performance. No data were presented on the evolution of impedance at the lithium electrode, which would have been the likely cause of degradation of cell capacity performance.

The Watanabe Group⁶⁷ has also presented a study of the influence of the anions present in a series of pyrrolidinium and tetra-alkylammonium ionic liquid electrolytes. They compared the behaviour of a series of Li-S cells in which the electrolyte consists of the C_3mpyr^+ (N-propyl-N-methyl-pyrrolidinium) cation, 0.5 M LiTFSI, and an anion is taken from the homologous series: FSI – $[(FSO_2)_2N]^-$; TFSI – $[(CF_3SO_2)_2N]^-$; BETI – $[(C_2F_5SO_2)_2N]^-$. The findings showed that while the all-TFSI system did not give the highest initial discharge capacity, it did register by far the strongest charge-discharge cycling performance, with 50 cycles completed at (initially) 800 mAh g^{-1} , down to ~ 700 mAh g^{-1} . With $C_3mpyrFSI$, the initial capacity was significantly higher (1000 mAh g^{-1}) but the capacity then dropped rapidly to < 200 mAh g^{-1} within 10 cycles.⁶⁷ The authors suggested that the FSI anion was the least stable of the three related anions and that it was, according to the synthetic chemistry literature, susceptible to nucleophilic attack. They suggested that the most likely nucleophiles in the electrolyte were polysulfides and that this would then explain the presence of lithium sulfate in the cathode after cycling. Clearly this indicates that researchers wishing to realise the benefit of the lower viscosity of FSI ionic liquids in Li-S electrolytes need to now consider the impact this likely reaction pathway can have on cell performance. Viscosity is certainly an important consideration in these ionic liquid electrolytes as the performance of the third anion (BETI), which confers relatively high viscosity on its ILs, was defined by a steady fall in discharge capacity from a low initial value of 600 mAh g^{-1} down to ~ 200 mAh g^{-1} by cycle 50.

From the Watanabe Group also comes an interesting parallel study on a new class of ionic liquid media. Equimolar mixtures of the short chain oligo-ethers, known as glymes, and

certain lithium salts form complexes which, because of the strength of the ether-lithium bonding, can be regarded as ionic liquids of the general formula $[\text{Li}(\text{glyme})]^+\text{A}^-$.⁹⁴ Based on the premise that polysulfides are less soluble in such strongly ionic media, Watanabe and co-workers⁷² evaluated the charge-discharge behaviour of sulfur-carbon composite electrodes in electrolytes comprising either triglyme (G3) or tetraglyme (G4) and lithium TFSI. For the composition $[\text{Li}(\text{G4})]\text{TFSI}$, Li-S cells maintained discharge capacity of around 800 mAhg^{-1} at a high coulombic efficiency ($\sim 97\%$), while with the shorter chain glyme, the capacity was initially higher ($\sim 1000 \text{ mAhg}^{-1}$) and was still at a useful value of $\sim 700 \text{ mAhg}^{-1}$ after 400 cycles, at close to 100% charge efficiency.⁷² In an extension of this work, consideration was also given to the influence of other anions on the performance of this type of electrolyte. While substituting TFSI with each of nitrate, triflate and tetrafluoroborate produced a sharp fall in both capacity and capacity retention, the use of BETI, the next longer homologue to TFSI, produced reasonably good performance – initial capacity of 700 mAhg^{-1} , which fell to just under 600 mAhg^{-1} after 100 cycles.⁷³

From the preceding discussion, it is obvious that the use of ionic liquids as electrolyte (or a component of) is virtually predicated on the presence of TFSI as the major anion. As we have noted briefly for the relevant studies, this is largely because this anion contributes to the formation and maintenance of an effective SEI on the lithium anode. Within the Li-S cell, the operation of the SEI is part of several equilibria involving the key sulfur redox species and, therefore some further discussion is justified.

Low-oxidation-state forms of sulfur have been detected in the SEI that forms on lithium electrodes that are charge-discharge cycled in TFSI-containing ionic liquid electrolytes.⁵¹ Evidence from surface X-ray analytical methods (e.g., XPS) indicates that sulfide is among the reduction products, which also include (predominantly) lithium fluoride as well as a host of fragments from the break-up of the bis(trifluoromethanesulfonyl)imide anion. In the presence of free lithium ions, the sulfide presumably forms the lithium compound, although direct detection of Li_2S has so far not been reported.

Importantly, insoluble short-chain lithium sulfides can react with sulfur or long-chain lithium polysulfides to produce soluble polysulfides as shown in equations (7) and (8). Thus, unlike in the simple ionic liquid electrolyte mixtures employed in the first studies, the presence of sulfur and polysulfides renders the SEI on lithium to some extent labile. With some dissolution of sulfide from the electrode now likely, the thickness and probably the permeability of the surface film will be determined by the interplay between the deposition and dissolution processes (equations 5 to 8). This in turn makes more difficult the task of establishing and maintaining an effective SEI.

Another aspect of the increased complexity of the behaviour of the lithium electrode in Li-S cells is the formation of oxyanions of sulfur and nitrogen, which is promoted by the use

of lithium nitrate as an additive to the electrolyte. As noted earlier, a range of oxysulfur species is produced by the reduction and breakdown of TFSI. In general terms, the abundance of these species is enhanced by the addition of TFSI-based ionic liquid and/or the presence of LiNO_3 . Unlike sulfide, the higher oxidation state forms of sulfur do not appear to be involved in any exchange reactions with solution-based species. No information is yet available on whether these compounds continue to accumulate during cell service and hence whether they contribute to loss of discharge capacity.

Overall, at this stage in the development of liquid electrolyte solutions for Li-S batteries, it is clear that none of the combinations of IL and organic solvent, together with variations in the identity of lithium salt (including additives such as nitrate), has proven able to limit significantly the steady decrease in discharge capacity that is always present from the commencement of cycling service. Presumably, even in configurations where combined electrode impedance does not appear to continue growing with cycling, some other process, perhaps as simple as precipitation of lower order lithium sulfides, progressively drains the electrodes of dischargeable material. Although limited in number, the studies that have considered ionic liquid anions other than TFSI suggest that this anion, compared with other fluorosulfonyl species, confers the best characteristics, in terms of both liquid properties and chemical reactivity with the lithium electrode. A summary of the main performance characteristics for modified liquid electrolytes is included in Table 1.

6. Solid and Solidified Electrolyte Configurations

From the discussion of liquid electrolyte solutions, it seems clear that the causes of capacity loss in Li-S cells are intimately associated with the processes and phenomena that often define behaviour in liquids: diffusion, migration, solubility, precipitation. In battery technology, the development of a solid electrolyte is always attractive as it makes any device inherently safer, in terms of preventing leakage of a potentially dangerous liquid. With respect to the operation of the lithium-sulfur system, some form of solid electrolyte may directly alleviate, or prevent, the processes that appear to be unavoidable in the liquid electrolyte systems investigated to date.

6.1. Polymer Electrolytes

6.1.1 ABSORBED LIQUID/GELLED ELECTROLYTES

The notion of allowing a liquid organic electrolyte solution to be absorbed by an appropriate polymer medium is common in lithium-ion technology where the resultant devices are well-known as ‘lithium polymer’ batteries. A popular polymer for this purpose is poly(vinylidene difluoride) (PVdF) which can be processed relatively easily into thin, microporous membranes. Choi et al.⁴² evaluated the performance of Li-S cells with electrolyte media that were based on ~ 100 micron thick PVdF

membranes that had been soaked with a range of TEGDME/DOL (1 M LiCF_3SO_3) solutions. The presence of the polymer caused an approximate doubling of electrolyte resistance and, at 100 micron, the electrolyte thickness was well above what would be optimum in a commercial cell. Nevertheless, the discharge capacities for the best polymer-based cells were comparable with those of liquid-only control cells and, over 50 cycles, registered a similar rate of capacity loss. Overall, though, these results, together with those from studies of similar systems⁹⁵, suggest that the presence of the polymer simply slows down ion movement somewhat, without any apparent effect on solution chemistry.⁹⁵

Wang et al.⁸⁰ prepared Li-S cells with a PVdF-HFP electrolyte (PVdF crosslinked with hexafluoropropylene). Thin (60 micron) sheets of polymer were solvent-cast from acetone, and then gelled with a typical organic carbonate (+LiPF₆) lithium-ion battery solution. The cells demonstrated good cycling stability, although the reversible capacity was quite low, at about 440 mAhg⁻¹, due to a low loading of sulfur in the cathode. At around the same time, Shin et al.⁷⁷ prepared plasticized polymer electrolytes by mixing PVdF-HFP with solutions of several lithium salts in TEGDME. The resulting mixtures were solvent-cast from acetone. When ball-milling was used to prepare the polymer electrolyte, and the salt was LiPF₆, the PVdF-TG composites reached the highest conductivity of $4.99 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. In a typical Li-S cell configuration, this electrolyte delivered the highest initial discharge capacity of $\sim 1500 \text{ mAhg}^{-1}$ at the rate of 0.14 mA/cm². However, the rate of capacity loss was dramatic for this and all other cells, such that the typical residual capacity after 10 charge-discharge cycles was around 450 mAhg⁻¹ (with respect to mass of sulfur). There was no evidence to suggest how the performance of this type of electrolyte might be improved.

As for PVdF, the use of polyethylene oxide (PEO) in lithium battery technology has a long history. While the use of gelled PEO electrolytes in lithium-ion batteries has been extensive, there are few notable examples in the use of PEO for lithium-sulfur battery electrolytes. In an early work, Jeon et al.⁹⁶ prepared Li-S (carbon black) cells in which the electrolyte was comprised of LiClO₄ dissolved in TEGDME that was absorbed by a PEO support. These cells yielded a modest capacity of around 400 mAhg⁻¹, which was steady for ten charge-discharge cycles. Later, Hassoun et al.^{97,98} employed PEO in a gelled composite that was comprised of an EC-DMC-LiPF₆ liquid component and a nano-structured zirconia additive. Performance at C/20 was initially quite impressive with a discharge capacity of 1200 mAhg⁻¹ (on the basis of the mass of sulfur in the cathode) but this fell away by approximately one third over 35 cycles.⁹⁷

More recently, attention has turned to tuning the composition of the polymer base so as to exert direct influence over the movement of polysulfide species. Jin et al.⁹⁹ prepared PEG borate esters and incorporated these into PEG-methacrylate copolymer blends which were then cast as membranes. On the premise that Lewis acid-base interactions

between the borate and polysulfide ions should enhance the mobility of lithium ions, the authors noted an increase in lithium transference number, but only during the first 20 cycles, after which it began to fall. The same period of cycling coincided with steady discharge capacity ($\sim 850 \text{ mAhg}^{-1}$ for the thinnest electrolyte membrane) as well as reasonably steady values of impedance for both the bulk electrolyte and the lithium electrode. However, the impedance of the cathode (including the electrolyte interphase region) rose significantly and was more than 50% higher (cf. initial value) at cycle 20. From this point, cell discharge capacity began to fall steadily with lithium electrode impedance now increasing but cathode impedance sitting at an almost constant value. The authors note that after 50 cycles XPS data show a markedly thicker layer of predominantly lower lithium sulfides (Li₂S and Li₂S₂) while at the 25 cycle point, there is much more diversity in the composition of the SEI.

Although not discussed by the authors, it would seem that the separator has a definite maximum capacity for absorbing (binding to) polysulfide species. In addition, the impedance-time profile for the cathode indicates that it too probably accumulates discharge products in the interphase layer and that this process is essentially complete after around 20 cycles. Beyond this point, liberated polysulfides are basically free to migrate across to the lithium electrode and undergo the well-known reactions that drive up impedance, as clearly shown in this work.⁹⁹ Perhaps the one main issue that this paper illustrates is that the electrolyte / separating medium between the electrodes, even when it is vastly massive compared with commercial equivalents, still does not have the capacity to do more than slow down the inevitable movement of polysulfides towards the negative electrode. At the very least, such a strategy must be matched with one for protecting the anode.

Arguably the most impressive performance for a Li-S cell that has been published to date has very recently been reported for another absorbed-liquid polymer electrolyte system. Chen and co-workers¹⁰⁰ have reasoned that adding nanoscale particulate silica to the polymer, to create a mesoporous network, will assist the movement of lithium ions while greatly inhibiting the movement of polysulfide species. The composite of methacrylate (PMMA), PVdF-HFP and mesoporous silica was cast from acetone and ether, dried under vacuum, then soaked in EC-DEC (1 M LiPF₆) to form the composite polymer electrolyte (CPE). With a composite sulfur-polyacrylonitrile cathode and lithium metal anode, these cells produced discharge capacity (with respect to the mass of sulfur) of close to the theoretical limit initially, which fell within ten cycles to and almost steady value of around 1200 mAhg⁻¹. After 100 cycles at 0.2 C, this had fallen slightly, to around 1150 mAhg⁻¹. Examination of the cells after service indicated that the combination of this cathode and electrolyte had been very effective in limiting the movement of sulfur through the CPE towards the anode. Interestingly, the voltage-time curve for discharge was quite different to that normally seen. It was essentially a smooth linearly sloping curve from 2.2V through to around 1.8 V, at which point the final discharge phase (to

form Li_2S) commenced. This calls into question the effect that this cathode-electrolyte system is having on the presence of some of the known intermediate reduction products of sulfur. A summary of the main performance characteristics for absorbed liquid (including gelled polymer) electrolytes is included in Table 1.

6.2.1 SOLID POLYMER ELECTROLYTES

A number of groups have investigated¹⁰¹ the use of solid polymer electrolytes, with or without the addition of ceramic fillers, mainly on the premise that the movement of polysulfides will effectively be blocked. As a starting point, though, the literature on this type of electrolyte shows that conductivities at room temperature are invariably very low, which greatly limits electrochemical performance. Some systems offer promise, however, as suggested by Marmorstein et al.⁷⁸ who characterised Li-S cells with three different polymer electrolytes; (i) PEO/LiTFSI; (ii) Poly (ethylene-methylene oxide) (PEMO) with LiTFSI; (iii) a composite made by mixing fumed silica with PEGDME and LiTFSI. The PEO cells yielded high initial discharge capacities (close to 1600 mAhg^{-1} with respect to sulfur), but only for the first cycle, and only when operated at 104°C . With a loading of 50 wt.% of sulfur in the cathode, these authors reported a rapid fall of discharge capacity to just over 200 mAhg^{-1} by cycle 20. Of interest was that the discharge V-t curve showed that the first stage discharge process, with a plateau at above 2.4 V, was only prominent for the first cycle and disappeared within 2-3 cycles. This coincided with the most severe fall in capacity and indicates that virtually no recharging of reduction products proceeds beyond the lower polysulfides (notionally S_4^{2-}). This behaviour is clearly one of the side-effects of changing the solution-phase chemistry of the sulfur cathode and may be a function of a range of factors, including the specific morphology and surface properties of these polymers. Of the other polymers examined, PEMO-LiTFSI exhibited qualitatively similar behaviour, and actually reached lower capacities more rapidly, while PEGDME yielded the most stable discharge capacity behaviour by delivering a steady value of just under 500 mAhg^{-1} (sulfur) for almost 25 cycles. The latter electrolyte also contained fumed silica and a methacrylate derivative so its performance is a little more difficult to interpret.

In another approach, Jeong et al.^{102,103} prepared $(\text{PEO})_6\text{LiBF}_4$ polymer electrolytes under three different mixing conditions: stirred polymer electrolyte (SPE), ball-milled polymer electrolyte (BPE) and ball-milled polymer electrolyte with 10 wt% Al_2O_3 (BCPE). Electrolyte films were solvent cast from acetonitrile and incorporated into lithium (metal)-sulfur (acetylene black support) cells that were cycled at 80°C , at a modest rate of $70 \mu\text{A cm}^{-2}$. Complete utilization of sulfur was achieved by discharging to an end-of-discharge voltage of 1.7 V vs $\text{Li}|\text{Li}^+$ but, as also reported by Marmorstein et al.,⁷⁸ capacity fell to low levels ($< 400 \text{ mAh g}^{-1}$) within three cycles. Progressively lowering the utilization, through 50, 25 and finally 12.5%, by raising the cut-off voltage, yielded improved

capacity retention, but at the expense of energy density. Jeong et al.¹⁰³ presented a detailed study of the voltage-time behaviour during the first few cycles. This analysis revealed only fleeting involvement of the higher polysulfides in cell behaviour. Even at 12.5% DoD, the voltage at cut-off was trending to lower values at the third cycle. Moreover, this behaviour was for the alumina-containing electrolyte, which yielded the best performance of the three formulations that were investigated. The improvement in cycling with the addition of Al_2O_3 was attributed to the promotion of the formation of Li_2S , however there was no way of gauging the likely durability of this benefit.¹⁰³

More recently, Liang et al.¹⁰⁴ showed greatly improved behaviour for a cell with a solid-state $\text{PEO}_{18}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}-10 \text{ wt}\%\text{SiO}_2$ electrolyte, lithium anode, and a mesoporous sulfur ordered mesoporous carbon (S-OMC) cathode. These cells maintained close-to-constant discharge capacity of about 800 mAhg^{-1} for 25 cycles, at 70°C and 0.1 mAcm^{-2} . The voltage-time characteristics of these cells were also notably constant through the cycling period evaluated. Interestingly, while there was evidence of discharge to octasulfide on the first cycle, the subsequent cycles showed a V-t profile that was devoid of the first ($\text{S}_8 - \text{S}_8^{2-}$) discharge plateau and which from that point retained the same profile throughout subsequent cycles. This clearly indicated that some greater stabilization of discharge products had been achieved in this combination of cathode and PEO electrolyte.

Finally, Hassoun and Scrosati⁷⁹ presented a further development of their earlier work with gelled PEO-based electrolytes in which they were able to remove the organic solvent and operate a series of cells with a composite LiTf-PEO- ZrO_2 electrolyte. While these cells delivered significantly better performance at 90°C , the discharge capacity at 70°C was still around 600 mAhg^{-1} and this was shown to be steady for at least 30 cycles.

6.2. Non-Polymer Electrolytes

While the inherent flexibility and low cost of polymer-based electrolytes are attractive features, it is clear from the previous discussion that the performance of solid polymer Li-S batteries to date has been in general quite poor, compared with liquid-based systems, and that the former are at this stage hampered by the requirement for operation at above ambient temperatures (typically at least 70°C). As a compositionally distinct alternative to these largely organic media, there has been long term interest in a family of sulfide compounds that form amorphous solid electrolytes in which the conductivity of metal ions such as lithium can be sufficiently high for battery applications. The group of Hayashi and Tatsumisago^{74,105-111} have been a significant influence in this area with their work on $\text{Li}_2\text{S} - \text{P}_2\text{S}_5$ glasses over more than a decade. In early work, they demonstrated that mechanical milling of $80\text{Li}_2\text{S} - 20\text{P}_2\text{S}_5$ (mol%) glasses gave rise to exceptionally high room temperature conductivity of $10^{-3} \text{ S cm}^{-1}$, which they attributed to the formation and stabilization of the high-temperature phase

Li_7PS_6 ¹¹². In fact, they describe these materials as ‘superionic’ and crystallographic analogues of thio-LISICON ($\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$).¹⁰⁷ When later deployed in energy storage devices, these electrolytes allowed reasonable cycling behaviour at current densities of around $65 \mu\text{Acm}^{-2}$.^{74,108} Further development, in which full Li-S cells were produced, saw demonstration of devices that could maintain discharge capacity above 850mAhg^{-1} for 200 charge–discharge cycles at $1.3 \text{mA}\text{g}^{-1}$.⁷⁵ The same devices could also deliver around 500mAhg^{-1} at almost $20 \text{mA}\text{g}^{-1}$ when the temperature was raised to 80°C . These cells featured a relatively simple cathode, which was comprised of milled sulfur, acetylene black and the solid electrolyte. It would be reasonable to expect that performance could be raised by further development of the cathode used in these cells. Agostini et al.⁷⁶ have also reported quite good cycling performance with this type of electrolyte although their discharge capacities, albeit with intercalating carbon anodes, were quite a bit lower.

In an interesting parallel effort, the group of Liang et al.¹¹³ at Oak Ridge National Laboratory have recently taken up the development of all solid-state Li-S cells with similar glassy sulfide electrolyte materials. In the first report, they describe beginning with the same starting materials (Li_2S and P_2S_5) but carrying out the reaction in THF solution to produce a nanoporous form of the highly conductive compound $\beta\text{-Li}_3\text{PS}_4$. Cyclic voltammetry at a platinum electrode shows reversible lithium deposition and symmetrical cells cycle without dendrite formation, even at 25°C , albeit with obvious increases in impedance over 15 cycles. In the next development of this electrolyte material, nano-sized particles of lithium sulfide were coated with $\beta\text{-Li}_3\text{PS}_4$ and then bound into cathodes with carbon black and PVC binder. With the thiophosphate also serving as the electrolyte, and utilizing a lithium anode, test cells delivered quite good initial discharge capacity ($\sim 1200 \text{mAhg}^{-1}$) but also suffered around 30% capacity loss over 100 cycles. It should be noted that the cathode was based on relatively low surface area carbon and the resultant lack of possibility for extensive interaction between sulfur/sulfide and a functional substrate is, based on comparison with other studies, a likely contributor to the loss of performance.¹¹⁴

Finally, Lin et al.¹¹⁵ have also investigated the effect of these sulfide materials on the behaviour of typical liquid-electrolyte Li-S cells. They added $\text{Li}_2\text{S-P}_2\text{S}_5$ (1:1 mole ratio) to a standard TEGDME (LiTFSI) electrolyte solution at a dosing of 5 wt.% and with standard cathode and lithium metal anode they obtained a discharge capacity that peaked at over 1300mAhg^{-1} and then levelled off at just under 1000mAhg^{-1} . This performance was much better than the control cells (no addition to the electrolyte) the discharge capacity of which fell to less than 400mAhg^{-1} over the same period of service. The authors attributed the improvement with the addition of phosphorus pentasulfide to in situ formation on the lithium anode surface of $\beta\text{-Li}_3\text{PS}_4$ which, as a good lithium ion conductor, protects the anode from access by reactive species. A second mode of action for the P_2S_5 additive was that its presence raised the solubility of all sulfide and polysulfide species, thereby largely

preventing the accumulation of lower, more reduced, sulfide species in the electrodes. Importantly, the pentasulfide is also stable in the potential window in which the sulfur cathode is typically operated.

As indicated earlier, thio-LISICON ($\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$) is a well-known superionic conductor and would have been expected to feature prominently in the development of all-solid Li-S cells. However, it has been reported that thio-LISICON is not stable in contact with lithium metal due to reactivity of the germanium centres in the former.¹¹⁶ Nevertheless, Nagao et al.¹¹⁷ have reported that all solid-state cells with thio-LISICON as electrolyte and a composite electrode of sulfur and CMK-3 (mesoporous carbon) showed an initial reversible capacity of up to 1300mAhg^{-1} . However, the cells show significant degradation of charge-discharge capacities after several cycles. The degradation of the charge discharge characteristics was investigated further in a study that analysed data from small- and wide-angle X-ray scattering experiments.¹¹⁸ The results indicated that in this type of cell, two different crystallographic forms of Li_2S are formed and that the formation of the high pressure polymorph is likely linked to the strong interaction between carbon and sulfur in the mesoporous cathode. The same group of researchers have also developed a related compound – $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ – which shows even higher conductivity, around 10^{-2}Scm^{-1} at room temperature. However, this compound also seems to have limited stability in the presence of elemental lithium.¹¹⁹ The cells into which it was incorporated by Nagao et al.¹¹⁸ employed indium anodes, rather than lithium, and the voltammetric behaviour reported for reduction processes showed very limited reversibility of the lithium deposition. Unfortunately, at this stage, the great benefits possibly accessible through the use of this highly conductive solid will remain under-utilized in Li-S cells.

All-solid-state lithium secondary batteries with a glassy $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$ electrolyte and lithium sulfide-carbon ($\text{Li}_2\text{S-C}$) composite positive electrodes, prepared by the spark plasma sintering process have also been reported.¹²⁰ The electrochemical tests demonstrated that the $\text{Li}_2\text{S-C}$ cells showed the initial charge and discharge capacities of ~ 1010 and 920mAhg^{-1} (referenced to Li_2S), respectively, which showed higher discharge capacity and coulombic efficiency $\sim 91\%$ than those for the $\text{Li/Li}_2\text{S-C}$ cells with nonaqueous liquid electrolytes ($200\text{--}380 \text{mAh/g-Li}_2\text{S}$ and $\sim 27\%$, respectively). The ex-situ S K-edge X-ray absorption fine structure measurements suggested that the appearance and disappearance of elemental sulfur in the positive electrodes after charging and discharging, respectively, indicating that the ideal electrochemical reaction $\text{Li}_2\text{S} \rightleftharpoons 2\text{Li} + \text{S}$ proceeded in the all-solid state cell. Such ideal electrochemical reaction, due probably to the suppression of the formation of polysulfides in the electrolyte, would result in higher coulombic efficiency and discharge capacity as compared with those of the liquid-electrolyte cells. A summary of the main performance characteristics for the solid electrolytes surveyed is included in Table 1.

7. Concluding Remarks and Outlook

The standard lithium-sulfur cell, which operates with a liquid electrolyte in which the products of reduction of sulfur are to varying extents soluble, fundamentally embodies a compromise between opposing factors (both chemical and electrochemical). As a result, while this version of the technology typically delivers a high initial capacity, the retention of discharge capacity and charging efficiency are both generally poor, due to the complex behaviour of the polysulfides. To some extent performance can be improved by incorporating nitrate into the electrolyte composition, as this acts to decouple the polysulfide shuttle from one of its driving forces – interaction with the lithium anode. On the timescale of many charge–discharge cycles, though, nitrate is ultimately consumed, by both electrodes, and its influence disappears. The fact that the SEI on lithium remains in dynamic exchange with solution makes protecting this electrode from interaction with redox-active species extremely challenging. Arguably the best way forward on this front is to consider a shift away from the metallic lithium electrode to one of the other high-specific-energy options, notably silicon. As only a very small number of studies have considered this option³⁹, it would be unwise to rule it out on the basis of the relatively low levels of performance that have been achieved to date. A more important issue to consider is that the slightly less negative potential of the $\text{Li}_{4.4}\text{Si}|\text{Si}$ electrode is likely to significantly decrease the interaction between the anode and TFSI. This in turn offers scope to develop an SEI with a different composition, one that is better suited to the solution-based polysulfide chemistry.

A second approach to improving performance is by enhancing the ability of the cathode to retain sulfur and polysulfides, as shown in a host of recent publications. Even with a specially designed mesoporous electrode however, cells that are optimized with respect to sulfur:electrolyte ratio still suffer ~50% loss of discharge capacity, albeit after 1000 cycles.¹²¹ In a similar vein, the use of a cathode binder with enhanced affinity for sulfur species has also been shown very recently to provide a benefit that is of the same order.¹²² Ultimately though, binding sulfur compounds to the cathode can only slow down the effects of diffusion, in much the same way as a chromatographic stationary phase slows the passage of the eluted components, and the degradative aspects of the polysulfide shuttle are eventually observed.

As we have seen, there is now an extensive literature on the modification of the electrolyte for lithium-sulfur batteries, which is largely focused on minimizing the solubility of the polysulfides. The approaches used include blending of electrolyte solvents with ionic liquids, absorption (gelling) of electrolyte solution with a variety of polymers and use of additives that lower polysulfide solubility. Arguably the most impressive improvement based solely on electrolyte modification was presented recently by Suo et al.⁸³ in which very high concentrations of lithium salt are shown to greatly suppress solubility of polysulfides and deliver discharge capacity that falls at a much reduced rate (compared with

standard liquid electrolyte cells). Overall, though, there is no indication that any modification to the electrolyte solution, of itself, will produce a lithium-sulfur cell that can maintain good discharge capacity at a constant value for hundreds of charge–discharge cycles.

The ultimate modification that can be made in terms of the solubility of polysulfides is to deploy a true solid electrolyte, based on either a polymer or a ceramic conductor. To date none of the solid polymer systems has been able to demonstrate performance that is comparable with liquid systems, even when operating temperature is raised above 60 °C (a typical minimum temperature for solid polymer conductivity). The situation with inorganic compounds, such as those based on $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses is more promising, although even the best results to date are similar to those obtained in standard liquid electrolyte systems, with good initial capacity (around 1000 mAhg^{-1}) falling away steadily within 100 to 200 cycles.¹¹⁴ Given the distinctly different discharge voltage-time profiles reported for these true solid electrolyte cells, there is clearly more research effort required to understand the detailed mechanism of the main electrochemical reactions before attempts can be made to improve the performance of the all-solid lithium-sulfur battery.

The best performance recorded to date for laboratory-based lithium-sulfur cells comes, not surprisingly, when materials and configurations are chosen which control the migration of sulfur and polysulfides by more than one means. This review has found that while modifying the electrolyte to reduce the solubility of sulfur species generates an improvement relative to a standard configuration, achieving a discharge capacity of at least half the theoretical value (1675 mAh g^{-1}), and preserving this for hundreds of cycles, requires a combination of some form of active retention of polysulfides in the cathode, as well as suppression of solubility of these species in the electrolyte. Research by Ji et al.⁸⁶ provided an excellent example in their studies with a carefully designed cathode of high sulfur affinity (based on reduced graphene oxide) and an electrolyte solution which contained a high proportion of pyrrolidinium TFSI ionic liquid. This work, and others with a similar approach, looks to be a promising basis for development of a durable lithium-sulfur battery technology.

One aspect of the performance of Li-S cells that is rarely discussed in the literature is rate capability. This important issue, brought to our attention by a reviewer, currently represents a serious deficiency in the technology. Perusal of Table 1 reveals that studies rarely employ discharge current densities greater than 0.1 C. This is no doubt one of the main drawbacks to current approaches that seek to limit the solubility and mobility of the reduction products of sulfur. The fact that the reactions at the positive electrode are solution-based obviously means that the diffusive flux of the reduction products (polysulfides) can limit the rate of discharge. Only in the early work of Rauh et al., where very high concentrations of higher polysulfides (rather than elemental sulfur) were used as the cathode, were much higher rates of discharge achieved. While some increases can be made through the optimization of

cell configuration (electrode thickness, etc.) a major improvement in the rate capability of the lithium-sulfur system will require a substantially different approach to the hosting of sulfur-polysulfide electrochemistry. As an indication that such an approach may not require a major departure from the suite of materials currently in use, Kinoshita et al.¹²³ very recently showed that the performance of Li-S cells featuring the non-polymer solid electrolyte Li_3PS_4 can be dramatically improved by the apparently simple incorporation of around 1wt.% of an imidazolium ionic liquid ($\text{C}_2\text{mimTFSI}$). Importantly, the improvement persists at 25 °C, at which temperature this and many other solid electrolyte systems barely function. While this composite contains a liquid, there is so little that its properties are more like those of a solid, thereby making the improved behaviour remarkable.

Progress over the last 15 years of development of lithium-sulfur cells has seen significant improvements in specific energy and cycle-life in configurations that incorporate a range of different electrolyte media. The most recent studies suggest that careful combination of materials that help contain the migration of polysulfides with electrolytes that limit their solubility, without compromising lithium-ion transport, could ultimately lead to devices which realize the goals of specific energy above 500 Whkg⁻¹ for more than 1000 cycles. At this stage, while it seems more than likely that the electrolyte will be a solution (in the liquid-based sense of the word), the progress in solid and solid-like electrolytes, in the hands of a relatively small number of researchers, is quite remarkable. This may well lead to the inherently safer solid electrolyte version of the lithium-sulfur cell, which is all the more remarkable given that the corresponding lithium-ion cell has so far proved elusive.

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Glossary of Terms and Abbreviations

BETI	bis(pentafluoroethanesulfonyl)imide [[$(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$] ⁻	–
FSI	bis(fluorosulfonyl)imide – [[$(\text{FSO}_2)_2\text{N}$] ⁻	–
TFSI/TFSA	bis(trifluoromethanesulfonyl)imide [[$(\text{CF}_3\text{SO}_2)_2\text{N}$] ⁻ (also represented as NTf_2^-)	–
OTf	trifluoromethanesulfonate (triflate) CF_3SO_3^-	–
bmim	1-butyl-3-methyl-imidazolium (C_4mim)	
C_4dmim	1-butyl-2,3-dimethyl-imidazolium	

deme	N,N-dimethyl-N-methyl-N-methoxyethyl-ammonium
dmpim	1-propyl-2,3-dimethyl-imidazolium
emim	1-ethyl-3-methyl-imidazolium (C_2mim)
P_{2225}	P,P,P-triethyl-P-n-pentyl-phosphonium
$\text{P13/C}_3\text{mpyr}$	1-propyl-1-methyl-pyrrolidinium
$\text{P14/C}_4\text{mpyr}$	1-butyl-1-methyl-pyrrolidinium
$\text{PP13/C}_3\text{mpip}$	1-propyl-1-methyl-piperidinium
$\text{PP14/C}_4\text{mpip}$	1-butyl-1-methyl-piperidinium
DEC	diethyl carbonate – $\text{C}_2\text{H}_5\text{-O-C(O)-O-C}_2\text{H}_5$
DMC	dimethyl carbonate – $\text{CH}_3\text{-O-C(O)-O-CH}_3$
DME	1,2-dimethoxyethane – $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$
DOL	1,3-dioxolane – $\text{CH}_2(\text{O-CH}_2\text{-O})\text{CH}_2$
EC	ethylene carbonate – $\text{CH}_2(\text{O-C(O)-O})\text{CH}_2$
GBL	γ-butyrolactone – $\text{CH}_2(\text{O-C(O)})\text{CH}_2\text{CH}_2$
HFP	hexafluoropropylene
MA	methyl acetate – $\text{CH}_3\text{-OC(O)CH}_3$
PC	propylene carbonate – $\text{CH}_2(\text{O-C(O)-O})\text{C(H)CH}_3$
TEGDME	tetraethyleneglycol dimethylether – $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$ (also known as ‘tetraglyme’ or ‘G4’)
PEGDME	poly(ethylene glycol) dimethyl ether – $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ (typically a blend of glymes with $n \geq 4$)
PEMO	poly(ethylene-methylene oxide)
PEO	poly(ethylene oxide)
PMMA	poly(methyl methacrylate)
PVdF	poly(vinylidene difluoride)
SEI	solid electrolyte interphase
EIS	electrochemical impedance spectroscopy
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy

Notes

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