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Efficient electrolytes for lithium–sulfur batteries

Natarajan Angulakshmi*[1] *and Arul Manuel Stephan*[2]

[1] *Department of Materials Science and Engineering, Politecnico di Torino, Turin, Italy*
[2] *Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi, India*

Edited by:
Mariusz Walkowiak, Institute of Non-Ferrous Metals, Poland

Reviewed by:
Xiqing Wang, Nanotek Instruments Inc., USA
Jijeesh Ravi Nair, Politecnico di Torino, Italy
Mariusz Walkowiak, Institute of Non-Ferrous Metals, Poland

Correspondence:
Arul Manuel Stephan, Central Electrochemical Research Institute (CSIR-CECRI), Karaikudi 630 006, India
e-mail: arulmanuel@gmail.com; amstephan@cecri.res.in

This review article mainly encompasses on the state-of-the-art electrolytes for lithium–sulfur batteries. Different strategies have been employed to address the issues of lithium–sulfur batteries across the world. One among them is identification of electrolytes and optimization of their properties for the applications in lithium–sulfur batteries. The electrolytes for lithium–sulfur batteries are broadly classified as (i) non-aqueous liquid electrolytes, (ii) ionic liquids, (iii) solid polymer, and (iv) glass-ceramic electrolytes. This article presents the properties, advantages, and limitations of each type of electrolytes. Also, the importance of electrolyte additives on the electrochemical performance of Li–S cells is discussed.

Keywords: lithium–sulfur batteries, poly sulfides, polymer electrolytes, charge–discharge studies, interfacial properties, ionic liquids, super ionic conductors, electrolyte additives

INTRODUCTION

The global warming and depletion of fossil fuel resources have accelerated immense research on energy storage devices unquestionably (Tarascon, 2001). In response to the modern society, it is now essential to develop new, low-cost and environmental friendly energy conversions and storage systems with new advanced materials (Arico et al., 2005; Bruce et al., 2008; Goodenough and Kim, 2010; Scrosati, 2011). Undoubtedly, lithium-ion battery is one of the great successes of modern electrochemistry due to its appealing properties such as high single cell voltage, no-memory effect, long cycle life, and high energy density. The fundamental aspects of lithium-ion batteries, working principles, and their limitations can be understood from numerous review articles (Whittingham, 2004) and dedicated books (Schalkwijk and Scrosati, 2002). The state-of-the-art lithium-ion batteries are composed of a carbonaceous anode and lithium transition metal oxide cathode separated by a polyolfine porous separator soaked in a non-aqueous liquid electrolyte (Manuel Stephan, 2006). The lithium-ion battery has become an inevitable power source not only for portable electronic devices such as laptop computers, cellular phones, and MP3 players but also find applications in satellites (Santoni et al., 2002) and in medical equipments (Bock et al., 2012). Nevertheless, with the existing insertion cathode materials (e.g., $LiCoO_2$, $LiFePO_4$, etc.), lithium-ion batteries have attained a maximum discharge capacity of approximately 250 mAh g^{-1} (with a theoretical energy density of 800 Wh kg^{-1}), which is not sufficient to meet out the demand of key markets such as transport and power grid applications (Lee et al., 2011). Obviously, intense research has been accelerated to find alternative electrochemical lithium-based power systems across the world. Among the systems known today, both Li–S and Li–O_2 are expected to fulfill the requirements of mankind with enhanced capacity and energy density. Nevertheless, so many technological and scientific problems remain unsolved in Li_2O systems (Bruce et al., 2012). The Li–S batteries have inspired many researchers recently, because sulfur is electrochemically active and can accept up to two electrons per atom approximately at 2.1 V vs. Li/Li^+. It has a high-theoretical capacity of 1675 mAh g^{-1}, which corresponds to an energy density of 2600 Wh kg^{-1} or 2800 Wh l^{-1} based on weight or volume, respectively. However, their practical applications are impeded by several major issues (Cakan et al., 2013; Xia et al., 2013).

Unfortunately, sulfur undergoes a series of compositional and structural changes during cycling, which involves soluble polysulfides and insoluble sulfides (Cheon et al., 2003a,b; Mikhaylik and Akridge, 2004). The typical Li–S batteries are composed of a lithium metal anode, an organic liquid electrolyte, and a sulfur composite cathode as depicted in **Figure 1**.

Although the concept of elemental sulfur as positive electrode material was introduced almost five decades ago by Hebert and Ulam (1962) its technological importance was only recognized in the beginning of year 2000. In the recent years, many review articles are available in the literature describing the working principles, advantages, and limitations of lithium/sulfur batteries (Ji and Nazar, 2010; Barghamadi et al., 2013; Bresser et al., 2013; Manthiram et al., 2013; Nazar and Evers, 2013). Also, numerous

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Abbreviations: AFM, atomic force microscope; CGPE, composite gel polymer electrolyte; DEC, diethyle carbonate; DIOX, 1,3-dioxolane; DMAc, dimethyl acetamide; DME, dimethyl ether; DMSO, dimethyl sulfoxide; EC, ethylene carbonate; EDX, energy dispersive X-ray; EMS, ethyl methane sulfonate; GPE, gel polymer electrolyte; Li_2S, lithium sulfide; $LiB(C_2O_4)_2$, lithium bis(oxalate)borate (LiBOB); $LiBF_2C_2O_4$, lithium bid(difluoro oxalate)borate (LiDFOB); $LiBF_4$, lithium tetrafluoroborate; $LiClO_4$, lithium perchlorate; $LiCF_3SO_3$, lithium trifluoromethanesulfonate; $LiPF_6$, lithium hexafluorophosphate; LiTFSI, lithium bis(trifluoromethylsulfonyl)imide; P_2S_5, phosphorous pentasulfide; PC, propylene carbonate; PEO, poly(ethylene oxide); PMMA, polymethylmethacrylate; PVDF, poly(vinylidene fluoride); PVDF-HFP, poly(vinylidene fluoride-co-hexafluoropropene); PYR_{14}TFSI, *N*-methyl-*n*-butyl-pyrrolidinium-bis(trifluoromethylsulfonyl)imide; SEM, scanning electron microscope; TEGDME, tetra (ethylene glycol) dimethyl ether; TEOS, triethoxysilane; THF, tetrahydrofuran; XRD, X-ray diffraction.

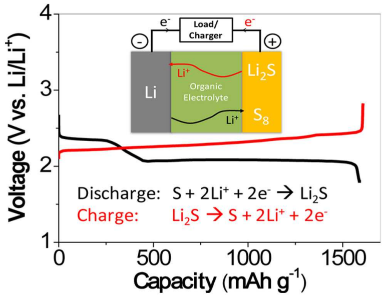

FIGURE 1 | Schematic diagram of a typical Li–S cell [adopted from Manthiram et al. (2013)].

articles appear on the fundamental chemistry (Akridge et al., 2004; Zhang, 2013a), performance of modified cathode materials (Ji et al., 2009; Liang et al., 2009; Yang et al., 2011; Fu et al., 2012), their fading mechanism (Diao et al., 2013), AFM, and Raman characterizations (Aurbach et al., 2009; Elazari et al., 2010; Yeon et al., 2012; Hagen et al., 2013) *in situ* XRD (Canas et al., 2013a) and impedance analysis (Yuan et al., 2009; Canas et al., 2013b). The preparation and characterization of cathode and anode materials for Li–S batteries are beyond the scope of this article. This article mainly encompasses the basic properties of electrolytes, their types, electrolyte additives, their advantages and limitations for the applications in Li–S batteries. The electrolytes for Li–S batteries can be classified as (i) non-aqueous liquid, (ii) ionic liquids, (iii) solid polymer electrolytes, and (iv) superionic conductors.

Lithium-ion reacts with elemental sulfur (S_8) and produces lithium polysulfides of general formula Li_2S_n, e.g., Li_2S_8, Li_2S_6. Upon discharge the length of the polysulfide is shortened as the sulfur is being further reduced. The overall reaction is

$$16Li^+ + 16e^- + S_8 \rightarrow 8Li_2S \tag{1}$$

The elemental sulfur is a promising electrode material, which is available abundantly, cheap, non-toxic, and environmentally benign. Despite all these advantages sulfur suffers from poor electronic conductivity.

Figure 2 shows typical discharge–charge profile of a Li–S cell. The discharge process is generally divided into four reduction regions depending upon the phase changes of sulfur species.

According to Zhang (2013a), the first upper voltage plateau between 2.2 and 2.3 V corresponds to a solid–liquid two-phase reduction from elemental sulfur to Li_2S_8. This process results in formation of huge voids in cathode due to the dissolution of Li_2S_8 into liquid electrolyte.

$$S_8 + 2Li^+ + 2e^- \rightarrow Li_2S_8 \tag{2}$$

In the second region, the cell voltage suddenly reduced with an increase in viscosity of electrolyte solution. The solution's viscosity reaches a maximum value at the end of the discharge region, which corresponds to the equation;

$$Li_2S_8 + 2\,Li^+ + 2e^- \rightarrow Li_2S_{8-n} + Li_2S_n \tag{3}$$

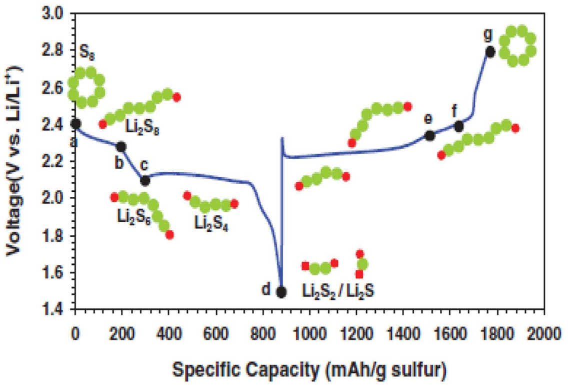

FIGURE 2 | First discharge and charge profiles of a Li–S cell between 1.5 and 2.8V vs. Li$^+$/Li [adopted from Barghamadi et al. (2013)].

The low voltage plateau, which occurs between 1.9 and 2.1 V offers majority of the total capacity of Li–S cell. In this third region, a liquid-solvent two-phase reduction takes place in which dissolved low-order polysulfide (PS) to insoluble Li_2S_2 or Li_2S.

$$2Li_2S_n + (2n-4)\,Li \rightarrow nLi_2S_2 \tag{4}$$

$$Li_2S_n + (2n-2)\,Li \rightarrow nLi_2S \tag{5}$$

In the fourth region, a solid–solid reduction from insoluble Li_2S_2 to Li_2S process takes place, which is kinetically slow and suffers from high polarization due to the non-conductive and insoluble natures of Li_2S_2 and Li_2S.

$$Li_2S_2 + 2Li^+ + 2e^- \rightarrow 2Li_2S \tag{6}$$

According to Mikhaylik and Akridge (2004), during the first charge polysulfides do not transform into elemental sulfur in a Li–S cell. Instead, in the second and subsequent charges, the higher-order polysulfides, which are generated at the sulfur electrode diffuse to lithium electrode and form lower-order polysulfides due to parasitic reaction. These species diffuse back again to the sulfur electrode as polysulfide and where polysulfide, of higher order are formed as a result of shuttle mechanism.

The sulfur and lithium sulfides, which are strong insulators, will easily dissolve in common organic liquid electrolytes. Spontaneously, they diffuse through the liquid electrolyte and subsequently leads to self-discharge and thereby increasing the viscosity of the electrolyte solution. These drawbacks lead the lithium/sulfur batteries to poor cycle life, low specific capacity, and lower efficiency.

NON-AQUEOUS LIQUID ELECTROLYTES

In order to improve the electrochemical performance of Li–S batteries, different strategies have been adopted, which also include the optimization of the electrolyte compositions (Barchasz et al., 2013a). The dissolution of polysulfides, LiS_x, leads to an unfavorable side reactions and adversely deteriorates the performance of the Li–S cells. It is well known that the carbonate-based solvents such as ethylene carbonate (EC) and diethyl carbonate (DEC) react with polysulfides irreversibly (Barchasz et al., 2013b; Barghamadi et al., 2014). In the beginning, dimethyl sulfoxide (DMSO) was explored as a possible electrolyte solvent for lithium–sulfur batteries; however, the sulfur can be reduced only to S_4^{2-} with an efficiency of 25% (Brummer et al., 1976). On the other hand, a 50% efficiency was achieved when dimethyl acetamide (DMAc) was used with a corresponding reduction of S_2^{2-} (Abraham et al., 1978). Although, tetrahydrofuran (THF) exhibited about 100% efficiency at 50°C, unfortunately, it is found to be thermodynamically unstable with lithium metal (Kock and Young, 1977; Yamin and Peled, 1983).

In a pioneering work, Rauh et al. (1979) reported electrolytes with high basicity can dissolve huge amount of lithium polysulfides. Also, the sulfur solubility can go up to 10M in DMSO or ethers like THF. Based on the electrochemical and spectroscopic studies of poly sulfides in non-aqueous solutions, the same group (Rauh et al., 1977) concluded that dynamic equilibrium, redox chemistry, kinetics are strongly affected by solvent complexation. Unquestionably, the selection of solvents, which is stable against nucleophilic attack of polysulfides is mandatory. 1,3-dioxolane (DIOX) has a good polysulfide solubility and high stability in contact with lithium metal forms a passive solid-electrolyte interphase. Tetraethylene glycol dimethylether (TEGDME) has a glyme structure with high donor number (DN = 18.6) and with low dielectric constant of $\varepsilon_r = 7.9$, which can dissociate both lithium salt and sulfur active material. The ether-based electrolytes have high donor number and co-ordinate with Lewis acidic cation of Li^+. 1,2-dimethoxyethane (DME) also has high lithium polysulfide dissolution ability and can provide sufficient amount of active materials (Tachikawa et al., 2011).

Generally, both DIOX and glyme solvents exhibit higher sulfur solubility (Peled et al., 1989; Chu et al., 2000; Shim et al., 2002). The impedance spectroscopic studies on Li–S cells containing 1M solution of $LiClO_4$ in sulfonane have been reported by Kolosnitsyn et al. (2011). It is suggested that the electrochemical processes in Li–S cells were controlled by diffusion in the surface layer on the sulfur electrode at high degrees of charge–discharge and by the transport properties of the electrolyte system at moderate degrees of charging. More importantly, the rate of shuttling of sulfur is determined by the solubility of lithium polysulfides in electrolytes, the transport properties of electrolyte systems and the dissolution rates on the electrodes. The structure of the positive electrode also significantly affects the transfer rate (Kolosnitsyn and Karaseva, 2008). The shuttling of polysulfide, although protects the Li–S batteries from overcharging, it adversely induces the self-discharge. Moreover, in Li–S batteries, the dentritic formation is much lower than other type of lithium batteries with metallic lithium (Chang et al., 2002). Due to the instability of ether solvents at higher potential values, they are not widely used in lithium batteries; however, they find applications in Li–S system because of 3 V vs. Li^+/Li (Choi et al., 2008; Mikhaylik, 2008; Mikhaylik et al., 2010). The importance of solvation ability and additives has been illustrated by Barchasz et al. (2013b) by using different combinations of TEGDME/DIOX binary electrolytes. The authors have also demonstrated that the lithium salt concentration also plays a vital role for the formation of good passivation and helps to reduce the shuttle mechanism and capacity loss. The solvation ability is also a key parameter for better electrochemical performance of Li–S cells.

By employing electrochemical and *in situ* X-ray absorption spectroscopy, Gao et al. (2011) demonstrated the influence of electrolytes on the charge–discharge studies of Li–S cells. A discharge capacity of about 1000 mAh g^{-1} was delivered by the Li–S cell when TEGDME and DOL/DME were used as electrolytes. While using PC/EC/DEC and EMS/DEC as electrolyte the cell delivered almost no capacity. On the basis of the electrochemical study, DOL/DME and TEGDME have been suggested as appropriate and promising solvents for the electrolytes of Li–S batteries. Although the discharge products of sulfur in DOL/DME and TEGDME are similar, the authors found a faster self-discharge and a more complete reduction of solution-phase sulfur species upon discharge for the combination of electrolytes, DOL/DME. While comparing the effect of lithium salts, $LiPF_6$, $LiCF_3SO_3$, and $LiClO_4$ a relatively stable capacity is seen for $LiClO_4$; however, poor safety concerns hamper it from practical application.

The electrochemical performance of $LiClO_4$/DOL/DME as electrolyte was reported by Wang et al. (2010). Impedance analysis indicated that the formation of impermeable layer on the surface of cathode considerably increased the interfacial resistance of the battery. They also suggested the combination of electrolyte DME:DOL of 2:1 v/v is capable of delivering a discharge capacity of 1200 mAh g^{-1} during its initial stage and retained a discharge capacity of 800 mAh g^{-1} even after 20 cycles.

The cycling behavior of Li/TEGDME/S cells was examined at low temperature by Rhu et al. (2006). The cell delivered a discharge capacity of 1030 and 357 mAh g^{-1} at 20 and −10°C, respectively. Upon addition of 1,3-dioxalane and methyl acetate to the TEGDME the discharge capacity was enhanced to 1342 and 994 mAh g^{-1}, respectively. The better performance of the cell has been attributed to the reduced viscosity of the electrolyte at lower temperature. The electrochemical properties of ether-based electrolytes have also been reported by Barchasz et al. (2013b). The same group (Barchasz et al., 2012) has added polysulfide (0.1M Li_2S_6) as co-salt in order to provide additional capacity and compensate the active mass loss. Unfortunately, it adversely reduced the capacity and cycle life of the cell. On contrary, to the above work Chen et al. (2013) achieved a dramatic increase in capacity, cyclability, and rate capability by optimizing the concentration of polysulfide species and the amount of electrolyte in the cell. As sulfur is a conversion type-cathode material, it does not require Li^+-ionic electrolyte and the discharge can be performed even with an ammonium solution. In an unconventional way of thinking, Zhang (2013c) found that the introduction of quarternary ammonium into liquid electrolyte could effectively suppress the disproportion of polysulfide intermediate, which increased the Li–S cells capacity retention; however, it is not able to stop the redox shuttle of polysulfide. Very recently, Agostini et al. (2014) exploited the use of non-flammable TEGDME-based electrolyte containing Li_2S_8 electrolytes. The electrochemical properties of the cell were effectively enhanced by the addition of $LiNO_3$, which provided a stable and protective solid-electrolyte interface on a lithium surface. An excess amount of electrolyte and low loading of sulfur have significantly enhanced the cycle life and capacity retention of Li–S cells (Brückner et al., 2014). However, the energy density of the cell was reduced due to the dead weight of the liquid electrolyte.

IONIC LIQUIDS AS ELECTROLYTES

Ionic liquids are identified as an electrolyte system for lithium-ion batteries due to their unique properties such as non-flammability, wide electrochemical stability, non-volatility, high ionic conductivity, and environmental friendliness (Galinski and Lewandowski, 2006). However, the reports on ionic liquids as electrolytes for Li–S batteries are very scanty. Very recently, Watanabe and co-workers reviewed the ionic liquids as electrolytes for lithium–sulfur batteries (Park et al., 2013). The same group also demonstrated the anionic effect as solvate ionic liquid electrolytes in rechargeable Li–S batteries (Ueno et al., 2013). Wang et al. (2008) compared the cycling profile of Li/S cells consisting of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide and lithium bistrifluoromethanesulfonylimide with a sulfur coated carbon cathode. The cell delivered higher discharge capacity with ionic liquid than the conventional organic solvent electrolyte. The physical and chemical properties of a ternary mixture comprising TEGDME as a polymer solvent in mixed electrolytes composed of *N*-methyl-*n*-butyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ($PYR_{14}TFSI$) and LiTFSI were reported by Shin and Cairns (2008). The ternary compound was employed as electrolyte for Li–S cells. The cell delivered a discharge capacity of 887 and 440 $mAh\,g^{-1}$at ambient temperature and at 0°C, respectively. With *N*-butyl-*N*-methyl-piperidinium–TFSI as electrolyte solvent and sulfur cathode, Yuan (2006) reported the cycling behavior of Li–S cells. Although, the cells delivered an initial discharge capacity of 1055 $mAh\,g^{-1}$ in its first cycle an abrupt decrease in discharge capacity (about 770 $mAh\,g^{-1}$) was found after a few cycles. The effect of imidazolium cation on the cycle life of Li–S batteries has been analyzed by Kim et al. (2007). Wang and Byon (2013) designed a new ionic liquid-based organic electrolyte, which swaps solubility and diffusion rate of polysulfides by a combination of 1,2-dimethoxyethane and highly viscous *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane sulfonyl) imide (PP13-TFSI). This engineered electrolyte offered high Coulombic efficiency, capacity retention, and suppressed internal shuttling of polysulfides.

POLYMER ELECTROLYTES

In the last three decades, extensive research has been devoted on the development of polymer electrolytes as they find applications not only in lithium batteries but also other electrochemical devices such as supercapacitors, fuel cells, and electrochromic devices (Manuel Stephan, 2006). The advantages of polymer electrolytes, their types, advantages, and limitations have already been reported elsewhere (Manuel Stephan et al., 2009; Quartarone and Mustarelli, 2011). In lithium sulfur batteries, polymer electrolytes play a vital role in suppressing the dissolution of poly sulfides in lithium/sulfur cells resulting in good cyclability and enhanced capacity retention (Hassoun and Scrosati, 2010, 2012). Hassoun and Scrosati (2010) demonstrated an all-solid-state lithium/sulfur cells composed of a Li_2S/C cathode, lithium metal anode, and a nanocomposite polymer as electrolyte. The cell was capable of delivering a discharge capacity of 300 $mAh\,g^{-1}$ at 70°C. The added-ZrO_2 filler in a PEO-$LiCF_3SO_3$ filler significantly promoted the ionic conductivity of the composite polymeric membrane. Efforts have also been made to replace the highly reactive anode material with alloy anodes with same type of nanocomposite polymer electrolytes (Jeng et al., 2007). Jeddi et al. (2013a,b) proposed a novel polymer electrolyte by blending poly(vinylidene fluoride-co-hexafluoropropene) (PVdF-HFP) with monofunctional poly(methyl methacrylate) (PMMA) containing inorganic trimethoxysilone domains. The gel polymer electrolyte (GPE) was found to be capable of upholding the electrolyte solution and preventing polysulfide diffusion, which improved the cycling performance of the sulfur-based electrode material.

Marmorstein et al. (2000) reported the charging–discharging characteristics of Li/S cells with three different polymer electrolytes at various operating temperatures ranging from ambient temperature to 100°C. Among the systems studied the cell operated between 90 and 100°C with poly ethylene oxide as electrolyte delivered highest discharge capacity. Unfortunately, these systems suffer from poor rate capability.

According to Zhang and Tran (2013d), the selection of electrolyte materials for lithium/sulfur batteries is very limited. Being a very strong nucleophilic agent, the polysulfides can react with many electrolyte solvents such as esters and carbonates and lithium salts such as $LiPF_6$, $LiBF_4$, $LiB(C_2O_4)_2$, and $LiBF_2C_2O_4$. Further, elemental sulfur and polysulfides can replace fluorine from fluorinated polymers such as (PVDF-HFP). Eventually, this leads the formation of thiols and vulcanization of unsaturated polymers. In view of the chemical stability, the lithium salts such as $LiSO_3CF_3$, LiTFSI, linear or cyclic ethers such as 1,2-dimethyl ether (DME), DIOX as solvents and poly (ethylene oxide), PEO as the ultimate polymer host for polymer electrolyte researchers. The authors also illustrated the influence of GPEs on the cycling performance of Li–S cells (Zhang, 2013b). The authors prepared a composite gel polymer electrolyte (CGPE) composed of PEO and SiO_2. Results showed that the incorporation of SiO_2 in the polymeric matrix has significantly trapped the polysulfide species in the separator and reduced the utilization of sulfur active materials. The authors also concluded the benefits of GPEs and CGPEs are adversely compensated by sulfur specific capacity. Zhang and Tran (2013d) reported the electrochemical properties lithium/sulfur cell with a flexible and free-standing CGPE membrane composed of 50% PEO–50% SiO_2.

Lécuyer et al. (2013) analyzed the structural evolution of Li/S cells based on PEO-based dry polymer electrolytes by employing SEM and EDX. Diffusion of sulfide species resulted in volume changes of both electrode and electrolyte. Attempts have been to enhance the mechanical property of cathode material by incorporation of PVdF in the composite cathode. Although incorporation of PVdF significantly enhanced the mechanical integrity, it could not solve the problems associate with the cyclability.

The cycling profile of Li–S cells with PEO-based gel electrolytes with $LiClO_4$ and TEGDME. The cell delivered higher discharge capacity than the subsequent cycles and a flat discharge has been observed at 2.0 V. The capacity fading has been attributed to low utilization of sulfur, which arises to the aggregation of sulfur (polysulfide) upon cycling (Jeon et al., 2002). The electrochemical and interfacial properties TiO_2-laden PEO-$LiCF_3SO_3$ complexes have been reported by Shin et al. (2002). The addition of TiO_2 into PEO-$LiCF_3SO_3$ complexes has substantially promoted not only the ionic conductivity but also interfacial resistance between composite polymer electrolyte and lithium metal anode. The remarkable decrease in the interfacial resistance is attributed to the lowering contact area between lithium and electrolyte. The increased discharge capacity of Li–S cells is attributed to the better interfacial property of composite polymer electrolyte and lithium metal anode.

SUPERIONIC CONDUCTORS

The appealing properties such as high safety, non-flammability, high thermal stability, reliability, and prevention of polysulfide formation and migration qualify the ionically conducting solids as potential electrolytes for lithium sulfur batteries. Based on their properties they are classified as (i) sulfides, (ii) oxides, and (iii) phosphates (Fergus, 2010). Among the three types, oxides are more stable in air than sulfides (Machida et al., 2004). The search for glass-ceramic materials with high stability in contact with lithium metal combined with a high ionic conductivity has been intensified for the fabrication of all-solid-state lithium batteries in order to ascertain the safety aspects. The major challenge for all solid-state batteries depends mainly on the electrode/electrolyte interfaces (Kim et al., 2006).

Nagao et al. (2011) fabricated an all solid-state lithium sulfur cell comprising sulfur-carbon electrode with Li_2S–P_2S_5 glass–ceramic electrolytes and examined their electrochemical performances. The authors performed the charge-discharge analysis between −20 and 80°C. The cells retained a reversible capacity higher than $850\,mAh\,g^{-1}$ for 200 cycles at 25°C. The enhanced discharge capacity of the cell was attributed to the reduced crystallinity of sulfur and particle size of the electrode materials achieved by milling, which facilitated better contacts between the particles.

Hayashi et al. (2003) have successfully introduced a novel all-solid-state Li/S batteries with Li_2S–P_2S_5 as a highly conductive glass–ceramic electrolytes. The cathode materials consisting of sulfur and CuS were synthesized by mechanical milling using sulfur and copper crystals as starting materials. The cell was capable of delivering over $650\,mAh\,g^{-1}$ for 20 cycles. The time of ball milling was found to influence the electrochemical properties of Li–S cell.

In a similar way, Kobayashi et al. (2008) reported the cycling performance of an all-solid-state-lithium sulfur battery with sulfur electrode and thio-LISICON electrolyte. The same group also reported the cycling behavior for mesoporous electrode with thio-LISICON electrolyte (Kobayashi et al., 2013).

ELECTROLYTE ADDITIVES

Electrolyte additives play an extraordinary role in lithium-ion batteries. Although the amount of additive in the electrolyte is around 5% either by volume or by weight it plays a significant role in the electrochemical performance of lithium-ion batteries. It significantly improves the solid-electrolyte interface on the surface of graphite, reduces irreversible capacity, enhances thermal stability, promotes physical properties of the electrolyte such as ionic conductivity, viscosity, and wettability of the polyolifine membrane (Zhang, 2006). It also protects battery safety by lowering flammability of organic electrolytes, increases tolerance, and stops battery operations in abuse conditions.

In a similar way, the electrolyte additives play a vital role in lithium/sulfur batteries. The polysulfides involve reactions with cathode and anode during cycling and therefore protection of lithium anode from chemical reactions is mandatory. This will significantly eliminate the shuttling of polysulfide and effectively promotes the columbic efficiency and cycling performance. Lithium nitrate ($LiNO_3$) reacts with metallic lithium and forms a rigid passivation layer that prevents the chemical reactions of polysulfides with metallic lithium and is attributed to the decomposition of $LiNO_3$ in the non-aqueous liquid electrolyte (Xiong et al., 2012; Zhang and Read, 2012). Very recently, Lin et al. (2013) illustrated that the addition of P_2S_5 as additive promoted the dissolution of Li_2S and alleviates the loss of capacity caused by the precipitation of Li_2S and also eliminated the shuttling of polysulfides by passivating metallic lithium.

SUMMARY AND FUTURE OUTLOOK

Li–S batteries are considered as one of the ultimate power source by virtue of its appealing properties such as low cost, non-toxic, abundance, and above all higher discharge capacity ($1640\,mAh\,g^{-1}$) and energy density ($2400\,Wh\,kg^{-1}$) than lithium-ion batteries. Regarding the non-aqueous liquid electrolytes for lithium–sulfur batteries, no one system is found to be optimal in all aspects. In this area, more work is certainly needed. Although, extensive research work has been pursued on the development of cathode materials for lithium/sulfur batteries, reports on solid polymer electrolytes and superionic conductors are very scanty. A few reports illustrate the glass-ceramic electrolytes with ionic conductivity exceeding $10^{-3}\,Scm^{-1}$ at ambient temperature. However, attention should be focused on the major drawbacks such as fragility at low thickness, high cost, and poor interfacial property at electrode/electrolyte interfaces. Prevention of shuttling of polysulfides by suitable polymeric/solid electrolytes will be appreciable and exotic. Ionic liquids in conjunction with polymer electrolytes and sulfurized carbon electrodes may offer a safe, reliable, and polysulfide shuttle-free lithium–sulfur batteries.

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