# Perspective of polymer-based solid-state Li-S batteries

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## Abstract

Li-S batteries, as the most promising post Li-ion technology, have been intensively investigated for more than a decade. Although most previous studies have focused on liquid systems, solid electrolytes, particularly all-solid-state polymer electrolytes (ASSPEs) and quasi-solid-state polymer electrolyte (QSSPEs), are appealing for Li-S cells due to their excellent flexibility and mechanical stability. Such Li-S batteries not only provide significantly improved safety but are also expected to augment the all-inclusive energy density compared to liquid systems. Therefore, this perspective briefly summarizes the recent progress on polymer-based solid-state Li-S batteries, with a special focus on electrolytes, including ASSPEs and QSSPEs. Furthermore, future work is proposed based on the existing development and current challenges.

**Keywords:** Solid-state Li-S batteries, polymer electrolytes, quasi-solid-state polymer electrolyte, energy-density estimations

## INTRODUCTION

Rechargeable lithium-ion batteries have attracted prodigious attention as energy storage systems to power portable electronics and electronic vehicles, owing to their high cycle life and energy efficiencies[1-4]. However, future scenarios cannot be fully accomplished given the insufficient energy density of current Li-ion batteries (i.e., < 350 Wh kg$^{-1}$)[5-7] and thus the development of electrochemical storage technologies with enhanced energy density is crucially needed. Among all the post Li-ion technologies, lithium-sulfur (Li-S) batteries are considered to be the most auspicious and viable alternatives considering their extraordinary energy density (i.e., theoretical capacity of 2600 Wh kg$^{-1}$), environmental friendliness and cost effectiveness[8-10].

Li-ion conducting electrolytes, as indispensable battery components, play a pivotal role in determining the performance of rechargeable Li-S batteries[11]. Commonly used liquid electrolytes (LEs) for Li-S batteries include lithium salts [e.g., lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)] and organic ether solvents [e.g., 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL)][12]. However, such LEs have intrinsic problems, including proneness to leakage and flammability, which may cause fire, explosion and other safety issues[13]. In addition, soluble polysulfide (PS) $Li_2S_n$ $4 \leq n \leq 8$ intermediates can diffuse between the sulfur cathode and lithium metal (Li°) anode during the charge/discharge processes (known as the PS "shuttle effect"), which leads to the irreversible loss of electroactive materials and deterioration of the electrode-electrolyte interphases, particularly for the Li° anode, thus significantly shortening the cycle life of the cell[12,14]. Due to their negligible volatility, appealing flexibility and mechanical stability, polymer electrolytes (PEs)[15,16], including all-solid-state polymer electrolytes (ASSPEs)[17] and quasi-solid-state polymer electrolytes (QSSPEs)[18,19], not only significantly improve battery safety, but are also expected to augment the all-inclusive energy density compared to liquid systems[14].

Considering the aforementioned points and the intrinsic advantages of PE-based Li-S batteries, herein we present an overview of the recent progress and advancement in PE-based (ASSPEs and QSSPEs) Li-S batteries and a systematic analysis of the projected energy density of Li-S batteries based on different electrolytes. Furthermore, this perspective also includes the remaining challenges that need to be solved for the practical applications and future prospects of PE-based Li-S battery technologies.

## ALL-SOLID-STATE POLYMER ELECTROLYTES

Generally, ASSPEs composed of lithium salts, polymer matrices and/or solid additives have been considered as some of the most appealing candidates to replace LEs due to their high safety, excellent flexibility and processability, and superior physical contact with the electrodes, in contrast to inorganic-based solid electrolytes[20]. Among all the different polymer matrices, poly(ethylene oxide) (PEO) is the most prevailing choice for developing ASSPE-based Li-S batteries, owing to its superior solvation ability, excellent mechanical properties, low cost and facile processability[21-25]. In PEO-based ASSPEs, lithium salts are dissociated and solvated by Lewis-base ether units (i.e., ethylene oxide) and the transportation of lithium cations is associated with the segmental motion of PEO chains by intrachain and/or interchain hopping[26]. It is widely acknowledged that lithium salts play a decisive role in decreasing the glass transition temperature ($T_g$), facilitating the segmental motion and increasing the ionic conductivity of ASSPEs[27]. More importantly, the nature of the salt anions determines the properties and qualities of the solid electrolyte interphase (SEI) and cathode electrolyte interface (CEI) layers formed on the electrodes, as well as the flexibility and wettability of the electrolytes[28].

LiTFSI was firstly employed as a conducting salt in ASSPEs by Armand *et al.*[29,30] in 1986 and has since become the most widely used lithium salt in recent decades because of its excellent chemical stability and anionic flexibility generated from the delocalized negative charge over flexible S-N-S bonds. However, LiTFSI/PEO-based ASSPEs provide inferior SEI formation in contact with the Li° anode due to the unfavorable anion chemistry. Furthermore, PS can still be dissolved in PEO at high temperatures (i.e., 70 °C), resulting in infinite charging (PS shuttle) already in the first cycles and notorious lithium dendrite growth[28,31]. The same phenomenon and cell performance are also observed in Li-S cells with lithium trifluoromethanesulfonate (LiTf)/PEO-based ASSPEs[32,33]. The cycling performance of PEO-based Li-S cells was improved for the first time by Ma *et al.*[34], where LiTFSI was replaced by an asymmetric imide salt, lithium (trifluoromethanesulfonyl)(*n*-nonafluorobutanesulfonyl) imide. This improvement was ascribed to the participation of the $-C_4F_9$ group in forming stable interphases with the electrodes.

In another work, Judez *et al.*[35] demonstrated a significant improvement in PEO-based Li-S cells when replacing LiTFSI with another imide salt, lithium bis(fluorosulfonyl)imide (LiFSI). A remarkably high Coulombic efficiency (CE) and prolonged cycle life were achieved and ascribed to the formation of a LiF-rich SEI layer on the Li° anode. However, the Li-S cell with LiFSI/PEO-based ASSPEs presented a lower capacity compared to the LiTFSI-based cell [e.g., < 800 mAh $g_{sulfur}^{-1}$ (LiFSI) *vs.* > 900 mAh $g_{sulfur}^{-1}$ (LiTFSI)] because of the poorer wetting properties of the $-SO_2F$ *vs.* $-SO_2CF_3$ groups[28,35]. In a subsequent study, another imide salt with an asymmetric structure, lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (LiFTFSI), consisting of both the $-SO_2F$ and $-SO_2CF_3$ moieties, was proposed by Eshetu *et al.*[28] with the aim of combining the merits of both the FSI⁻ and TFSI⁻ anions. It was anticipated that the electrochemical decomposition of the FTFSI⁻ anion could form a synergistic SEI layer with well-balanced organic and inorganic species [Figure 1A]. Effectively, such cells delivered a high specific capacity (1394 mAh $g_{sulfur}^{-1}$) and areal capacity (1.2 mAh cm⁻²), excellent CE (nearly 100%) and prominent rate capabilities (~500 mAh $g_{sulfur}^{-1}$ at 0.5 C). All these results emphasize that a chemically and mechanically stable SEI layer is prominent for the cycle life and rate performance of ASSPE-based Li-S batteries[36-38].

To further alleviate the lithium dendrite growth and inhibit the "shuttle effect" of aggressive PS, the same group reported a novel designer anion, (difluoromethanesulfonyl) (trifluoromethanesulfonyl)imide (DFTFSI⁻)[38]. This anion is capable of simultaneously facilitating Li cation transport ($T_{Li}^+$) and improving the interfacial compatibility towards the Li° electrode, thereby enhancing the Li-S cell performance[39]. It was demonstrated that hydrogen bonding could be formed between the H atoms of the newly introduced $-CF_2H$ functional group and the O atoms of PEO, to diminish the anion mobility and enhance $T_{Li}^+$. In particular, the $-CF_2H$ moiety in the DFTFSI⁻ is electrochemically labile, which is facilely decomposed to form ionically conductive LiH and mechanically stable LiF species as a SEI layer on the Li° anode, thereby ensuring excellent interfacial properties [Figure 1B]. Meanwhile, DFTFSI⁻ also shows a superior chemical stability towards the aggressive PS species, as revealed by density functional theory calculations. All these aspects guarantee an ultrahigh cycle life (more than 1300 cycles) with CEs close to 100% [Figure 1C], albeit with a decline in capacity.

In addition to fluorine-containing imide salts, non-fluorinated salt anions have also attracted significant attention. In this respect, lithium tricyanomethanide (LiTCM), a cost-effective and low toxicity fluorine-free salt was proposed and employed as the main salt or additive in PEO-based ASSPEs for Li-S batteries, demonstrating the unique interfacial properties and high CE of the cell[38,40]. As shown in Figure 1D, unlike the lithium deposits of the fluorine-containing LiTFSI, the LiTCM-based electrolyte shows more uniform and compact deposits with a bluish black color, owing to the formation of highly conducting $Li_3N$ and carbon-containing species (e.g., polymeric C=N network), which are generated from the reduction of the
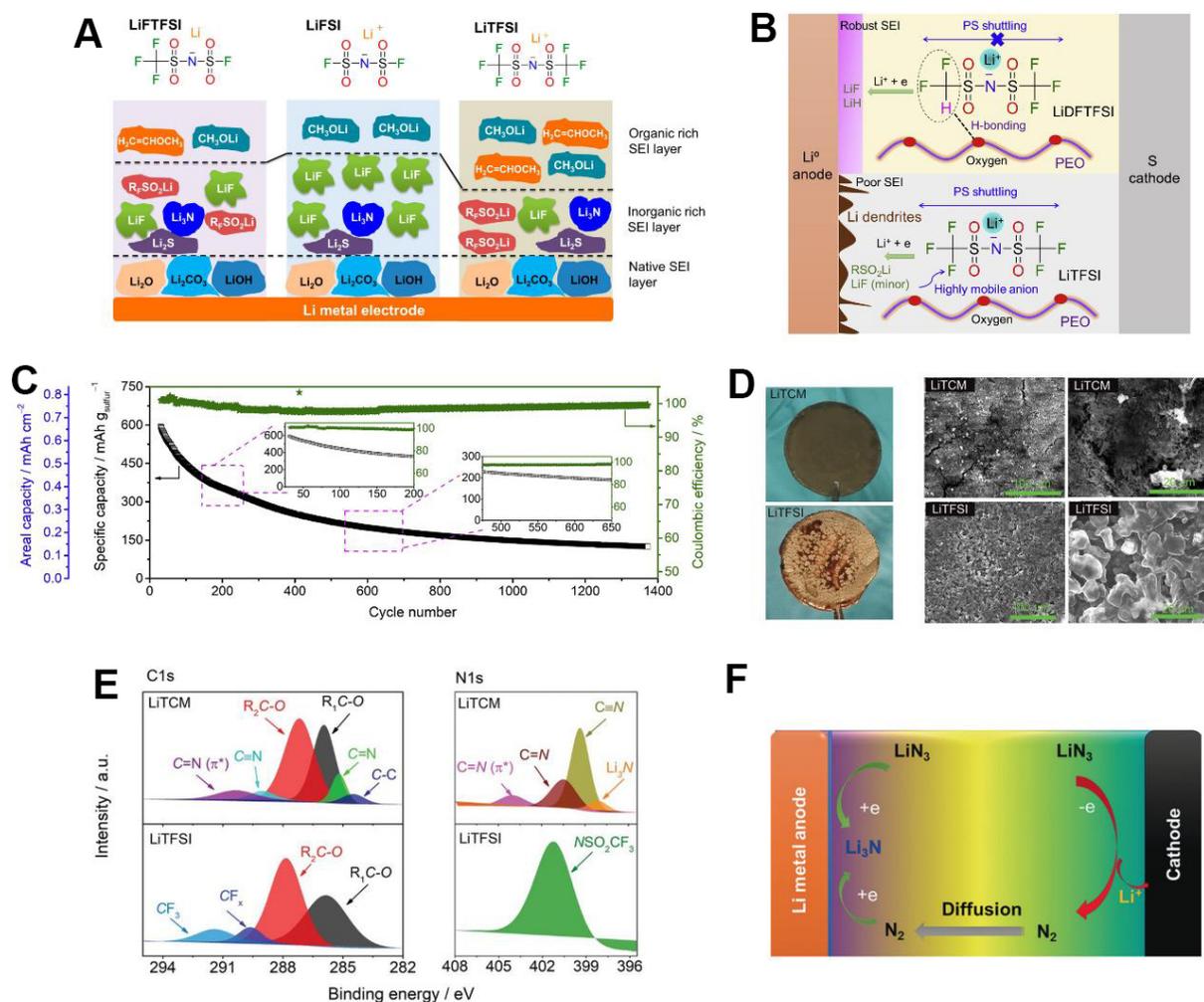
**Figure 1.** (A) Schematic illustration of the solid electrolyte interphase layer formed on a Li° anode in electrolytes with different lithium salts. Reproduced from Ref.[28] with permission. Copyright 2018 American Chemical Society. (B) Role of the two salts in SPE-based Li-S batteries. (C) Long-term cycling stability of Li-S cells based on the LiDFTFSI/PEO electrolyte (0.1/0.1 C, after C-rate test, *erratic Coulombic efficiency at around 400th cycle). Figure 1B and C reproduced from Ref.[39] with permission. Copyright 2019 Cell Press. Optical and scanning electron microscopy images (D) and X-ray photoelectron spectroscopy spectra (E) of lithium deposited onto Cu substrates in LiX/DME (X = TCM or TFSI) LEs. Reproduced from Ref.[40] with permission. Copyright 2019 Wiley-VCH. (F) Schematic illustration of electrochemical reactions of LiN$_3$ in lithium-metal batteries. Reproduced from Ref.[43] with permission. Copyright 2017 Wiley-VCH.

TCM$^-$ anion, as suggested by the X-ray photoelectron spectra in Figure 1E.

However, the practical application of the aforementioned emerging salts is still hindered by multi-step, time-consuming and laborious syntheses or the currently small production scale, resulting in high costs. It is accepted that the employment of electrolyte additives is a feasible, economical and facile strategy (small doses for large effects) to meet the requirements for achieving an ideal SEI layer and long-term cyclability[41,42]. As an additional step to the use of the above listed salts (LiFSI, LiFTFSI, LiDFTFSI and LiTCM) as additives into LiTFSI/PEO ASSPEs, lithium azide (LiN$_3$) has been proposed as a novel additive that can be reduced into Li$_3$N species to form a highly conductive SEI layer. Simultaneously, LiN$_3$ can also be oxidized on the cathode to form molecular nitrogen (N$_2$), which can then migrate to the Li° side and become further reduced into Li$_3$N to reinforce the ion conduction of the SEI layer [Figure 1F], resulting in a

Li-S cell with a high reversible capacity of ~800 mAh g$^{-1}$, even after 30 cycles[43].

Tuning the anion chemistry in ASSPEs to achieve robust SEIs on Li° in order to improve the cycle life of Li-S cells is one of the approaches utilized in the literature. Another effective approach is to optimize the cathode, with the aim of confining PS species within the cathode matrix to further suppress the shuttle effect and avoid poisoning of the Li° and active material loss upon cycling. The work of Gao *et al.*[44] demonstrated a nanoscale encapsulation concept based on Li$_2$S@TiS$_2$ core-shell particles, which was originally developed for liquid systems, to also be effective in ASSPEs, with > 400 mAh g$^{-1}$ reached after 150 cycles. Not limited to the physical confinement of PS, organosulfur-type active materials have been used to replace elemental S as an example of the chemical confinement of PS. An improved cycle life of a Li-S cell has been illustrated, even with a poor SEI formation ability electrolyte (LiTFSI/PEO), using a cathode composed of a S-containing copolymer (prepared via the inverse vulcanization of sulfur with divinylbenzene)[45].

It is generally accepted that sulfur cathodes have an intrinsic drawback in that elemental sulfur possesses inferior electronic and ionic conductivity, resulting in sluggish reaction kinetics of the cathodes[46-48]. Unfortunately, this issue is amplified in ASSPE-based Li-S cells due to the poor wettability and compatibility of the ASSPE toward the sulfur electrode. Therefore, the incorporation of extra electronic/ionic conductors into the cathode materials for ASSPE-based Li-S cells is highly needed. Previous studies have demonstrated that carbon materials [e.g., acetylene black (AB)[49,50], Ketjenblack (KB)[51], graphene oxide (GO)[52,53] and graphene-carbon nanotubes[54]] and Li$^+$ conductive polymers [e.g., polyethylene glycol (PEG)] are the most effective and appealing candidates for use in Li-S cells to enhance the electronic/ionic conductivities of sulfur cathodes. For example, a composite cathode with PEG-grafted graphene oxide (GO) was reported by Zhang *et al.*[52], serving as a Li-ion conductor, with the grafted PEG in direct contact with the electron conductor (i.e., GO), which greatly enhanced the Li-ion transport efficiency. In addition, cathode preparation methods, e.g., gas-phase mixing, ball-milling and liquid deposition methods, also have a significant impact on improving the ionic conductivity of cathodes[48]. Zhou *et al.*[55] prepared a well-dispersed S@KB composite via a solution deposition of sulfur onto KB directly. Compared to the simply mixed S/KB composite, the prepared S@KB composite showed better sulfur/carbon contact, a smaller (nano) sulfur particle size and a more homogeneous distribution, resulting in a high capacity and CE, as well as fast kinetics.

## QUASI-SOLID-STATE LI-S CELLS

As discussed above, ASSPEs suffer from low ionic conductivity and poor contact with electrodes at room temperature, which hinder their application as electrolytes for high-performance Li-S batteries from a practical perspective. One of the most feasible approaches to alleviate the above dilemma of ASSPEs is the use of QSSPEs, which are also known as gel polymer electrolytes (GPEs). These electrolytes are based on the incorporation of an organic liquid compound, known as a plasticizer, into a solid polymer matrix. The improvement in ionic conductivity originates from the enhanced segmental mobility of polymer backbones in the presence of plasticizing agents, thus offering rapid ionic transport. The significant research efforts carried out in recent years have led to substantial scientific progress in improving the performance of QSSPE-based Li-S cells, such as their mechanical properties[56], Li-ion transference number[57,58] and/or thermal stability [Table 1][59].

Conventionally, *ex-situ* methods (generally physical methods), like solvent-casting, phase inversion and electrospinning, have been used to prepare QSSPEs for Li-S cells. However, one of the main issues is the weak interactions between the electrolyte components, which is inherent for QSSPEs prepared by such methods. This can lead to oozing of the liquid plasticizer, which induces a deterioration in both

**Table 1. State-of-the-art in QSSPE-based Li-S batteries**

| Entry | Electrolyte components | $\sigma^{[a]}$/mS cm$^{-1}$ | $T_{Li}+^{[b]}$ | $C_i^{[c]}$/mAh g$^{-1}$ | $C_e^{[d]}$/mAh g$^{-1}$ (cycle life) | SL$^{[e]}$/mg cm$^{-2}$ | C-rate | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1 | PETEA + 1.0 M LiTFSI in DOL/DME + 1 wt.% LiNO$_3$ | 11.3 (25 °C) | 0.47 | 647 | 530 (400th cycle) | 1.2-1.5 | 0.5 C | [60] |
| 2 | PEO/LAGP + 1.0 M LiTFSI in TEGDME | 1.15 | 0.28 | 725 | 700 (300th cycle) | 1.0 | 0.5 C | [61] |
| 3 | PDADMATFSI + 1.0 M LiTFSI in PY14TFSI | 1.0 (RT) | - | 1400 | 400 (30th cycle) | 1.0 | 0.1 C | [62] |
| 4 | PVDF + 1.0 M LiTFSI + 0.4 M LiNO$_3$ in DOL/DME | 3.0 (70 °C) | 0.45 | 1675. | 1000 (100th cycle) | 2.0 | 56 mA g$^{-1}$ | [63] |
| 5 | PVDF/PEO/ZrO$_2$ + 1.0 M LiTFSI in DOL/DME | 0.53 (25 °C) | 0.71 | 1058 | 847 (500th cycle) | 1.7 | 1.0 C | [64] |
| 6 | PDADMATFSI + 1.0 M LiTFSI in EMIM-TFSI | - | - | 693 | 142 (500th cycle) | - | 0.5 C | [65] |
| 7 | PVDF/PDA + 1.0 M LiTFSI in DOL/DME | 0.57 (RT) | - | 1215 | 869 (200th cycle) | 1.0-1.3 | 0.1 C | [66] |
| 8 | PETEA/Ester + 1.0 M LiTFSI in DOL/TEGDME + 1 wt.% LiNO$_3$ | 0.28 (RT) | - | 713 | 499 (300th cycle) | 1.0-1.2 | 0.5 C | [67] |
| 9 | PVDF-HFP/Fumed SiO$_2$ + 1.0 M LiTFSI + 0.1 M LiNO$_3$ in DOL/DME | 1.3 (25 °C) | - | 895 | 845 | 1.5-2.0 | 0.1 C | [68] |
| 10 | PPC/SiO$_2$ + 1.0 M LiTFSI in DOL/TEGDME + 1 wt.% LiNO$_3$ | 0.16 (23 °C) | 0.83 | 1672 | 1422 (500th cycle) | - | 100 mA g$^{-1}$ | [69] |
| 11 | PAN/PEO/LATP + 1.0 M LiTFSI in DOL/DME + 1 wt.% LiNO$_3$ | 0.86 (25 °C) | 0.55 | 904 | 704 (100th cycle) | 1.0-1.3 | 0.1 C | [70] |
| 12 | PVDF-HFP/PETT-Ester + 1.0 M LiTFSI in DOL/DME + 1 wt.% LiNO$_3$ | 0.34 (25 °C) | 0.39 | 601 | 415 (300th cycle) | 1.2 | 0.5 C | [71] |
| 13 | PMIA/DDSDHE + 1.0 M LiTFSI + 0.1 M LiNO$_3$ in DOL/DME | 1.8 | - | 1122 | 713 (600th cycle) | 1.2 | 0.5 C | [72] |
| 14 | PVDF/OP + 0.6 M LiTFSI + 0.4 M LiNO$_3$ LiNO$_3$ in DOL/DME | 0.71 (25 °C) | 0.58 | 843 | 484 (300th cycle) | 2.0 | 0.5 C | [73] |
| 15 | PEGDA-P(VCA-*co*-BA) + 1.0 M LiTFSI in DOL/DME + 1 wt.% LiNO$_3$ | 2.9 | 0.63 | 1080 | 715 (300th cycle) | 4.5 | 0.1 C | [74] |

[a]Ionic conductivity. [b]Lithium-ion transference number. [c]Initial capacity. [d]End of life capacity. [e]Sulfur loading. DDSDHE: di-(2-(5,5-dimethyl-2-sulfido-1,3,2-dioxaphosphinan-2-yl)hydrazineyl)-*P*-ethylphosphinic; DME: 1,2-dimethoxyethane; DOL: 1,3-dioxolane; LAGP: Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$; EMIM-TFSI: ethylmethylimidazolium bis(trifluoromethanesulfonyl)imide; LATP: Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$; LiTFSI: lithium bis(trifluoromethanesulfonyl)imide; OP: organo-polysulfides; PDA: polydopamine; PEO: poly(ethylene oxide); PEGDA: poly(ethylene glycol) diacrylate; PDADMATFSI: poly(diallyldimethylammonium) bis(trifluoromethane) sulfonimide; PETEA: pentaerythritol tetraacrylate; PETT: pentaerythritol tetrakis(3-mercaptopropionate); P(VCA-*co*-BA): poly(vinyl carbonate-co-butyl acrylate); PVDF: poly(vinylidene fluoride); PVDF-HFP: poly(vinylidene fluoride-hexafluoropropylene); PY14TFSI: 1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide; RT: room temperature; TEGDME: tetraethylene glycol dimethyl ether.

electrochemical performance and becomes a safety hazard during battery operation[75]. In addition, these methods generally present wettability issues due to the poor contact between both components, especially in high-loading Li-S carbon-based porous cathodes, leading to poor interfacial contact and battery cyclability, as shown in Figure 2A[76].

Therefore, it is clear that the development of QSSPEs can simultaneously provide enhanced interfacial properties, improved safety and simple and effective preparation methods for large-scale applications that are essential. In this scenario, chemical methods, also known as "*in-situ* synthesis", are considered as the most promising alternatives. As shown in Figure 2B, these techniques can greatly improve the interfacial compatibility, owing to the intimate contact established between the electrodes, thereby providing an uninterrupted flow channel for lithium ions[76]. Likewise, the low cost, high efficiency and fabrication speed of these methods make them compatible with battery assembling processes. Different *in-situ* preparation methods have been used in the literature in
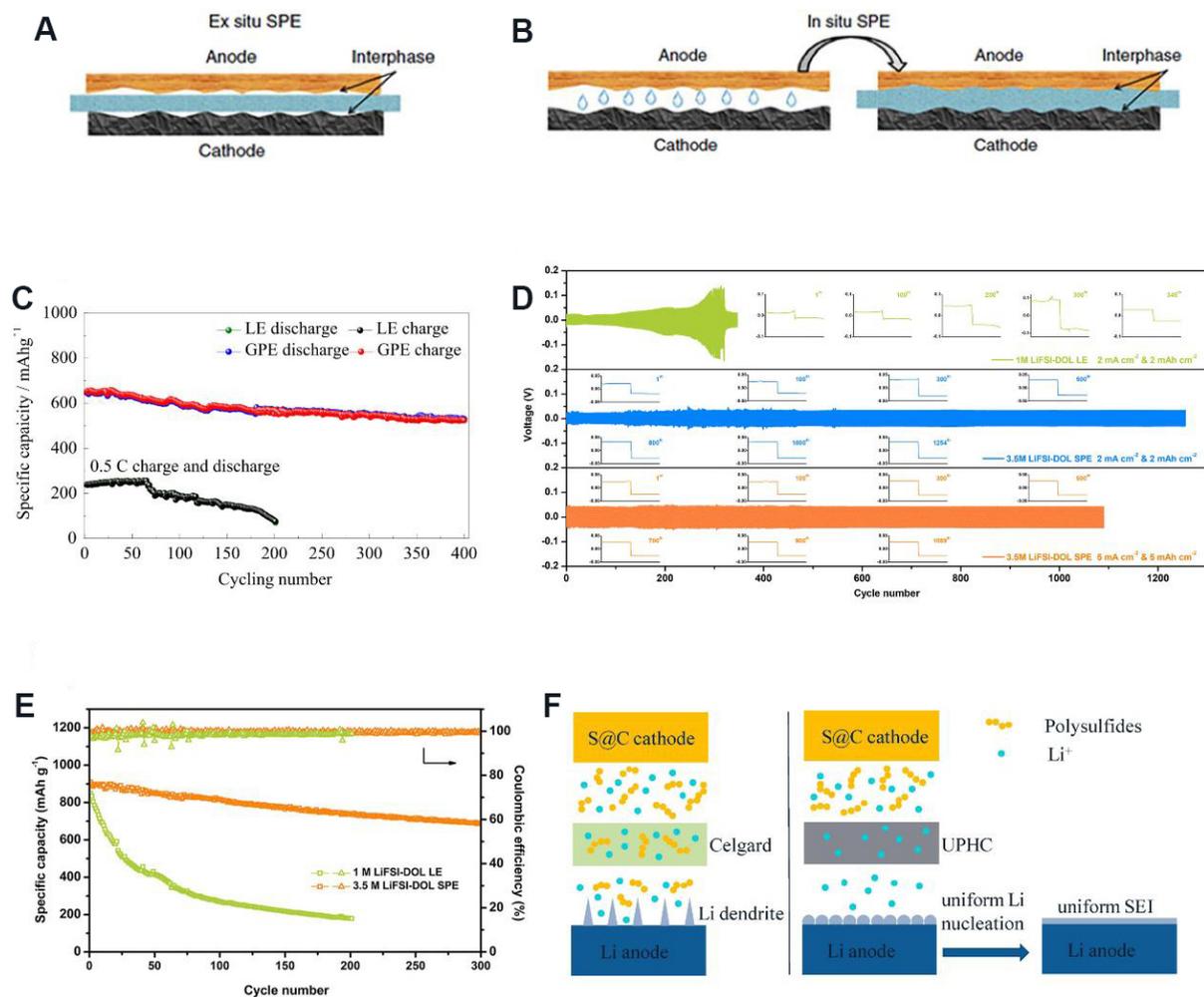
**Figure 2.** Schematic illustration of (A) *ex-situ* and (B) *in-situ* synthesis and the interfacial contact with the different cell elements. Figure 2A and B are reproduced from Ref.[76] with permission. Copyright 2021 Wiley-VCH. (C) Comparison of Li-S cycling performance between LE and thermal crosslinked QSSE at 0.5 C. Reproduced from Ref.[60] with permission. Copyright 2016 Elsevier. (D) Galvanostatic cycling of Li || Li symmetric cell of 1 M LiFSI-DOL-based LE (2 mA cm$^{-2}$ and 2 mAh cm$^{-2}$) and 3.5 M LiFSI-DOL-based QSSE (2 mA cm$^{-2}$ and 2 mAh cm$^{-2}$, and 5 mA cm$^{-2}$ and 5 mAh cm$^{-2}$). (E) Cycling performance of 1 M LiFSI-DOL-based LE and 3.5 M LiFSI-DOL-based QSSE at 0.2 C. Figure 2D and E are reproduced from Ref.[77] with permission. Copyright 2021 Elsevier. (F) Schematic illustration of Li nucleation and PS diffusion in S@C/LE/Li and S@C/UPHC-QSSE/Li. Reproduced from Ref.[79] with permission. Copyright 2020 Elsevier.

recent years, with three of them being particularly important for their application in Li-S batteries: thermochemical cross-linking, room temperature polymerization and ultraviolet (UV) induced crosslinking.

Of these three methods, thermochemical crosslinking, which consists of the formation of a three-dimensional (3D) polymer network structure via a thermally induced free radical reaction, is by far the most used and analyzed method due to its simplicity and reproducibility. Liu *et al.*[60] reported a QSSPE, prepared by *in-situ* synthesis with pentaerythritol tetraacrylate, which presented a remarkably high ionic conductivity of 1.13 × 10$^{-2}$ S cm$^{-1}$ at RT. This, in combination with the ability to retain polysulfides, resulted in a high-performance Li-S cell with remarkable rate performance (~600 mAh g$^{-1}$ at 1 C) and capacity retention (81.9% after 400 cycles at 0.5 C), as displayed in Figure 2C. However, this method requires the use of azobisisobutyronitrile as an initiator, which can cause stability issues due to its reactivity with the Li° anode.

With the aim of solving the reactivity issue of thermal initiators with Li°, researchers have made significant efforts to move to RT polymerization without the need to incorporate any type of initiator. This kind of synthesis method seeks to save energy during the process and also avoids the possible side reactions due to the non-reacted initiators. Cheng *et al.*[77] reported a resourceful initiator-free gelation method by the ring-opening polymerization of DOL. This work demonstrates a superior dendrite-free behavior, as shown in Figure 2D, and good compatibility in a Li-S battery, delivering a capacity of 687 mAh g^{-1} after 300 cycles (capacity retention of 76%) with a CE of 99.6% [Figure 2E].

Finally, although it is sometimes not strictly considered an *in-situ* technique due to the difficulty of applying it in preassembled cells, the UV light-induced crosslinking method, commonly used in the ink industry, has become greatly important both at the academic and industrial levels[78,79]. This method has attracted attention mainly for its low cost, reduction or even elimination of the use of solvents and its low energy consumption. In recent years, the group of Tu have carried out extensive studies on a modified poly(vinylidene fluoride)-*co*-hexafluoropropylene (PVDF-HFP)-based GPE with a 3D network constructed from the photopolymerization of pentaerythritol tetrakis-divinyl adipate (PETT-DA). This 3D network results in the diminished formation of dendrites and the "shuttle effect" [Figure 2F], while PVDF-HFP guarantees the mechanical properties of the GPE[71,79,80]. In addition to academic studies, the practical application of *in-situ* synthesis techniques has also been studied at an industrial level. Miltec successfully proved the viability of *in-situ* light-induced crosslinking for both electrode and QSSPE manufacturing for lithium-metal batteries (including Li-S batteries). These industrial initiatives represent a significant boost to finally demonstrating the industrial viability of these electrolytes for Li-S batteries.

Other than the preparation methods of QSSPEs, the electrolyte components, including plasticizers and polymer matrices, are also important to determine the electrochemical performance of a Li-S cell. In the literature, research attention has been focused on the investigation of different polymer hosts while using the standard state-of-the-art (SOA) LE as a plasticizer, i.e., DOL/DME-based electrolyte[13]. As a consequence, the "shuttle effect", the intrinsic issue of Li-S technology, still remains when using such QSSPEs. In order to tackle this challenge, in addition to carbon composites that can capsulate sulfur, avoiding the migration of polysulfides, different studies have intended to replace the elemental sulfur ($S_8$) by organosulfur as the active material in quasi-solid-state Li-S cells. These compounds consist of sulfur chains of variable sizes covalently bonded with organic frameworks.

The main example is the widely used sulfurized polyacrylonitrile (SPAN). Figure 3A shows a schematic illustration of the differences between the redox process of elemental sulfur and SPAN. The first discharge plateau disappears when using SPAN in the cell, which is related to the solid to solid reaction and the absence of solubilized long chain PS in the electrolyte, leading to a very stable performance and high specific capacity[81,82]. In the work of Liu *et al.*[83], SPAN was prepared by heating sulfur powder and polyacrylonitrile (PAN) at 300 °C under an argon atmosphere and this material was coupled with a QSSPE to obtain long cycling and a high capacity (~550 mAh g^{-1} in the first cycle and 500 mAh g^{-1} after 180 cycles) at 50 °C [Figure 3B]. Since this work, many studies have been developed in order to improve its performance[84]. However, there are still improvements to be made, especially in the case of high sulfur compositions (> 50 wt.%) in the chemical structure of the organosulfur, due to the persistence of long chain PS formation, as illustrated in Figure 3C[85]. In order to solve the persistent "shuttle effect", new organosulfur structures have been developed recently, such as the one presented by Yan *et al.*[86]. This compound, based on fluorinated quinone with a high S content, shows an outstanding performance of ~800 mAh g^{-1} of sulfur (560 mAh g^{-1} of organosulfur) after 600 cycles at 0.5 C [Figure 3D].
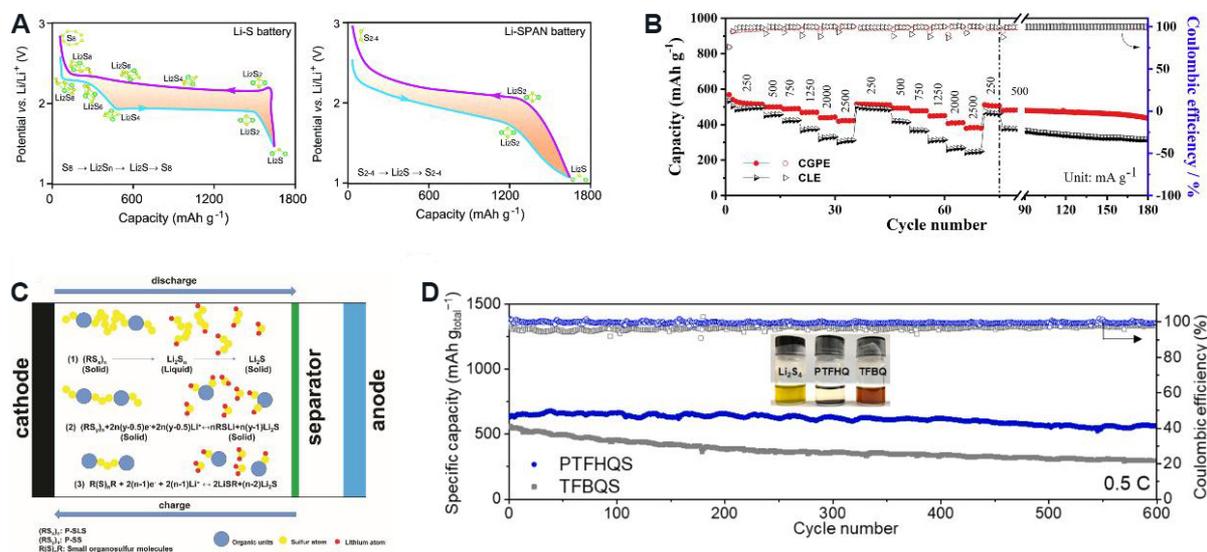
**Figure 3.** (A) Schematic illustration of the different redox reactions between Li-S and Li-SPAN batteries. Reproduced from Ref.[81] with permission. Copyright 2021 Royal Society of Chemistry. (B) Electrochemical performance of SPAN-based cathode material at 50 °C using a LE or GPE at different C-rates and long cycles. Reproduced from Ref.[83] with permission. Copyright 2019 Cell Press. (C) Different electrochemical processes depending on the S content in the organosulfur structure. Reproduced from Ref.[85] with permission. Copyright 2020 Royal Society of Chemistry. (D) Long cycling performance for recently developed fluorinated organosulfur quinone at 0.5 C. Reproduced from Ref.[86] with permission. Copyright 2019 American Chemical Society.

## PROJECTED ENERGY DENSITY AND PERSPECTIVES

Most of the abovementioned work on Li-S cells using ASSPEs and QSSPEs is mainly focused on materials development and selection. With regards to practical applications, it is important to know the potential energy density that can be achieved using different types of electrolytes and the key parameters required to reach the target energy density. Herein, estimations of the energy density of Li-S cells, as shown in Figure 4, have been carried out under realistic conditions (e.g., S utilization, loading and negative to positive capacity ratio), with variation of the thickness (t) of the electrolyte membrane in the case of ASSPEs and liquid content in the case of QSSPEs. In order to assess the energy density at the cell level, the following formula was utilized:

$$E_{cell}^{g} = \frac{C_{cell}^{a} \cdot V_{cell}}{m_{cell}^{a}}$$

where $C_{cell}^{a}$ is the areal capacity of the cell, $V_{cell}$ is the average discharge voltage and $m_{cell}^{a}$ is the sum of the areal mass of every cell component, including the current collector, separator (when necessary), anode, cathode and electrolyte.

The estimation of different electrolytes was carried out using different methods. For ASSPEs, the mass ($m_{elec}^{a}$) is calculated by the product of the electrolyte thickness ($t_{elec}$), the density of PEO ($\rho_{elec}$) and porosity: $m_{elec}^{a} = t_{elec} \cdot \rho_{elec} \cdot (1 - \varepsilon_{elec})$. For LEs, the mass of the electrolyte is obtained considering the areal sulfur loading ($m_{S}^{a}$), the electrolyte to sulfur ratio (E/S) and the electrolyte density ($\rho_{elec}$): $m_{elec}^{a} = m_{S}^{a} \cdot E/S \cdot \rho_{elec}$. Finally, for QSSPEs, a combined strategy was followed. Initially, the mass of the solid membrane was calculated for a PVDF membrane, following the strategy of ASSPEs. Additional LE mass added to wet this membrane was then calculated based on this mass. Furthermore, the additional LE to wet the cathode was calculated based
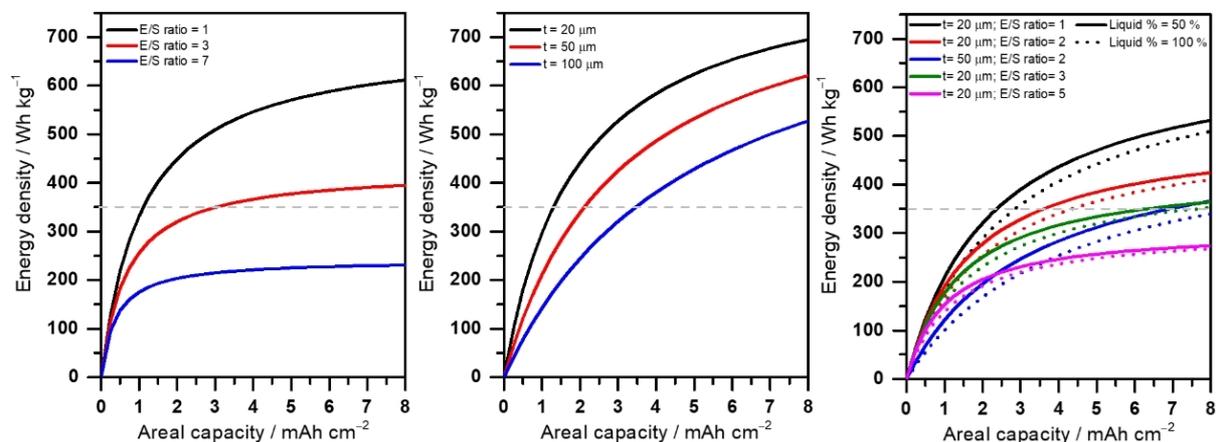
**Figure 4.** Energy density estimations for ASSPE-, QSSPE- and LE-based Li-S cells with various electrolyte thicknesses ($t$, in ASSPE systems), liquid content (wt.%, in QSSPE systems) and E/S ratios (in LE systems). Calculations were performed with the following parameters: 1200 mAh $g_{sulfur}^{-1}$ for cathode capacity; 64 wt.% sulfur loading for LE and 50 wt.% sulfur loading for ASSPE Li-S cells. In all the cases, the negative to positive capacity ratio was set to 3.

on the E/S ratio, as for LEs. Liquid systems are not the focus of this perspective but they are also included as a reference for comparison.

### ASSPE systems

It has been shown that Li-S technology is not competitive with SOA Li-ion cells in terms of volumetric energy density; therefore, the estimations of energy density shown in Figure 4 include only gravimetric values based on the total weight of the cell components (without packaging). A target of 350 Wh kg$^{-1}$ was chosen to surpass today's SOA Li-ion batteries at the cell level. To reach this value, in the case of Li-S cells with ASSPEs, the electrolyte membrane must go down to 50 μm, with a cathode of 2 mAh cm$^{-2}$. This seems more feasible compared to liquid systems, where an E/S ratio of 3 μL mg$^{-1}$ and an areal capacity of > 3 mAh cm$^{-2}$ are needed in order to reach 350 Wh kg$^{-1}$. This difference between both systems is explained by the double role of the ASSPE in both the cathode and electrolyte. In the cathode, the ASSPE acts as both a binder and catholyte, wetting electrode materials and eliminating the need for any additional electrolyte. In the electrolyte, the ASSPE not only conducts Li$^+$, but is also used as a physical barrier between two electrodes to prevent short circuiting of the cell (no additional separator is needed). This allows for a reduction in the weight of the inert compounds, thereby increasing the energy density of the system.

However, experiments have suggested that, when a ASSPE-based Li-S cell is coupled with a bench-marking cathode, which has been optimized based on the parameters of a LE, reaching an areal capacity of > 2 mAh cm$^{-2}$ is rather challenging[19]. This is due to the fact that the intrinsic properties of ASSPE systems that determine the S utilization are different from LEs, i.e., viscosity, wettability and ionic conductivity, leading to different optimum conditions of pore size and porosity in the cathode. When studying ASSPEs for Li-S cells, the cathode limitations should be taken into consideration to interpret the results. Unlike liquid-based Li-S systems, where the cathode is no longer an issue after decades of development, the optimization of cathodes for ASSPE-based Li-S cells should be conducted and extended in order to reach areal capacities higher than 2 mAh cm$^{-2}$.

### QSSPE systems

To decrease the operating temperature of ASSPE-based Li-S cells, QSSPEs were used to increase the ionic conductivity at RT, whilst simultaneously providing improved safety compared to LE-based cells. In QSSPE

based Li-S cells, due to the presence of the liquid phase plasticizer, the cathode used is the same as the ones in LE-based Li-S cells in terms of formulation. Hence, the estimations of energy density of QSSPE-based Li-S cells consider the parameters of both the catholyte (E/S ratio) and electrolyte (liquid content and thickness of the electrolyte membrane).

The results clearly show that the amount of liquid in the electrolyte varying from 50 to 100 wt.% does not have a significant impact on the energy density. On the contrary, the E/S ratio of the catholyte and the thickness of the electrolyte dominate the variation of the total weight of the cell. Comparably to the LE system, in QSSPE-based Li-S cells, if the electrolyte membrane thickness is 20 μm with a catholyte E/S ratio of 1 or 2, the areal capacity should be between 2.5 and 4 mAh cm$^{-2}$ in order to reach the targeted 350 Wh kg$^{-1}$. Unfortunately, current QSSPE-based Li-S cells are not able to achieve these criteria. Note that, even for Li-S cells comprising bench-marking DME/DOL-based LEs, it is still a challenge to operate for more than 100 cycles with such criteria values at a large pouch level[87-91]. Noteworthy, due to the presence of the liquid phase in the QSSPE system, the discharge/charge reaction and the Li/electrolyte interface are comparable to the LE system. Therefore, although the LEs for Li-S cells are not the main focus of this perspective, it is important to provide a brief discussion of LEs as plasticizers in QSSPEs.

It is generally accepted that Li-S cell failure is mainly due to Li anode degradation or consumption[87,92-94]. Following this conclusion, studies have focused on Li protection development, including *in-situ* SEI formation by additives, *ex-situ* protection by different coatings and 3D Li metal anodes. Nevertheless, the effectiveness of these approaches is questionable due to the dynamic Li stripping and plating on the Li anode upon cycling (cracks occur on the SEI and coatings) and the high reactivity between Li and the electrolyte (even higher when increasing the surface area in the case of 3D Li metal), with the LE possibly being the most decisive cell component to determine the electrochemical performance. Nevertheless, the reported developments of QSSPEs for Li-S cells mainly concentrate on preparation methods and the selection of new materials as polymer matrices[95]. More attention should therefore be paid to plasticizers, which are equally or even more critical for QSSPE-based Li-S cell performance. Currently, 1 M LiTFSI in a binary mixture of DME/DOL (1:1 v/v) containing LiNO$_3$ as an additive is widely regarded as a benchmark for QSSPE-based Li-S cells. The introduction of LiNO$_3$ significantly improves the interfacial stability of the lithium anode through the *in-situ* formation of a favorable SEI, which facilies homogeneous and dendrite-free Li deposition and a highly reversible plating/stripping process. Inspired by this principle, all the valuable salts and additives reported in ASSPE-based Li-S cells can also be employed in QSSPE-based systems, such as LiDFTFSI, LiTCM and LiN$_3$, to regulate the Li deposition and form excellent SEI layers[13].

As discussed above, the commonly used solvents for QSSPE-based Li-S cells are ether solvents, such as DME and DOL. However, the intermediate PS are prone to dissolution in ether-based solvents, followed by shuttling from the sulfur cathode to lithium anode during the repeat charge/discharge process, leading to a fast capacity decay. It is reported that ionic liquids (ILs) with high viscosity can effectively diminish the "shuttle effect" due to the low solubility of PS in ILs[19]. Furthermore, the Lewis acid cations of ILs are capable of effectively trapping PS from diffusion based on the hard and soft acid and base theory, which also contributes to suppressing PS shuttle[96]. Therefore, QSSPE-based Li-S cells comprising IL-based plasticizers showed good sulfur utilization and capacity retention at lower C-rates (< 0.5 C). However, IL-based QSSPEs show a lower ionic conductivity compared to ether-based ones, resulting in inferior electrochemical performance when a high current density is applied[13].

Beyond the SOA DME/DOL LE, which has a high solubility of PS (near 7 M), another type of LE with a limited or absent solubility of PS has also been investigated. The simplest approach is to increase the Li salt

concentration from 1 to 7 M while using the same DME/DOL solvent[97-99]. However, the density and viscosity of such electrolytes are very high and the cost is also simultaneously dramatically increased. Consequently, Cuisinier *et al.*[100], Lee *et al.*[101], Shyamsunder *et al.*[102] proposed new different concepts of "sparingly solvating electrolytes", which consists of a low donor number solvent as a co-solvent or as a solo solvent when a low ion-pairing Li salt is used. Following this concept, other research groups, such as Nakanishi *et al.* in Japan and Piwko *et al.* in Germany, also actively contributed to this regard[103-107]. It is noteworthy that with the change from electrolytes with high PS solubility to such "sparingly solvating electrolytes", the whole cell chemistry is changed simultaneously. Indeed, the discharge/charge profile of S cathodes using such electrolytes is distinct compared to the DME/DOL system. Although the formation of long chain PS still occurs, their conversion to shorter chain PS is instantaneous due to the limited solubility of long chain PS in the electrolyte. This change in S reduction mechanism results in a difference in the optimum condition of the cathode in terms of porosity, pore size and E/S ratio. Moreover, the absence of long chain PS in the electrolyte could also affect the Li/electrolyte interface, meaning less harsh conditions for Li metal.

It is still too early to draw a conclusion of whether "sparingly solvating electrolytes" will enable a long cycle life Li-S cell with competitive gravimetric energy density but this kind of LE can be an option as a plasticizer for QSSPEs. As discussed earlier, in order to study the real effect of such QSSPEs, the cathode should not be a limiting factor, which needs to be suitable for "sparingly solvating electrolytes". Furthermore, although the amount of the liquid content (50 or 100 wt.%) in the QSSPE does not remarkably affect the energy density of the cell, it does have a significant impact on the Li/electrolyte interface. All the above-mentioned aspects need to be taken into consideration when designing a QSSPE-based Li-S cell using "sparingly solvating electrolytes" as plasticizers.

## CONCLUSION AND OUTLOOK

This perspective has briefly summarized the recent progress on polymer-based solid-state Li-S batteries, with a special focus on the electrolytes, including all-solid-state polymer electrolytes (ASSPEs) and quasi-solid-state polymer electrolyte (QSSPEs). Advances have been mainly made in tuning the anion chemistry in ASSPEs, with the aim of forming a robust SEI on the Li anode to improve the stability of the cell and enable a long cycle life. The majority of published studies of QSSPE-based Li-S cells are related to the preparation method to achieve a facile, cost-effective, eco-friendly and scalable processing route. Moreover, strategies for improving Li/electrolyte interfaces have also been addressed in numerous works through the enhancement of the physical contact between the QSSPE and Li anode using an appropriate preparation method. Despite the aforementioned improvements in both ASSPE- and QSSPE-based Li-S cells, the cycling performances (especially the cells with a high S loading) of these two electrolyte-based cells are still far from the LE-based one [Table 2]. These can be attributed to the following issues and challenges: (1) low ionic conductivity at room temperature, especially for ASSPE-based cells; (2) uncontrollable dissolution and "shuttle effect" of polysulfides (PS); (3) adverse electrode/electrolyte interfaces, e.g., inferior chemical/electrochemical stability. To make them competitive with LE-based Li-S cells and enhance the overall performance of ASSPE- and QSSPE-based Li-S cells, the following aspects are critical:

(1) The role of salt anions in dictating the properties of the electrolytes and electrolyte/electrode interfaces has been spotlighted in ASSPE-based Li-S cells. Designing and developing novel lithium salt anions with super-delocalized structure and superior SEI (or CEI) formation properties is of paramount significance, which not only facilities enhanced ionic conductivity but also boosts the formation of excellent interfaces.

**Table 2. Comparison of ASSPE-, QSSPE- and LE-based Li-S cells**

| Electrolytes | Cathode composition/wt.% | SL[a]/mg cm$^{-2}$ | Electrolyte composition | IC[b]/mAh g$^{-1}$ | FC[c]/mAh g$^{-1}$ | Rate | Cycle life | Ref. |
|---|---|---|---|---|---|---|---|---|
| ASSPEs | S (40) + KB (15) + SE (45) | 1 ± 0.1 | PEO/LiFSI | 550 | 100 | 0.1 C | 1000 | [35] |
| | S (40) + KB (15) + SE (45) | 1 ± 0.1 | PEO/LiFTFSI | 790 | 626 | 0.1 C | 50 | [43] |
| | S (40) + KB (15) + SE (45) | 1 ± 0.1 | PEO/LiDFTFSI | 600 | 150 | 0.1 C | 1300 | [39] |
| | S (40) + KB (15) + SE (45) | 1 ± 0.1 | PEO/LiTFSI + 10% LiDFTFSI | 810 | 400 | 0.1 C | 100 | [38] |
| | S@KB (80) + AB (10) + PVDF (10) | 0.6-1.0 | PEO/LiClO$_4$ | 600 | 600 | 0.1 C | 30 | [108] |
| QSSPEs | S@CMK-3 (80) + AB (10) + PVDF (10) | 1.2-1.5 | PETEA activated in 1 M LiTFSI-DME/DOL + 1% LiNO$_3$ | 650 | 580 | 0.5 C | 400 | [60] |
| | S@CNT (90) + PVDF (10) | 4.9 | PEO/LiTFSI activated in 1 M LiTFSI-DME/DOL + 1% LiNO$_3$ | 850 | 600 | 0.1 C | 50 | [109] |
| | S@AB (80) + AB (10) + PVDF (10) | 1.5-2.0 | PETT-DA + PVDF activated in 1 M LiTFSI-DME/DOL + 2% LiNO$_3$ | 700 | 620 | 0.5 C | 300 | [79] |
| | SPAN (60) + AB (30) + PAN (10) | N/A | LiPF$_6$-EC/DMC/DEC | 1200 | 975 | N/A | 50 | [83] |
| | S (60) + AB (30) + PVDF (10) | 4 | LiTFSI/DOL polymerization | 700 | 600 | N/A | 80 | [77] |
| LEs | S@AB (80) + AB (20) + PG (10) | 9 | 1 M LiTFSI-DME/DOL + 2% LiNO$_3$ | 855 | 500 | 0.13 C | 40 | [110] |
| | S (70) + C (20) + CMC/Gl (6.7/3.3) | 6.5 | 0.5 M LiTFSI-0.5 M LiNO$_3$-DME/DOL | 1320 | 1100 | 0.1 C | 120 | [111] |
| | S@CoS$_2$-G (80) + KN (10) + PVDF (10) | 2.9 | 1 M LiTFSI-DME/DOL + 1% LiNO$_3$ | 1100 | 820 | 0.2 C | 30 | [112] |
| | S-Fe-Ni-NC (60) + AB (20) + PVDF (10) | 4.1 | 1 M LiTFSI-DME/DOL + 0.1 M LiNO$_3$ | 1000 | 580 | 1.0 C | 800 | [113] |
| | S@Co-N/G (75) + KB (15) + PVDF (10) | 6 | 1 M LiTFSI-DME/DOL + 2% LiNO$_3$ | 850 | 833 | 0.2 C | 100 | [114] |

[a]Sulfur loading. [b]Initial capacity. [c]Final capacity. AB: Acetylene black; AM: active material; C: carbon; CMC: carboxymethyl cellulose; CMK-3: CMK-3 carbon; CNT: carbon nanotubes; Co-N-G: cobalt in nitrogen-doped graphene; CoS$_2$-G: cobalt disulfide-graphene mixture; DA: divinyl adipate; DEC: diethylene carbonate; DMC: dimethyl carbonate; DEC: diethylene carbonate; DME: dimethoxyethane; DOL: dioxalane; EC: ethylene carbonate; Fe-Ni-NC: Fe-Ni nanoparticles encapsulated in nitrogen-doped carbon; G: graphene; Gl: glucose; KB: Ketjenblack; LiDFTFSI: lithium (difluoromethanesulfonyl) (trifluoromethanesulfonyl)imide; LiFSI: lithium bis(fluorosulfonyl)imide; LiFTFSI: lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide; LiTFSI: lithium bis(trifluorosulfonyl)imide; MWCNT: multi-walled carbon nanotubes; NC: nitrogen-doped carbon; NG: nitrogen-doped graphene; PAN: polyacrylonitrile; PEO: poly(ethylene oxide); PETEA: pentaerythritol tetraacrylate; PETT: pentaerythritol tetrakis; PG: peach gum; PVDF: polyvinylidene fluoride; PVDF-HFP: poly(vinylidene fluoride)-*co*-hexafluoropropylene); S: sulfur; SE: solid electrolyte.

It is well anticipated that PS can be dissolved and diffuse easily in the PEO-based matrix. In pursuit of high-performance Li-S cells with paramount PS inhibition, new polymer hosts containing an oxygen/nitrogen functional group (e.g., -O-C=O, -C=O, -C-O-C, -C=N and so on), which shows strong interactions with LiPS, are of interest for building excellent Li-S batteries. In addition, the development of single-ion conductive GPEs, which not only transport Li$^+$ but also block negatively charged LiPS, are gaining particular attention for overcoming the PS shuttle effect. In parallel, investigations of new plasticizers, e.g., "sparingly solvated electrolytes" and ionic liquids, should be more considered due to their key roles in terms of prolonging the cycle life of the practical large-scale cells, which is of a paramount challenge for Li-S technology.

(3) A better understanding of the interfaces (e.g., SEI and CEI layers), particularly regarding their morphologies, compositions, formation mechanisms and properties, is essential. Both in the case of ASSPEs and in the case of QSSPEs, the use of advanced characterization techniques such as nuclear magnetic resonance, *in-situ* studies using X-ray photoelectron spectroscopy, electron microscopy (transmission or scanning), density functional theory calculations and so on, are highly recommended, as essential tools to understand and clarify the operational problems commonly associated with Li-S batteries. The understanding of the issues with these techniques would inspire potential strategy solutions. These improvements would definitely boost the long-awaited development of high-energy density polymer-based Li-S batteries.

(4) Future work should be conducted on the specific cathode development for ASSPE- and QSSPE-based Li-S cells in order to reach the requested criteria to surpass the competitive gravimetric energy density of 350 Wh kg$^{-1}$ as indicated by estimations.

## DECLARATIONS

**Authors' contributions**
Conceived the research and supervised the work: Li C, Zhang H
Wrote the manuscript: Castillo J, Qiao L, Santiago A, Judez X, Sáenz de Buruaga A, Jiménez-Martín G, Armand M, Zhang H, Li C
Homogenized the final version and took a prominent role during the corrections: Qiao L, Castillo J
All authors have given approval to the final version of the manuscript.

**Availability of data and materials**
Not applicable.

**Conflicts of interest**
All authors declared that there are no conflicts of interest.

**Ethical approval and consent to participate**
Not applicable.

**Consent for publication**
Not applicable.

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