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Batteries

Electrolyte Regulation towards Stable Lithium-Metal Anodes in Lithium–Sulfur Batteries with Sulfurized Polyacrylonitrile Cathodes

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Lithium–sulfur (Li–S) batteries are highly regarded as the next-generation energy-storage devices because of their ultrahigh theoretical energy density of 2600 Wh kg^{-1}. Sulfurized polyacrylonitrile (SPAN) is considered a promising sulfur cathode to substitute carbon/sulfur (C/S) composites to afford higher Coulombic efficiency, improved cycling stability, and potential high-energy-density Li–SPAN batteries. However, the instability of the Li-metal anode threatens the performances of Li–SPAN batteries bringing limited lifespan and safety hazards. Li-metal can react with most kinds of electrolyte to generate a protective solid electrolyte interphase (SEI), electrolyte regulation is a widely accepted strategy to protect Li-metal anodes in rechargeable batteries. Herein, the basic principles and current challenges of Li–SPAN batteries are addressed. Recent advances on electrolyte regulation towards stable Li-metal anodes in Li–SPAN batteries are summarized to suggest design strategies of solvents, lithium salts, additives, and gel electrolyte. Finally, prospects for future electrolyte design and Li anode protection in Li–SPAN batteries are discussed.

1. Introduction

The concerning issues of fossil-energy shortage and environment crisis stimulate the development of various clean and renewable energy sources.[1] The demand for high-energy-density secondary batteries becomes significant with the booming electrical and electronic industry in the past few decades.[2] Lithium (Li) metal with an ultrahigh theoretical specific capacity of 3860 mAh g^{-1} and the lowest negative electrochemical potential of −3.040 V versus the standard hydrogen electrode (SHE) is considered as the „Holy Grail“ anode,[3] and the lithium–sulfur (Li–S) battery is considered as one of the most promising next-generation energy-storage devices as a result of its ultrahigh theoretical energy density of 2600 Wh kg^{-1} and the advantages of the cathode brings in terms of low cost, high abundance, and environmental benignity of sulfur.[4] Nevertheless, conventional Li–S battery cathodes using carbon/sulfur (C/S) composite raises several issues that strongly hinder the practical application of Li–S batteries including: 1) electronic and ionic insulation of sulfur and lithium sulfide (Li_2S) to render low sulfur utilization; 2) huge volume expansion of sulfur and Li_2S leading to electrode structure collapse during charge and discharge; 3) lithium polysulfide (LiPS) intermediates that dissolve into the electrolyte and diffuse to the anode side to corrode the Li-metal and reduce the Coulombic efficiency, a process noted as the notorious shuttle effect.[1,4b,5] Therefore, Li–S batteries with the conventional C/S cathode suffer from low Coulombic efficiency, rapid capacity decay, and severe anode decomposition resulting in a limited lifespan.[6]

From the view of cathode design, various strategies have been proposed to surmount the above-mentioned shortcomings of the C/S cathode.[7] Among them, employing sulfurized polyacrylonitrile (SPAN) as the sulfur cathode to construct a Li–SPAN battery is considered as a promising direction to realize high-performance Li–S batteries. The SPAN cathode was first reported by Wang and co-workers in 2002.[8] SPAN is synthesized by simply annealing the mixture of sulfur and polyacrylonitrile (PAN) under an inert atmosphere, and the SPAN cathode is prepared with additional conductive carbon and polymer binder. Compared with the C/S cathode, SPAN has a greater conductivity because the pyrolized PAN conjugated chain provides channels for electron conduction.[9] More importantly, active sulfur within SPAN is atomically dispersed and covalently bonded to the conductive skeleton without elemental sulfur thus there is very limited soluble LiPSs in the electrolyte during cycling. Consequently, the SPAN cathode demonstrates a unique discharge/charge behavior of solid–solid conversion different from the solid—liquid–solid pathway of the C/S cathode. The electrochemical reaction pathway without soluble LiPS promotes the utilization of active sulfur and inhibits the corrosion of the Li-metal anode during cycling, resulting in a higher Coulombic efficiency of near to 100 % and much improved cycling stability.[10] In addition the independence of the sulfur redox reactions from interference with soluble LiPS raises opportunities of using high-areal-loading cathode and reducing the electrolyte volume to realize high-energy-density Li–S batteries beyond 400 Wh kg^{-1}. Taking the above advantages, Li–SPAN batteries have attracted growing attention as a promising Li–S battery configuration.[11]

Despite the advances in SPAN cathode design, the unstable Li-metal anode emerges as a problem and retards

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the practical applications of Li–SPAN batteries. In principle, Li-metal can react with almost all kinds of working electrolyte to form a solid electrolyte interphase (SEI) because of its ultrahigh reactivity.[12] The as-formed SEI is in close contact with the surface of the Li-metal and is considered to be a self-limiting protective layer to prevent further reaction with the electrolyte. Although the structure and composition of the SEI remain controversial, a general understanding is that the SEI plays a determining role to influence the Li plating/stripping behavior and consequently the performance of the Li-metal anode. Therefore, constructing a robust and sustainable SEI is of great significance for Li-anode protection. Unfortunately, most SEIs formed by routine electrolytes exhibit unsatisfactory properties. The heterogeneity of the SEI is recognized as the initiator of uneven Li deposition resulting in random Li growth into Li dendrites. Dendrite growth of Li-metal raises severe safety concerns, such as internal circuit and thermal runaway. Meanwhile, Li dendrites generate inert „dead Li“ during continuous Li plating/stripping, accounting for dramatic dimensional change, rapid loss of active material, and limited lifespan of the battery.[13] In addition, the SEI is unstable and cracks into fragments during cycling. The exposed fresh Li-metal continuously consumes the electrolyte to result in premature battery failure.[3e,13a] Apart from the issues of the Li-metal itself, the SPAN cathode also has negative effects on the Li-metal anode especially in ether-based electrolytes, in which LiPSs are partially dissolved. The dissolved LiPSs shuttle between the cathode and the anode, destroy the SEI and react with the Li-metal underneath, and aggravates anode corrosion to increase the instability of the Li-metal anode.[14] Moreover, the above-mentioned problems of the Li-metal anode will be particularly magnified under practical conditions, under which high-areal-loading cathodes, thin anodes, and lean electrolyte volume have to be employed to meet the requirements for high-energy-density Li–SPAN batteries.[15] Facing these challenges, the effective protection of the Li-metal anode is required in the Li–SPAN system to achieve reliable high performance for practical applications.

Focusing on Li-anode protection, various strategies have been proposed including constructing Li hosts,[16] using Li alloys,[17] artificial SEIs,[18] and electrolyte engineering.[19] Considering the protective SEI is predominantly afforded by the electrolyte through surface reaction, regulation of the electrolyte by selecting suitable solvents, Li salts, and additives is a logical strategy.[3d,4a,20] The composition of the electrolyte has great influence on structure and composition of the SEI. The ability of electrolyte to repair the cracked SEI during cycling affords a sustainable SEI which allows stable anode running. In addition, a favorable electrolyte contributes to high ionic conductivity to reduce ohmic polarization and allows a uniform Li-ion flux across the SEI to give even Li deposition.[4d,21] Additional benefits can also be achieved in cathode activation, polysulfide shuttling inhibition, and reducing electrolyte volume. Therefore, regulating the electrolyte is strongly regarded as a direct and efficient method towards stabilizing Li-metal anodes for high-performance Li–SPAN batteries. However, anode protection are still at an early stage for Li–SPAN batteries. This calls for more attention and efforts in this field to understand the basic electrochemistry in the Li–SPAN system to construct rational design strategies on further electrolyte regulation and to manufacture high-performance Li–SPAN batteries.

Fifty years after of the first proposal of the Li–S configuration and almost twenty years of the first applicable SPAN cathode (Figure 1), Li anode protection has become the core issue for the realization of not only the Li–SPAN system, but also other rechargeable batteries based on Li-

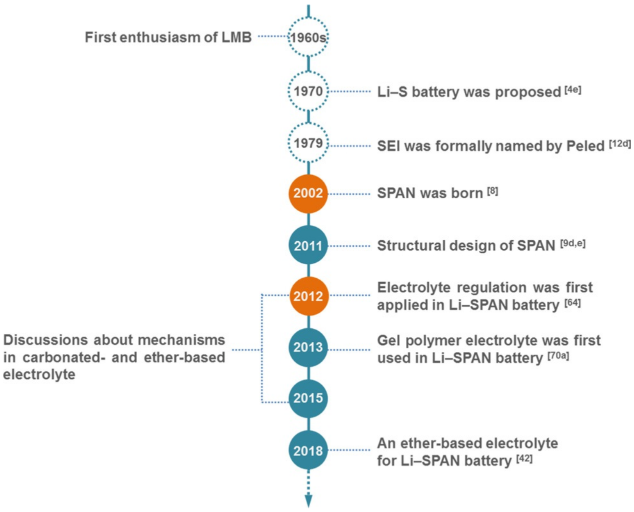
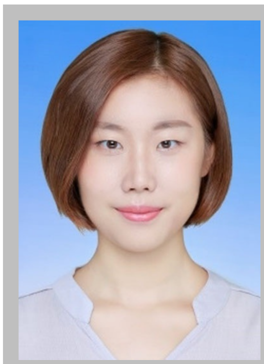


Figure 1. A brief timeline about the development of Li–SPAN batteries.



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metal anodes. To promote further progress in the design of stable Li-metal anodes for rechargeable batteries, in this Minireview we aim to address the current strategies of electrolyte engineering toward Li-metal protection in the Li–SPAN system. The basic electrochemistry of the Li–SPAN system is first introduced to afford a general overview. The strategies for electrolyte design regarding the selection of solvents, lithium salts, and additives in liquid electrolyte are included. Gel polymer electrolytes in Li–SPAN batteries are also discussed. Finally, insights and perspectives on rational electrolyte design and Li-metal protection are presented.

2. Li–SPAN batteries

Typically, a Li–SPAN cell consists of a Li-metal anode, an SPAN cathode, a separator, and electrolyte (Figure 2 a,b). The Li-metal anode goes through a reversible electrochemical reaction of $\mathrm{Li}+e^- \leftrightarrow \mathrm{Li}^+$. The SPAN cathode is usually a composite of SPAN, conductive carbon, and binders. SPAN is typically prepared by ball-milling a mixture of sulfur and PAN and subsequent annealing at a temperature in the range from 300 to 500 °C under a protective atmosphere to undergo a dehydrogenation process and possible partial carbonization (Figure 2 c).[22] The exact chemical structure of SPAN has been extensively investigated but remains controversial. Nevertheless, it is generally accepted that the sulfur species (S_x, $2 \leq x \leq 4$) are chemically bonded to the pyrolyzed pyridine skeleton instead of being physically confined, this conclusion is based on the fact that no elemental sulfur is detected in SPAN. The pyrolyzed PAN chain serves as the conductive backbone and sulfur in the sidechain affords the reversible capacity.[23] During the discharge/charge process, conversion between SPAN and lithiated SPAN takes place with reversible breaking and reformation of C−S and S−S bonds, yet further exploration is requested to illustrate the structure and mechanism of SPAN-related electrochemistry.[14b] In addition, a separator between cathode and anode is essential to avoid direct contact of the electrodes and internal short circuits. The separator needs to be uniform, robust, and porous to guarantee sufficient transportation of Li ions internally. Further functionalization of the separator can give better battery performance.[24]

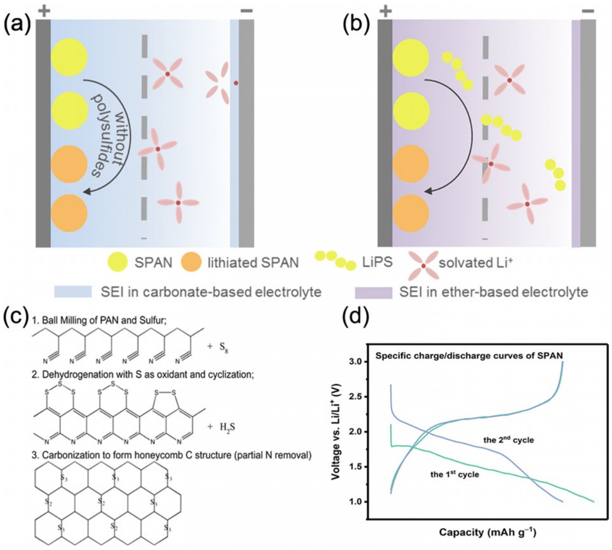

Figure 2. Schematic configuration and probable mechanism of Li–SPAN in a) carbonate-based electrolyte and b) ether-based electrolyte. The vertical dashed line is the separator. c) Proposed structure variation during the synthesis of SPAN.[14b] Copyright 2015, American Chemical Society. d) Typical charge/discharge curves of a Li–SPAN battery with conventional carbonate-based electrolyte at the first and second cycle.

Electrolyte is an indispensable component of a working battery. Electrolyte basically serves as the medium for ion transportation between cathode and anode. According to their phase at room temperature, electrolytes can be categorized as liquid, quasi-solid-state,[25] and all-solid-state.[26] For Li–SPAN batteries, liquid electrolyte is the main focus. It can be roughly categorized into carbonate- and ether-based electrolytes on the basis of the organic solvents employed. Carbonate solvent is broadly employed with the Li–SPAN system, exhibiting ideal compatibility with the SPAN cathode and good performances.[9a] The equal volume mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1.0 M lithium hexafluorophosphate ($\mathrm{LiPF_6}$) is the most common electrolyte system in Li–SPAN batteries. Meanwhile, ether solvents are also used in the Li–SPAN system, which are believed to afford additional protection toward Li anode but suffer from dissolved LiPSs and the resulting polysulfide shuttle effect. Therefore, the application of ether-based electrolyte is not yet widespread compared with carbonate-based electrolyte in Li–SPAN batteries.

Typical charge/discharge curves of a Li–SPAN battery with routine carbonate-based electrolyte are shown in Figure 2 d. Distinct from Li–S batteries with conventional C/S composite cathodes, there is only one plateau during the charge and discharge process in Li–SPAN batteries. Based on the charge/discharge behavior, a „solid–solid“ conversion mechanism is proposed and widely accepted regarding the Li–SPAN system rather than „solid–liquid–solid“ conversion of the C/S composite cathode.[23b] Such a difference is attributed to the atomic dispersion and chemical bonding of sulfur within SPAN, as well as the limited solubility of LiPS in carbonate-based electrolyte. Another notable difference is that the first discharge process is different from the subsequent cycling in Li–SPAN batteries while routine C/S composite cathodes affords similar discharge behaviors throughout its lifespan. The initial discharge voltage of the SPAN system in the first cycle is around 1.8 V and is around 2.3 V at the second cycle, which becomes stable during the subsequent cycles. Corresponding discharge plateaus are also different considering the first and the subsequent cycles. In addition, the capacity of the initial discharge process usually exceeds the theoretical capacity based on sulfur (1672 $\mathrm{mAh\,g^{-1}}$), of which nearly 200–400 $\mathrm{mAh\,g^{-1}}$ capacity is irreversible in the following cycles. This characteristic behavior of Li–SPAN is possibly ascribed to the capacity of the conjugate skeleton structure (C=C and C=N) that Li ions are irreversibly intercalated, yet this argument is not solid and requires further investigation.[23a,27] Notably, the capacity of

SPAN can be calculated on the basis of either sulfur or the SPAN composite. The sulfur content of the SPAN composite (usually 40–50 wt% in SPAN) and the areal sulfur loading within the cathode also vary among the published results. These parameters have a great impact on the electrochemical performances and therefore should be seriously considered when comparing the reported battery performances. Another noteworthy issue is the tap density of the sulfur cathode which is closely associated with the battery volumetric energy density. The SPAN cathode demonstrates potential advantages to realize a higher tap density over the routine C/S composite cathode, but further material innovation is required to improve the sulfur content in the SPAN cathodes.

Generally under ideal conditions with excessive electrolyte and Li anode, the widely employed electrolyte of 1.0 M $LiPF_6$ in EC/DEC demonstrates acceptable performances with the SPAN cathode regarding initial capacity and cycling lifespan. However, under practical conditions with limited Li anode excess and low electrolyte volume (low electrolyte/sulfur ratio) to pursue high energy density, the EC/DEC carbonate electrolyte is not able to protect Li-metal anode as shown by rapid capacity decay and short lifespan.[28] Specifically, the SEI formed by the EC/DEC system mainly comprises Li_2O and Li_2CO_3 in the inner inorganic layer and metastable ROCOOLi in the outer organic layer. The structure of such SEIs follows the „mosaic model“ which is undesirably fragile and vulnerable during cycling.[4d] Therefore, as a result of an unstable and inhomogeneous SEI and the consequent unstable Li-metal anode, the standard carbonate-based electrolyte cannot satisfy the requirements of high-energy-density and long-term cycling stability in Li–SPAN batteries. On the other hand, ether-based electrolyte (commonly 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL)/dimethoxy ethylene glycol (DME)) is considered to be more compatible with Li anodes and offers evident dendrite suppression,[12c,13a] where DOL goes through a self-polymerization process on the Li-metal surface to form a protective layer.[29] Nevertheless, the current Li–SPAN system fails to accommodate the ether-based electrolyte to afford better electrochemical performances than the carbonate-based electrolytes. Dissolved LiPSs in ether solvents are deemed as the main hindrance and cause polysulfide shuttling, cathode capacity decay, and anode corrosion. Therefore, how to mitigate or inhibit the dissolution of LiPSs becomes an extra concern for anode protection in Li–SPAN batteries with ether-based electrolytes.

As is discussed above, the current electrolyte system cannot satisfy the demands of Li–SPAN batteries and prevents them from exhibiting the expected advantages especially for the anode side. Electrolyte regulation is therefore highly required to stabilize Li-metal anodes in Li–SPAN batteries. Insights into the electrolyte structure and its influence on Li electrochemistry are highly regarded. Principles for rational electrolyte design and application are of great value for not only the Li–SPAN system, but also in other Li-metal batteries.[12c,13a,14c,28b,30] Fundamental understanding and regulation of the SEI should be the core issue to direct electrolyte design, while the structure of the Li-ion solvation sheath predominantly determines the structure and properties of the SEI because the solvents and anions in the Li-ion solvation sheath preferentially precipitate in the reduction process on Li-metal anodes to generate the SEI. Therefore, modulating the structure and components of the Li-ion solvation sheath, mainly through selecting solvents and anions, constitutes an effective strategy to realize ideal SEIs and thus Li anode protection.[31] In addition, the Li ion solvation sheath also influences the bulk ion conductivity and desolvation of Li ions on SEI. In this way, the design and selection of favorable solvents, Li salts, and additives are reasonable approaches to regulate the Li-ion solvation sheath and consequently considered as the main focuses of current research. A solid electrolyte affords a different pathway to address the unstable interface between the Li-metal anode and the electrolyte. Quasi-solid gel electrolytes and potential all-solid-state electrolytes can bring new opportunities in this field. Therefore, in the next Section, we will make a systematic summary of electrolyte regulation strategies in Li–SPAN batteries according to the above-discussed aspects including solvents, Li salts, additives, and gel-electrolyte.

3. Liquid Electrolyte Regulation in Li–SPAN Batteries

Liquid electrolytes are broadly applied in rechargeable batteries because of the advantages they bring of high ionic conductivity, low surface tension, low viscosity, and the capability to wet the electrode surface. The influence of liquid electrolytes on Li plating/stripping is mainly determined by the structure of the Li-ion solvation sheath and the properties of the resultant SEI layers on Li-metal anodes. Generally, Li ions are solvated by solvents in liquid electrolytes and accompanied by anions associated with the Li salts and additives in most cases. The solvated Li ions and surrounding environment constitute the solvation sheath with specific components and structures.[28b,31,32] The solvents and anions in the solvation sheath are more likely to react with Li-metal for SEI generation.[3c,28b] The structure of the solvation sheath greatly influences Li-ion desolvation and migration through the SEI. Therefore, rational design of the solvents and anions in the Li-ion solvation sheath is highly regarded as a way to regulate Li deposition and improve the anode performance. Solvent regulation is mainly a choice between two mainstream systems, that is, into carbonate and ether solvents. Anion regulation is mainly based on selecting Li salts. Besides, additives analogous to solvent and Li salt also demonstrate performance promotion.[33] Examples of the above-mentioned strategies are discussed in the following sections regarding the Li ion solvation sheath, the as-formed SEI, and their effects on Li-metal protection in Li–SPAN batteries.

3.1. Carbonate Solvents

Carbonate solvents can be categorized into cyclic and linear carbonates according to the molecular structure.[20] Common cyclic carbonates include ethylene carbonate (EC)

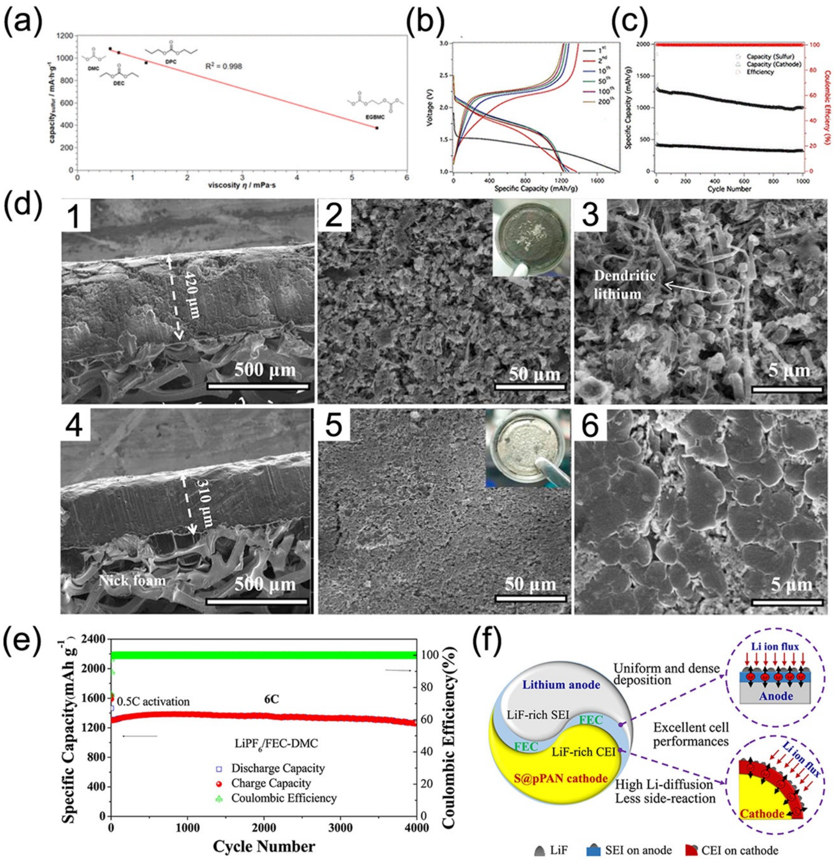

Figure 3. Electrolyte regulation in carbonate-based liquid electrolyte. a) Linear correlation between the viscosity and the discharge capacity in the 2nd cycle using different carbonates.[34] Copyright 2018, The Electrochemical Society. b) Electrochemical discharge and charge curves of various cycles at 0.4 C and c) cycling performances of Li–SPAN cells.[14b] Copyright 2015, American Chemical Society. d) Morphology of Li mental anodes in different carbonate electrolytes. Cross-section views (d_1, d_4) and top views (d_2, d_3, d_5, d_6) of Li electrodes recovered from Li|Li cells cycled at 1.0 mA cm^{-2} after 100 cycles using conventional EC-based electrolyte (d_1, d_2, d_3) and FEC-based electrolyte (d_4, d_5, d_6). Insets: are optical pictures of the corresponding cycled Li anodes. e) Long-term cycling performances of Li–SPAN cells in FEC-based electrolyte at 6.0 C. f) Schematic illustration of FEC-based electrolyte in a Li–SPAN battery.[35] Copyright 2018, Elsevier.

and propylene carbonate (PC). Dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) are the most frequently applied linear carbonate solvents. Many studies have indicated that Li ions are preferentially solvated by cyclic carbonate solvents owing to their higher permittivity and dipole moments in comparison with linear carbonate solvents.[20b,36] However, linear carbonates are necessary as co-solvents to compensate the problem of the high viscosity of cyclic carbonates. Buchmeiser and co-workers systematically investigated the effects of the molecular structure of carbonate solvents on the electrochemical performances for the Li–SPAN system.[34] This provides important basic guidance for the selection of carbonate solvents. A linear correlation between the viscosity of carbonate solvents and cell performances was presented that lower viscosity affords higher capacity (Figure 3 a). Furthermore, temperature was confirmed to influence the capacity and rate performance of Li–SPAN batteries by the regulation of electrolyte viscosity.[37] The performance of the proposed mixed carbonate solvent of EC/DEC was further investigated by Archer and co-workers. The Coulombic efficiency was stable nearly 100 % over 1000 cycles at 0.4 C. The initial capacity was 1843 mAh g^{-1} and remained over 1000 mAh g^{-1} after 1000 cycles (Figure 3 b,c).[14b] The achieved performances were remarkable at that time considering the usage of conventional EC/DEC electrolyte, encouraging following efforts in this field to realize further promotion.

Despite satisfactory cathode performances, some studies showed that the EC-based electrolyte is not compatible to the Li-metal anode. Dendritic and mossy Li is more prone to form in this system increasing safety hazards.[4d] Consequently, substitution of EC with other anode-favorable carbonates is highly required. Fluorinated carbonate solvents, such as fluoroethylene carbonate (FEC), has been verified to achieve a more uniform SEI and inhibit Li dendrite growth.[28,38] Because of the lower level of the lowest unoccupied molecule orbital (LUMO: −0.87 eV), FEC is more prone to be reduced on Li-metal anodes than EC and DEC. As a result, more LiF is generated within the SEI, which is considered as a beneficial component to form homogeneous SEIs and induce uniform Li deposition.[39] FEC has been confirmed to be effective in many Li-metal batteries and was introduced to the Li–SPAN system as the main solvent by Wang and co-workers.[35,40] Compared with the SEI formed in EC-based electrolytes, a LiF-rich SEI was confirmed by X-ray photoelectron spectroscopy after introducing FEC. The uniform and compact Li deposition morphology further indicated the LiF-rich SEI can shield Li anodes effectively (Figure 3d). The FEC-based electrolyte also contributed to superb performances in Li–SPAN cells. The ultra-long lifespan (capacity retention of 96.3% and Coulombic efficiency of 99.9% over 4000 cycles at 6.0C; Figure 3e,f) and excellent rate performance (1459.3 $mAh\,g_{sulfur}^{-1}$ at 30.0C) corroborated the function of FEC in Li–SPAN batteries. Carbonate-based electrolyte exhibits promising performances in Li–SPAN cells, which can be further improved with fluorinated solvents. Nevertheless, electrolyte consumption and uncontrolled Li deposition are still not fully addressed in carbonate-based electrolytes, especially under practical conditions with limited electrolyte volume and Li excess. Therefore, further optimization of the carbonate solvent is needed to achieve reliable performances for practical applications.

3.2. Ether Solvents

Ether solvents are more compatible with Li anodes than carbonates as with the ether solvents protecting oligomers form in the SEIs on Li surfaces.[41] The most commonly used ether solvents are 1,3-dioxolane (DOL), dimethoxy ethylene glycol (DME), and tetrahydrofuran (THF).[14d,20] Although ether-based electrolytes are widely used in Li–S batteries with standard C/S composite cathodes, their use usually results in poor electrochemical performances with Li–SPAN batteries.[9b,11b,14b] A reasonable explanation is that LiPSs can partially dissolve into ether-based electrolytes to induce the shuttle effect and severe corrosion of the Li-metal anode (Figure 4a).[14b] Therefore, inhibition of LiPS dissolution in ether-based electrolytes is the key issue to demonstrate the advantages of ether solvents on Li-metal protection in Li–SPAN batteries.

Modification of the SPAN cathode is an effective method to inhibit LiPSs dissolution. Xie and co-workers designed a Se_xSPAN composite cathode with faster kinetics (Figure 4b).[14a] The dissolution of LiPSs is therefore inhibited resulting in reduced shuttle effect and improved performances. Consequently, the Se_xSPAN cathode delivered a high reversible capacity (1300 $mAh\,g^{-1}$ at 0.13C) and high rate (900 $mAh\,g^{-1}$ at 6.5C based on S and Se). This work makes a breakthrough in the performances of Li–SPAN with ether solvents and validates cathode modification as a promising direction. More importantly, it shows that ether-based electrolyte is potentially advantageous for Li anode protection in Li–SPAN batteries. Developing new ether-based electrolytes

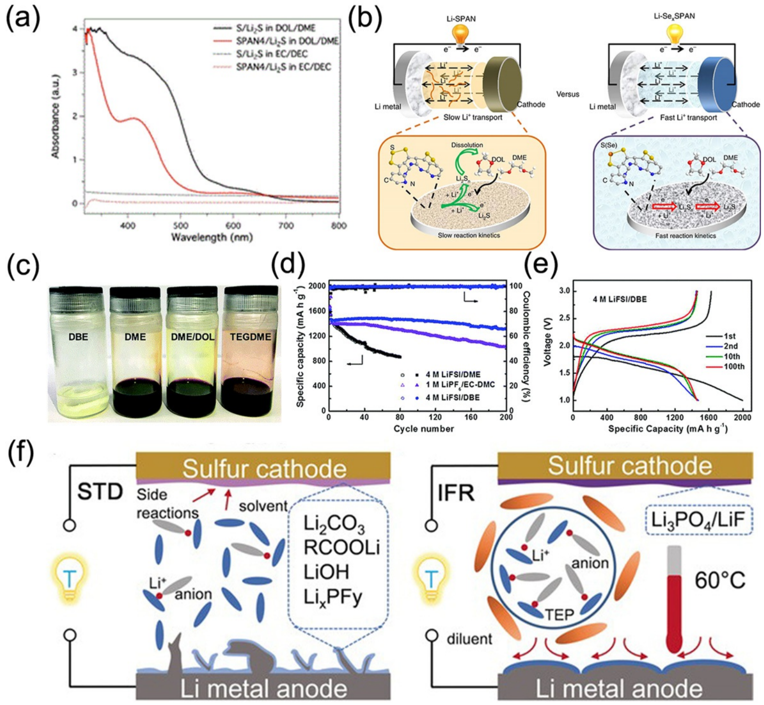

Figure 4. Electrolyte regulation in ether-based liquid electrolyte. a) Ultraviolet-visible spectroscopy spectra of the samples of S/Li_2S, $SPAN/Li_2S$ in DOL/DME and EC/DEC electrolytes after 10 days.[14b] Copyright 2015, American Chemical Society. b) Scheme of the proposed reaction process. Small amount of Se-doping significantly enhances the redox kinetics of polysulfide conversion, leading to ether-compatibility and superior performances of Li-$Se_{0.06}$SPAN battery.[14a] Copyright 2019, Nature Publishing Group. c) Solubility evaluation of 0.25 M Li_2S_6 in typical ether solvents, DBE affords the lowest solubility toward LiPSs. d) Cycling performance of Li–SPAN cells in 4.0 M LiFSI/DBE, 4.0 M LiFSI/DME, and 1.0 M $LiPF_6$/EC-DMC at 1.67 $A\,g^{-1}$. e) Discharge/charge profiles of Li–SPAN cells in 4.0 M LiFSI/DBE electrolyte, the current density is 0.33 $A\,g^{-1}$ at the first cycle and 1.67 $A\,g^{-1}$ during the following cycles.[42] Copyright 2018, Royal Society of Chemistry. f) Illustration of Li–S batteries using 1.0 M $LiPF_6$/EC-DMC (STD) electrolyte and 1.1 M LiFSI/TEP-TTE (IFR) electrolyte, respectively.[43] Copyright 2019, Wiley-VCH.

with low LiPSs solubility can thus inhibit LiPS shuttling and promote the stability of Li-metal anodes. One strategy is to increase the salt concentration to reduce the fraction of free solvents that are capable to solvate LiPSs. In addition, the structure of the ion–solvent complex in highly concentrated electrolyte is different from in conventional electrolyte, which may result in a more uniform and stable SEIs.[44] High-concentrated ether-based electrolytes have been shown to be effective in suppressing the growth of Li dendrites.[45] For instance, it was found that a 4.0 M LiFSI/DME electrolyte enabled high Coulombic efficiency in Li | Cu half cells.[46] Similarly, Wang and co-workers selected dibutyl ether (DBE) with 4.0 M Lithium bis(fluorosulfonyl)imide (LiFSI) as electrolyte in Li–SPAN batteries.[42] Because of the limited solubility of LiPSs in DBE (Figure 4 c) and the ability of high-concentrated electrolyte to suppress Li dendrite formation, the cycling stability and electrochemical reversibility of Li–SPAN cells with 4.0 M LiFSI/DBE surpassed those in 4.0 M LiFSI/DME and 1.0 M $LiPF_6$/EC-DEC (Figure 4 d,e). This is the first application of high-concentrated ether electrolytes in Li–SPAN batteries to address this issue. Wang et al. reported another ether-based electrolyte mainly consisting of 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl (TTE) and triethyl phosphate (TEP).[43] LiF and Li_3PO_4, as two key components in the SEI, were derived from the decomposition of TTE and TEP, respectively, and are considered to afford a micro-sized and dense-packing Li deposition (Figure 4 f). This kind of ether-based electrolyte was also stable at high temperature owing to the high flash point of TTE. A stable Columbic efficiency of 99.5 % and good rate performance of 620.1 mAh $g_{composite}^{-1}$ at 10.0 C with temperature of 60 °C were also realized using this electrolyte.

In summary, ether-based electrolyte offer advantages toward Li-metal protection but suffer from LiPS dissolution and the resultant side effects. Inhibiting LiPS dissolution in ether electrolytes is the key point to promote battery performances in Li–SPAN batteries. Cathode modification and electrolyte engineering are both promising strategies, whereby the electrolyte route is more challenging to fulfill. Nevertheless, efforts at developing high-performance ether-based electrolytes are important despite achievements in carbonate-based Li–SPAN batteries in terms of anode protection.

3.3. Lithium Salts

To develop a suitable Li salt in a particular battery system, multiple factors, including solubility, ionic conductivity, electrochemical/chemical stability, thermal stability, and cost must be considered.[20b,47] As an indispensable component in electrolytes, Li salts not only afford the source of dissociated ions for ion conduction, but also take part in the SEI formation through the reduction of anions.[41,48] Attempts at varying the anions have shown that both the constituents and concentration of Li salts impact the composition of the SEI and further determine the Li deposition behaviors.[49]

Lithium hexafluorophosphate ($LiPF_6$) is the most commonly employed salt in carbonate-based Li–SPAN batteries because of its electrochemical stability and high ionic conductivity in electrolyte. Nevertheless, $LiPF_6$ is thermodynamically unstable, sensitive to moisture, and insufficient to passivate the Li anode.[50] Hence, efforts have been pursued to modulate the Li salts to reinforce the stability of whole electrolyte system and optimize the SEI in Li–SPAN batteries. Lithium borates, such as lithium bis(oxalate)borate (LiBOB) and lithium difluoro(oxalate)borate (LiDFOB), are introduced to substitute $LiPF_6$. Because of the lower reduction potential, LiBOB is more prone to decompose on the Li anode.[49b,c] The resultant SEI with boron species contribute to improved long-term cycling performance with a capacity decay of 0.05 % per cycle by constructing robust and sustainable SEI layers in Li–SPAN batteries.[51] LiDFOB has the merits of thermal stability, optimized ionic conductivity over a wide temperature range, and the ability to promote a LiF-rich SEI as well.[52] Based on the previous attempts in Li-ion batteries and Li–S batteries, LiDFOB was introduced into Li–SPAN systems to replace $LiPF_6$. It was found that the introduction of LiDFOB distinctly improved the cycle performances.[53] With the electrolyte formula of 1.0 M LiDFOB/EC-DMC-FEC, an initial capacity of 1400 mAh g_{sulfur}^{-1} with the capacity retention of 89 % for 1100 cycles at 1.0 C was realized in Li–SPAN cells (Figure 5 a), simultaneously with obvious dendrite-free morphology of Li anodes (Figure 5 b). The improved performances were ascribed to the combined effects of LiDFOB and FEC on forming a unique SEI to allow uniform Li plating/stripping. LiFSI is also considered as a promising Li salt in Li–SPAN because FSI^- anions can react with Li metal to afford a thinner and denser inorganic SEI layer enriched with LiF.[44,54] The Li–SPAN battery with 1.0 M LiFSI in EMC/FEC exhibited prominent performances of 1270 mAh g_{sulfur}^{-1} reversible capacity with 98 % capacity retention after 1000 cycles at 2.0 C (Figure 5 c). The rate performance was also promoted to maintain the capacity of 1210 mAh g_{sulfur}^{-1} at 10.0 C (Figure 5 d). In Li–SPAN batteries with ether-based electrolyte, LiFSI also contributed to uniform Li plating/stripping by forming the LiF-rich SEI.[42,43] Nevertheless, the performance is not as good as that in carbonate-based electrolyte.

Generally, anions of the Li salt participate in the Li ion solvation sheath. The concentration of Li salts also influences the structure of the solvation sheath.[12a] In concentrated electrolyte, anions provide a greater contribution to the SEI than in dilute electrolytes.[44] The anions decompose preferentially to the solvents.[44] The strategy of using highly concentrated electrolyte is therefore expected to be effective in Li–SPAN batteries with ether-based electrolyte on stabilizing Li anodes.[20a,45b] With 4.0 M LiFSI introduced in DOL/DME,[55] more FSI^- anions participated in SEI formation to enrich the LiF content. The resulting SEI gave more stable and uniform Li plating/stripping, and superior cycle stability of the whole cell was achieved (Figure 5 e).

The anions of the Li salts participate in the Li-ion solvation sheath and contribute to the formation of SEI. Careful selection of Li salts has a positive influence on stable Li-metal anodes. The concentration of Li salts and the matched solvents also influences the overall performance. Therefore, the Li salt constitutes an important component in

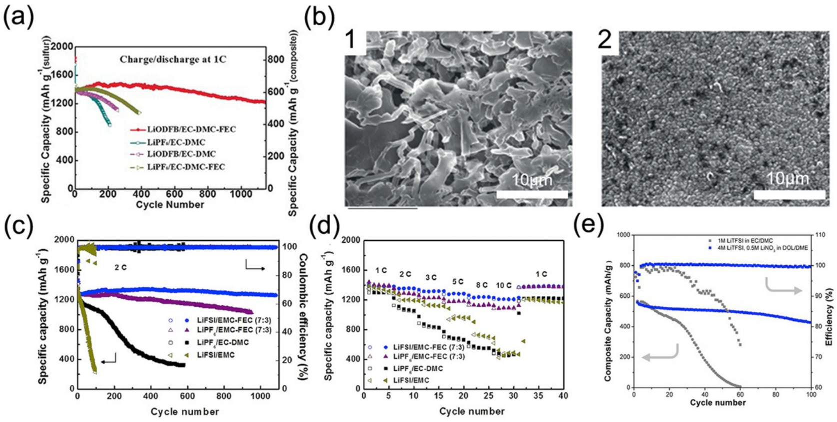

Figure 5. Electrolyte regulation of Li salts in liquid electrolyte. a) Long-term cycling performance of Li–SPAN cells at 1.0 C in LiDFOB/EC-DMC-FEC electrolyte. b) SEM Images of Li electrodes in Li | Li cells at 0.28 mA cm^{-2} after 100 cycles using LiPF$_6$/EC-DMC (b$_1$) and LiDFOB/EC-DMC-FEC electrolytes (b$_2$), respectively.[53] Copyright 2019, Wiley-VCH. c) Cycling performance (0.2 C for the 1st cycle and 2.0 C for the rest ones) and d) rate performance of Li–SPAN cells in 1 M LiFSI/EMC-FEC electrolyte.[40] Copyright 2018, Elsevier. e) Cycling performance of Li–SPAN cells at 100 mA g^{-1} in 4.0 M LiFSI/DOL-DME electrolyte.[55] Copyright 2019, Elsevier.

the electrolyte and considerable attention should be paid to it. Strategies from other battery systems, such as dual-salt and local high-concentration, can also be applied to the Li–SPAN system.

3.4. Additives

Besides solvents and Li salts, additives are recognized as another vital ingredient of electrolyte.[33c] Additives are usually designed to react with Li metal prior to the solvents and Li salts to contribute beneficial components to the SEI. Although additives are only employed in small amounts, usually below 5–10 % by weight or volume percentage, they can bring about obvious changes in electrochemical performances.[12a,13a,33c] Briefly, additives can be categorized into four types according to their compositions: solvent analogues, Li salts, metal ions, and others.[12a] It is also rational to classify additives by their specific functions, which includes SEI-forming additives and Li-ion plating additives.[13a]

As an effective carbonate to induce a stable SEI,[56] FEC can also be used as an additive in electrolytes to enhance the stability and uniformity of the SEI in Li–SPAN batteries. With 5 wt % FEC addition in 1.0 M LiPF$_6$/EC-DEC, Li–SPAN batteries with a high sulfur loading of 3.0 mg$_{sulfur}$ cm^{-2} still exhibited a capacity of 1530 mAh g$_{sulfur}{}^{-1}$ at 0.5 C and the capacity retention of 98.5 % after 100 cycles (Figure 6 a,b).[57] Vinylene carbonate (VC) can construct a stable SEI because its unsaturated structure makes it easily reduced on Li anodes through ring-opening polymerization.[58] Wang et al. designed a duplex component additive with 2 % VC/1 % tris(trimethylsilyl) phosphite (TMSP) in EC/DMC electrolyte (Figure 6 c).[59] The reversible capacity of the Li–SPAN cells reached 1385.6 mAh g$_{sulfur}{}^{-1}$ after 500 cycles at 1.0 C, which exceeded the performances of the cells with TMSP or VC added individually.[59] The combined effect of TMSP and VC

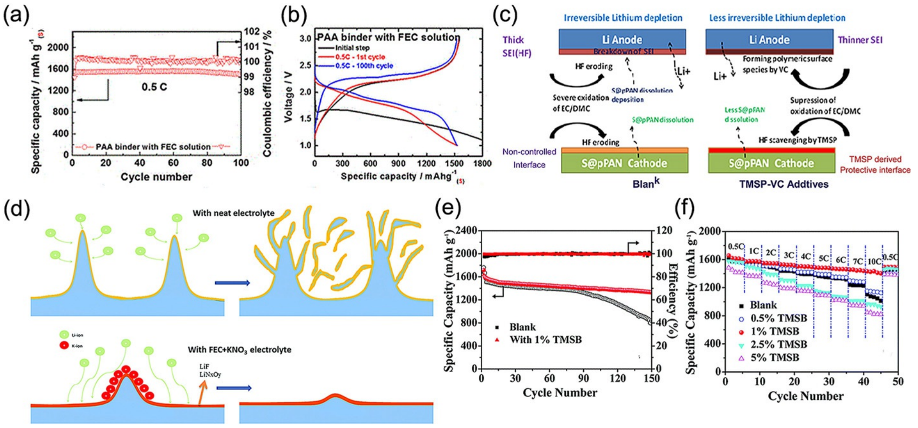

Figure 6. Electrolyte regulation by using additives in liquid electrolyte. a) Cycling performance and b) charge–discharge curves of the Li–SPAN cell with PAA binder and 5 wt % FEC solution after 100 cycles.[57] Copyright 2017, American Chemical Society. c) Schematic illustration of TMSP-VC for improving the electrochemical performance of Li–SPAN cells.[59] Copyright 2018, Elsevier. d) Illustration of the Li-plating process with neat electrolyte and the FEC + KNO$_3$ electrolyte.[62] Copyright 2019, Royal Society of Chemistry. e) Cyclic performance at 0.5 C and f) rate performance of Li–SPAN batteries in the electrolytes with different amounts of TMSB additives.[63] Copyright 2016, Royal Society of Chemistry.

is therefore proposed to be beneficial toward anode protection, but further mechanism investigation is required.

Li salt additives can regulate the Li-ion flux in the SEI by changing the content and the species making up the inorganic components of the SEI.[12a] Lithium nitrate ($LiNO_3$) is a widely used additive to prevent LiPS shuttling and to protect Li anodes from LiPS corrosion in Li–S batteries with traditional C/S composite cathodes.[60] The reduction products of $LiNO_3$ on Li-metal are identified to be Li_xNO_y species. The Li_xNO_y species, together with the oxidation products of LiPSs which is Li_xSO_y, form a stable SEI to protect the Li anode and suppress Li dendrites.[33c,60d,61] The addition of $LiNO_3$ is also effective in Li–SPAN batteries. By adding 0.5 M $LiNO_3$ to the highly concentrated electrolyte of 4.0 M LiFSI in DOL-DME, the solubility of LiPSs in ether solvents was further reduced to clearly enhance the Coulombic efficiency from 95.3 % to 98 %.[55] Recently, Shuai et al. proposed a multifunctional additive of FEC and potassium nitrate (KNO_3) to construct a stable hybrid SEI consisting of LiF and Li_xNO_y in Li–SPAN batteries (Figure 6 d).[62] Potassium ions are adsorbed on the surface of Li anode and accumulate around the tip of Li dendrites to form an electrostatic shield, which suppresses further growth of the dendrites. This effect of FEC, NO_3^-, and K^+ results in a considerable specific capacity of 650 mAh $g_{composite}^{-1}$ and rate performance of 600 mAh $g_{composite}^{-1}$ at 1.0 C.

Another additive, tris(trimethylsilyl)borate (TMSB) was first reported by Wang and co-workers for Li–SPAN batteries and was elucidated to be effective in stabilizing interphases as well as accelerating Li-ion diffusion.[63] With only 1 % TMSB added into FEC/EMC, the Li–SPAN batteries delivered a reversible capacity of 1600 mAh g_{sulfur}^{-1} with capacity retention of 81 % after 150 cycles at 0.5 C (Figure 6 e). Superior rate performance of 1423 mAh g_{sulfur}^{-1} at 10.0 C was also achieved (Figure 6 f). Moreover, Wang and co-workers reported a series phosphorus-rich additives for Li–SPAN batteries, including dimethyl methylphosphonate (DMMP),[64] tris(2,2,2-trifluoroethyl) phosphite (TTFP),[65] triphenyl phosphite (TPPi),[66] triethyl phosphate (TEP),[51] and tris(trimethylsilyl) phosphite (TMSP).[59] These compounds are not only available as flame retardants to improve the safety of Li–SPAN full cells, but also proved to be beneficial for dense-packing Li deposition.

Varying additives is an efficient and feasible strategy to stabilize the Li anode by forming an SEI consisting of the reaction products between the additives and Li metal. For Li–SPAN batteries, much more work has been carried out on additives than on regulating solvents and Li salts. However, the gradual depletion of additives in the long-term cycling is an inevitable consequence that must be addressed especially in light of the low amounts used. Thus, it is highly desired to avoid the rapid consumption of the additives. Also, additives which can contribute to a more sustainable SEI are preferred.

4. Gel Polymer Electrolytes in Li–SPAN Batteries

Gel polymer electrolytes (GPE) consist of an organic aprotic dipolar solvent and polymer matrix, which afford electrochemical properties and mechanical strength, respectively.[25a,49a,67] The preparation methods of GPEs can be classified into physical and chemical methods, while the chemical preparation is also called „in situ synthesis“.[68] The merits of GPEs are considered to include flexible structure, good wettability, high ionic conductivity, and higher safety. Moreover, GPEs can serve as an ex situ coating on Li metal to suppress Li dendrite growth and to reduce interfacial resistance.[69]

Chen et al. reported a series of results on the use of GPE in Li–SPAN batteries.[70] Based on the mixed polymer matrix of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride hexafluoro propylene) (PVDF-HFP), inorganic components, such as mesoporous silica (MPS) (Figure 7 a) or montmorillonite nanoclay (MMT) (Figure 7 b), were added to prolong the mechanical stability. The as-prepared GPE compromising polymer matrix and MPS particles not only facilitated rapid Li-ion transportation, but also prevent the LiPSs generated from shuttling. Consequently, electrochemical performances of the Li–SPAN batteries were improved with the initial capacity of 1648 mAh g_{sulfur}^{-1} and the reversible capacity of 1143 mAh g_{sulfur}^{-1}.[70c]

GPE is considered to be useful at inhibiting Li dendrite growth and has been applied in lithium-ion batteries, lithium–air batteries, and Li–S batteries. Whereas only a few studies

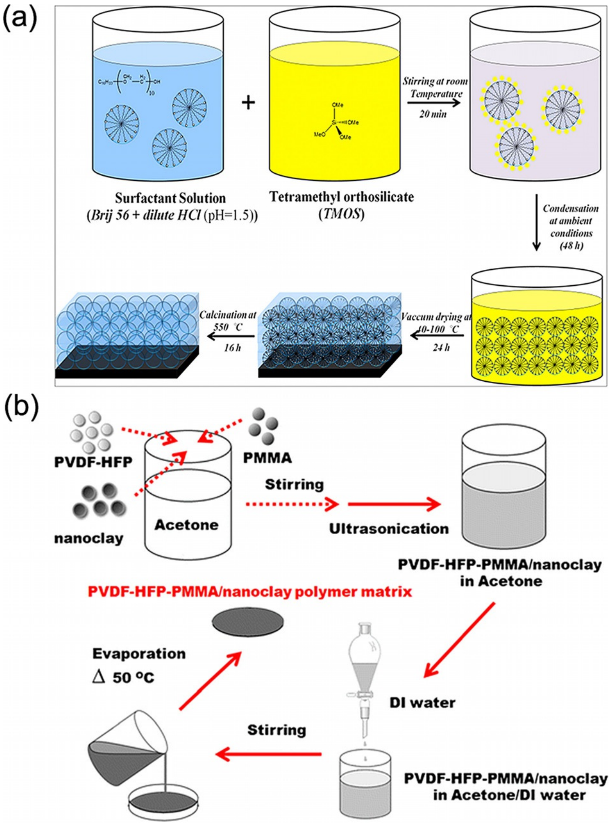

Figure 7. Gel polymer electrolyte regulation in Li–SPAN batteries. a) Schematic of the synthesis of mesoporous silica particles used in GPE.[70c] Copyright 2014, Elsevier. b) Schematics of the preparation of PVDF-HFP/PMMA/MMT polymer matrix as GPE in Li–SPAN batteries. Copyright 2014, Springer.[70b]

on GPE are reported for Li–SPAN batteries, there exists huge potential to expand the application of GPE in this field. In addition, the employment of solid-state electrolytes to construct all/quasi-solid-state Li–SPAN batteries is an emerging direction. $Li_{10}GeP_2S_{12}$ (LGPS), $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, Li_3PS_4, and $Li_7P_3S_{11}$ are typical solid-state-electrolytes for the Li–S system[71] and several pioneering studies have been reported to address the interfacial impedance[72] and enhance the electronic/ionic conductivity.[73] Yet solid-state Li–SPAN batteries have not been reported, leaving this direction unexplored. However, issues of ionic conductivity, interfacial contact, mechanical and chemical stability, and flexibility in battery applications, are still to be sufficiently addressed for solid-state Li–SPAN batteries. Further efforts are needed regarding these issues.

5. Conclusions and Perspective

Li–S batteries constitute an outstanding representative of high-energy-density electrochemical energy storage devices. The Li–SPAN configuration has attracted growing attention considering its cathode advantages of high stability, high Coulombic efficiency, and high capacity. The unstable Li-metal anode emerges as the bottleneck which limits the lifespan and increases safety hazards through uncontrollable Li deposition with dendrite growth and dead Li formation, all of which hinder the application of Li–SPAN batteries. To generate a robust and sustainable SEI on the Li-metal anode is of great significance. Electrolyte regulation is widely accepted as an effective strategy to construct a desirable SEI for Li-anode protection. For liquid electrolytes in Li–SPAN batteries, carbonate solvents afford the best performance and fluorinated carbonates are even better. Ether-based electrolytes possess potential advantages toward stabilizing the Li-metal anode but currently suffer from LiPS dissolution and shuttling. Rational selection of Li salts and additives also promote the battery performances. In addition, solid-state Li–SPAN batteries with gel polymer electrolytes or potential ceramic electrolytes afford possibilities to improve the Li–SPAN system. To rationalize the electrolyte engineering strategy, the structure of the Li-ion solvation sheath and the properties of the as-formed SEI are believed to determine the Li deposition behavior. Therefore, from a fundamental point of view, to rationally design an advantageous solvation sheath of ions (including solvents and anions) and the corresponding SEI is highly desired. Herein we have summarized the current advances in electrolyte engineering for Li–SPAN batteries and attempted to provide understandings on the relationships between the electrolyte structure and the as-formed SEI and to associate the performances with interfacial properties. The strategies summarized herein are also potentially applicable in Li-metal batteries with other cathodes. Yet, more efforts are required in this field to promote our understanding and battery performances.

As to the direction for further developments, more fundamental investigation is needed in the principles for electrolyte design. To this end, in situ and operando characterizations are highly required to afford more information on the structure of SEIs and the behavior of Li plating/stripping. Optimizing the electrolyte system is also required, for which strategies from other battery systems using Li-metal anodes can be investigated. In addition, the influence of the SPAN cathode on the Li-metal anode must be considered. Especially for Li–SPAN batteries with ether-based electrolytes, determining how the dissolved LiPSs affects the Li anode and how to inhibit such deteriorations will enhance the electrochemical performances.

For the further application of Li–SPAN batteries, the current electrochemical evaluation conditions need to be designed in accord with practical demands. High-sulfur-content and high-areal-loading cathodes are essential to achieve high-energy-density batteries. Low electrolyte volume and limited anode excess are also important. High-capacity cathodes result in reduced excess of Li-metal anode and increased Li utilization in each cycle, while low electrolyte volume requires reduced electrolyte consumption with Li-metal anode during cycling. Under such rigorous conditions, the protection of Li-metal anodes becomes even more important. Correspondingly, electrolyte regulation under practical conditions must meet more rigorous requirements, such as lower viscosity, higher ionic conductivity, better wettability as well as improved capability to protect the Li-metal anode through forming a more stable SEI. In addition, the size of the electrodes and other non-active materials, such as current collector and separator, also influence the practical energy density. Therefore, when evaluating or comparing the electrochemical performances, such as specific capacity and cycling stability, these parameters must be given serious consideration. To this end, Li–SPAN pouch cells are recommended to be a more realistic configuration to better address the application issues. Further progress in battery engineering is urgently needed.

Despite the efforts to address the challenges on anode protection in Li–SPAN batteries, investigations on such a complicated system afford strategies and methodologies that may potentially inspire other electrochemical energy-storage systems. The focus on the interfaces between electrode/electrolyte multiphases is highlighted especially for the conversion-type reactions, in which the ion solvation sheath, the desolvation process, and the interphases (if existing) play a determining role in the electrochemical performances. To upgrade the current cathodes, the SPAN configuration implies a direction to integrate conversion-type and intercalation-type reactions within the cathode region to afford both high capacity and high stability, yet this argument requires further study. As for anode design, the cathode influence on the anode behavior needs more attention because parasitic reactions originating from the cathode active materials may significantly destroy anode stability. Therefore, a rational design strategy should integrate issues of all the battery components for not only the Li–SPAN batteries, but also other systems including Li–S and Li-metal batteries. To generally address scale-application of Li–SPAN and other high-energy-density battery systems, the whole industrial chain from material supplement and battery assembly to recycling needs to be comprehensively considered. The application of batteries beyond 400 $\text{Wh}\,\text{kg}^{-1}$ calls for intensive efforts into all these aspects.

In summary, the advances of Li–SPAN batteries strongly depend on the Li-anode performance, yet more attention needs to be paid to Li-anode protection. Facing both challenges and opportunities, the strategy of electrolyte regulation towards stable Li-metal anode is highlighted in Li–SPAN batteries. Considering the recent advances made in this field, it is believed the Li–SPAN system is a high-energy-density rechargeable battery which can make a vital contribution to sustainable energy supply and the global energy economy.

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Conflict of interest

The authors declare no conflict of interest.

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