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Review

Sulfone-based high-voltage electrolytes for high energy density rechargeable lithium batteries: Progress and perspective

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ABSTRACT

Further enhancement in the energy density of rechargeable lithium batteries calls for high-voltage cathode materials and stable anodes, as well as matched high-voltage electrolytes without compromising the overall property of batteries. Sulfone-based electrolytes have aroused great interest in recent years owing to their wide electrochemical window and high safety. However, significant challenges such as the complexity of synthesis, high melting point (typically above room temperature), high viscosity, and their poor compatibility with graphite-based anodes have drastically impeded their practical applications. In this review, recent progress of sulfone solvents in high energy density rechargeable lithium batteries is summarized theoretically and experimentally. More importantly, general improvement methods of sulfone-based electrolytes, such as adding additives and cosolvents, structural modifications of sulfone, superconcentrated salt strategy are briefly discussed. We expect that this review provides inspiration for the future developments of sulfone-based high-voltage electrolytes (SHVEs) and their widespread applications in high specific energy lithium batteries.

1. Introduction

Driven by high energy density, high security and long cycle lifespan, lithium-ion batteries (LIBs) have been extensively applied in the field of portable electronic devices, smart grids, electric transportations and large-scale energy storage systems [1]. For a typical LIB, the theoretical energy density of the battery is dependent on theoretical capacity (C_0) of the active electrode material and thermodynamic equilibrium potential (E) of the cell together [2–4]. Therefore, searching for high-voltage cathode materials with a charging voltage up to 5 V plays a crucial role in improving the energy density of LIBs [5]. But its overall performance is also affected by the electrochemical stability of the electrolyte, an indispensable part of LIBs, and which has been demonstrated have a significant impact on cycling and safety performances, *etc.* [6]. However, the electrolytes used nowadays are mainly traditional carbonate-based electrolytes, which has poor oxidation stability at a high voltage over 4.5 V *vs.* Li/Li^+ [7]. Moreover, the side reactions between cathode materials and electrolytes could be intensified by the catalysis of transition metal ions during charging, which will lead to battery capacity fading, cycling stability degradation and the combustible gas generation with safety concerns [8]. Therefore, how to design suitable high-voltage electrolytes that can be well-matched with advanced electrode materials is a key issue in the development of the next-generation LIBs.

Several effective methods have been explored to design suitable electrolyte systems that well-matched with high-voltage cathodes of LIBs, and one of the most common approaches is to develop new high-voltage solvents. Among various high-voltage solvents, sulfones are often investigated due to their excellent flame resistance and high anodic stability, and these characteristics have been confirmed by experiments and theoretical calculations [9,10]. Obviously, the strong electron-withdrawing sulfonyl group can further increase the oxidation potentials [11]. Besides, sulfone solvents can be used not only in high-voltage LIBs but also in other lithium-based high specific energy cells, such as lithium-metal batteries (LMBs) and lithium-air batteries (LABs). However, the great challenges that severely restrict the applications of sulfone-based electrolytes in the industrial batteries are: the complexity of synthesis, high melting point (typically above room temperature), high viscosity, and disability in forming a stable passive protective film on the graphite-based anodes [12]. Therefore, it will be a great breakthrough in the development of high energy density batteries

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to find suitable optimization methods to conquer the challenges of existing sulfone solvents and design a series of SHVEs with excellent performance.

In this review, we introduce some knowledge about the theoretical basis for the design of SHVEs at first. Then, previous progress of SHVEs in high-voltage LIBs is summarized, with the consideration of the modification strategies of sulfone-based electrolytes to keep up with the electrolyte evolution. These strategies include adding film-forming additives, adding cosolvents, structural modification of sulfones, and superconcentrated salt electrolytes. Thirdly, applications of SHVEs in other high specific energy lithium batteries like LMBs and LABs are also presented. Finally, we briefly discussed the limitations and prospects of ongoing SHVE.

2. Theoretical basis for the design of SHVEs

Compared with the electrochemical methods, the theoretical calculation methods can not only explain the experimental results, but also predict some chemical properties of functional molecules, and provide reliable guidance for research work.

For one thing, the energy level of the frontier molecular orbit largely reflects the physicochemical properties of the molecules, especially for the redox stability. According to the frontier orbital theory [13], the highest occupied molecular orbital (HOMO) corresponds to the electron donor, and the lowest unoccupied molecular orbital (LUMO) corresponds to the electron acceptor. Generally, the higher the LUMO energy of a molecule, the better its resistance to reduction, and the lower the HOMO energy of a molecule, the better its resistance to oxidation. When the HOMO energy of the cathode material is lower than the HOMO energy of the electrolyte, it will cause electrons to transfer from the electrolyte to the cathode and eventually result in the oxidation of the electrolyte [13,14]. Therefore, for a high-voltage electrolyte, the lower the HOMO energy of the electrolyte components is, the higher the electrochemical potential of the cathode is. The correlation between HOMO energy levels and oxidation potentials can provide useful guidance for computational screening of electrolytes with high oxidation potentials. For example, Jiang *et al.* [15] computed the electrochemical windows of five commonly used sulfone solvents by different calculation methods combined with various solvation models. The result showed that Second-Order Moller-Plesset Perturbation Theory (MP2) method combined with the polarizable continuum model (PCM) can well repeat the experimentally tested oxidation potential of the sulfone solvents, and further demonstrated the wide electrochemical window of sulfone-based electrolytes is since sulfone groups can help reduce the HOMO energy level of electrolyte systems (Figs. 1a and b).

For another thing, recent molecular dynamics simulations displayed that anions and surrounding solvents can strongly affect the oxidation potential and electrochemical stability of the sulfone-based electrolytes [16,17]. The research found that anions and extra solvent molecules (cosolvents) could participate in the oxidation and decomposition reactions, reducing the calculated oxidation potentials of sulfones, such as sulfolane (SL), trimethylene sulfone (TriMS) and 1-methyltrimethylene sulfone (MTS) clusters [17]. Therefore, the design of SHVEs must consider the molecular clusters environment around the sulfone solvents to ensure that its oxidation stability will not be reduced by the additional additives and cosolvents. Importantly, it is known that H transfer reactions during the oxidation reactions generate corrosive HF, which can poison cathode materials and impair the performance of the battery, and can be detected in all investigated electrolytes composed of carbonate solvents and a fluorinated lithium salt. However, simulation results showed that HF would not be produced when the sulfone solvents and anion clusters were oxidized together [7,17], so sulfone could improve the cycling performance of the batteries, which also provided a theoretical basis for the design of the SHVEs.

SHVEs usually have an oxidation decomposition potential of more than 5 V *vs.* Li/Li^+, which can meet the requirements of high-voltage applications. However, most sulfone solvents have a high melting temperature due to high molecular symmetry, so except for TMS-based electrolytes, most of SHVEs could not be prepared by a single sulfone and had a poor low-temperature performance. Fortunately, it was found that modifications that breaking the molecular symmetry of sulfones could reduce their melting point. In addition, we must consider the low ion conductivity and high viscosity of SHVEs. Ionic conductivity is determined by both viscosity and dielectric constant of solvent molecules. The dielectric constant determines the dissociation degree of lithium ions, and the viscosity determines the ion migration rate. Generally, the dielectric constant of the sulfone solvents is bigger than 10, especially the dielectric constant of TMS is 44 [18], which facilitates the dissociation of the lithium salts. Therefore, the main factor limiting ionic conductivity is viscosity. Consequently, for the optimization of SHVE's physical and electrochemical properties, we mainly consider reducing its viscosity and melting point.

It is foreseeable that the future central researches of electrolyte will focus on the combination of theoretical calculations and electrochemical methods to find appropriate quantitative parameters, so as to design and optimize the excellent SHVEs for commercially available high energy density rechargeable lithium

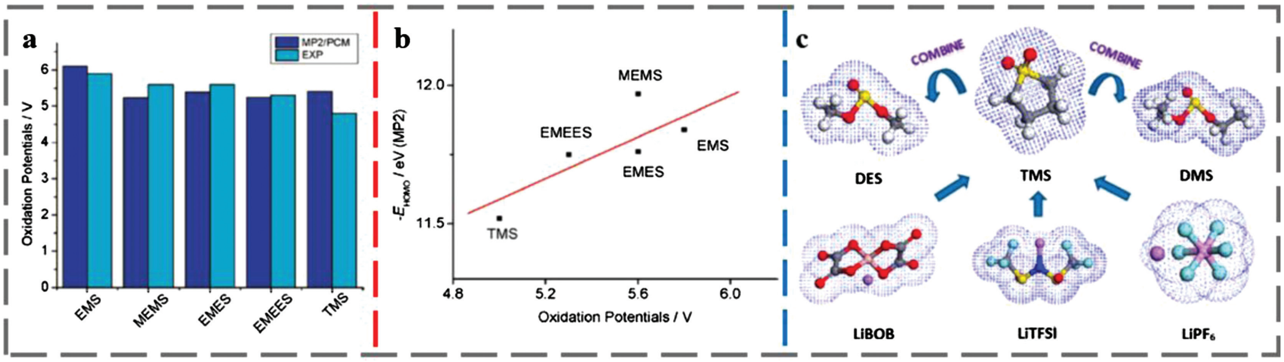

Fig. 1. (a) Oxidation potentials calculated at the MP2/6-31+G(d, p)/PCM model and compared with the experimental contrast. (b) Correlation between the HOMO energies and the experimental oxidation potentials. Copied with permission [15]. Copyright 2011, American Chemical Society. (c) Electron cloud structures of lithium salts and sulfone solvents: it reflects the affinity between Li^+ and the oxygen atom of different solvent molecules. Copied with permission [19]. Copyright 2015, American Chemical Society.

batteries. Our previous work [19] combined the theoretical quantum chemistry (QC) calculation *via* density functional theory (DFT) and experimental tests to research the physical and electrochemical performance of several sulfone/cosolvent systems. The successful research had provided a more efficient and reliable way to explore and design SHVEs, especially for solvent screening and analysis of anion-cation interactions (Fig. 1c).

3. Applications and optimization methods of SHVEs in high-voltage LIBs

3.1. Applications of SHVEs in LIBs

The growing demand for electric vehicles and mass energy storage systems has put forward higher requirements for the energy density of LIBs, which has stimulated the development of LIBs towards high voltage. Although excellent active electrode materials (especially high-voltage cathode materials) have been developed, the application of LIBs is still limited by the severe oxidation decomposition of the traditional carbonate-based electrolytes under high voltage. Alternatively, the commonly used sulfone-based electrolytes exhibit high anodic stability (> 6.0 V), high dielectric constant (43.4), high flash point (166 °C) and good compatibility with other cosolvents [20]. For example, the use of 2% SL an additive for the 1.0 mol/L lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v) contributed to improve the oxidation potential of the initial carbonate-based electrolyte from 4.25 V to 5.0 V, thus effectively suppressing the subsequent decomposition of the solvent and dissolution of transition metal ions on the cathode [20]. In addition, the TMS-containing (40 wt%) electrolytes based on an ionic liquid (*N*-butyl-methyl piperidiniumbis (trifluoro-methyl-sulfonyl) imide, $PP_{14}TFSI$) exhibited higher lithium salts solubility, ionic conductivity ($\sim 10^{-3}$ S/cm), and better electrode compatibility than the pure ionic liquid electrolyte. And the discharge capacity of the battery constructed with $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode was over 230 mAh/g cycled in the TMS-$PP_{14}TFSI$ mixed electrolyte after 30 circles, which is more stable than that of 215.2 mAh/g cycled in the conventional electrolyte composed of 1 mol/L $LiPF_6$/EC/DMC under the same situations [21]. Moreover, except for the sulfone-containing electrolyte (the molecular weight is usually < 50%) above-mentioned, sulfone solvents can also be used as the main solvent of the electrolyte in high-voltage LIBs to form SHVEs (the molecular weight is usually > 50%) with high oxidation stability and security, it is also what this review will focus on. As we mentioned above, even though sulfone-based electrolytes are extensively researched owing to their excellent oxidation stability, their practical application is also restricted in some unfavorable factors, especially its high viscosity, high melting point, inferior wettability with the membrane and the electrode materials, and inability in protecting graphite electrode. Accordingly, it is fairly urgent to find some effective methods to solve these problems.

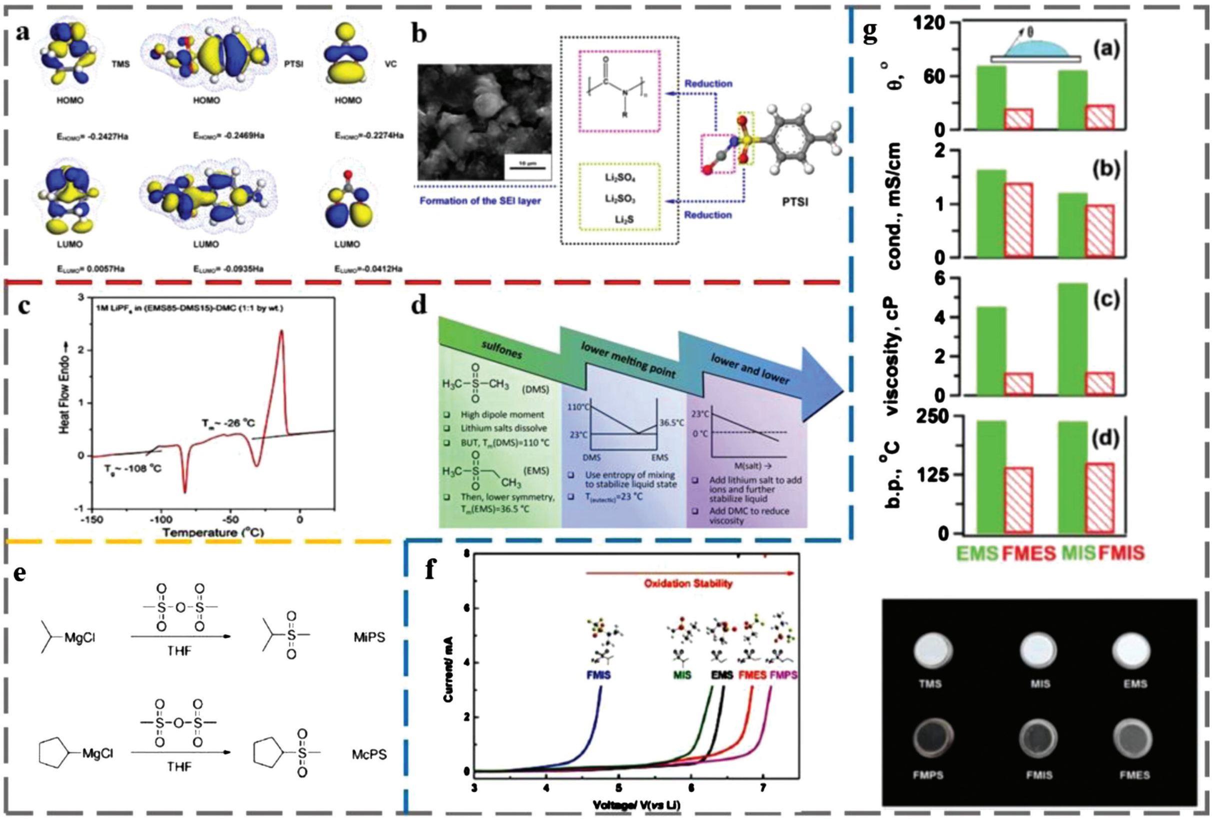

Fig. 2. The role of film-forming additives: (a) Frontier molecular orbitals and energies of PTSI, TMS and VC. (b) The possible mechanism and intermediate products of an SEI layer formed by PTSI on the graphite anode. Copied with permission [22]. Copyright 2012, Elsevier. The role of cosolvents: (c) DSC thermogram analysis: used to investigate the low temperature stability of the mixed electrolyte. (d) Schematic presentation of the design of composite sulfone-carbonate ternary electrolyte based on changes of their melting points. Copied with permission [9]. Copyrights 2015, Elsevier. Alkyl substituted sulfone electrolytes: (e) The procedure and structure of aliphatic sulfones (MiPS and MaPS). Copied with permission [26]. Copyrights 2016, Wiley VCH. Fluorinated sulfone electrolytes: (f) The oxidation stability of the fluorinated sulfones and their nonfluorinated counterparts tested by linear sweep voltammograms. (g) Physical characteristics of homologous fluorinated and non-fluorinated sulfones. Copied with permission [27]. Copyrights 2017, Royal Society of Chemistry.

3.2. Optimizations of SHVEs

3.2.1. Additives for film-forming

The first major challenge of SHVEs is poor compatibility with graphite anodes because a good solid electrolyte interface (SEI) layer cannot be formed on graphite anodes for the pure sulfone-based electrolytes. The SEI layer can prevent the exfoliation of the graphite layer resulted from solvent intercalation and avoid the continuous decomposition of electrolyte caused by excessive irreversible reduction. To tackle these challenges, plenty of researches proved that introducing an appropriate trace substance (< 5 wt% or 5 vol%, namely SEI-forming additives) into the electrolyte is one of the most effective and economical methods for improving the performance of SHVEs on the graphite anodes.

Wu *et al.* [22] investigated the effects of isocyanate as a film-forming additive of 1 mol/L bis(trifluoromethane sulfonyl) imide (LiTFSI)-TMS electrolyte on lithium/mesocarbon microbeads (Li/MCMB) battery system. The results showed that the mixed electrolytes with 5% *p*-toluenesulfonyl isocyanate (PTSI) had ionic conductivities nearly above 10^{-3} S/cm and excellent anodic stability in excess of 5 V *vs.* Li/Li$^+$. Furthermore, the reversible capacity of the battery kept at 360 mAh/g after 50 cycles with the help of PTSI. All these enhanced physicochemical properties and battery performance benefited from the presence of -NCO functional group on the PTSI, which could reduce the melting point of the electrolyte, and improve its flash points, boiling points, electrochemical window, and wettability. Most importantly, the energy level of PTSI shown in the Fig. 2a clearly indicated that PTSI can redox before TMS and VC to form a protective film on the MCMB electrode and stabilize the electrochemical performance of the electrolyte, thereby achieving satisfactory cell performance. The possible film-forming mechanism and a multi-layered structure of SEI film were proposed in the Fig. 2b, a sulfur-containing inorganic layer (Li_2SO_4, Li_2SO_3, Li_2S) was formed by the reduction of sulfonyl groups, and the reduction of -NCO functional groups was responsible for the formation of a polymer layer.

Watanabe and coworkers introduced vinylene carbonate (VC) as a film-forming additive into the electrolyte of 1 mol/L $LiBF_4$-TMS /EA (1:1, v/v), and the mixed electrolyte could remarkably improve the coulombic efficiency and capacity retention of the Li/$LiCoO_2$ [23]. They found that the interface resistance between electrode and electrolyte without VC was in the range of 50 and 100 Ω after the first cycle, and further climbed in the latter cycles. In contrast, the addition of VC could promote the formation of stable SEI film on the cathode during the first cycle, thereby holding the resistance in the circulation at a low level of 20 Ω. Similarly, adding VC to the electrolyte had the same improvement effect on the 5 V battery system with Li/$LiNi_{0.5}Mn_{1.5}O_4$ as the electrode.

3.2.2. Cosolvents for better ion mobility and wettability

Apart from the progress made in the addition of film-forming additives to protect the graphite electrodes, introducing cosolvents to pure sulfone electrolyte is another economical and convenient way to improve its physical and chemical properties without changing the main components of the electrolytes. For example, the strategy of intermixing an appropriate amount ratio of low viscosity cosolvent and high dielectric constant cyclic carbonate to decrease the viscosity of the traditional carbonate-based electrolyte systems can be used as a reference for viscosity reduction of sulfone-based electrolytes.

Angell *et al.* [24] introduced DMC into 1 mol/L $LiPF_6$/EMS, and the oxidation stability (> 5.9 V *vs.* Li$^+$/Li) of the intermixed EMS-based electrolyte was the same as the previously reported EMS itself. And also, the electrolyte remarkably enhanced the performance of high-voltage $LiNi_{0.5}M_{1.5}O_4$ (LNMO) cathode, that is, the coulombic efficiency reached 99% after 30 cycles and capacity retention reached 97% after 100 cycles. At the same time, it also had good compatibility with spinel lithium titanate $Li_4Ti_5O_{12}$ (LTO) anode. Additionally, they also developed a three-component system (1 mol/L $LiPF_6$ in (EMS85-DMS15)-DMC (1:1, w/w) with good ionic solution, improved ionic conductivity, oxidation resistance, and ideal low-temperature stability. The result suggested that the melting point of the mixture composed of 85 mol% ethyl methyl sulfone (EMS; T_m = 36.5 °C) and 15 mol% dimethyl sulfone (DMS; T_m = 110 °C) dropped to 23 °C may be due to their co-crystallization behavior (Figs. 2c and d). Besides, other improvements of the electrolyte, such as low viscosity and further increases stability of the liquid phase, benefited from DMC as less-viscous cosolvents. What is more, Abouimrane *et al.* [25] applied a binary system that was blended tetramethyl sulfone (TMS) with ethyl methyl carbonate (EMC) (1:1, v/v) as a cosolvent to construct LTO||LNMO cell. The cell had outstanding electrochemical stability and cycle stability, exhibiting a high capacity retention rate up to 88.6% over 1000 cycles at 2 C rate. They also found that the improved properties of the battery were owing to the decrease of viscosity and increase of both the ionic conductivity and wettability of the electrolyte by EMC.

Introducing less-viscous cosolvent to improve ion mobility and separator wettability of SHVEs is undoubtedly effective and convenient, but low viscosity is usually accompanied by low boiling point, so much attention should be paid to the problem of reduced security that is simultaneously introduced by the low boiling point of the cosolvent.

3.2.3. Structural modification of sulfones for a better intrinsic comprehensive performance

Changing the molecular structure of sulfone solvents themselves is regarded as another important approach to enhance the characteristics of SHVEs in the high-voltage LIBs, with the introduction of a molecular group like $—CH(CH_2)_4$ [26], $—CF_3$ [27], $—OCH_3$ [12], $—CH(CH_3)_2$, and so on. Guided by the effects of fluorinated substituted on the carbonate-based electrolyte. Zhang *et al.* [27] synthesized a new class of trifluoromethyl ($—CF_3$) sulfone and systematically studied their physical and electrochemical properties for the preparation of high-voltage electrolytes. These new sulfones were proved to have an enhanced separator wettability, oxidation ability (Fig. 2f) and security compared with their non-fluorinated counterparts. Also, the viscosity of fluorinated sulfones was relatively low in general (Fig. 2g). More importantly, a unique feature of fluorinated solvents was that the introduction of fluorine atoms into sulfones could aid to passivate the graphite anode. And the cycling tests showed that high-voltage NMC532/graphite cells constructed with fluorinated sulfone electrolytes have a perfect capacity retention rate of up to 80% after 500 cycles at 4.6 V.

On the other hand, alkyl substituent has a distinctive influence on the melting point and oxidation stability of the sulfone solvents. The introduction of the cyclohexyl group and cyclopentyl group to the EMS and DMS (Fig. 2e) decreased their melting point from 36.5 °C to 9 °C and from 110 °C to 19 °C respectively [26], thus broadening the operating temperature range of sulfone solvents on the low-temperature side. A series of methoxy substitutions of EMS also achieved a similar effect in lowering the melting point [12]. Unfortunately, the above-mentioned alkyl substitutions of sulfone also reduced its original ionic conductivity and oxidation potential to some extent. Nonetheless, the immature alkyl substitution technology of sulfone still provides us with more choices to improve the performance of sulfone solvent in high-voltage electrolytes.

3.2.4. Superconcentrated salt electrolytes for peculiar solvation and interface structure

All the above optimization methods are based on diluted electrolytes that their concentration of lithium salt is optimized at around 1 mol/L to obtain the maximum ionic conductivity. Recently, Xu *et al.* [28] found a new strategy to use highly concentrated (3.25 mol/L) lithium salt (lithium bis(fluorosulfonyl) imide (LiFSI)) dissolved in the SL without any additives and cosolvents to obtain extraordinary electrolyte. As shown in Fig. 3, both experimental measurements and quantization calculations show the electrolyte system had the advantage of fast electrode reactions, non-flammability and stability in a wide operating temperature range. QC calculations and molecular dynamics simulations predicted that in the high concentrated SL-based electrolytes, all SL molecules were coordinated by Li^+, and no H-transfer-reaction, which strengthened the Mn-O bonds to inhibit the transition metal dissolution and increase the oxidation stability of electrolyte, leading to polymerizable of SL instead of gaseous products. Simultaneously, the electrolyte was able to form stable cathode electrolyte interphase (CEI) on the high-voltage cathode interface due to the synergetic effects of SL and super-concentrated salt, thereby supporting efficient and stable cycling performance of high-voltage cathodes. Furthermore, a stable LiF-rich and Li_2O-rich SEI film was generated in the early cycles, which could effectively suppress continuous side-effects and graphite exfoliation, thus enabling outperformed high reversible cyclic stability and ~70% capacity retention after 1000 cycles for full lithium-ion battery with MCMB||LMNO at 4.85 V. Therefore, the superconcentrated salt strategy on the sulfone-based electrolytes provide a bright future for the design and optimization of SHVEs.

4. Applications of SHVEs in other high specific energy lithium batteries

4.1. Applications of SHVEs in LMBs

The exploitation of the cathodes with high-voltage to maximize the operating voltage of the battery and the development of the anodes with high specific capacities has attracted great attention, with the purpose of increasing the energy density of the battery. Li metal has become one of the most ideal anodes over the past few decades due to its high theoretical specific capacity (3862 mAh/g) accompanied by the most negative standard electrochemical potentials (−3.040 V) [29,30]. Nevertheless, the uncontrollable overwhelming parasitic reactions between Li metal and electrolyte have always been a bottleneck problem restricting its development. The high porosity and dendritic morphology of Li deposition resulted from the parasitic reactions would lead to a low utilization rate of Li and limited cycle life of the LMBs, even dendrite Li can easily penetrate through the membrane and impose a serious threat to security [31]. In recent years researchers devoted great efforts to overcome these challenges mainly bent on the modification of Li metal anodes and SEI film, optimization of electrolyte. For instance, Wu's group [32] developed a thin and porous LiF-rich layer on the Li metal surface by the *in-situ* reaction of ammonium hydrogen difluoride (NH_4HF_2) and Li metal, thus significantly reduce the interface impedance. Zhang *et al.* [33] introduced a novel electrolyte additive (a mixed fiber microporous membrane) effectively inhibiting the formation and growth of Li dendrites, and achieved improving cycling performance, the security of the cells. Besides, the incorporation of the solid electrolyte and a small amount of liquid electrolyte was prepared to provide excellent interfacial stability in LMBs [34]. The trimethylene sulfate was developed as an electrolyte additive to regulate Li deposition to generate homogeneity and Li_2O-rich of SEI [35]. Beyond that, employing SHVEs to stabilize Li metal for high energy density batteries was once considered as a promising strategy. Unfortunately, the high oxidizability of sulfur (S_6^+) in sulfone and the high reducibility of Li metal will lead to irreversible side reactions between sulfone solvents and Li anodes, thereby destroying the stable and efficient circulation of Li anodes in the sulfone-based electrolyte.

Recently, Zhang and coworkers [36] developed sulfone-based electrolytes that can be applied to high-voltage (4.9 V) LMBs and detected a high cycling performance with 300 cycles. The number of free solvent molecules in the electrolyte was decreased due to the increased salt-to-solvent molar ratio, which inhibited the harmful interactions between the electrolyte and Li metal (Fig. 4a). They demonstrated that a high coulomb efficiency of Li metal over 98% was achieved in the highly concentrated sulfone-based electrolyte (HCSE) formed by LiFSI dissolved in TMS. Furthermore, localized highly concentrated sulfone-based electrolyte (LHCSE)

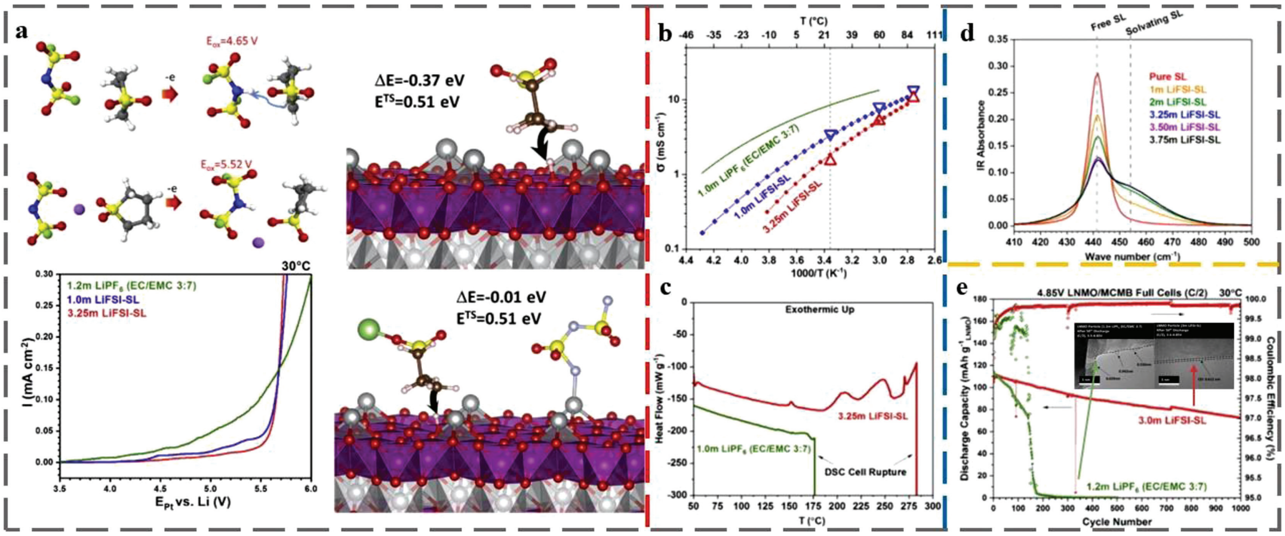

Fig. 3. (a) Prediction the oxidation stability of SL (FSI^-) by QC calculations. (b) Comparision of temperature-dependent conductivities and (c) DSC heat flow measurement between LiFSI / SL and reference carbonate electrolyte. (d) FTIR measurements of SL-FSI at different salt concentrations to study the solvation behavior of Li^+. (e) Galvanostatic cycling capacity and CEI structural changes during cycling were characterized with cryo-(S)TEM for carbonate electrolyte and 3 mol/L LiFSI-SL. Copied with permission [28]. Copyright 2018, Elsevier.

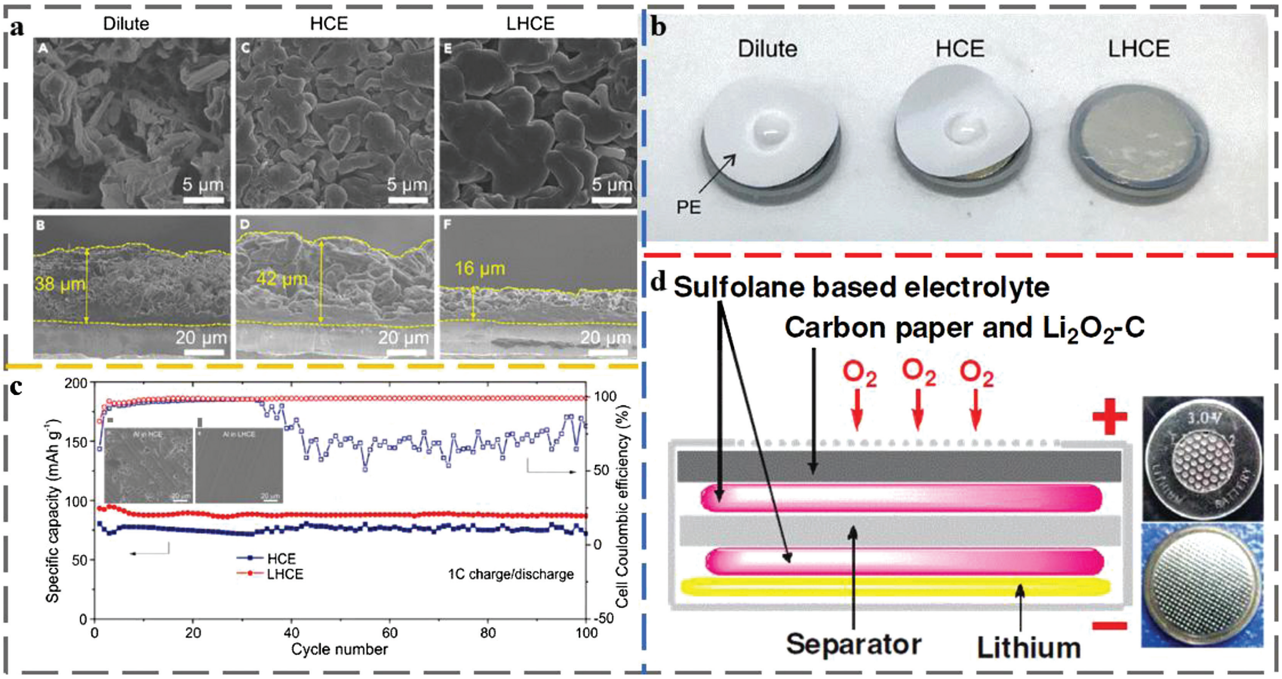

Fig. 4. SHVEs for LMB: (a) SEM images of Li deposition morphologies in different sulfone-based electrolytes. (b) Wettability tests of sulfone-based electrolytes on polyethylene (PE) separators. (c) Cycling performance tests of Li||LNMO cells constructed with HCE and the LHCE, and SEM images inside are the morphologies of Al foils after testing. Copied with permission [36]. Copyright 2018, Elsevier. SHVEs for LAB: (d) Schematic and cycle performance of a LAB using a LiTFSI-SL electrolyte. Copied with permission [45]. Copyright 2014, Wiley VCH.

with an extra non-solvating fluorinated ether (TTE) additive showed reduced viscosity, improved separator wettability (Fig. 4b), and also effectively improved the coulombic efficiency (98.8%) of LMBs (Fig. 4c) and corrosion resistance ability of cathode current collector Al.

4.2. Applications of SHVEs in LABs

In recent years, the rechargeable LABs have attracted unprecedented attention in virtue of their extremely high theoretical energy density of 11,140 Wh/kg, which is 8 times higher than that of current state-of-art LIBs excluding the oxygen quality, and LABs have the potential to extend the driving mileage of electric vehicles to 500 km between charges [37,38]. However, early investigations of nonaqueous LABs displayed an insufficient cycle life less than 100 cycles due to the severe irreversible decomposition of carbonate-based and ether-based electrolytes at the cathode, and there were almost no reversible formation/decomposition of lithium peroxide (Li_2O_2) in the cycle [39–41].

Sulfone-based electrolytes are once again considered as promising electrolyte candidates for LABs owing to its superior oxidative stability, and recent studies have shown that TMS has relatively high electrochemical and chemical stability against O_2 radicals [42–45]. Zhang *et al.* [46] employed dimethyl sulfoxide (DMSO) as an electrolyte solvent for rechargeable Li-O_2 batteries (Fig. 4d). The electrolyte had enough electrochemical stability with a wide electrochemical window from 2.0 V to 4.5 V *vs.* Li^+/Li, and the existence of Li_2O_2 further confirmed the feasibility of DMSO for Li-O_2 batteries. Although the formation of Li_2O_2 was still unable in a long period and accompanied by many undesired by-products, inspired by the encouraging results obtained above, they conducted a study on TMS with similar superior properties to DMSO. Fortunately, there were few side reactions, and the formation of Li_2O_2 was a predominant and stable discharge product in Li-O_2 batteries constructed with a TMS-based electrolyte [43]. Furthermore, sulfone-based electrolyte composed of 1 mol/L LiTFSI in TMS had been used to construct LABs and exhibited a high energy efficiency of 78.32%, accompanied by 18–525 cycles at a current density varying from 1.00 mA/cm^2 to 0.05 mA/cm^2 [44]. Although severe capacity fading is still a major problem of the LABs, sulfone-based electrolytes are expected to promote the development of LABs with green, sustainable and high performance.

5. Outlooks

Significant progress demonstrates the great promise of sulfone solvents as high-voltage electrolyte components (namely SHVEs) in high energy density rechargeable lithium batteries (such as LIBs, LMBs, LABs) due to their high anodic stability and incombustibility. However, serious capacity decay and poor rate performance of batteries are caused by high viscosity, poor wettability and difficulty in forming stable SEI film on the graphite anode of the current SHVEs. In response to these limitations, four feasible

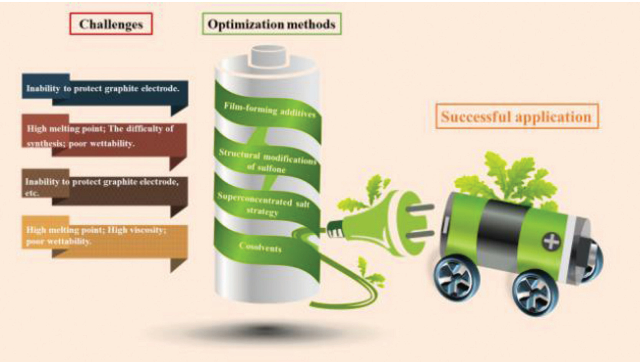

Fig. 5. Future perspective of sulfone-based high-voltage.

optimization methods of SHVEs for current investigations are discussed, as shown in Fig. 5.

(i) Film-forming additives are used to enable stability of graphite anode/SHVE interface.
(ii) Low viscosity cosolvents are used to decrease the viscosity and increase the ionic conductivity of SHVEs. Introducing a small amount of film-forming additive as a sacrificial component or suitable cosolvent that makes a synergistic effect with the electrolyte into conventional electrolytes can effectively improve the physicochemical and electrochemical characteristics of the cells.
(iii) Structural modifications aim to obtain more sulfone solvents with inherently excellent properties. Especially for fluorination of sulfones is expected to improve all of the existing shortcomings of SHVEs.
(iv) The superconcentrated salt strategy can produce peculiar solvation structure in the SHVEs with a high salt concentration, which is conducive to the formation of SEI on the graphite surface, while major problems such as high viscosity, and poor wettability limit its applications.

So far, there is still a lack of an ideal way to completely tackle all the existing challenges of SHVEs, so the attempt to combine two or more advantages based on the aforementioned ways will be a great concern to improve the performance of SHVEs, and intensively and systematically researches are still be needed.

Furthermore, lots of work on electrolytes have shown that the relationship between frontier molecular orbital energy of the molecules and its redox ability is very helpful for evaluating and finding new solvents and additives, meanwhile, theoretical calculations can simulate molecular solvation behavior and electrode/electrolyte interface reaction mechanism, thus providing a convenient strategy for the design and research of SHVEs. Consequently, the combination of quantum theoretical calculations and experiments is expected to be an efficient way to explore suitable SHVEs for practical applications in high energy density rechargeable lithium batteries. Overall, it is believed that SHVEs are expected to be practically used in high energy density rechargeable lithium batteries if their difficulties of high viscosity and poor compatibility with the graphite electrode can be surmounted through joint efforts.

Declaration of competing interest

The authors report no declarations of interest.

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