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Recent Progress of Electrolyte Design for Lithium Metal Batteries

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Lithium metal batteries (LMBs) bring a bright future for the industrialization with higher voltage and energy density than conventional lithium ion batteries (LIBs) as lithium metal offers an ultra-high specific capacity and the lowest electrochemical potential. However, they tend to confront unstable interface with electrolytes, uncontrollable dendrite growth and notorious safety concerns, seriously blocking the practical application of lithium metal anodes. Electrolyte is always considered as the

most critical factor, directly affecting the overall battery behavior. In this case, the rearrangement of active components or designing novel electrolytes become indispensable approaches and tremendous efforts are required to seek for positive solutions. Herein, we provide recent advancements in prevailing liquid, solid and gel electrolytes from the perspective of their potential application in LMBs. The key scientific issues related to enhanced performance have also been highlighted.

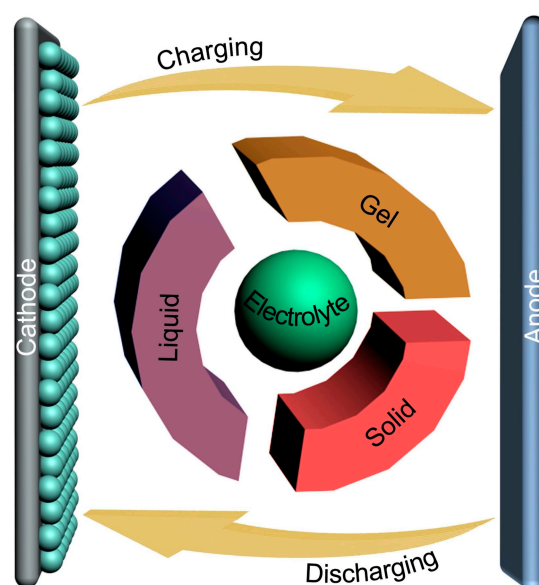
1. Introduction

Electrochemical energy storage is a driving force for the rapid development of modern society, which gradually revolutionizes the traffic and lifestyle from many aspects. Despite the successful application of lithium ion battery as a competitive energy storage system to power portable devices and even electric vehicles, its corresponding volumetric and gravimetric energy densities have almost reached the limit, failing to satisfy the ever-increasing demands. Advanced anode materials are urgently desired for pursuing evolving electrical equipment.

Lithium metal is considered as the “Holy Grail” and displays incomparable merits versus other anode materials, promoting the enthusiastic pursuit for lithium-sulfur and lithium-air batteries.^[1] It exerts an ultra-high specific capacity (3860 mA h g⁻¹) and the lowest electric potential (−3.040 V vs the standard hydrogen electrode).^[2] Accordingly, reviving the exploration of rechargeable lithium metal batteries (LMBs) is the key precondition to achieve high energy density.

Unfortunately, inherent tough issues of poor safety and cycling performance, usually impede the application of lithium metal, which mainly stems from its electrochemically unstable interface and easily deformed structure, especially in conven-

tional organic electrolyte systems. Merely relying on composite electrodes or novel current collectors, these problems may still challenge the ultimate application. Under this background, researchers inevitably turn their attention to rearranging active components or designing novel electrolytes to further push forward the progress. There are three main types of routine electrolytes for rechargeable LMBs, including solid, liquid and gel species (Scheme 1). Liquid electrolytes usually provide fast lithium ion transport and rate performance due to their free fluidity while solid electrolytes mainly focus on the excellent mechanical strength and safety behaviors. Gel electrolytes exhibit moderate performance from both liquid and solid counterparts. In this paper, we are devoted to provide remarks of recent studies on electrolyte modifications and designs, aiming to promote electrochemical performance and probably meet the expectation of LMBs.



Scheme 1. Schematic of electrolyte types in lithium metal batteries.

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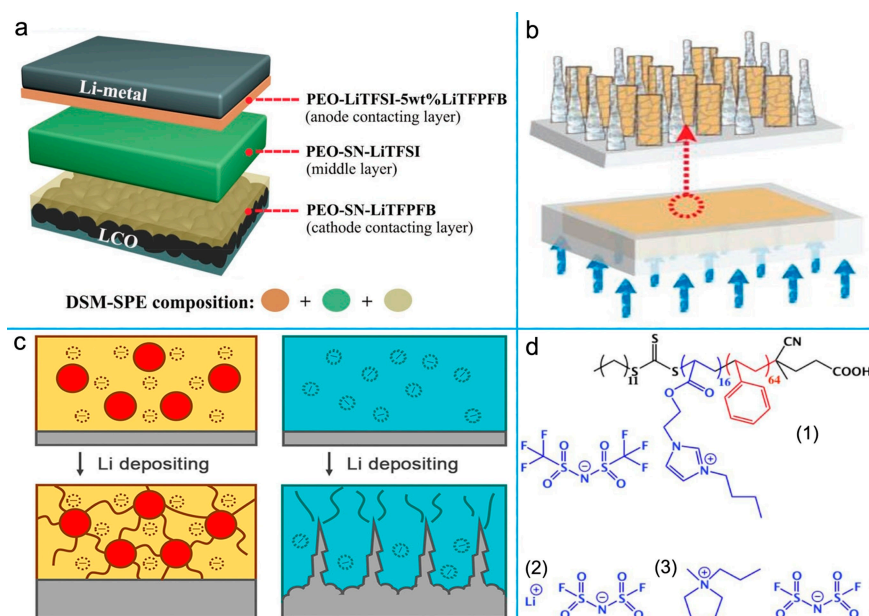
2. Solid Electrolytes

Solid electrolytes usually possess unique merits in contrast to liquid counterparts, including superior mechanical property and suppressed flammability. Among these species, we mainly place emphasis on extensively studied solid polymer electrolytes (SPEs) since they usually deliver low density, excellent flexibility and interface adhesion to electrodes, as well as the simple synthetic methods and battery assembly process over inorganic solid electrolytes (ISEs). SPEs generally refer to the system that lithium salts dissolve in polymer block with relative high molecular weight. Segmental motions of polymer chains ensure the smooth transmission of lithium ions. As the holy candidate, poly(ethylene oxide)-contained SPEs received comprehensive attention in the past few decades, mainly because of their low glass transition temperature and the advantage in solvating alkaline salts. However, long-standing bottlenecks still maintain, such as inadequate ionic conductivity, poor oxidative stability and undesired side reactions with lithium anode, deteriorating its large-scale commercialization. Recently, Cui's group demonstrated a multilayer structure of PEO-based electrolyte to tackle these tough issues.^[3] They chose succinonitrile (SN) as the effective plasticizer and combined it with PEO polymer, delivering favorable ionic conductivity by destructing the internal crystallization. To pursue desirable behavior of LMBs, wide potential window and excellent reductive stability of SPEs are generally cited as key factors. However, SPE obtained by simply mixing PEO and SN may suffer from unamiable anode/cathode interface properties.

In this situation, the group presented a sandwich-like electrolyte composed of PEO skeleton, SN and functional lithium salts (Scheme 2a). Amorphous middle layer with a thickness of 40 μm consisted of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt, PEO and SN. TFSI⁻ anions with dispersed negative charge facilitated salt dissociation and ionic migration along with bereft crystallinity of PEO. Interestingly, bilateral layers via in-situ polymerization could achieve reinforced interface adhesion, while the ion transport was probably insufficient. Therefore, controlling their thicknesses in allowable ranges is the requirement.

Lithium trifluoro(perfluoro-tert-butyloxy) borate (LiTFPFB) with large fluoroalkoxyl anion displayed low LUMO energy and tended to decompose on lithium anode, leading to ameliorative interface stability. Besides, interactions between Li⁺ ions and PEO affected the electron cloud distribution of ether oxygen groups, facilitating lower HOMO energy with improved oxidation resistance. It was noted that poor mobility of bulky TFPFB⁻ anions also contributed to high t_{Li^+} . This work provides a new perspective in designing functional SPEs compatible with both electrodes.

Employing protective layers usually result in limited effectiveness and accelerated dendrite growth along the crack edge once they break down during cycling. Therefore, fundamentally changing the ionic transmission mode is the ultimate goal to pursue. Tang et al. recently reported a two-dimensional vertically aligned vermiculite sheets (VAVS) as the versatile filler of PEO-based SPE.^[4] Due to the layered structure of magnesium aluminosilicate, vermiculite sheets with a thickness of 1.5 nm could easily be exfoliated from bulk crystals via



Scheme 2. (a) Schematic of differentiated salt-based multilayered solid polymer electrolyte (DSM-SPE). Bilateral layers are in-situ formed on the electrodes. Reproduced with permission from Ref. [3]. Copyright (2019) Wiley-VCH. (b) Schematic of vertical temperature gradient freezing of VS dispersion in a Teflon mold placed on the top of liquid nitrogen to induce the directional freezing casting. Reproduced with permission from Ref. [4]. Copyright (2019) Wiley-VCH. (c) The deposition behavior of lithium metal anode with LLZTO modified SPE (left) and routine liquid electrolyte (right). Reproduced with permission from Ref. [5]. Copyright (2017) National Academy of Sciences. (d) Chemical components of the ternary polymer electrolyte. Reproduced with permission from Ref. [12]. Copyright (2019) Wiley-VCH.

a straightforward ion-exchange method and then uniformly dispersed in polymer framework with certain orientation. Herein, we would highlight the elaborate preparation method of excellent VAVS.

At the initial stage, they prepared VAVS by directional freeze casting from the bottom to the top in liquid nitrogen environment with a subsequent freeze-drying process (Scheme 2b) and then the PEO-acetonitrile solution was introduced. However, the following procedures easily destroyed the primary structure of prefabricated VAVS. Therefore, the authors added some PEO into VS suspension in advance as the binder to anchor dispersed VS sheets, avoiding the structure collapse. Generally, aluminum ions were inclined to replace part of Si^{4+} ions in tetrahedral silicate of VS, leading to electronegative sheets for absorbing lithium ions. As a result, favorable ion conductivity of $1.89 \times 10^{-4} \text{ S cm}^{-1}$ and salt dissociation could be achieved with the aid of directional, continuous and run-through VS filler. Moreover, this PEO-VS based composite SPE delivered superior mechanical strength, alleviating the dendrite growth. Similar to vermiculite sheets, even-dispersed $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (LLZTO) ceramic particles have been applied as favorable filler in PEO-lithium salt matrix by Zhang's group.^[5] LLZTO particles could break the crystallization of PEO and anchor the anions effectively (Scheme 2c), enabling high cation conductivity of $1.12 \times 10^{-5} \text{ S cm}^{-1}$. Interestingly, ceramic fillers gave rise to suppressed dendrite growth and extended electrochemically window. These researches pave new approaches for next-generation lithium metal batteries.

In addition to the application of functional lithium salts or fillers, directly modifying the polymer framework attracts much attention as well. The Mecerreyes group revealed an upgraded polymer electrolyte with ethylene oxide, carbonate ester and lithium-sulfonimide, which could work as a single-ion conductor,^[6] mainly due to the utilization of carbonate units by offering proper decoupling effect with lithium cations. Chen's group also designed a carbonate contained solid polymer electrolyte, combining the merits of PEG and polycarbonate.^[7] In fact, researches on polycarbonate have encompassed both fundamental study and solid electrolyte field since 2010.^[8] Recently, members of Tominaga group demonstrated an end-capped poly(ethylene carbonate) (PEC) based electrolyte with 120 mol% lithium salt^[9] and the introduction of acetate end-groups improved the thermal stability over 30°C . With the combined effect of PEC matrix and concentrated lithium salt, this electrolyte delivered desired lithium ion conductivity, transfer number, oxidation stability (5.4 V vs. Li/Li^+), as well as suppressed corrosion on current collector. This work proved the applicability of concentrated solid polymer electrolyte and promoted the use of polymers with high T_g at room temperature. In addition, they also evaluated the performance of PEC/lithium salt composite with TiO_2 nanoparticles,^[10] which was conducive to enhanced lithium ion diffusion.

Another alternative ion-conducting material with widespread attention lies in the family of polymerizing ionic liquids (PILs).^[11] Besides the remarkable process-ability and non-leakage behavior as common polyelectrolytes, PILs deliver applicable ion conductivity, electrochemical and thermal

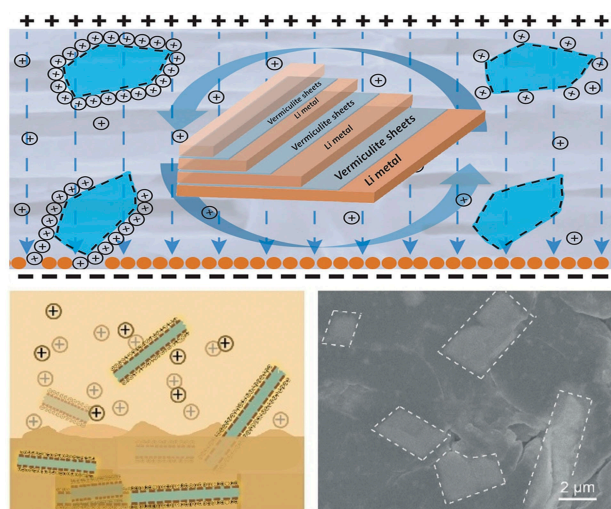
stability as well. However, homo-polymeric units of PIL matrix usually lead to easier degradation of pristine mechanical strength and compromised performance. To shake off the tough situation, Forsyth's group described a PIL-based copolymer, serving as the host of ternary polymer electrolyte (Scheme 2d) and providing reinforced mechanical property.^[12] By tuning the molar ratio of anion to Li^+ , PIL-based electrolyte with optimized conductivity was applied in solid-state lithium battery. Moreover, they demonstrated that concentrated IL could be confined into PIL matrix and decreased the glass transition temperature, resulting in higher ionic conductivity.^[13] With the aid of previous research, they successfully employed PIL electrolytes into rechargeable zinc and sodium batteries.^[14] According to the discussion above, taking multiple measures to design versatile SPEs owning desirable ion migration, operating voltage range as well as sufficient mechanical property may be the sally port for future investigation.

3. Liquid Electrolytes

Admittedly, liquid electrolytes with free fluidity exhibit natural merits in LMBs over the solid counterparts, such as high ion conductivity and tight interfacial contact with the electrodes. However, conventional carbonate solutions usually give rise to continuous anode corrosion and inhomogeneous lithium plating as well as the resulting dendrite growth with risks of short-circuit and burning, restricting the large-scale application. Employing artificial interface layers or various additives are still the main research approaches until now. In addition, searching alternative electrolytes, such as ether-based or other versatile electrolytes, has gained comprehensive attention either.

To get rid of the dilemma and withstand uneven surface deposition of lithium anode, Ma et al. conceived a bio-inspired design of soft-hard organic-inorganic composite, consisting of two dimensional colloidal vermiculite sheets as the hard ingredient and lithium as the soft segment.^[15] Its excellent performance was closely associated with the unique structure design. As mentioned above, vermiculite sheet was electro-negative and easily adsorbed by cations. Thence, authors realized the co-deposition of lithium-vermiculite composite and adjusted the morphology of deposited lithium metal (Scheme 3). Hereafter, the vermiculite sheets delivered negative charged again and detached from metal anode with the help of electric field force, thereby continuing to adsorb lithium ions. What needs to be emphasized was the ingenious idea of the shuttle movement of vermiculite sheets in this experiment. This simple design with abundant raw materials exhibited broad prospects of practical application. However, great efforts in other ways are still required to eliminate unfavorable parasitic reactions around the anode surface.

Solid-electrolyte interphase (SEI) layers exert important effects on the interface corrosion and deposition behavior of lithium anode. Kubo's group discovered a LiBr-LiNO_3 dual-anion electrolyte which induced ultrathin, homogeneous SEI layer during lithium stripping process and subsequent epitaxial growth of deposited lithium metal.^[16] Actually, interactions of



Scheme 3. Co-deposition mechanism of vermiculite sheets with Li in electrolyte and the corresponding SEM morphology after co-deposition process. Reproduced with permission from Ref. [15]. Copyright (2019) Wiley-VCH.

solvent, anions/cations and solvation of lithium ions are closely related to the SEI components.^[17] Therefore, Zhang's group regulated the Li^+ solvation in fluorinated electrolyte, achieving a $\text{LiF/LiN}_x\text{O}_y$ based SEI layer as well as smooth anode morphology.^[18] Moreover, chemistry of SEI layer also depends on the concentration of lithium salt by modulating the reductive stability of salt anions and solvents. Wang's group obtained a fluorinated interphase in concentrated carbonate electrolyte with about 10 M LiFSI salt.^[19] This F-rich layer contributed to dendrite-free surface and desirable efficiency over 99%. However, concentrated solution usually confronted high viscosity, high cost and poor wettability on cathode and separators. At this point, localized high-concentration electrolyte as reported by Xu^[20] might be an optimized way to alleviate these tough issues.

4. Gel Polymer Electrolyte

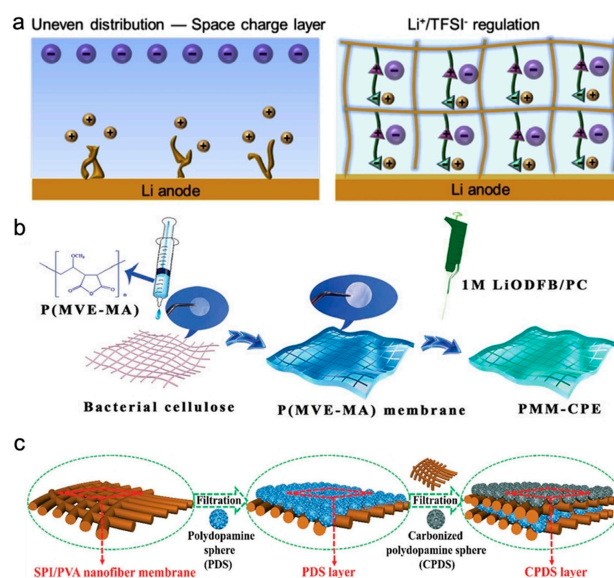
Gel polymer electrolytes (GPEs) represent composite systems, consisting of polymer framework and evenly dispersed liquid solution with proper lithium salts. They usually integrate features from both solid and liquid systems.^[21] As a result, multipurpose GPEs have received extensive attention up to now. From the perspective of regulating lithium ion flux and inhibiting dendrite growth, Li et al. stated a functional cross-linked zwitterionic gel polymer electrolyte (ZGE), mainly composed of zwitterionic component [2-(methacryloyloxy) ethyl]dimethyl-(3-sulfopropyl) (SBMA) and poly(ethyleneglycol) diacrylate (PEGDA).^[22] According to the widely recognized space charge theory from Chazalviel, space charge effect around lithium metal anode could easily appear under the circumstance of anion depletion, resulting in mussy distribution of ion flux and ramified lithium growth. The authors reported that the migration of TFSI⁻ anions in ZGE was restrained significantly via the interactions with cationic segments,

facilitating desired plating morphology and enhanced t_{Li^+} of 0.63. Moreover, evenly arranged anionic components also provided regular distribution of lithium ion flux (Scheme 4a). Unique internal structure of ZGE endowed lithium anode with superior behavior over 400 hours. Besides, appropriate mechanical behavior took certain effect in alleviating partial metal deposition and vertical growth.

For purpose of high energy density, functional GPEs compatible with both lithium anode and high-voltage cathodes such as transition metal oxide are eagerly required. Dong et al. reported a bacterial cellulose supported poly(methyl vinyl ether-alt-maleic anhydride) composite electrolyte (PMM-CPE, Scheme 4b) with high ionic conductivity and wide electrochemical window.^[23] This GPE could stabilize lithium anode and LiCoO_2 cathode simultaneously by forming favorable SEI/CEI layers, delivering excellent capacity retention and rate performance. Zhu et al. also designed a bio-based composite GPE (Scheme 4c) to tackle both dendrite growth of lithium anode and Mn^{x+} dissolution of LiMn_2O_4 cathode.^[24] The GPE mainly composed of environmental friendly soy protein isolate (SPI) and porous polydopamine spheres (PDSs). However, versatile GPEs usually suffer from increased thickness and battery volume due to the combination of various components, so further optimization should be included.

5. Towards Future Electrolytes

Developing new-type electrolytes can significantly promote the industrialization of lithium metal batteries and will be a worthy



Scheme 4. (a) Illustration of the morphologies of lithium with LE (left) and ZGE (right) during the Li plating. Reproduced with permission from Ref. [22]. Copyright (2020) Elsevier. (b) Representation of the PMM-CPE fabrication process. Reproduced with permission from Ref. [23]. Copyright (2018) Royal Society of Chemistry. (c) Fabrication process of skeleton materials for composite bio-based gel polymer electrolyte (c-GPE). Reproduced with permission from Ref. [24]. Copyright (2018) Wiley-VCH.

research field in the future. Nevertheless, regulating electrolyte components and the bulk distribution of lithium ion flux are still at the early stage, though abundant progresses already exist. To satisfy the demands of practical application, areal capacity typically over 4 mAh cm^{-2} of lithium metal anode is necessary. However, tough challenges may appear with ultra-high plating/stripping capacity. Frequent interface fracture/repair and excess electrolyte consumption accelerate the battery failure inevitably.^[25] In spite of appropriate mechanical strength to alleviate lithium dendrites, solid and gel polymer electrolytes usually result in inferior volumetric energy density, consequently reducing the commercial advantage over graphite-based batteries. In addition, poor wettability to high-loading cathode with high press density deteriorates effective ion migration and causes severe voltage polarization, especially for viscous liquid and stretchy solid electrolytes. Further, many ambiguous scientific and technical bottlenecks will emerge if we employ these novel electrolytes into industrialized pouch cells. Consequently, approaches from multiple aspects are more favorable for achieving safe and durable lithium metal batteries with high energy and power density.

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