

Review

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# Recent progress of multilayer polymer electrolytes for lithium batteries

Nan Zhang<sup>#</sup>, Shaoping Wu<sup>#</sup>, Hongpeng Zheng, Guoyao Li, Hezhou Liu, Huanan Duan\*

State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

<sup>#</sup>Contributed equally to this work.

\*Correspondence to: Prof. Huanan Duan, State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Rd., Shanghai 200240, China. E-mail: hd1@sjtu.edu.cn

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## Abstract

The significant market for electric vehicles and portable electronic devices is driving the development of high-energy-density solid-state lithium batteries. However, the solid electrolyte is still the main obstacle to the development of solid-state lithium batteries, mainly due to the lack of a single solid electrolyte that is compatible with both high-voltage cathodes and lithium metal anodes. These problems can potentially be solved with multilayer electrolytes. The property of each layer of the electrolyte can be tuned separately, which not only meets the different needs of the cathode and anode but also makes up for the shortcomings of each layer of the electrolyte, thereby achieving good mechanical properties and chemical and electrochemical stability. This review first presents a brief introduction to homogeneous single-layer electrolytes. The design principles of multilayer polymer electrolytes and the application of these principles using examples from recent work are then introduced. Finally, several suggestions as guides for future work are given.

**Keywords:** Solid-state lithium batteries, solid electrolytes, multilayer polymer electrolytes, high energy density

## INTRODUCTION

Lithium anodes are used in high-energy-density batteries because of their high theoretical capacity and low reduction potential<sup>[1]</sup>. By combining a lithium metal anode and a high-voltage cathode, the energy density of a lithium battery can exceed 260 Wh kg<sup>-1</sup><sup>[2]</sup>, which is appropriate for electric vehicles<sup>[3]</sup>. However, as anodes,



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alkali metals are faced with key problems, such as dendrite growth and side reactions with electrolytes, which lead to potential safety hazards<sup>[4,5]</sup>. Polymers are considered promising electrolytes to address the safety problems of lithium batteries<sup>[6]</sup>. Generally, polymer electrolytes can be divided into solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs). Fillers and additives can also be added to the polymer matrix to make composite polymer electrolytes. The investigation of SPEs started with Fenton *et al.* in 1973, who proved that alkali metal salts can form conductive complexes in polyethylene oxide (PEO)<sup>[7]</sup>. Later, Feuillade *et al.* added organic plasticizers into a polymer-salt system to prepare a quasi-solid-state GPE in 1975<sup>[8]</sup>. Since these pioneering works, polymer electrolytes have made significant progress because of their outstanding advantages, such as low flammability and high flexibility. Their processability and resistance to mechanical deformation are better than those of traditional liquid electrolytes and their electrode/electrolyte interfacial contact and compatibility are better than those of inorganic solid electrolytes<sup>[9,10]</sup>.

An ideal polymer electrolyte should possess high ionic conductivity ( $> 10^{-4}$  S cm<sup>-1</sup> at room temperature) and lithium-ion mobility, excellent chemical and electrochemical stability, compatibility with high-voltage cathodes ( $> 4.5$  V *vs.* Li/Li<sup>+</sup>) and lithium anodes and resistance to the volume change of the electrode and lithium dendrite formation. However, integrating all these required properties into polymer electrolytes remains a challenging task. Common polymer electrolytes, such as polyethers, polyesters, polyacrylonitrile, fluoropolymers and their copolymers, cannot easily meet the above requirements simultaneously, so the emergence of multilayer electrolytes is imperative.

Multilayer polymer electrolytes (MLPEs), first reported in the 2000s<sup>[11]</sup>, refer to two or more polymer electrolytes with different components that are superposed by *ex-situ* or *in-situ* preparation methods. An oxidation-resistant/soft polymer is used for the cathode side, a reduction-resistant/high-strength polymer is used for the anode side and a polymer with high ionic conductivity can be used as the intermediate layer. This architecture ideally takes full advantage of each polymer electrolyte and makes up for their shortcomings to achieve excellent mechanical, chemical and electrochemical properties. As a result, significant achievements in the development of MLPEs, including research publications<sup>[12,13]</sup> and patents<sup>[14]</sup>, have been reported in recent years. For example, Zheng *et al.* introduced a PEO-Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub> (LLZTO)-ionic liquid (IL) transition layer at the P(VEC-co-EGDMA) (vinyl ethylene carbonate (VEC) as a monomer and poly (ethylene glycol) dimethacrylate (PEGDMA) as a cross-linking point) electrolyte/cathode interface through a solution-casting method to achieve a double-layer structure and improve the interfacial contact<sup>[15]</sup>. Li *et al.* designed a PEO-based multilayer electrolyte structure<sup>[16]</sup>. The sacrificial layer on the anode side could accommodate lithium deposition and hinder lithium dendrite growth<sup>[16]</sup>.

This review first presents an introduction to the different types of single-layer polymer electrolytes and their advantages and disadvantages. We then discuss the design principles of MLPEs, introduce the application of these principles, present recent progress in MLPEs and conclude with the development prospects of MLPEs. This review will aid the further development of MLPEs and promote their application in the future.

## SINGLE-LAYER POLYMER ELECTROLYTES: ADVANTAGES AND DISADVANTAGES

Common solid and quasi-solid polymer electrolytes can be divided into the following categories according to the functional groups/chemical bonds that interact with lithium ions: polyethers, polyesters (ester bonds in the main or side chain), fluoropolymers, polyacrylonitrile, hydrogen bonding materials and others. The different functional groups of polymers determine their performance as electrolytes regarding conductivity, oxidation and reduction resistance, flexibility and strength. These different kinds of polymer electrolytes are

briefly described below.

### Polyethers

The research of SPEs began with polyethers. Polyether-based SPEs, such as PEO, poly(propylene oxide), poly(ethylene glycol) methyl ether acrylate and poly(dioxolane), have strong electron-donating ether oxygen groups (-C-O-C-) and have good electrochemical compatibility with lithium metal. After adding lithium salts or additives, an ionic conductivity of  $10^{-4}$  S  $\text{cm}^{-1}$  can be achieved at room temperature<sup>[17]</sup>. In addition, polyethers usually have good flexibility and fit well with the electrode interface<sup>[18]</sup>. However, the oxidation resistance of polyether-based SPEs is poor because the  $\alpha$ -H of polyether is easy to lose and they cannot be coupled with high-voltage cathodes, such as  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) and  $\text{LiCoO}_2$  (LCO). Moreover, their low mechanical strength makes them unable to effectively block lithium dendrites<sup>[19]</sup>.

### Polyesters

Polyesters are polymers that contain -COO-, where the electron-withdrawing -C=O groups coordinate with  $\text{Li}^+$  to ensure the solvation and transportation of  $\text{Li}^+$ . Their highest occupied molecular orbital (HOMO) energy level is lower than polyether, so they have a wider electrochemical window. The ester group in the polyester can be in the main or side chain. Polycarbonates are a popular type of main-chain polyester. Although some polycarbonates, such as poly(ethylene carbonate), poly(propylene carbonate) (PPC) and poly(vinyl carbonate), have high a lithium-ion transference number ( $t_{\text{Li}^+}$ ) and high electrochemical stability<sup>[20-22]</sup>, they also have shortcomings, such as poor mechanical properties, insufficient flexibility and poor compatibility with lithium anodes<sup>[23,24]</sup>. For other polycarbonates, such as poly(trimethylene carbonate) and poly( $\epsilon$ -caprolactone) (PCL), the ion conductivity at room temperature is too low and the Coulombic efficiency and capacity retention of the resulting batteries are poor<sup>[25]</sup>.

Ester side groups can be introduced into the polymer chain to coordinate with  $\text{Li}^+$ . The most common ones are butyl polyacrylate (PBA) and polymethyl methacrylate (PMMA), both of which can resist high voltages and the latter is stable to lithium metal<sup>[26,27]</sup>. However, their ionic conductivity is so low that they can only be used in the form of GPEs with liquid electrolytes. Moreover, there is the issue of poor mechanical strength, with PBA being too soft to form a self-standing electrolyte and PMMA being hard and brittle after film formation<sup>[28]</sup>.

### Fluoropolymers and polynitriles

Strong electron-absorbing functional groups, such as F and cyano ( $\text{C}\equiv\text{N}$ ) groups, in the polymer chain can lower the HOMO of SPEs and endow them with high electrochemical oxidation stability. Both polyvinylidene fluoride (PVDF) and PVDF hexafluoropropylene copolymers (HFPPs) have high thermal stability and mechanical strength and a wide electrochemical window<sup>[29,30]</sup>; however, their high crystallinity is not conducive to ionic conductivity and their interfacial stability with lithium metal still needs to be improved<sup>[31]</sup>. Moreover, polynitriles contain  $\text{C}\equiv\text{N}$  groups, which can coordinate with the metal ions of high-voltage cathodes to alleviate the oxidation process at the electrolyte/cathode interface. The most common polynitrile is polyacrylonitrile (PAN), which has the advantages of oxidation resistance and high-temperature resistance and can be coupled with high-voltage cathodes<sup>[32]</sup>. However, the  $\text{C}\equiv\text{N}$  group undergoes a continuous side reaction with lithium metal, forming a thick solid electrolyte interphase (SEI) film with the main composition of  $\text{Li}_3\text{N}$ , thereby seriously damaging the electrolyte/anode interface and ultimately leading to limited battery performance<sup>[33]</sup>.

### Hydrogen bonding materials

Hydrogen bonding materials, such as polyalcohols and polyamines, can form a hydrogen bond network and dissolve a large amount of lithium salt. Polyvinyl alcohol (PVA) is a type of polyalcohol that contains

hydroxyl and acetate side groups. It has good chemical stability, hydrophilicity and mechanical strength<sup>[34]</sup>. However, plasticizers must be added to achieve reasonable ionic conductivity; moreover, they are unstable when in contact with lithium metal<sup>[35]</sup>. Similarly, polyethyleneimine is a type of polyamine with a structure and Li-ion transport mechanism similar to PEO. Li<sup>+</sup> ions coordinate and hop between different nitrogen sites in the main chain, branched chain and terminal group. The amine group reduces the binding energy of lithium ions and anions and improves the conductivity<sup>[36]</sup>, but its poor mechanical performance hinders its practical application. A comparison of the electrochemical and mechanical properties of different polymer electrolytes is presented in [Table 1](#).

Even though significant progress has been achieved for the above-mentioned polymer systems, it is difficult for a single-layer electrolyte to simultaneously meet the requirements of high conductivity, compatibility with high-voltage cathodes and lithium anodes (oxidation and reduction stability), resistance to lithium dendrites (strength) and the volume change of the cathode (flexibility), as summarized in [Figure 1](#). Interestingly, some of these requirements conflict with each other, e.g., oxidation and reduction stability, strength and flexibility. Therefore, to achieve a good combination, two or more component polymer electrolytes can be stacked to prepare MLPEs, as shown in [Figure 1F](#). MLPEs can be divided into all-solid-state and quasi-solid-state electrolytes. Next, we introduce the design principles that should be followed to develop desirable MLPEs.

## DESIGN PRINCIPLES OF MLPEs

MLPEs have the potential to meet the conflicting demands mentioned above and also improve battery safety. A desirable MLPE should follow the four design principles of high ionic conductivity, oxidation and reduction resistance, good flexibility and strength and compatibility with different polymer matrices.

### Design of MLPEs with high ionic conductivity

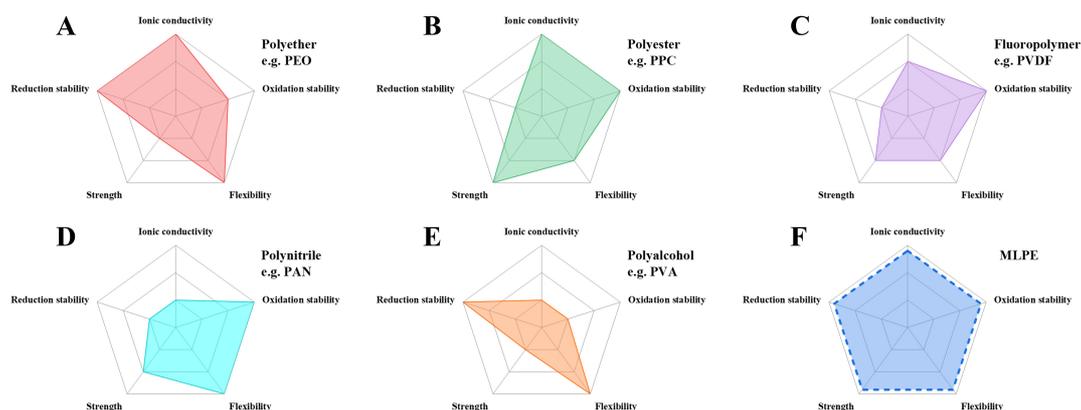
An electrolyte must have excellent ionic conductivity and electronic insulation to reduce self-discharge. The room-temperature ionic conductivity generally needs to reach the practical value of  $10^{-4}$  S cm<sup>-1</sup> to enable the normal charge and discharge of the battery. In this aspect, the design principles of MLPEs and SPEs are similar, i.e., improving the ionic conductivity by appropriately selecting polymer matrices, lithium salts, plasticizers and fillers.

To obtain high conductivity, the matrix of MLPEs needs to have electron-donating groups, such as ether (-C-O-C-) and ester (-C=O) groups, to form coordination bonds with cations, which enable facile ion transport<sup>[45]</sup>. Moreover, the amorphous region of the polymer electrolyte can be increased through polymer blending, which decreases the glass transition point and increases the ionic conductivity<sup>[46]</sup>. Similar to blending, copolymers formed by the copolymerization of different monomers can reduce the crystallinity of polymers, thus improving the movement of chain segments to enhance Li<sup>+</sup> transport<sup>[47]</sup>.

Lithium salts are the source of the charge carrier, Li<sup>+</sup>, in MLPEs, so their selection directly affects the ionic conductivity. The conductivity of an SPE or MLPE can be improved by selecting an appropriate type and content of lithium salt. To achieve high conductivity, the anions and cations in the lithium salt must be easily dissociated, i.e., the dissociation energy of the lithium salt should be low. Moreover, the high solubility in the electrolyte ensures a sufficient Li-ion concentration. One of the common types of lithium salt is lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), which has a large anion radius and is composed of N atoms with strong electronegativity and two S atoms connected with strong electron-withdrawing groups (-CF<sub>3</sub>)<sup>[48]</sup>. Increasing the concentration of lithium salts properly can increase the number of carriers in MLPEs to improve the ionic conductivity. However, too much lithium salt will hinder Li-ion conduction

**Table 1. Comparison of electrochemical and mechanical properties of different polymer electrolytes**

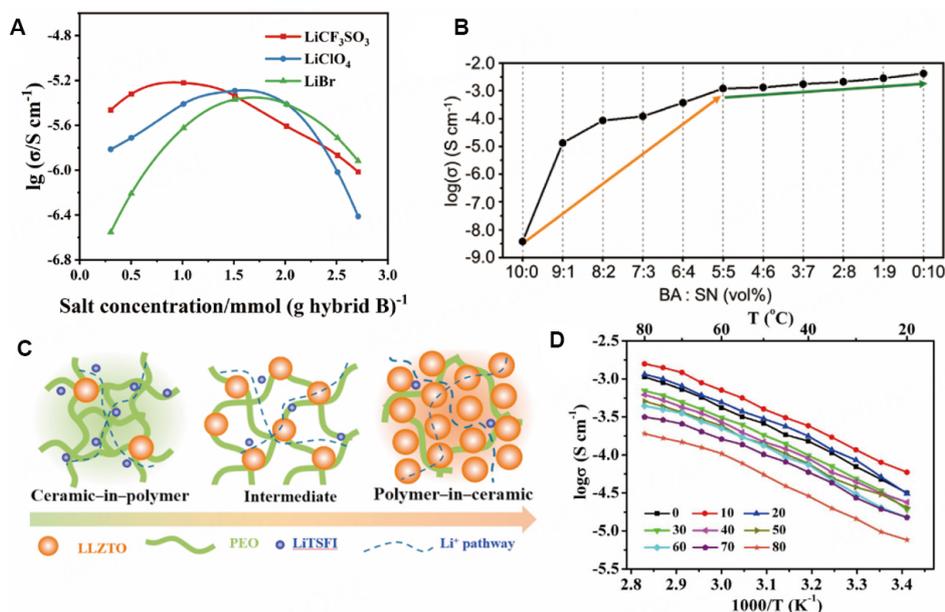
	Component	Ionic conductivity ( $S\text{ cm}^{-1}$ )	Electrochemical window (V)	Strength (MPa)	Strain (%)	References
Polyether	PEO/LLZO	$5.6 \times 10^{-4}$ (60 °C)	4.75	1.0 (shear)	2092	[37,38]
Polyester	PPC-LiTFSI/PPC-LiTFSI-SN	$5.77 \times 10^{-4}$ (55 °C)	4.7	30.3	56	[39]
Fluoropolymer	PVDF-LiBOB	$7.0 \times 10^{-5}$ (25 °C)	4.7	3.5	210	[40,41]
Polynitrile	PAN-LiClO <sub>4</sub>	$1.8 \times 10^{-5}$ (60 °C)	4.9	7.7	264	[42]
Polyalcohol	(PVA-PEG) + NaNO <sub>3</sub>	$4.32 \times 10^{-6}$ (20 °C)	4.0	1.39	68	[43,44]

**Figure 1.** Radar charts of properties of common polymer electrolytes: (A) PEO; (B) PPC; (C) PVDF; (D) PAN; (E) PVA; (F) desired MLPEs.

because of the increased viscosity and decreased Li-ion mobility. As a result, conductivity-salt concentration plots usually exhibit a maximum value, as shown in Figure 2A<sup>[49]</sup>. For LiCF<sub>3</sub>SO<sub>3</sub>, when the concentration is 1 mmol (g hybrid B)<sup>-1</sup>, the ionic conductivity can reach  $6.3 \times 10^{-6}$  S cm<sup>-1</sup>. Hybrid B refers to the copolymer containing a 20% molar ratio of 2-methylacrylic acid 3-(bis-carboxymethylamino)-2-hydroxy-propyl ester and 80% of poly(ethylene glycol) methyl ether methacrylate.

Plasticizers can be added to MLPEs to lower the glass transition point, promote the movement of chain segments and then improve the ionic conductivity. Plasticizers can generally be divided into three categories: plastic crystals<sup>[50]</sup>; organic solvents<sup>[26]</sup>; ILs<sup>[51]</sup>. For example, as shown in Figure 2B, when the content of succinonitrile (SN), a plastic-crystal plasticizer, increases to 50 vol.%, the conductivity of the gel electrolyte rapidly increases from  $10^{-6}$  to 1 mS cm<sup>-1</sup> (orange arrow), proving that the use of a plastic crystal plasticizer can effectively provide fast lithium-ion transport channels<sup>[50]</sup>.

Fillers in MLPEs can also improve the ionic conductivity of the battery by reducing the crystallinity of the polymer matrix through interaction with the polymer matrix and lithium salt. Fillers can be divided into two types, namely, in-active and active fillers. In-active fillers are usually lithium-free inorganic solid materials (e.g., Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub>), which can effectively reduce the crystallinity of the polymer matrix, improve the mobility of the chain segment and enhance the Li-ion conductivity. It is noteworthy that some in-active fillers can be used as Lewis bases to complex with Li ions to improve the dissociation of lithium salts and can also be used as Lewis acids to combine with anions to increase the Li-ion migration number of polymer electrolytes. Active fillers generally include solid-state electrolyte materials [e.g., LLZTO, Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) and Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LAGP)], which can provide a lithium source, directly participate in ion transmission and further improve the ionic conductivity. With increasing active filler



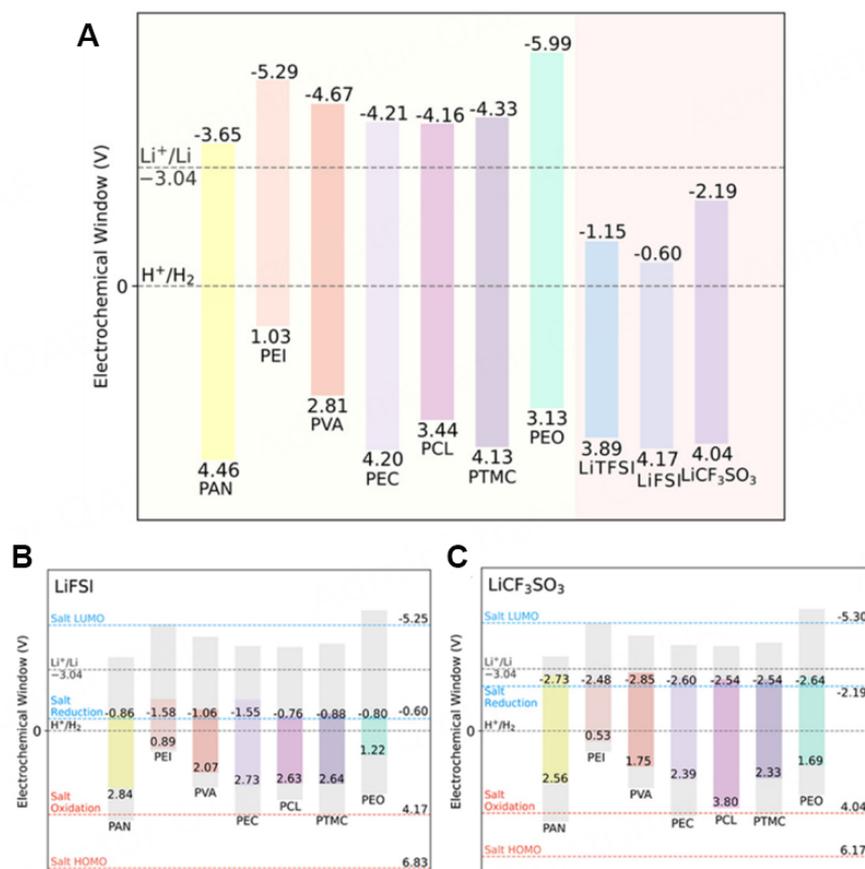
**Figure 2.** Methods to improve ionic conductivity of SPEs. (A) Relationship between content of different lithium salts and Li-ion conductivity. Reproduced with permission<sup>[49]</sup>. Copyright, Elsevier 2003. (B) Influence of SN plasticizer content on ionic conductivity. Reproduced with permission<sup>[50]</sup>. Copyright, Springer Nature 2022. (C) Schematic images of transfer process of composite electrolytes with different contents of ceramic fillers. (D) Arrhenius plots of (1-x) wt.%[PEO<sub>8</sub>-LiTFSI]-x wt.% LLZTO composite electrolyte. Reproduced with permission<sup>[52]</sup>. Copyright, Elsevier 2018.

content, the lithium conduction behavior of composite electrolytes changes dramatically. Figure 2C<sup>[52]</sup> exhibits schematic images of the Li transfer process of composite electrolytes with different contents of ceramic fillers. When the filler content is increased to a critical point (10 wt.%, shown in Figure 2D), i.e., the percolation threshold value, the Li transport pathways transition from the PEO matrix to the percolated LLZO network, significantly increasing the overall ionic conductivity of the composite electrolyte from  $6.30 \times 10^{-5}$  to  $1.17 \times 10^{-4}$  S cm $^{-1}$  at 30 °C.

### Design of MLPEs with good oxidation and reduction stability

The MLPEs used in batteries with high-voltage cathodes and lithium metal anodes should exhibit good oxidation and reduction resistance. On the cathode side, the large contact area between the electrolyte and the cathode makes MLPEs susceptible to oxidative decomposition with the catalytic effect of transition metal ions or conductive carbon<sup>[45,53]</sup>. In addition, some functional groups (C-O and C-H) have poor stability under high voltages, which can lead to problems such as unstable contact of the cathode/electrolyte interface, capacity attenuation and so on. For the anode side, the continual reduction of the polymer may cause the volume change of the polymer, leading to the formation of a thick SEI layer with poor Li-ion conduction. The oxidation and reduction stability can be effectively enhanced by combining appropriate polymer matrices and lithium salts or adding fillers.

The theoretical calculation of molecular orbitals provides a useful guide to developing polymers with low HOMO energy and high lowest unoccupied molecular orbital (LUMO) energy. The gap between the HOMO and LUMO can be used to estimate the electrochemical stability window (ESW) of the electrolyte. A polymer with a lower HOMO energy level will have stronger oxidation resistance, so it is more suitable for coupling with a high-voltage cathode. Similarly, the higher the LUMO energy level, the stronger the reduction resistance of the polymer and there will be no continuous side reaction when contacting the lithium anode. The ESWs of several pristine polymers are shown in Figure 3A<sup>[54]</sup>. PAN exhibits one of the

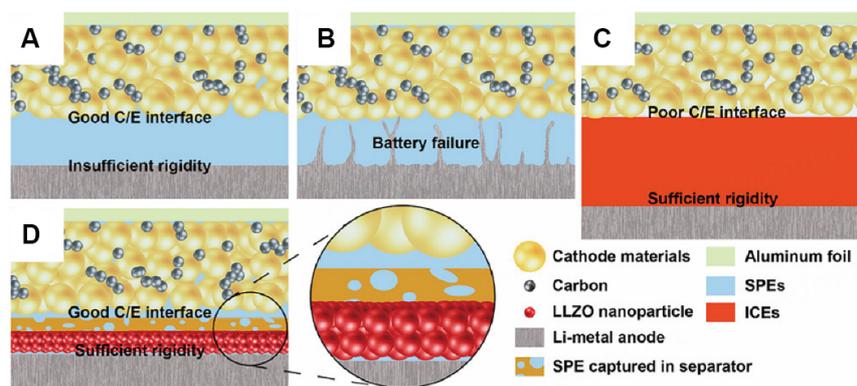


**Figure 3.** (A) Redox potentials for typical pristine polymers and lithium salts. (B) Redox potentials of (B) polymer/LiFSI and (C) polymer/LiCF<sub>3</sub>SO<sub>3</sub> complexes. Reproduced with permission<sup>[54]</sup>. Copyright, ACS 2020.

widest ESWs (~8.11 V vs. SHE) and has the highest oxidation potential (4.46 V vs. SHE). The calculation of HOMO and LUMO energy levels provides an intuitive basis for the design of MLPEs.

Figure 3A also shows the redox potentials of three kinds of common lithium salts (i.e., LiTFSI, lithium bis(fluorosulfonyl) imide (LiFSI) and LiCF<sub>3</sub>SO<sub>3</sub>), which also play an important role in improving the oxidation and reduction resistance of MLPEs. When the polymer interacts with lithium salts, the redox potential changes. Unfortunately, this interaction usually narrows the ESW of the electrolyte, as proved by Marchiori *et al.* who used density functional theory to compare the ESWs for pristine polymers, salts and the corresponding polymer/salt complexes<sup>[54]</sup>. For example, the PEO/LiFSI complex decreases the ESW of 9.12 V in pristine PEO to 2.02 V (vs. SHE, as shown in Figure 3B). The less positive oxidation potential of the polymer/salt complexes compared to the pristine materials was attributed to the structural reorganization after oxidation with the counter anion. They also found that the polymer/LiCF<sub>3</sub>SO<sub>3</sub> complexes displayed the largest ESW among the considered complexes (as shown in Figure 3B and C), with an order of polymer/LiCF<sub>3</sub>SO<sub>3</sub> > polymer/LiTFSI > polymer/LiFSI. This ESW assessment is helpful for designing desirable polymer/salt complexes for MLPEs.

Moreover, the filler itself, whether organic or inorganic, has good electrochemical stability. Organic fillers can be added to MLPEs to participate in the formation of the cathode electrolyte interphase (CEI) layer on the cathode surface and improve the stability of the cathode/MLPE interface<sup>[55]</sup>. On the anode side, the



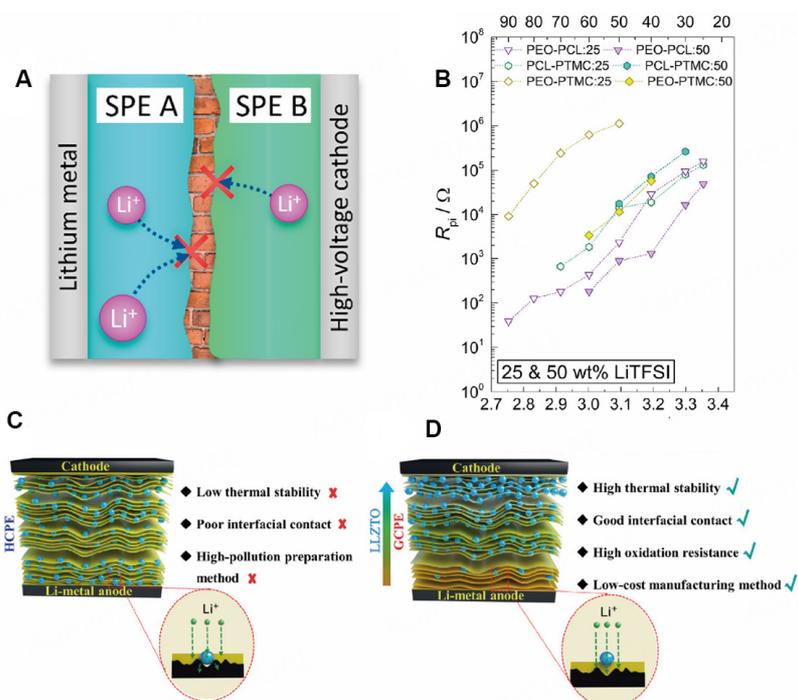
**Figure 4.** Schematic of solid-state Li battery with (A and B) conventional SPEs, (C) ICEs and (D) MLPEs. Reproduced with permission<sup>[60]</sup>. Copyright, ACS 2018.

improvement mechanism of reduction stability is due to the bond formation or interaction between the functional groups of the organic fillers and polymer matrices, which raises the LUMO energy of the polymers<sup>[56]</sup>. For ceramic fillers, the strategy is to take advantage of the Lewis acid-base interaction between the anions, ceramic particles and polymer chain to modify the chemical environment of the polymer matrix, thereby inhibiting the reductive decomposition of the polymer matrix at low voltages and facilitating the dissociation of lithium salts<sup>[57,58]</sup>.

#### Design of flexible and strong MLPEs

Poor interfacial contact between an MLPE and cathode usually causes large interfacial resistance, which may even prevent the battery from operating. Moreover, the volume change of the active material in the cathode caused by ion insertion/extraction leads to strain accumulation near the interfaces. Therefore, it is necessary to realize full and close interfacial contact between the cathode and electrolyte to enhance the electrochemical performance of polymer electrolytes. The SPE shown in Figure 4A has low interfacial resistance, but lithium dendrites will form due to its low mechanical strength [Figure 4B]. In contrast, the mechanical properties of inorganic ceramic electrolytes (ICEs) are sufficient to resist lithium dendrites, but the contact between rigid ICEs and electrodes is poor, resulting in high interfacial resistance [Figure 4C]<sup>[59]</sup>. Duan *et al.* used dense LLZO electrolytes on the lithium metal side and poly(ethylene glycol) methyl ether acrylate electrolytes with almost no LLZO on the cathode side [Figure 4D]<sup>[60]</sup>. The soft polymer electrolyte layer prepared by *in-situ* polymerization was in full contact with the active material, resulting in a good electrode/electrolyte interface and the promotion of the continuous transmission of Li ions.

To solve the problem of the polymer electrolyte/lithium anode interface, attention should not only be given to the formation of a stable SEI layer, and it should also be ensured that the MLPE has high mechanical properties. Only when the shear modulus of the electrolyte material ( $> 6$  GPa) is 1.8 times that of lithium metal ( $\sim 4.25$  GPa) can it effectively suppress dendritic growth on the surface of a lithium anode<sup>[61,62]</sup>. A polymer with good strength and high reduction resistance was selected as the matrix of a polymer electrolyte to form a stable anode/electrolyte interface, thus hindering the growth of lithium dendrites<sup>[63]</sup>. On this basis, a small amount of filler/skeleton can be added to the polymer electrolyte matrix to increase its elastic modulus. However, the increase in the elastic modulus of the MLPE leads to a decrease in the interfacial contact<sup>[64]</sup>. Therefore, it is of great importance to increase the compatibility of the interface while preserving the sufficient mechanical strength of the MLPE.



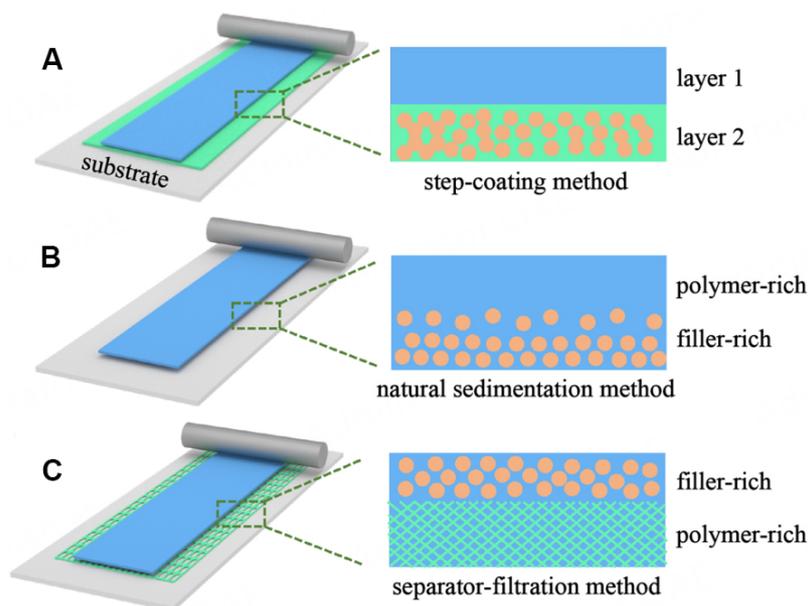
**Figure 5.** (A) Schematic diagram of interface between two SPEs. (B) Polymer interfacial resistance ( $R_{pi}$ ) with different Li salt contents at temperatures ranging from 25 to 90 °C. Reproduced with permission<sup>[65]</sup>. Copyright, ACS 2021. Schematics of (C) homogeneous composite polymer electrolyte and (D) gradient composite polymer electrolyte. Reproduced with permission<sup>[66]</sup>. Copyright, John Wiley and Sons 2021.

### Design of MLPEs with good compatibility between two polymer electrolytes

The polymer matrix in different layers in MLPEs may be different, so the interface between individual polymers cannot be ignored because of its high impedance. Previous studies have shown that due to the coordination strength difference or immiscibility between the two polymer bodies, the resistance of the polymer-polymer interface can be very large and even dominate the total resistance of the whole battery [Figure 5A]<sup>[65]</sup>. Several methods can be used to increase the interfacial miscibility and reduce the interfacial resistance. The first is to increase the concentration of lithium salts. With increasing lithium salt concentration, the glass transition temperatures of the two polymers gradually merge and the miscibility is gradually improved<sup>[65]</sup>. Figure 5B shows that when the LiTFSI concentration doubled from 25 to 50 wt.%, the resistance of the polymer-polymer interface ( $R_{pi}$ ) in PEO-poly(trimethylene carbonate) and PEO-PCL decreased by 100 and 10 times, respectively.

The second method is to use the same polymer matrix and different plasticizers. A quasi-double-layer polymer electrolyte was prepared by adding two plasticizers, i.e., propylene carbonate (PC) and diethylene glycol dimethyl ether (DGM), to the same matrix of PVDF/LLZO/LiTFSI. The same basic components, which can eliminate the contact interface of different electrolytes, reduce the interfacial resistance<sup>[56]</sup>.

The final method involves obtaining a filler concentration gradient within the MLPE. As shown in Figure 5C and D, LLZTO fillers with a concentration gradient change the traditional design of double-layer polymer electrolytes and have the following advantages: (1) the continuous change of composition and structure eliminates all macroscale interfaces; (2) the high and the low LLZTO content sides meet the needs of high-voltage cathodes and lithium metal anodes, respectively; and (3) the residual and thermal stresses of the interface are reduced and the good mechanical properties of the electrolyte are ensured<sup>[66]</sup>. The following



**Figure 6.** Preparation of MLPEs: (A) step-coating method; (B) natural sedimentation method; (C) separator-filtration method.

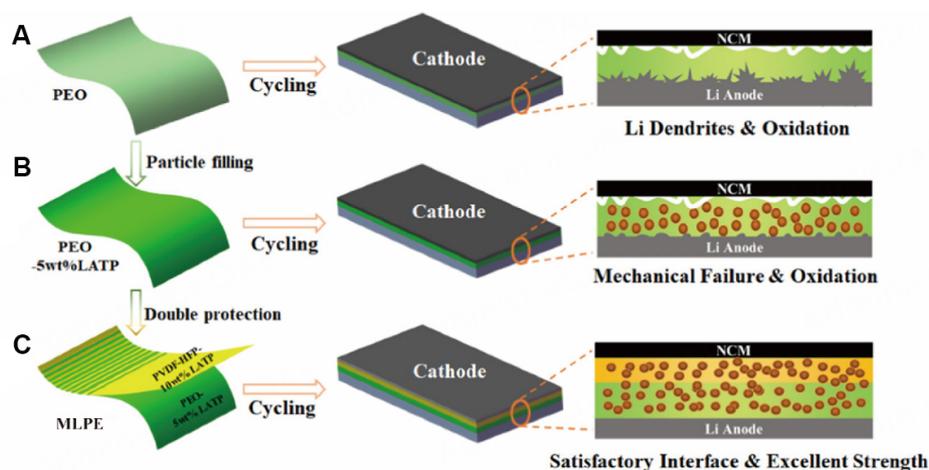
section introduces the application of these four design principles with some of the recent progress for MLPEs and highlights the electrolyte design, preparation methods and electrochemical properties.

## LITHIUM METAL BATTERIES BASED ON MLPEs

### Preparation protocols for MLPEs

So far, researchers have developed a variety of methods to prepare MLPEs, which can be mainly divided into step-coating, natural sedimentation and separator-filtration methods, as shown in [Figure 6](#). In the step-coating method, different polymer solutions consisting of different polymer matrices, lithium salts or different fillers are first prepared. These solutions are then coated stepwise on a cathode or anode substrate to make the MLPEs with the structure shown in [Figure 6A](#). This method is versatile, straightforward and effective in preparing MLPEs to meet the different demands of high-voltage cathodes and lithium metal anodes. However, the disadvantage of this approach is that a new interlayer interface is introduced and the compatibility between layers needs to be considered.

The natural sedimentation and separator-filtration methods are usually used to prepare MLPEs with the same polymer matrix and different fillers. In the natural settlement method, a polymer-filler mixture is coated directly on the substrate. A gradient distribution of the filler is achieved through a standing step by taking advantage of the density difference between the polymer and the filler to have the filler settle with gravity, as shown in [Figure 6B](#). In this manner, a rigid filler-rich layer helps suppress lithium dendrite formation and a soft polymer-rich layer helps to make good contact with the cathode. This method has few process steps, but the distribution of the filler is related to the particle size, solution viscosity, coating thickness and standing time, resulting in higher requirements for the raw materials and process control. To gain improved process control, the separator-filtration method is used, where a polymer-filler mixture is coated on a separator by reasonably selecting the pore size of the separator and the diameter of the filler. After settling, a heterogeneous structure, as displayed in [Figure 6C](#), is achieved, with a filler-rich layer above the separator and a polymer-rich layer within the separator. This method can effectively avoid the introduction of the new interface and the compatibility problem, but it needs a separator, which may complicate the electrolyte structure and affect the ionic conductivity.



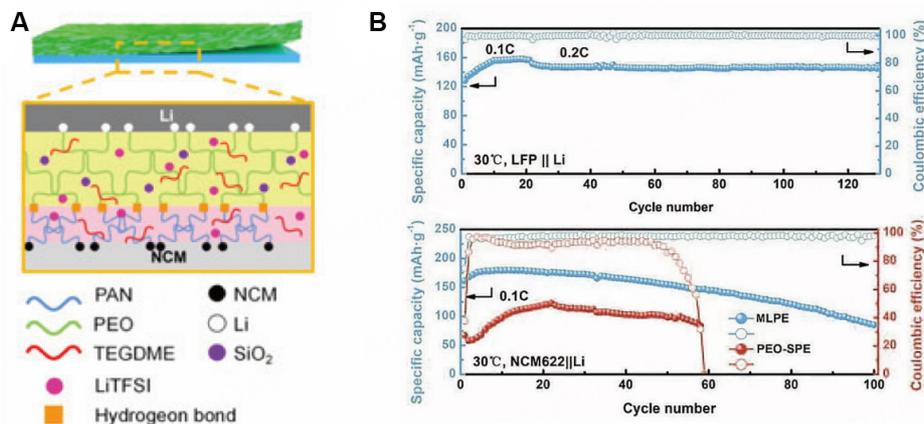
**Figure 7.** Schematic diagram of preparation method of (A) PEO SPE, (B) PEO-LATP electrolyte and (C) MLPE via an *ex-situ* two-step process. Reproduced with permission<sup>[67]</sup>. Copyright, ACS 2021.

### MLPEs using different polymer matrices

In combination with the design principles described above, the most common MLPE involves combining two polymer electrolytes with high ionic conductivity. The one on the cathode side is soft and oxidation resistant, while the one on the anode side is hard and reduction resistant. They are usually prepared by a two-step method via an *ex-situ* or *in-situ* route.

The *ex-situ* two-step process refers to the preparation of two kinds of solid electrolyte membranes by tape-casting and then combining the two membranes into a whole by hot pressing or other methods. The compatibility and adhesion between the two polymer matrices need to be high to reduce the interfacial impedance between them. For example, Yao *et al.* prepared LATP-reinforced PVDF-HFP-based composite electrolytes on the cathode side and PEO-LATP composite electrolytes on the anode side<sup>[67]</sup>. The MLPE was then formed by hot pressing at 60 °C with the help of the internal pressure of the battery itself. As shown in [Figure 7](#), PEO has good film-forming properties and excellent stability to lithium metal, while PVDF-HFP can be coupled with the NCM111 cathode because of its excellent oxidation resistance. The interfacial resistance between them can also be reduced by placing it at 60 °C. The  $t_{Li^+}$  reached 0.43 and the capacity of NCM111/MLPE/Li was still 105 mAh g<sup>-1</sup> after 100 cycles at 0.2 C.

The *in-situ* two-step synthesis method covers the second polymer precursor or solution onto the surface of the first layer and forms an integrated structure through photocuring or solvent volatilization, respectively. This method ensures good interfacial contact while avoiding mutual penetration between the two layers. Liu *et al.* first prepared a PAN-based electrolyte<sup>[33]</sup>, then covered it with a PEO precursor and photocured it under ultraviolet light to prepare an MLPE, as shown in [Figure 8A](#). PAN has good oxidation resistance, which can effectively solve the problem of PEO not being able to be coupled with a high-voltage cathode. Once PEO contacts PAN, the hydroxyl group in PEO can form O-HN hydrogen bonds with the cyano group in PAN, resulting in a good connection both physically and chemically. [Figure 8B](#) shows that the LiFePO<sub>4</sub> (LFP)/MLPE/Li battery exhibited excellent cycling performance. After 130 cycles at 30 °C, the Coulombic efficiency remained above 99.5%. In addition, the specific discharge capacity of the NCM622/MLPE/Li battery at 4.3 V vs. Li/Li<sup>+</sup> was 176.0 mAh g<sup>-1</sup> and the Coulombic efficiency remained at ~95% after 100 cycles.



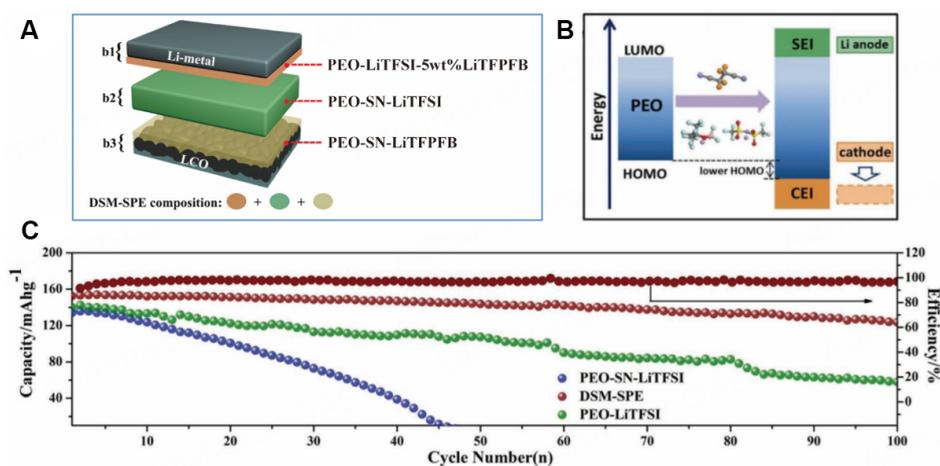
**Figure 8.** (A) Schematic of MLPE prepared via an *in-situ* two-step synthesis method. (B) Electrochemical performance of NCM622/Li using MLPE and PEO-SPE. Reproduced with permission<sup>[33]</sup>. Copyright, MDPI 2022.

Nevertheless, the interface between the two electrolytes cannot be ignored when two different polymers are used as the matrix. Considering the design principles discussed above, it may be desirable to use a single polymer as the matrix and change the type and/or content of lithium salt, plasticizer and ceramic filler to reduce the impedance between the interfaces and improve the ion transport efficiency.

#### Same polymer matrix and different lithium salts or additives

As described above, the choice of lithium salt is of particular importance in designing MLPEs. Specifically, the lithium salt is related to ionic conductivity, electrochemical stability, interface formation and lithium dendrite propagation<sup>[68]</sup>. The lithium salt also plays an important role in controlling the ESW of MLPEs. There are two mechanisms to broaden the ESW. One is to adjust the frontier orbital energy level of electrolytes through thermodynamics. The interaction between the polymer segment, salt (cation and anion) and additives can change the HOMO and/or LUMO of the electrolyte<sup>[69]</sup>. The other mechanism is to control the formation of the dynamically stable interphase (i.e., CEI and SEI) on the electrode surface to suppress direct reactions between the electrolyte and electrode materials. Anions that migrate to the electrode participate in the formation of a stable CEI and SEI.

MLPEs with the same polymer matrix can be prepared by changing the types of lithium salts. Wang *et al.* designed a three-layer polymer solid electrolyte, as shown in Figure 9<sup>[70]</sup>. The anode-side component was PEO-LiTFSI-lithium trifluoro(perfluoro-tert-butyloxy) borate (LiTFPFB), the cathode-side component was PEO-SN-LiTFPFB and the intermediate layer was PEO-SN-LiTFSI. LiTFPFB on both electrode sides helps to form a stable contact layer while preventing side reactions between SN and Li and widening the HOMO-LUMO gap of the electrolyte [Figure 9B]. Based on the complexation reaction between lithium salts and the polymer matrix, the ether oxygen donates the lone electron pairs to the Li ions of the lithium salts. Thus, the  $\alpha$ -H of PEO is not easy to lose, leading to the lowering of the HOMO energy level of PEO. The electrolytes on the cathode and anode sides were prepared by an *in-situ* method to reduce the interfacial impedance with the electrode. As a result, the Li/Li symmetric batteries could cycle for more than 600 h at a current density of 0.25 mAh cm<sup>-2</sup>. The high-voltage LiCoO<sub>2</sub>/Li battery could be cycled 100 times at 0.5 C with a discharge capacity of 119 mAh g<sup>-1</sup> and maintain a capacity retention rate of 83.3% at a rate of 0.1 C [Figure 9C].



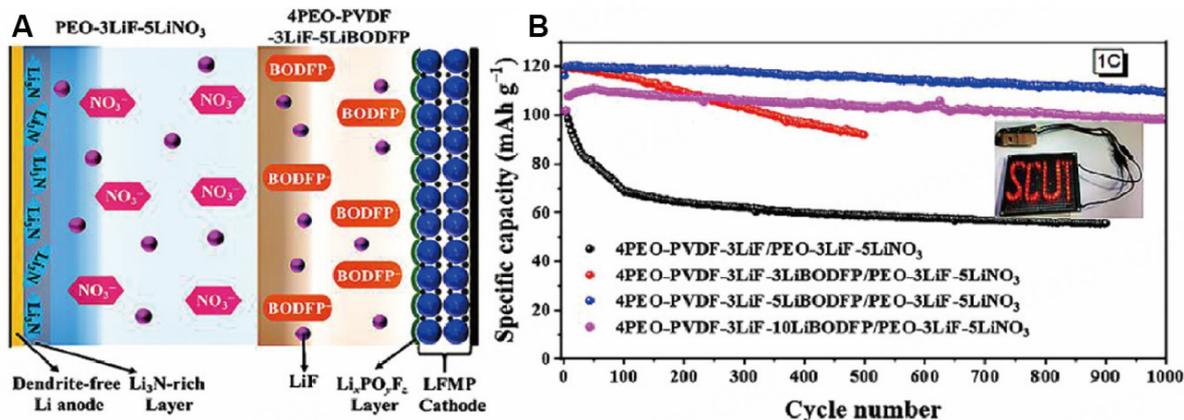
**Figure 9.** (A) Schematic of MLPE with different lithium salts. (B) Schematic of widened ESW of PEO matrix with interaction of lithium salts. (C) Cycling performance of LiCoO<sub>2</sub>/Li batteries with PEO-SN-LiTFSI, PEO-LiTFSI and MLPE at 0.1 C (1 C = 155 mAh g<sup>-1</sup>) with a voltage range of 2.5–4.3 V at 60 °C. Reproduced with permission<sup>[70]</sup>. Copyright, John Wiley and Sons 2019.

In addition, additives can be introduced into MLPEs to adjust the composition and structure of the CEI and/or SEI layers. Li *et al.* first reported a PEO-based heterogeneous MLPE containing a lithium bisoxalatodifluorophosphate (LiBODFP) additive on the cathode side<sup>[71]</sup>. LiBODFP can induce the formation of a stable CEI layer, prevent continuous decomposition and resist a high voltage of 5.0 V *vs.* Li/Li<sup>+</sup>. Simultaneously, the LiF on the LiFe<sub>x</sub>Mn<sub>1-x</sub>PO<sub>4</sub> (LFMP, 0 < x ≤ 0.5) cathode side can stabilize the PEO matrix and LLZTO can reduce the crystallinity of the polymer to improve the ionic conductivity and enhance the mechanical strength. Furthermore, the additive of LiNO<sub>3</sub> on the anode side promotes stable SEI formation to protect lithium from dendrite formation [Figure 10A]. After the LFMP/Li battery was cycled 1000 times in the range of 2.5–4.5 V *vs.* Li/Li<sup>+</sup> at 1 C, the capacity retention rate was still 90.6%, as shown in Figure 10B.

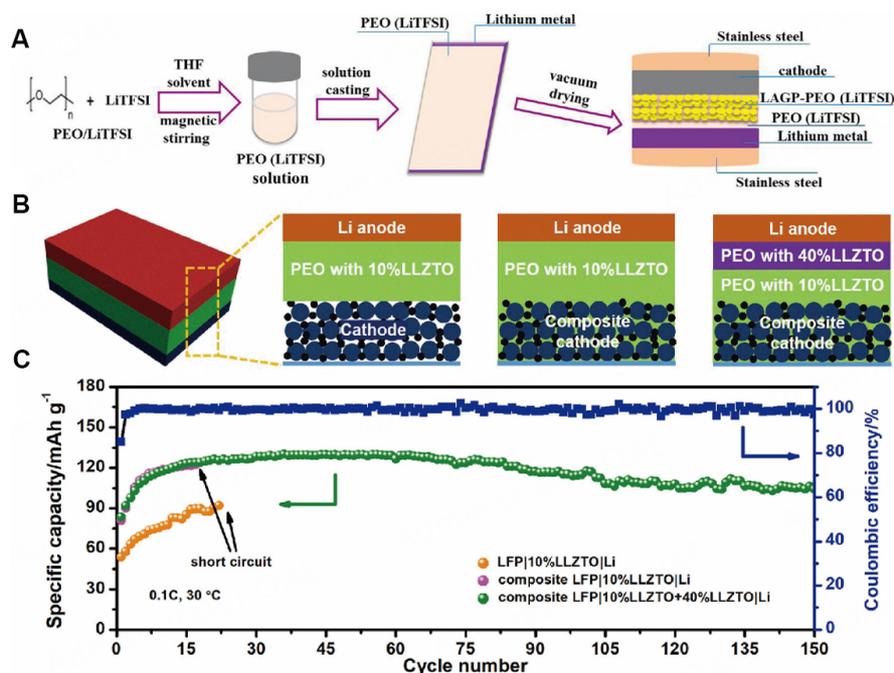
### Same polymer matrix and different fillers

The design of MLPEs can be realized by using different contents of fillers. Generally, increasing the filler content in the polymer electrolyte can effectively improve the mechanical properties and inhibit the growth of Li dendrites. Moreover, a polymer layer with a high filler content can possess a wide ESW, while a polymer layer with less filler content can provide good interfacial contact and help to release the capacity of the electrode. Therefore, through the reasonable design of MLPEs, both short-circuit resistance and good interfacial contact can be achieved simultaneously. Therefore, researchers have attempted to prepare MLPEs with asymmetric filler content by step-coating, natural sedimentation and separator-filtration methods.

The step-coating method includes an *ex-situ* and *in-situ* route. Wang *et al.* employed PEO as a matrix to design an MLPE based on LAGP and PEO through an *ex-situ* step-coating method<sup>[72]</sup>, as shown in Figure 11A. The optimized LAGP-PEO (LiTFSI) layer exhibits good electrochemical stability (> 5.12 V *vs.* Li/Li<sup>+</sup>), which means that this polymer layer can match with the high-voltage cathode material (LFMP). Moreover, the PEO (LiTFSI) layer exhibits good interfacial contact and mechanical properties, which can effectively improve the capacity retention rate and discharge-specific capacity of the half-cells. Under the combination of the use of these two layers, the all-solid-state half-cell delivered a discharge capacity as high as 160.8 mAh g<sup>-1</sup> at 50 °C. In another work, Bi *et al.* developed an *in-situ* step-coating method to prepare a MLPE composed of PEO and LLZTO filler [Figure 11B]<sup>[73]</sup>. In this MLPE, PEO with 10 wt.% LLZTO near the cathode side exhibits the optimum ionic conductivity while PEO with 40 wt.% LLZTO near the anode



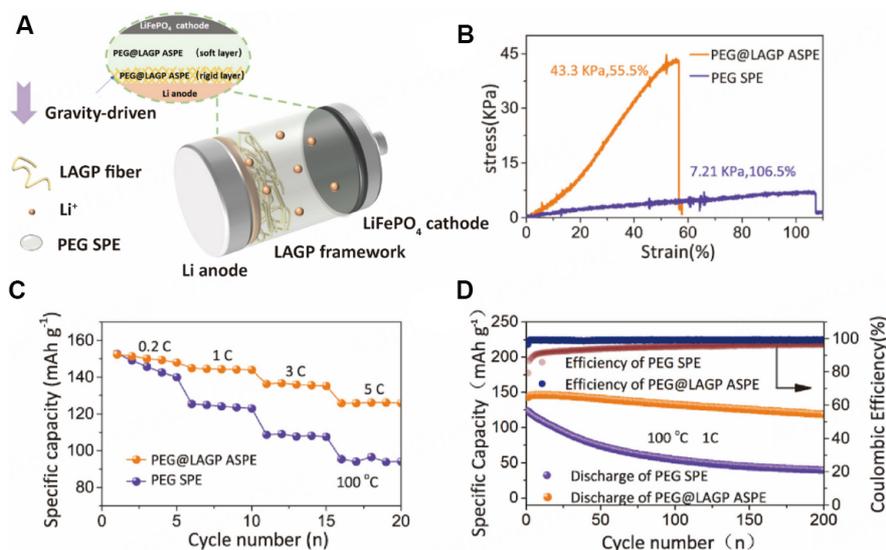
**Figure 10.** (A) Schematic of MLPE with different additives. (B) Cycling performance of LFMP@C/Li cells with MLPE at 1 C in the voltage range of 2.5-4.5 V. Reproduced with permission<sup>[71]</sup>. Copyright, Elsevier 2022.



**Figure 11.** (A) Preparation of Li/LFMP cells with MLPE through an *ex-situ* step-coating method. Reproduced with permission<sup>[72]</sup>. Copyright, ACS 2017. (B) Schematic of three kinds of battery configurations: LFP/10%LLZTO/Li; composite LFP/10%LLZTO/Li; composite LFP/MLPE/Li. (C) Cycling performance for these three batteries at 30 °C. Reproduced with permission<sup>[73]</sup>. Copyright, Elsevier 2021.

side possesses excellent mechanical properties for inhibiting the growth of lithium dendrites. Such a solid-state battery design presented a discharge capacity of 129 mAh g<sup>-1</sup> and a cycle life of over 150 cycles [Figure 11C].

The natural sedimentation method is a simple and operable method for the *in-situ* preparation of MLPEs. Yang *et al.* designed a gravity-driven MLPE, as shown in Figure 12A<sup>[74]</sup>. The rigid layer consisting of a polymer-embedded 3D continuous LAGP framework efficiently increases the  $t_{Li^+}$  and critical current density. The soft poly(ethylene glycol) methyl methacrylate layer prepared by thermal polymerization has



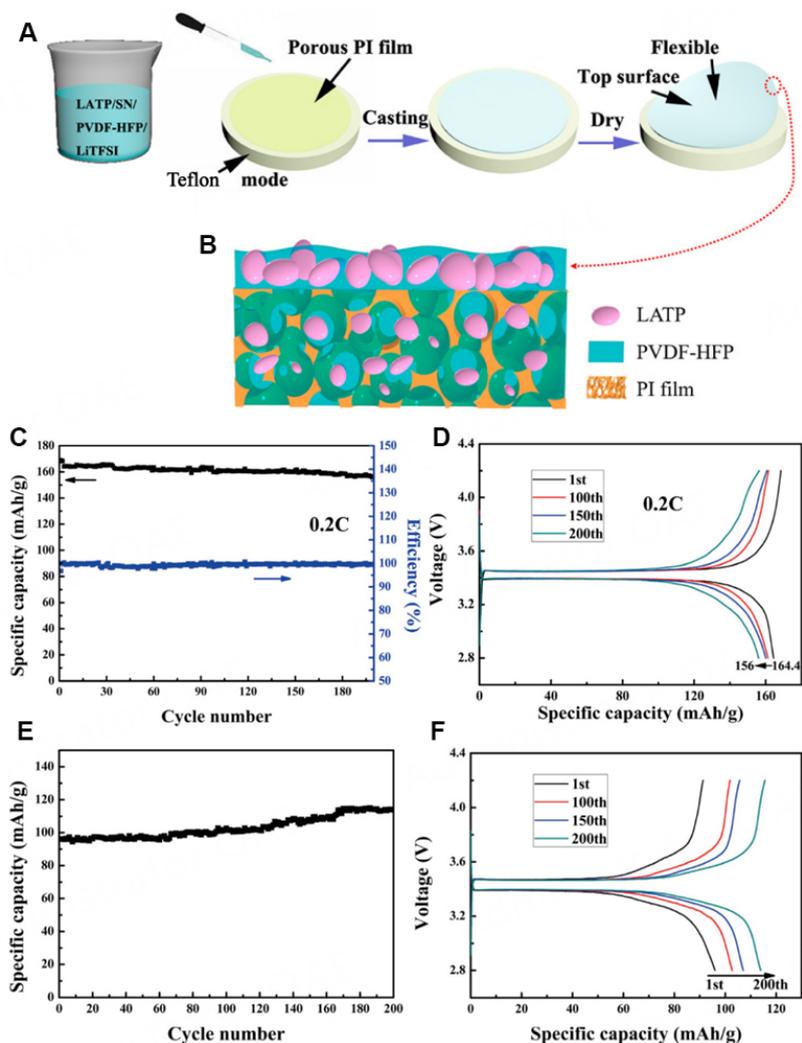
**Figure 12.** (A) Schematic diagram of gravity-driven MLPE structure. (B) Stress-strain curves of PEG SPE and PEG@LAGP MLPE. (C) Rate capabilities and (D) Cycling performance of LFP/SPE/Li and LFP/MLPE/Li cells at 1 C under 100 °C. Reproduced with permission<sup>[74]</sup>. Copyright, Elsevier 2022.

good interfacial contact with the cathode. These two layers are naturally layered by gravity during polymerization. The electrolyte showed a tensile strength of up to 43.3 kPa, as shown in [Figure 12B](#), while LFP/PEG@LAGP/Li cells provided significantly improved electrochemical performance compared to LFP/PEG/Li cells at high current density and 100 °C [[Figure 12C](#) and [D](#)].

A membrane with micropores can allow the permeation of the polymer to the lower layer while leaving the ceramic fillers in the upper layer to form an MLPE. Gai *et al.* prepared an MLPE using a porous polyimide film, as shown in [Figure 13A](#) and [B](#)<sup>[75]</sup>. PVDF-HFP and LATP are used as the polymer matrix and ceramic filler, respectively, and SN is added to achieve high conductivity ( $1.28 \times 10^{-4} \text{ S cm}^{-1}$ ). The LFP/MLPE/Li battery exhibits a reversible discharge capacity of  $156 \text{ mAh g}^{-1}$  after 200 cycles at a rate of 0.2 C and the Coulombic efficiency is greater than 98% [[Figure 13C](#) and [D](#)]. It is noteworthy that the battery can work at 4 °C and the discharge capacity is still  $110 \text{ mAh g}^{-1}$  after 200 cycles of 0.2 C [[Figure 13E](#) and [F](#)].

The above-mentioned methods can also be combined to prepare MLPEs. For example, Deng *et al.* combined the step-coating and natural sedimentation methods<sup>[66]</sup>. They first settled LLZTO in (poly(ethylene glycol) diacrylate (PEGDA) under gravity and cured it once under ultraviolet light. Next, when PEGDA without LLZTO was added, the LLZTO content in the MLPE after complete curing showed a gradient distribution, as shown in [Figure 5D](#). The as-prepared MLPEs did not have any macroscale interfaces and exhibited reduced residual and thermal stress with phase separation avoided during charging and discharging.

It is noteworthy that there is some discrepancy in which side of the MLPEs, the filler-concentrated side or the polymer-rich side, faces the cathode in the above examples. In Refs.<sup>[66,72,75]</sup>, the filler-concentrated side was chosen to face the cathode, while in Refs.<sup>[73,74]</sup>, the polymer-rich side was chosen. The former group claims that the porous filler-concentrated side with a wide ESW is oxidation resistant to the cathode and the thin dense polymer-rich side provides good interfacial contact to reduce Li dendrite growth. In contrast, the latter group states that the filler-concentrated side brings enhanced mechanical strength and  $\text{Li}^+$  transference number to resist lithium dendrites, while the soft polymer-rich layer makes good interfacial

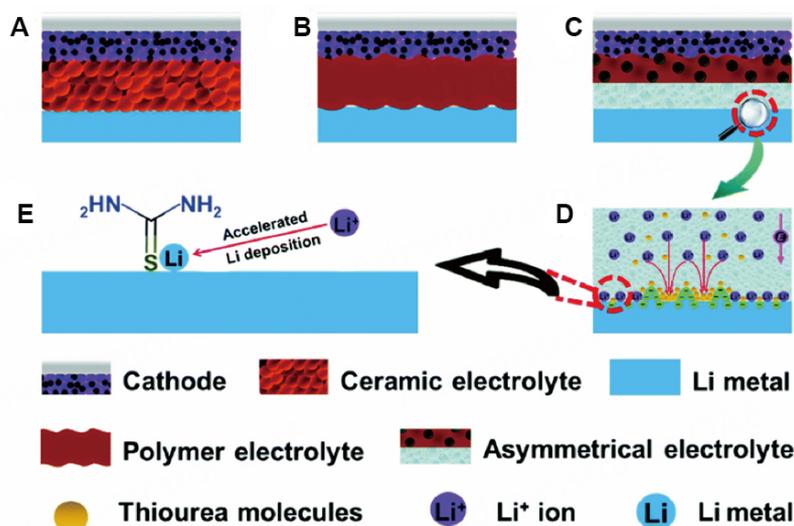


**Figure 13.** (A and B) Schematic diagrams of fabrication process of MLPE with separator-filtration. (C and E) Long-term cycling performance of LFP/MLPE/Li cell for 0.2 C at (C) 25 and (E) 4 °C. (D and F) Voltage-capacity profiles of 1st, 100th, 150th and 200th cycles for 0.2 C at (D) 25 and (F) 4 °C. Reproduced with permission<sup>[75]</sup>. Copyright, ACS 2019.

contact with cathodes. Different MLPE arrangements can be selected according to different considerations, e.g., the specific electrode configuration and demands of the battery.

### Quasi-solid-state multilayer GPEs

Despite the flexibility of MLPEs provided by the polymer matrix, there may still exist inherent gaps and unstable connection reactions at the solid-solid interface between the electrolyte and the electrode. Accordingly, a small amount of liquid electrolyte can be added to form a multilayer gel polymer electrolyte (MLGPE) for potential comprehensive performance advantages, including high ionic conductivity, good interfacial contact and a wide operating temperature range. Similar to the classification of MLPEs, this section classifies MLGPEs according to their components and divides them into MLGPEs with different polymer matrixes, namely, MLGPEs with the same polymer matrix and different plasticizers and MLGPEs with the same polymer matrix and different fillers.

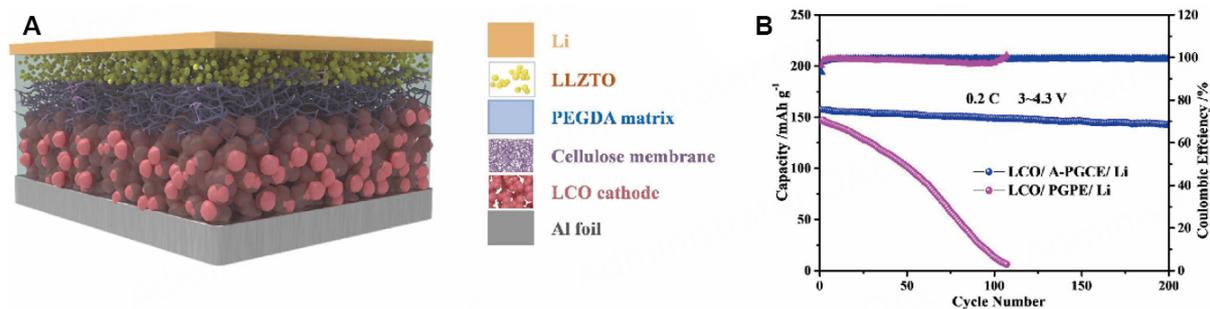


**Figure 14.** Schematic comparison of solid-state Li batteries with three different electrolytes: (A) an inorganic ceramic electrolyte; (B) a typical polymer electrolyte; (C) MLGPE. (D and E) Schematic description of effect of THU additive in MLGPE on Li deposition. Reproduced with permission<sup>[76]</sup>. Copyright, Royal Society of Chemistry 2020.

Different layers of MLGPEs may have different polymer matrices. For instance, Wang *et al.* coated a soft PEO-LLZO composite electrolyte on one side of a separator facing the cathode to guarantee good interfacial compatibility and coated a thin PVDF-HFP gel-electrolyte with thiourea (THU) additive on the other side towards the Li metal<sup>[76]</sup>. The separator contained a large number of submicron-connected pores to adsorb liquid [Figure 14]. The THU additive on the anode side could accelerate the speed of lithium adsorption on the anode, thereby forming a flat SEI to inhibit the formation of lithium dendrites and promote the electrochemical kinetic process. Compared with a pure ceramic electrolyte [Figure 14A] and a polymer electrolyte [Figure 14B], the 45  $\mu\text{m}$ -thick MLGPEs showed improved electrochemical performance. The LFP/MLGPE/Li battery showed stable cycling performance over 200 cycles at 1 C with a Coulombic efficiency of 99.6%.

Low anodic reactivity and high voltage compatibility can be achieved by adding different kinds of plasticizers to the same polymer matrix. Pan *et al.* added different plasticizers, namely, PC and DGM, to a PVDF/LLZO/LiTFSI composite<sup>[56]</sup>. The side with the PC faces the cathode because the *in-situ*-polymerized PC can serve as a CEI film and enhance the antioxidation ability. In contrast, on the anode side, the nucleophilic substitution of DGM with PVDF increases the reduction stability and suppresses the formation of lithium dendrites. Moreover, because of the use of the same matrix, there is no interfacial resistance of different electrolytes, so the MLGPE exhibits an ionic conductivity of  $1.3 \times 10^{-4} \text{ S cm}^{-1}$ . The cycling stability of NCM811/MLGPE/Li and NCM811/MLGPE/hard carbon batteries is better than that with GPE added with PC and DGM only. The capacity retention rate of NCM811/MLGPE/hard carbon batteries was 80.2% after 200 cycles at 1 C and 25 °C.

MLGPEs can also be prepared by controlling the filler content at different positions in the same polymer matrix. Cai *et al.* developed a simple and environmentally-friendly *in-situ* polymerization method by dropping a mixture of PEGDA monomer<sup>[77]</sup>, liquid electrolyte and LLZTO ceramic particles on a cellulose membrane and using gravity to allow it to settle naturally [Figure 15A]. After thermal polymerization, an MLGPE rich in LLZTO at the top could be obtained. The LLZTO-rich side faced the lithium anode during cell assembly to take advantage of its improved mechanical properties to inhibit the growth of Li dendrites.



**Figure 15.** (A) Schematic of LCO/MLGPE/Li cells via an *in-situ* fabrication process. (B) Long-term cycling performance of cell at 0.2 C and room temperature. Reproduced with permission<sup>[77]</sup>. Copyright, Elsevier 2022.

Subsequently, the MLGPE showed an ionic conductivity of  $1.25 \times 10^{-3} \text{ S cm}^{-1}$  and  $t_{\text{Li}^+}$  of 0.57. The LCO/MLGPE/Li cell showed an initial discharge capacity of  $157.6 \text{ mAh g}^{-1}$  in the voltage range of 3.0 to 4.3 V vs. Li/Li<sup>+</sup> and a capacity retention rate of 90.7% after 200 cycles at 0.2 C, indicating good cycling stability [Figure 15B].

Regarding the MLGPE preparation, some MLGPEs may traditionally need an additional *ex-situ* step to incorporate plasticizers by immersing the dry film into the liquid electrolyte. In this method, toxic organic solvents are employed to dissolve polymers and lithium salts, which are then removed by environmentally unfriendly evaporating and/or heating. In addition, the residual solvent in the MLGPE may react with the electrode, resulting in the degradation of battery performance. Furthermore, many recent studies have attempted an *in-situ* polymerization technology, which directly converts liquid precursors into solid electrolytes by crosslinking polymer monomers under controlled conditions. This not only eliminates the use of polluting and toxic organic solvents but also reduces the electrolyte/electrode interfacial resistance by injecting the liquid precursor directly into the battery during cell assembly<sup>[78]</sup>. The *in-situ* polymerization also helps to improve the mechanical strength of polymer electrolytes<sup>[18]</sup>. In addition, the mechanical strength of MLGPEs with ceramic fillers can also be significantly improved. Therefore, *in-situ* polymerized MLGPEs reinforced with mechanically strong ceramic fillers are especially promising as serious electrolyte contenders for future high-energy-density lithium batteries.

## CONCLUSION AND PERSPECTIVES

This review has systematically summarized the typical polymer electrolytes and their advantages and disadvantages, introduced the concept and design principles of MLPEs and presented the recent progress in MLPEs and MLGPEs from the aspects of matrices, additives, lithium salts and ceramic fillers. MLPEs have the potential to meet the mechanical properties and voltage requirements of the cathode and anode while simultaneously having high conductivity and good electrochemical performance. We propose the following directions as being worthy of future research.

### *In-situ* preparation process

The preparation process of MLPEs is mainly divided into two methods: *ex-situ* and *in-situ*. Although the *ex-situ* preparation method can prepare MLPEs and realize the gradient distribution of additives, such as ceramic fillers, the bonding between different layers is not tight, thereby easily causing large internal resistance. The *in-situ* preparation method described above can effectively enhance the bonding between the two layers of the electrolyte<sup>[33]</sup>, which is conducive to ion transport and improved safety. Future efforts can be dedicated to the two-step *in-situ* preparation method to achieve good interfacial contact while simplifying the process. It is noteworthy that the *in-situ* preparation process can also enhance the interfacial

contact between the electrolyte and the electrode<sup>[79]</sup>. The two electrolytes can be combined with the two electrodes with the *in-situ* method, and then the third polymer precursor can be introduced between them similarly to form a multilayer structured electrolyte with the contact at each interface enhanced. In addition, the *in-situ* method can eliminate the environmental pollution caused by solvent volatilization without using any toxic solvents.

### Computation-guided polymer design

Though the present review of the recent progress in MLPEs has mainly focused on experimental work, theoretical computation is expected to have a profound influence on exploring the properties of MLPEs and designing new MLPEs. For instance, one of the advantages of MLPEs is their wide ESW. The experimental determination of the ESW (e.g., optical absorption spectra and cyclic voltammetry) is normally time-consuming and provides insufficient electronic information, such as the polymer band edges. Density functional theory (DFT) has been used to unravel the role of the polymer matrix in determining the ESW of polymer electrolytes<sup>[80]</sup>. With the rapid development of computing power, future work can be directed to the utilization of computation to understand the complex interplay of other factors affecting the ESW of MLPEs, such as the chemical and morphological variations present in the polymer matrix, interactions between the polymer matrix and the lithium salts, and the evolution of the electrode/electrolyte interfaces. As an example, Yuan *et al.* used a multi-physical field model to simulate the change in the growth direction and shape of lithium dendrites by adding heterogeneous reinforcements to the polymer matrix and comprehensively studied the factors controlling the dendrite inhibition effect<sup>[81]</sup>.

More recently, the field of polymer informatics has emerged, which aims to accelerate polymer property prediction and design via surrogate machine learning models that are built on reliable previous data. An online platform known as the Polymer Genome has been set up by Doan Tran<sup>[82]</sup> to incorporate various models and datasets. This paradigm shift based on high-throughput computation and data science approaches promises to speed up polymer-matrix screening, novel polymer discovery and even the optimization of composition and experimental conditions. Recent work by Liu *et al.* compares various machine learning models based on a dataset from both literature and independently conducted experiments and finds that the random forest model is the best among six (i.e., linear regression, ridge regression, lasso regression, random forest, decision tree and a support vector machine) in terms of accuracy and predictive ability<sup>[83]</sup>. This data science approach could be extended to include other types of polymer matrices and commonly used salts, even bi- and tri-salt components.

### Evaluation of interfacial compatibility between two polymers

For multilayer electrolytes, the commonly used evaluation indicators, such as the electrochemical window, lithium-ion transference number, cycling stability, and so on, mainly come from the electrochemistry community. To set up a more comprehensive evaluation system, indicators from other communities are needed. One of the greatest differences between MLPEs and homogeneous electrolytes is that the interface between different layers cannot be ignored. The interfacial resistance may play a decisive role in the overall resistance of the battery, so the compatibility between interfaces is worth optimizing and evaluating. In previous studies, the polymer-polymer interface impedance has been separated and the impedance can be related to the frequency through DRT and other methods to more accurately describe and evaluate the interfacial resistance. Simultaneously, the concept of the solubility parameter is proposed for the evaluation of the interfacial compatibility of two polymers, which is originally a parameter characterizing the polymer-solvent interaction. This concept can be applied to describe the polymer-polymer interaction. When the solubility parameters of the two materials are similar, they can be blended and have good co-solubility. It is noteworthy that the solubility parameter can also evaluate the affinity between the plasticizer and polymer matrix, and thus a better combination can be selected to prepare MLPEs.

Given the molar gravitational constant ( $F$ ,  $J^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}$ ) and internal pressure square root ( $\lambda$ ,  $J^{1/2} \text{ cm}^{-3/2}$ ) of the common groups in the polymer and the molar volume of the repeating unit ( $V_m$ ,  $\text{cm}^3 \text{ mol}^{-1}$ ), the density ( $\rho$ ,  $\text{g cm}^{-3}$ ) and the molar mass ( $M_0$ ,  $\text{g mol}^{-1}$ ) of the polymer, the internal pressure square root and solubility parameter ( $\Delta$ ,  $J^{1/2} \text{ cm}^{-3/2}$ ) of the polymer can be calculated from<sup>[84]</sup>:

$$\lambda = \rho \Sigma(\lambda V_m)_i / M_0$$

$$\Delta = \delta^2 / \lambda = \frac{\rho (\Sigma F_i)^2}{M_0 \Sigma(\lambda V_m)_i}$$

where  $\delta$  is the cohesive energy density of the polymer,  $J^{1/2} \text{ cm}^{-3/2}$ .

Two kinds of polymer can be applied to the adjacent layers of electrolytes if the difference between their solubility parameters is less than 3. For example, the solubility parameters of PCL and poly(ethylene adipate) are 18.0 and 18.1  $J^{1/2} \text{ cm}^{-3/2}$ , respectively, meaning that the co-solubility of these two kinds of polymer is good and the impedance of the polymer-polymer interface is small.

## DECLARATIONS

### Authors' contributions

Conceptualization: Wu S, Duan H

Data curation, formal analysis, writing - original draft: Wu S, Zhang N

Resources, technical support: Zheng H, Li G, Liu H

Funding acquisition, supervision: Duan H

Writing - review and editing: Wu S, Zhang N, Duan H

### Availability of data and materials

Not applicable.

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate.

Not applicable.

### Consent for publication

Not applicable.

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