Mitigating Interfacial Instability in Polymer Electrolyte-Based Solid-State Lithium Metal Batteries with 4 V Cathodes

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ABSTRACT: Solid polymer electrolytes (SPEs) are attractive for next-generation energy storage, because they are more thermally stable compared to conventional liquid electrolytes and simpler for scalable manufacturing than ceramic electrolytes. However, there is a growing body of research suggesting that the interfacial instabilities between SPEs and other battery components (e.g., electrodes and electrolyte fillers) hinder their practical applications. This Perspective highlights the degradation mechanisms at these interfaces revealed by recent works, especially in lithium/4 V cathode systems with high energy density. We also review recent progresses on mitigating such instabilities and provide perspectives on how to further understand and address these issues, such as advanced characterizations and simulations, which deliver a valuable guide for future studies to accelerate the development of SPE-based solid-state batteries.

Enhancing energy density and safety is critical to developing next-generation rechargeable batteries for various applications, such as electric vehicles and portable electronics.1−3 However, cells with higher energy density are prone to thermal runaway, which compromises safety.4 One attractive solution to such conflict is to replace flammable liquid electrolytes by solid electrolytes with much higher thermal stability, especially when high-capacity electrodes are used, such as Ni-rich oxides and the lithium metal anode.5,6

There are two major types of solid electrolytes: ceramic electrolytes (e.g., Li3PS4, garnet Li3La2Zr2O12/LLZO, Li1.3Al0.3Ge1.3(PO4)3/LAGP)7−9 and solid polymer electrolytes/SPEs (e.g., poly(ethylene oxide)/PEO, polyacrylonitrile/PAN)10,11. Ceramic electrolytes usually have ionic conductivities over 0.5 mS cm−1, much higher than polymer electrolytes (10−5 to 10−4 Sc m−1).17−19 On the other side, the interfacial stability has not received enough attention. However, it represents critical challenges for practical applications of solid polymer batteries.20 For example, while 3 V PEO-based solid-state batteries have been commercialized, the instability of PEO above 4 V prevents its application in high-energy-density batteries.21 The instability of SPEs, such as poly

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propylene carbonate (PPC), with lithium metal also impedes their applications in lithium metal batteries. Increasing interest has been witnessed during the last several years on understanding and engineering interfacial instability in polymer electrolyte-based batteries, which point out important directions for advancing understanding and enhancing the performance of next-generation batteries. Various types of degradation mechanisms exist at the polymer electrolyte/electrode interfaces, including chemical, electrochemical, and mechanical degradations (Figure 1). Such instabilities affect not only the electrolyte phase but also solid electrodes themselves. Moreover, in polymer/ceramic composite electrolytes, the polymer/ceramic interface may also degrade over time. As different issues present at different interfaces, we will divide our discussions into the polymer/cathode interface, the polymer/anode interface, and the polymer/ceramic electrolyte interface in sequence. Recent progress will be reviewed first, followed by our perspectives on further directions to accelerate understanding of these interfaces and practical applications of solid polymer electrolyte-based solid-state batteries. Because the target of this Perspective is solid-state batteries with high energy density, we focus on 4 V Li(Ni$_x$Co$_y$Mn$_z$)O$_2$ (NCM) cathode and high-capacity lithium anode. Sulfur and air cathodes will not be included here because their electrode potentials are typically within the stability window of polymer electrolytes.

Cathode/SPEs Interfaces. Degradation Mechanism at the Cathode/SPEs Interface. Polymers tend to lose electrons at high electrode potential. The oxidation electrode potential is related to the Fermi level of a polymer electrolyte. Among common polymer electrolytes, those with carbonyl group are stable at moderately high voltage (e.g., 4–4.5 V vs Li$^+$/Li$^-$) but polymers with an ether group are widely accepted to be unstable above 4 V vs Li$^+$/Li$^-$, such as PEO. Because PEO is widely studied, and it has been commercialized in 3 V Li/LiFePO$_4$ (LFP) batteries, addressing the interfacial stability between 4 V cathodes (e.g., NCM and LiCoO$_2$/LCO) and PEO has the potential to enable practical 4 V solid-state batteries in the future. Hence, this section will mainly focus on the PEO/4 V cathode interface.

In the literature, the stability of PEO above 4 V vs Li$^+$/Li$^-$ has been mainly evaluated by two strategies: scanning voltammetry with an inert stainless steel (SS) substrate and galvanostatic cycling with a 4 V cathode. Linear sweep voltammetry (LSV) tests typically show no obvious oxidation current below 4.3 and even 4.5 V vs Li$^+$/Li$^-$, but in galvanostatic cycling, 4 V cathodes without any modification typically show poor performance (e.g., <80% capacity retention after only 20–50 cycles). The discrepancy is suspected to arise from distinctly different activities between the inert SS substrate and catalytic...
Ni, Mn, and Co ions or oxides on the 4 V cathode surface. Such catalytic properties have been proposed and discussed in the literature, and serious attention should be paid to them. For example, Kosova et al. and Liu et al. suggested that the surface coating of LCO would cover Co4+ catalytic sites, therefore restrain the decomposition of electrolytes.\textsuperscript{36,37} It also points out the importance of understanding mechanisms of PEO oxidation based on a catalytic perspective.

Recently there have been increasing studies on the oxidation mechanisms of PEO, and the results show that the oxidation affects both the PEO electrolyte and the solid electrode. First, Nie et al. show that the onset electrode potential for gas release is 4.5 V vs Li+/Li on an inert SS substrate but decreases to \textasciitilde 4.2 V on a LCO electrode.\textsuperscript{23} The gas composition is complicated, including H2, CH4, CO, etc. (Figure 2a), and the capacity of Li/PEO/LiTFSI/LCO cell also shows rapid drop during cycling under 4.5 V (Figure 2b). Li1.4Al0.4Ti1.6(PO4)3 (LATP) coating on LCO suppresses the gas release, which indicates that the substrate activity is critical. The oxidation process is proposed to be the dehydrogenation of PEO, which generates a strong acid HTFSI. HTFSI not only attacks lithium metal and produces H2 but also accelerates the decomposition of PEO. In another report, Yang et al. illustrates that the terminal group of PEO plays a critical role in its oxidation (Figure 2c).\textsuperscript{38} –OH-terminated PEO is electrochemically stable up to 4.05 V vs Li+/Li, but the –OCH\textsubscript{3}-terminated one shows an expanded stability window to 4.3 V vs Li+/Li. On the other side, the PEO oxidation also attacks the solid phase. Li et al. observed that the crystallinity of LCO was severely degraded upon cycling with PEO up to 4.3 V vs Li+/Li (Figure 2d,e), which reduced ionic diffusivity and increased cell impedance dramatically.\textsuperscript{35}

Beside the chemical/electrochemical stability of PEO and cathode materials, the physical contact between solid PEO and cathodes is also important.\textsuperscript{20} It is well-known that the volume of cathode particles changes upon state of charge. For example, the unit cell volume of NCM811 could shrink \textasciitilde 2.4% when 70% lithium ions are extracted from the lattice.\textsuperscript{39} The volume change of cathode particles upon cycling can result in their delamination from the PEO electrolyte (Figure 2f,g). Nakayama et al. pointed out that such delamination will lead to hotspots in current density, which consequently amplifies the electrochemical polarization and even accelerated the decomposition of lithium salts.\textsuperscript{40}

Other polymers, such as PAN, PPC, and poly(vinylidene fluoride) (PVDF), are generally considered to be stable with 4 V cathode, but they are typically unstable with the anode,\textsuperscript{26,41,42} which will be discussed in Lithium Anode/SPEs Interfaces.

Strategies to Mitigate Cathode/SPEs Interfacial Instabilities. As discussed above, instabilities at this interface mainly arise from oxidation of the polymeric phase. Hence, suppression of polymer oxidation will be effective to address this challenge,
Figure 3. Selected strategies to mitigate cathode/SPE interfacial instability. (a) A conformal LiTaO₃ coating is formed on both active materials and carbon additives by ALD, which prevents PEO oxidation at high electrode potential. (b) An LCO particle with a dual-layer protection formed by nano-LAGP coating and salt decomposition. (c) The cycling performance of a Li/LAGP-LCO cell between 3 and 4.5 V. (d) Schematics of bare NCM and NCM with stable CEI composed of anionic groups from LiBOB decomposition. (e) Cycling performance of Li/Li(DME)ₓFSI-PEO₀.₆/NCM111 cell under different cutoff voltages. The inset is the chemical structure of Li(DME)ₓFSIPEO₀.₆, quasi ionic liquid electrolyte. (f) Structures of cells with ex situ SPE (top) and in situ SPE (bottom). In situ formed SPEs improve the interfacial ion transport compared to ex situ formed SPEs. Panel a is reproduced with permission from ref 43. Copyright 2019 The Royal Society of Chemistry. Panels b and c are reproduced with permission from ref 35. Copyright 2020 Elsevier. Panel d is reproduced from ref 45 with permission from a Creative Commons Attribution 4.0 International License. Panel e is reproduced with permission from ref 24. Copyright 2019 John Wiley and Sons. Panel f is reproduced with permission from ref 46. Copyright 2019 Springer Nature.

and this concept has been explored in multiple approaches, such as inert coating on cathode surface, tuning the electronic structure of electrolytes, and reducing mechanical delamination.

The distinct oxidation behavior of SS and 4 V cathodes suggests that different surfaces have different catalytic capabilities toward PEO oxidation. Hence, passivating the catalytically active sites by inert materials is likely to suppress PEO oxidation. One popular method is surface coating, such as inactive oxides (e.g., Al₂O₃ and ZnO). Conformal surface coating can be realized by atomic layer deposition (ALD). Liang et al., used ALD to coat a thin LiTaO₃ (LTO) layer on LCO surface, and results showed that a coating on an as-prepared electrode is more effective than coating on individual particles, because of a more stable interface between carbon black additives and polymers (Figure 3a).³⁵ Zhai et al. coated Al₂O₃ on NCM111 by ALD. A 2 nm Al₂O₃ layer is effective in suppressing PEO oxidation when charged up to 4.2 V vs Li⁺/Li.⁴¹ Beside ALD, ball-milling and sol–gel methods are scalable for surface coating. Li et al. used a combination of ball milling and sintering to introduce LAGP nanoparticles on the surface of LCO and NCM523. The as-formed LAGP coating and the passivation layer from salt decomposition together reduce the PEO decomposition (Figure 3b). Stable cycling with capacity retention of 84.7%/200 cycles and 93.8%/100 cycles is achieved in LCO (Figure 3c) and NCM523 systems, respectively.

Besides an ex situ oxide layer, cathode electrolyte interfaces (CEI) formed in situ by salt decomposition are also effective to suppress PEO oxidation and help desolvate lithium ions. Choudhury et al. demonstrated that an anionic polymer coating from lithiated Naflon or decomposition of lithium bis(oxalate)borate (LiBOB) can prevent NCM from being exposed to ethers, and facilitate the transport of lithium ions between the electrolyte and cathode (Figure 3d).⁴⁵

Tuning the electronic structure of polymer electrolytes is another promising strategy to enhance the anodic stability of polymer electrolytes. Wu et al. realized this strategy by mixing PEO with quasi-ionic liquids (QILs), such as concentrated lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxy-ethane (DME) (Li(DME)ₓFSI-PEO₀.₆, x = 0.7–1.2).²⁴ PEO and DME form complex pairs with overabundant Li⁺, making it much harder to separate lone electron pairs from PEO and DME; thus, its oxidation stability is evidently enhanced. The onset oxidation potential on Pt electrode increases to 4.7 V vs Li⁺/Li in Li(DME)₀.₇FSI-PEO₀.₆ (Table 3).²⁴ PEO-QILs electrolytes are not strictly solid-state at the operation temperature, because it contains liquid DME inside (~17 wt %), it verified that tuning the electronic structure of the polymer is a feasible method to stabilize polymer electrolytes at high potential.
Regarding mechanical failure due to delamination between SPEs and cathodes, in situ polymerization has been proposed so that the liquid precursor can form intimate contact with cathode particles first. Zhao et al. used 1,3-dioxolane (DOL) as the liquid precursor to improve the interfacial contact, followed by in situ polymerization. Such in situ polymerization successfully reduces the interfacial impedance and improves the electrocatalytic conductivity (Figure 3f). When combined with sulfur, NCM622, and LFP cathodes, the full cells display higher coulombic efficiencies and more stable cycling performance than cells without the in-built structure.

**Lithium Anode/SPEs Interfaces.** Degradation Mechanisms at the Lithium Anode/SPEs Interface. A lithium metal anode is attractive for next-generation batteries because of its high specific capacity (3860 mAh g\(^{-1}\)) and low electrode potential (3.04 V vs standard hydrogen electrode/SHE). The combination of polymer electrolytes and lithium metal is attractive because it enhances both energy density and safety. However, both chemical and mechanical instabilities are present at the interface between the polymer electrolyte and the lithium metal, which limit applications of the SPE-based lithium metal batteries.

**Surface coating, engineering electronic structure and mechanical properties of the electrolyte, and enhancing interfacial adhesion are effective methods to suppress interfacial failures in polymer electrolyte-based solid-state batteries.**

Most polymers, like PEO, PPC, and PAN-based electrolytes, exhibit chemical reactions with lithium metal upon cycling. Li et al. found that the reduction of PEO electrolyte by lithium metal leads to increasing charge-transfer resistance of the Li/PEO interface (Figure 4a). Moreover, Zhou et al. further proved the polymer decomposition by the addition of impurity scavenger, which remarkably enhances cycle life and reduces cell impedance. In PPC, Wang et al. showed that lithium scissor PPC to smaller fragments and even liquid short chains, which leads to high conductivity (\(3 \times 10^{-4}\) S cm\(^{-1}\) at 20 °C) but fast degradation (Figure 4b). Shen et al. also found that side reactions exist between PAN and lithium metal. However, information is still lacking regarding the exact products and pathways of the reaction between polymer electrolytes and the lithium anode.

Another grand challenge of the lithium/polymer interface is its mechanical vulnerability, which results in the well-known phenomenon of lithium dendrites. Dendrite growth has multiple causes, such as mechanical strength of electrolytes, electronic conductivity of electrolytes, and uneven grain boundaries. Among these factors, low shear modulus of polymer electrolyte is one crucial factor, because the value is typically much less than the critical value to block the dendrite growth (1–10 GPa). The uncontrollable dendrite growth and stripping in repeated cycling will cause the formation of dead lithium and promote side reactions between polymer electrolytes and the lithium anode. These issues can become more severe when liquid or polymeric plasticizers are added to enhance conductivity, because they also further soften the polymer electrolyte.

**Strategies to Mitigate Lithium Anode/SPEs Interfacial Problems.** Various strategies have been explored in recent years to improve the stability between lithium metal and SPEs. The general approaches include reduction of contact area and forming a high-quality SEI to enhance chemical stability and the addition of ceramic fillers to enhance mechanical stability.

To address the chemical instability between PPC and lithium discussed above, Wang et al. used cellulose as a scaffold to minimize their contact area, and Li/Li cells with cellulose-PPC electrolyte is stable over 300 h while Li/Li cells with pure PPC electrolyte failed immediately (Figure 4c). Such strategy may be generalized to other polymers that are not stable with lithium metal. The quasi-IL strategy by Wu et al. also changes the composition of SEI on lithium surface and improve the cycling stability of the lithium anode.

On the other side, multiple reports show that ceramic electrolyte particles can greatly enhance the modulus of SPEs to suppress lithium dendrites (Figure 4d). For example, Chen et al. used PEO with garnet \(Li_6La_5Zr_2Ta_5O_{16}\) (LLZTO) particles as composite electrolytes to fabricate an all-solid-state battery. The LLZTO not only provides fast transport channels for lithium ions but also improves the mechanical properties of the solid electrolyte. Therefore, the composite electrolyte successfully suppresses lithium dendrite growth during cycling (Figure 4e,f), and Li/PEO-LLZTO/Li symmetric cells are stable over 670 h with almost no fluctuation in overpotential.

Another feasible strategy to suppress lithium dendrite is to modify the polymer/lithium interface by high-quality SEI or interlayer. For example, Yan et al. introduced intermediary \(Mg_2N_2\) between PEO and lithium anode. \(Mg_2N_2\) could react with lithium anode and form LiN and Mg metal during cycling. LiN has high ionic conductivity (10\(^{-3}\) S cm\(^{-1}\)) at room temperature, which could mitigate Li concentration gradient, and is stable with Li metal. The formed Mg improve the uniform distribution of current density. The homogeneous Li\(^+\) distribution combined with uniform current density successfully suppressed lithium dendrite growth and enhanced the stability of PEO/Li interfaces.

**Polymer/Ceramic Interfaces in Composite Electrolytes.** As discussed above, polymer/ceramic composite electrolytes are effective to enhance the ionic conductivity of polymer electrolytes and suppress the growth of lithium dendrite. Various kinds of ceramic fillers have been explored in the literature, such as nonconductive fillers (e.g., SiO\(_2\) and Al\(_2\)O\(_3\)) and conductive fillers (e.g., LATP, LLZO, and sulfides). The effects of fillers on ion transport are complicated, because fillers affect crystallinity/structures of the polymer matrix and space charge region at the polymer/ceramic interface and thus ion transport. These effects have been discussed in recent reviews, but interfacial instability and degradation are rarely discussed. Nonconductive fillers are typically stable with a polymer because they are inert. Meanwhile, ionic conductive fillers appear to be more active, and may have side reactions with the polymer phase, especially sulfides and LLZO. This is a rarely explored topic, but critical to both scientific understanding and technological advancement.

Recently, Riphaus et al. investigated the interface between PEO and \(Li_{10}SnP_2S_{12}\) (LSPS). They suggested that the chemical reactions between PEO and LSPS cause the growing impedance of the composite electrolyte. The chemical reactions generate polysulfides, PS\(_{3}^-\) units, and sulfite as...
The ceramic/polymer interface inside polymer electrolytes may also degrade, which can remarkably affect transport properties of solid electrolytes in long-term operation. Mitigating such instability is critical to developing robust solid-state batteries.

major decomposition products, which is confirmed by multimode characterizations, such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR, Figure 5a), and solid-state NMR spectroscopy. They also suggested that the −OH group at the end of PEO promotes the formation of sulfite from the decomposition of LSPS (Figure 5b).

Moreover, garnet LLZO particles could react with CO2 in air and form a Li2CO3 passivation layer.63 Huo et al. shows that such a passivation layer with ultralow ionic conductivities hinders the ionic transport between PEO and Ta-doped LLZO (LLZTO).64 Hence, Li+ can move only inside the polymer phase with low ionic conductivity. After the removal of surface Li2CO3 by annealing at 600 °C, the interfacial resistance between PEO and LLZTO pellet drops significantly from 93.1 to 8.9 Ω at 25 °C. Consequently, ions can readily move across the PEO/LLZTO interface, and the ionic conductivity of the LLZTO/PEO (80 wt % LLZTO) composite electrolyte also increases from $7.2 \times 10^{-6}$ S cm⁻¹ with Li2CO3-containing LLZTO to $2.4 \times 10^{-5}$ S cm⁻¹ with Li2CO3-free LLZTO (Figure 5c).

**Perspectives.** As shown above, significant efforts have been devoted to enhancing interfacial stabilities between polymer electrolytes and electrodes/fillers. The current development trend in material engineering includes (1) development of new coating materials and surface doping to suppress oxidation at the cathode and form high-quality CEI; (2) tuning mecanochemical response at the lithium/electrolyte interface to realize reversible and smooth lithium deposition, such as by the addition of fillers with different shapes and various mechanical properties and by SEI modification;65 and (3) control chemical composition at the ceramic filler/polymer interface to stabilize interfacial ion transport. As more and more interests have been paid to polymer electrolyte-based solid state batteries with high energy density, new material engineering solutions are expected to emerge in the coming years.

Currently fundamental understanding on polymer/electrode interfaces and polymer/ceramic electrolyte interface are still limited. To tackle this challenge, more characterizations, especially in situ and in operando studies, are needed. To date, most research on this topic is ex situ, and samples suffer from possible modifications from post treatments such as washing by solvents. Moreover, vulnerable samples could be...
oxidized or contaminated during external sample transfer. One outlier is that Chusid et al. studied the interface between lithium metal and PEO by *in situ* FTIR, which proved direct evidence of interfacial reactions such as the decompositions of salt anions.66 In addition, *in operando* transmission X-ray microscopy has been used to monitor the dendrite and mossy growth over time.67 Deeper investigation of Li dendrite growth would provide more insights about how to mitigate the interfacial instability on the anode side. Apart from *in situ* studies, the cryo-EM (electron microscopy) is another promising method to study this interface without interference from post treatment (Figure 5d,e).68,69 Polymers are very sensitive to beam damage, and this is one reason why they are difficult to be studied by EM at room temperature. Because of the low operation temperature of cryo-EM, the beam damage can be reduced, which helps protect the pristine state of the samples.

Along with advanced characterizations to probe the embedded solid/solid interfaces above, simulation is another powerful tool to circumvent challenges in experiments and help better understand interfacial instabilities. Possible directions include the range of electrochemical windows, compatibility between different polymers, and electrode materials. For instance, Ebadi et al. used molecular dynamic (MD) simulation to study the interface of PEO/lithium metal, and they found the aggregation of cations and anions around the interface is the main reason for the slow dynamics of Li+ transportation (Figure 5f).70 It should be noted that this simulation is without electrical field, so more work needs to be done in the future to understand chemical distribution closer to real conditions (with electrical field).

In addition, besides characterizations at room temperature, it is also very important to understand how temperature affects the interfacial stabilities. Higher temperature can have both positive and negative effects on interfacial stabilities. It may promote side reactions and soften polymers, reducing their capabilities to suppress dendrites. On the other side, they may change SEI compositions and even form SEI with better quality to suppress dendrites. This was reported in liquid electrolytes,71 which may also exist in polymeric ones.

With the combination of advanced experimental and modeling research, new fundamental understanding of interfacial stabilities in polymer electrolyte-based solid-state batteries will be obtained, which will accelerate their adoption in commercial markets to realize safe energy storage with high energy density.

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