

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

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Cite This: *ACS Energy Lett.* 2020, 5, 3244–3253



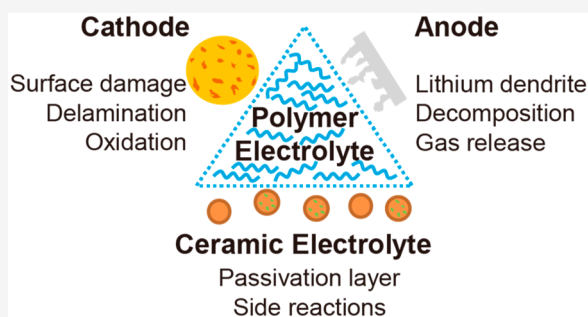
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ABSTRACT: Solid polymer electrolytes (SPEs) are attractive for next-generation energy storage, because they are more thermally stable compared to conventional liquid electrolytes and simpler for scalable manufacturing than ceramic electrolytes. However, 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 SPEs-based solid-state batteries.



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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., Li_3PS_4 , garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}/\text{LLZO}$, $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3/\text{LAGP}$)^{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^{-6} – $10^{-4} \text{ S cm}^{-1}$). However, they encounter significant challenges in scalable manufacturing, thickness reduction, large interfacial impedance, and optimization of operation pressure.^{12,13} On the other side, SPEs are compatible with current tape-casting-based manufacturing processes of batteries.¹⁴ Moreover, SPEs have a much lower density (~ 1 – 1.5 g cm^{-3}) compared to their ceramic counterparts (e.g., $\sim 1.9 \text{ g cm}^{-3}$ for Li_3PS_4 and $\sim 5.1 \text{ g cm}^{-3}$ for LLZO),^{15,16} which helps increase gravimetric energy density at the cell level. It should

be noted that here we focus on polymer electrolytes with solid polymer as the dominant phase, but not gel electrolytes where the majority is liquid.

The two major challenges for SPEs are their low bulk conductivities at room temperature and interfacial instability with other components inside (e.g., electrodes and ceramic electrolyte additives). Great progress has been reported on improving the conductivity of SPEs, especially with the addition of highly conductive ceramic electrolyte particles, such as LLZO and LAGP, enhancing the conductivity from 10^{-5} to $10^{-4} \text{ S cm}^{-1}$.^{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

Received: July 8, 2020

Accepted: September 14, 2020

Published: September 14, 2020

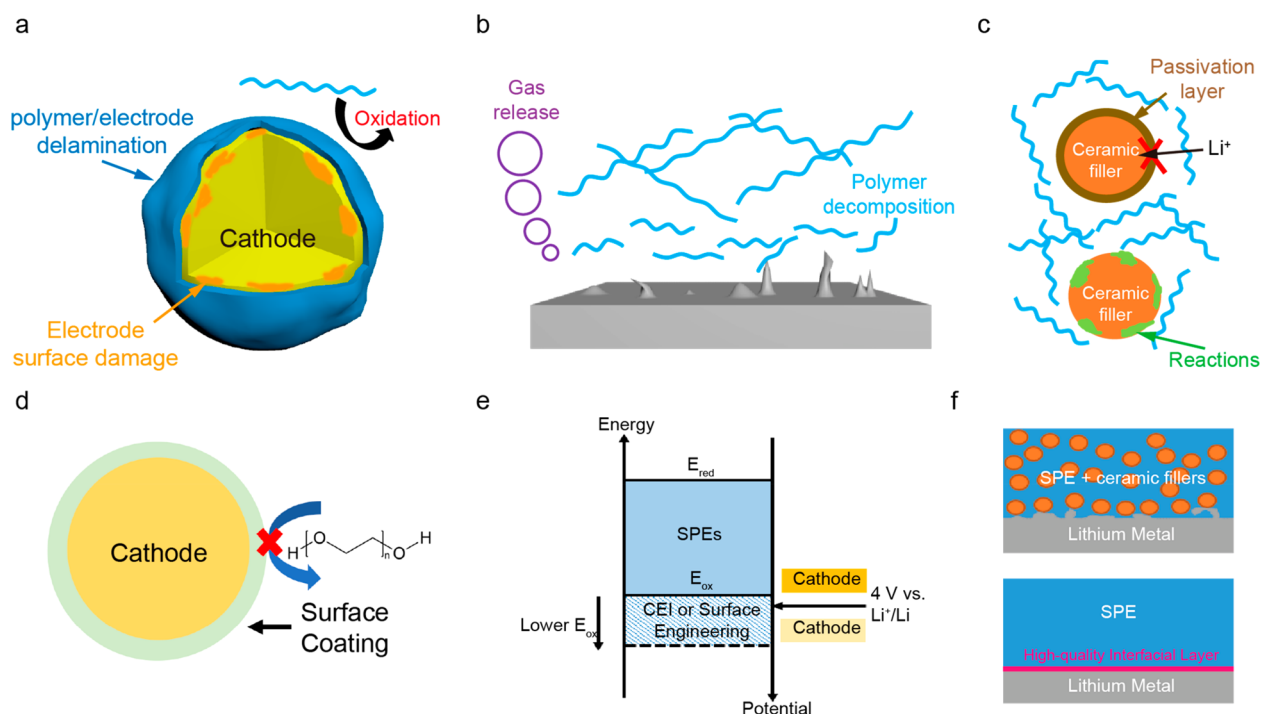


Figure 1. Schematics of selected degradation mechanisms at different interfaces in polymer electrolyte-based solid-state batteries and potential solutions for mitigating the interfacial instabilities. (a) The cathode/polymer electrolyte interface, such as oxidation of polymer electrolytes above 4 V vs Li^+/Li , surface damage of cathode materials, and delamination between polymer and electrode. (b) The lithium/polymer electrolyte interface, such as dendrite growth, gas generation, and polymer decomposition. (c) The ceramic electrolyte/polymer electrolyte interface, such as passivation layer and side reactions between ceramic and polymer electrolytes. (d–f) Strategies to mitigate instabilities above. (d) Surface coating on solid particles to prevent polymer decomposition. (e) Tuning electronic structure of SPEs to reduce decomposition. (f) Adding ceramic fillers (top) or forming high-quality interfacial layer (bottom) to suppress lithium dendrites.

propylene carbonate (PPC), with lithium metal also impedes their applications in lithium metal batteries.²²

Increasing interest has been witnessed during the last several years on understanding and engineering interfacial instability in polymer electrolyte-based batteries,^{23–27} 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 $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ (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.²⁸ Among common polymer electrolytes, those with carbonyl group are stable at

moderately high voltage (e.g., 4–4.5 V vs Li^+/Li),^{29,30} but polymers with an ether group are widely accepted to be unstable above 4 V vs Li^+/Li , such as PEO.³¹ Because PEO is widely studied, and it has been commercialized in 3 V $\text{Li}/\text{LiFePO}_4$ (LFP) batteries,³² addressing the interfacial stability between 4 V cathodes (e.g., NCM and $\text{LiCoO}_2/\text{LCO}$) 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.

The instability at the polymer electrolyte/electrode interface is complicated and originates from various chemical and physical mechanisms. Understanding degradation mechanisms is critical to designing interfaces to mitigate such instability.

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 ,^{33,34} but in galvanostatic cycling, 4 V cathodes without any modification typically show poor performance (e.g., <80% capacity retention after only 20–50 cycles).³⁵ The discrepancy is suspected to arise from distinctly different activities between the inert SS substrate and catalytic

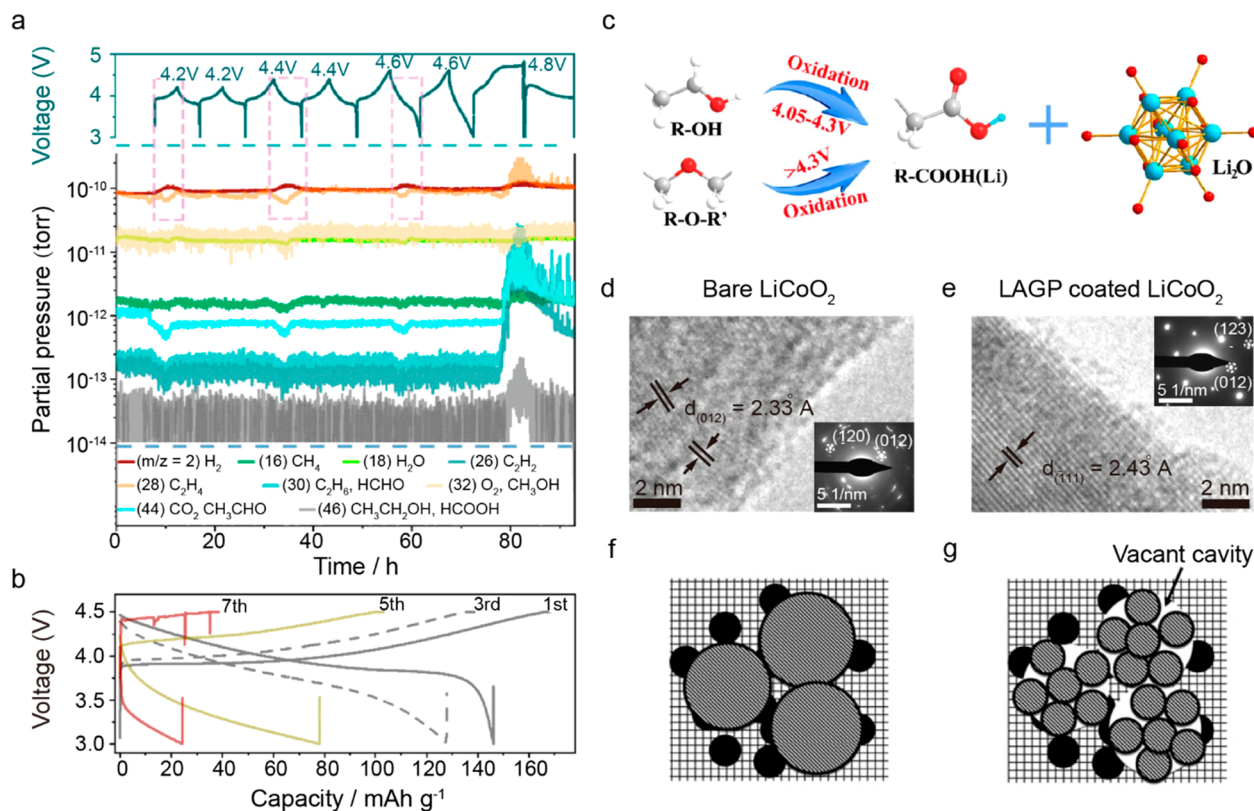


Figure 2. Degradation mechanisms at the cathodes/SPE interface. (a) Differential electrochemical mass spectrometry (DEMS) mass signals (m/z) and (b) corresponding voltage profile of a Li/PEO-LiTFSI/LCO cell. (c) Effects of terminating group on the oxidation stability of PEO electrolytes. (d and e) High-resolution TEM images of (d) bare LCO and (e) LAGP-coated LCO after 50 cycles in PEO electrolyte. The crystallinity of bare LCO is damaged while that of LAGP-coated LCO is not affected. The inset images are corresponding diffraction patterns. (f and g) The physical contact between PEO and LFP particles (f) before volume change and (g) after volume change during cycling. Panels a and b are reproduced from ref 23. Copyright 2020 American Chemical Society. Panel c is reproduced with permission from ref 38. Copyright 2020 The Royal Society of Chemistry. Panels d and e are reprinted with permission from ref 35. Copyright 2020 Elsevier. Panels f and g are reprinted with permission from ref 40. Copyright 2010 The Royal Society of Chemistry.

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.^{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 ~4.2 V on a LCO electrode.²³ The gas composition is complicated, including H₂, CH₄, CO, etc. (Figure 2a), and the capacity of Li/PEO/LCO cell also shows rapid drop during cycling under 4.5 V (Figure 2b). Li_{1.4}Al_{0.4}Ti_{1.6}(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).³⁸ -OH-terminated PEO is electrochemically stable up to 4.05 V vs Li⁺/Li, but the -OCH₃-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.³⁵

Beside the chemical/electrochemical stability of PEO and cathode materials, the physical contact between solid PEO and cathodes is also important.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 ~2.4% when 70% lithium ions are extracted from the lattice.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 amplified the electrochemical polarization and even accelerated the decomposition of lithium salts.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,^{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,

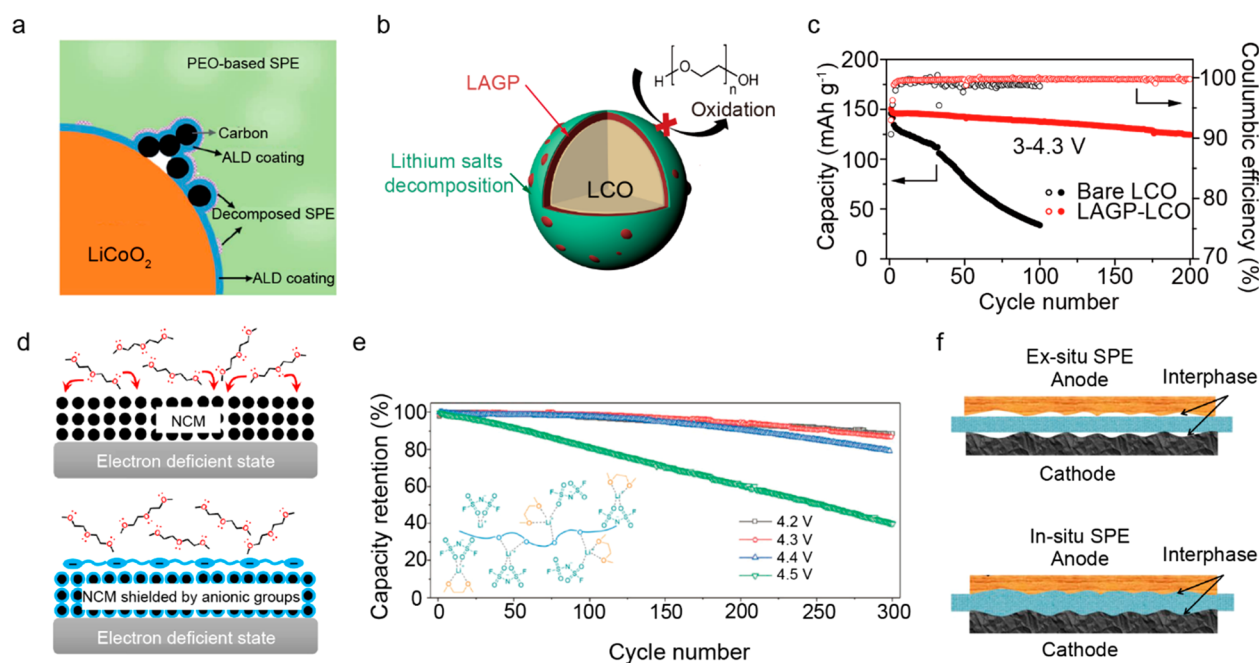


Figure 3. Selected strategies to mitigate cathode/SPE interfacial instability. (a) A conformal LiTaO_3 coating is formed on both active materials and carbon additives by ALD, which prevents PEO oxidation at high electrode potential. (b) An LCO particle with a dual-layer protection formed by nano-LAGP 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) $_{0.7}$ FSI-PEO $_{0.6}$ /NCM111 cell under different cutoff voltages. The inset is the chemical structure of Li(DME) $_x$ FSI-PEO $_{0.6}$ 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., Al_2O_3 and ZnO). Conformal surface coating can be realized by atomic layer deposition (ALD). Liang et al. used ALD to coat a thin LiTaO_3 (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).⁴³ Zhai et al. coated Al_2O_3 on NCM111 by ALD. A 2 nm Al_2O_3 layer is effective in suppressing PEO oxidation when charged up to 4.2 V vs Li^+/Li .⁴⁴ 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 NCM523.³⁵ 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 Nafion 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-dimethoxyethane (DME) (Li(DME) $_x$ FSI-PEO $_{0.6}$, $x = 0.7-1.2$).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) $_{0.7}$ FSI-PEO $_{0.6}$. Impressive capacity retention of 79.2% after 300 cycles is achieved in cycling NCM333 between 4.4 and 3 V vs Li^+/Li (Figure 3e). Moreover, they observed a 3–5 nm thick CEI on cathode surface, which effectively hampered the phase transition of NCM at high electrode potential. Such a CEI layer originates from oxidation of both FSI^- and DME. Higher electrode potential leads to more decomposition of FSI^- , which suppresses further decomposition of DME and PEO. Although the 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.⁴⁶ Such *in situ* polymerization successfully reduces the interfacial impedance and improves the electrolyte 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 ($\sim 3860 \text{ mAh g}^{-1}$) and low electrode potential (-3.04 V vs standard hydrogen electrode/SHE).² 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.^{25,41} 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).⁴⁷ Moreover, Zhou et al. further proved the polymer decomposition by the addition of impurity scavenger, which remarkably enhances cycle life and reduces cell impedance.⁴⁸ In PPC, Wang et al. showed that lithium scissors PPC to smaller fragments and even liquid short chains, which leads to high conductivity ($3 \times 10^{-4} \text{ S cm}^{-1}$ at $20 \text{ }^\circ\text{C}$) but fast degradation (Figure 4b).²⁶ Shen et al. also found that side reactions exist between PAN and lithium metal.⁴⁹ 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.⁵⁰ 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 ($1\text{--}10 \text{ GPa}$).⁵¹ 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.^{52,53}

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).²⁶ 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.²⁴

On the other side, multiple reports show that ceramic electrolyte particles can greatly enhance the modulus of SPEs to suppress lithium dendrites (Figure 4d).^{54,55} For example, Chen et al. used PEO with garnet $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) particles as composite electrolytes to fabricate an all-solid-state battery.⁵⁴ 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 interfacial layer.^{56,57} For example, Yan et al. introduced intermediary Mg_3N_2 between PEO and lithium anode.⁵⁸ Mg_3N_2 could react with lithium anode and form Li_3N and Mg metal during cycling. Li_3N has high ionic conductivity ($10^{-3} \text{ S cm}^{-1}$) at room temperature, which could mitigate Li concentration gradient, and is stable with Li metal. The as-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_2O_3) and conductive fillers (e.g., LATP, LLZO, and sulfides).⁵⁹ 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.^{60–62} These effects have been discussed in recent reviews,⁵⁹ 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, Riphaut et al. investigated the interface between PEO and $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (LSPS).²⁷ They suggested that the chemical reactions between PEO and LSPS cause the growing impedance of the composite electrolyte. The chemical reactions generate polysulfides, PS_4^{3-} units, and sulfite as

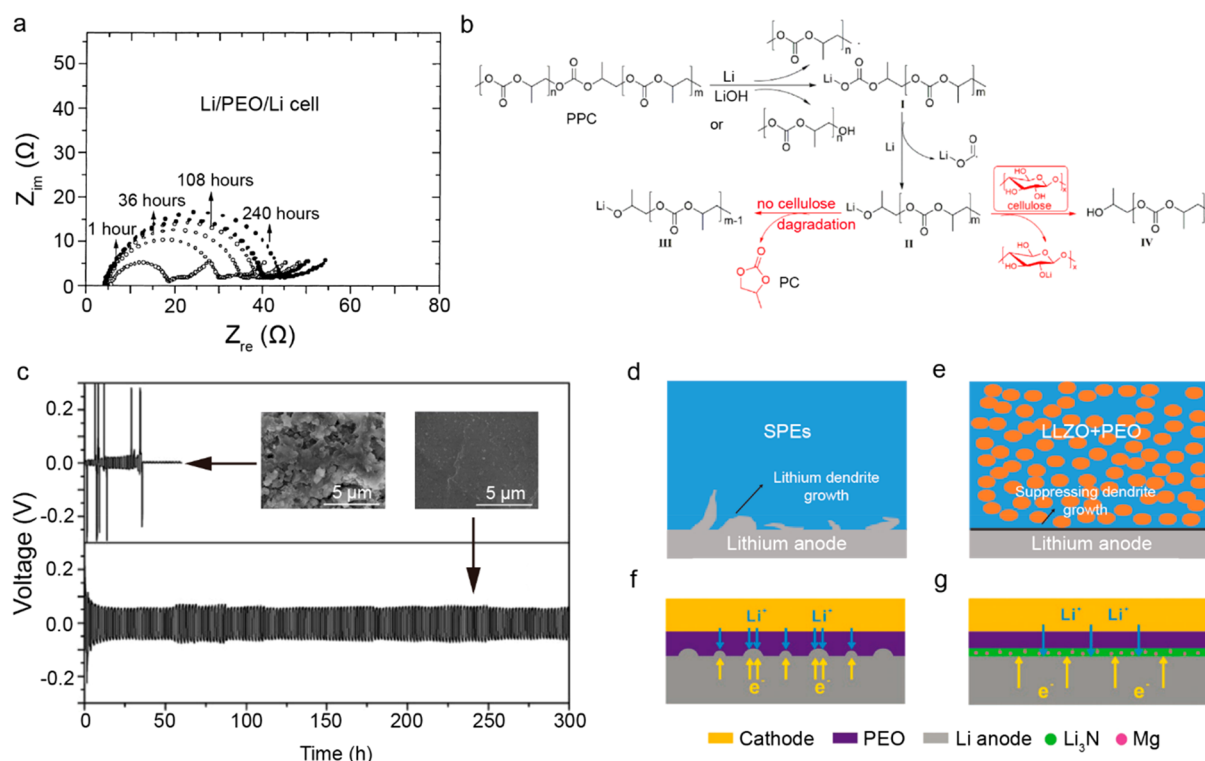


Figure 4. Degradation mechanisms at lithium anode/SPEs interfaces and corresponding solutions. (a) Increasing charge transfer impedance at the Li/PEO interface, which is considered to arise from the reduction of the PEO electrolyte. (b) Possible chemical and electrochemical degradation pathways of PPC-based electrolyte with cellulose or without cellulose during physical contact or electrochemical cycling with lithium metal. (c) Cycling of Li/PPC/Li (upper part) and Li/PPC-cellulose/Li (lower part) cells. Insets are SEM images of corresponding lithium metal electrode surfaces. (d and e) The schematics to demonstrate that the composite electrolyte with LLZO fillers suppresses lithium dendrite growth (e) compared to pure SPEs (d). (f and g) The schematic to show the distribution of Li ions and current density without (f) and with (g) intermediary Mg_3N_2 . The Li_3N and Mg are reaction products between Li metal and Mg_3N_2 . Panel a is reproduced with permission from ref 47. Copyright 2001 Elsevier. Panels b and c are reproduced with permission from ref 26. Copyright 2018 Elsevier. Panels f and g are reproduced with permission from ref 58. Copyright 2019 John Wiley and Sons.

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 $-\text{OH}$ 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 CO_2 in air and form a Li_2CO_3 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 Li_2CO_3 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 $7.2 \times 10^{-6} \text{ S cm}^{-1}$ with Li_2CO_3 -containing LLZTO to $2.4 \times 10^{-5} \text{ S cm}^{-1}$ with Li_2CO_3 -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 mechanochemical 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

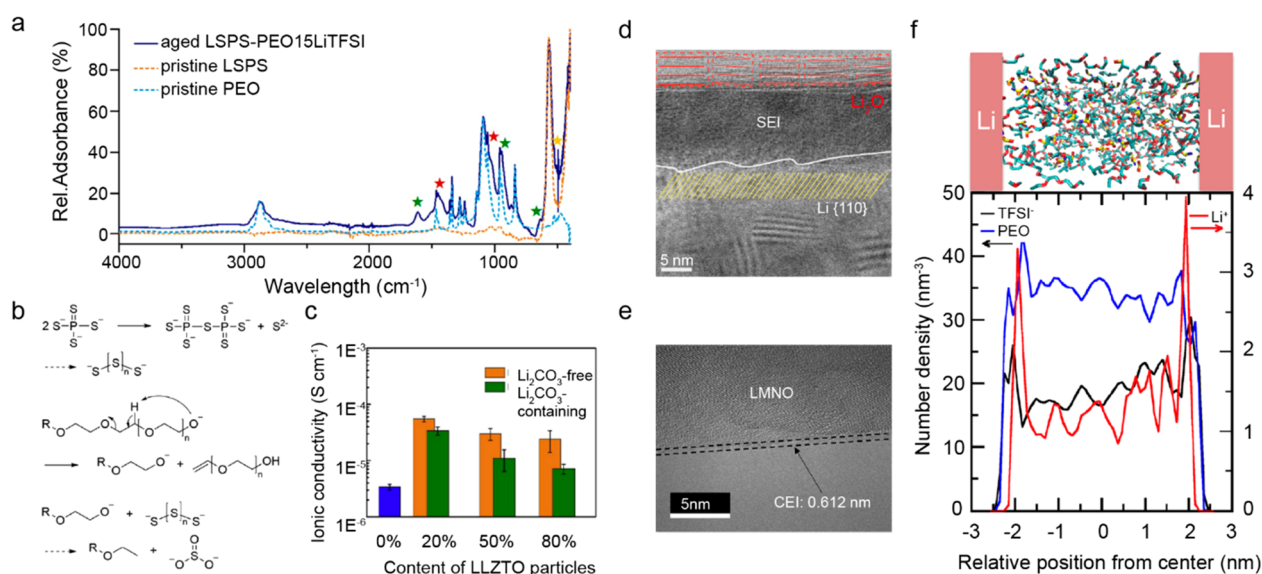


Figure 5. Interfacial issues between polymer and ceramic phases in composite electrolytes and examples of advanced characterizations and simulations for future directions. (a) The FTIR spectrum of a 7-day aged LSPS/PEO₁₅LiTFSI interface compared to pristine LSPS and pristine PEO. The new peaks at 635, 905, and 1615 cm⁻¹ indicate reduction of the polymer accompanied by release of hydrogen or water. (b) Possible reaction mechanisms of LSPS degradation in the PEO electrolyte. (c) Ionic conductivities of Li₂CO₃-free and Li₂CO₃-containing composite electrolytes with different contents of LLZTO particles. (d) A Cryo-TEM image of SEI formed in organic liquid electrolyte. (e) A Cryo-TEM image of CEI on the LiNi_{0.5}Mn_{1.5}O₄ cathode surface. (f) Modeling the partial density of Li⁺, TFSI⁻, and PEO in the presence of a Li metal surface. Panels a and b are reproduced from ref 27 with permission from a Creative Commons Attribution 4.0 International License. Panel c is reproduced with permission from ref 64. Copyright 2020 Elsevier. Panel d is reproduced with permission from ref 68. Copyright 2017 AAAS. Panel e is reproduced with permission from ref 69. Copyright 2018 Elsevier. Panel f is reproduced with permission from ref 70. Copyright 2017 Elsevier.

Advanced characterizations, especially *in situ* characterizations and cryogenic techniques, and modeling will inject new impetus into further revealing the degradation mechanism of SPEs and improving related battery performance.

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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ACKNOWLEDGMENTS

Y.Y. acknowledges funding support from AFOSR (FA9550-18-1-0410 and FA9550-20-1-0233). X.S. is supported by Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) Program, and the Western University.

REFERENCES

- (1) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; Meng, Y. S.; Subramanian, V. R.; Toney, M. F.; Viswanathan, V. V.; Whittingham, M. S.; Xiao, J.; Xu, W.; Yang, J.; Yang, X.-Q.; Zhang, J.-G. Pathways for practical high-energy long-cycling lithium metal batteries. *Nature Energy* **2019**, *4*, 180–186.
- (2) Liu, B.; Zhang, J.-G.; Xu, W. Advancing Lithium Metal Batteries. *Joule* **2018**, *2*, 833–845.
- (3) Albertus, P.; Babinec, S.; Litzelman, S.; Newman, A. Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries. *Nature Energy* **2018**, *3*, 16–21.
- (4) Lin, D.; Liu, Y.; Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotechnol.* **2017**, *12*, 194–206.

(5) Li, J.; Ma, C.; Chi, M.; Liang, C.; Dudney, N. J. Solid Electrolyte: the Key for High-Voltage Lithium Batteries. *Adv. Energy Mater.* **2015**, *5*, 1401408.

(6) Luo, W.; Gong, Y.; Zhu, Y.; Li, Y.; Yao, Y.; Zhang, Y.; Fu, K.; Pastel, G.; Lin, C.-F.; Mo, Y.; Wachsman, E. D.; Hu, L. Reducing Interfacial Resistance between Garnet-Structured Solid-State Electrolyte and Li-Metal Anode by a Germanium Layer. *Adv. Mater.* **2017**, *29*, 1606042.

(7) Liu, Z.; Fu, W.; Payzant, E. A.; Yu, X.; Wu, Z.; Dudney, N. J.; Kiggans, J.; Hong, K.; Rondinone, A. J.; Liang, C. Anomalous High Ionic Conductivity of Nanoporous β -Li₃PS₄. *J. Am. Chem. Soc.* **2013**, *135*, 975–978.

(8) Murugan, R.; Thangadurai, V.; Weppner, W. Fast Lithium Ion Conduction in Garnet-Type Li₇La₃Zr₂O₁₂. *Angew. Chem., Int. Ed.* **2007**, *46*, 7778–7781.

(9) DeWees, R.; Wang, H. Synthesis and Properties of NaSICON-type LATP and LAGP Solid Electrolytes. *ChemSusChem* **2019**, *12*, 3713–3725.

(10) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303–4418.

(11) Huang, B.; Wang, Z.; Li, G.; Huang, H.; Xue, R.; Chen, L.; Wang, F. Lithium ion conduction in polymer electrolytes based on PAN. *Solid State Ionics* **1996**, *85*, 79–84.

(12) Sakamoto, J. More pressure needed. *Nature Energy* **2019**, *4*, 827–828.

(13) Famprikis, T.; Canepa, P.; Dawson, J. A.; Islam, M. S.; Masquelier, C. Fundamentals of inorganic solid-state electrolytes for batteries. *Nat. Mater.* **2019**, *18*, 1278–1291.

(14) Chen, F.; Yang, D.; Zha, W.; Zhu, B.; Zhang, Y.; Li, J.; Gu, Y.; Shen, Q.; Zhang, L.; Sadoway, D. R. Solid polymer electrolytes incorporating cubic Li₇La₃Zr₂O₁₂ for all-solid-state lithium rechargeable batteries. *Electrochim. Acta* **2017**, *258*, 1106–1114.

(15) Yu, S.; Schmidt, R. D.; Garcia-Mendez, R.; Herbert, E.; Dudney, N. J.; Wolfenstine, J. B.; Sakamoto, J.; Siegel, D. J. Elastic Properties of the Solid Electrolyte Li₇La₃Zr₂O₁₂ (LLZO). *Chem. Mater.* **2016**, *28*, 197–206.

(16) Baranowski, L. L.; Heveran, C. M.; Ferguson, V. L.; Stoldt, C. R. Multi-Scale Mechanical Behavior of the Li₃PS₄ Solid-Phase Electrolyte. *ACS Appl. Mater. Interfaces* **2016**, *8*, 29573–29579.

(17) Li, X.; Wang, D.; Wang, H.; Yan, H.; Gong, Z.; Yang, Y. Poly(ethylene oxide)–Li₁₀SnP₂S₁₂ Composite Polymer Electrolyte Enables High-Performance All-Solid-State Lithium Sulfur Battery. *ACS Appl. Mater. Interfaces* **2019**, *11*, 22745–22753.

(18) Li, M.; Frerichs, J. E.; Kolek, M.; Sun, W.; Zhou, D.; Huang, C. J.; Hwang, B. J.; Hansen, M. R.; Winter, M.; Bieker, P. Solid-State Lithium–Sulfur Battery Enabled by Thio-LiSICON/Polymer Composite Electrolyte and Sulfurized Polyacrylonitrile Cathode. *Adv. Funct. Mater.* **2020**, *30*, 1910123.

(19) Zheng, J.; Tang, M.; Hu, Y.-Y. Lithium Ion Pathway within Li₇La₃Zr₂O₁₂-Polyethylene Oxide Composite Electrolytes. *Angew. Chem., Int. Ed.* **2016**, *55*, 12538–12542.

(20) Nie, K.; Hong, Y.; Qiu, J.; Li, Q.; Yu, X.; Li, H.; Chen, L. Interfaces Between Cathode and Electrolyte in Solid State Lithium Batteries: Challenges and Perspectives. *Front. Chem.* **2018**, *6*, 616.

(21) Qiu, J.; Liu, X.; Chen, R.; Li, Q.; Wang, Y.; Chen, P.; Gan, L.; Lee, S.-J.; Nordlund, D.; Liu, Y.; Yu, X.; Bai, X.; Li, H.; Chen, L. Enabling Stable Cycling of 4.2 V High-Voltage All-Solid-State Batteries with PEO-Based Solid Electrolyte. *Adv. Funct. Mater.* **2020**, *30*, 1909392.

(22) Zhang, J.; Zhao, J.; Yue, L.; Wang, Q.; Chai, J.; Liu, Z.; Zhou, X.; Li, H.; Guo, Y.; Cui, G.; Chen, L. Safety-Reinforced Poly-(Propylene Carbonate)-Based All-Solid-State Polymer Electrolyte for Ambient-Temperature Solid Polymer Lithium Batteries. *Adv. Energy Mater.* **2015**, *5*, 1501082.

(23) Nie, K.; Wang, X.; Qiu, J.; Wang, Y.; Yang, Q.; Xu, J.; Yu, X.; Li, H.; Huang, X.; Chen, L. Increasing Poly(ethylene oxide) Stability to 4.5 V by Surface Coating of the Cathode. *ACS Energy Letters* **2020**, *5*, 826–832.

- (24) Wu, H.; Xu, Y.; Ren, X.; Liu, B.; Engelhard, M. H.; Ding, M. S.; El-Khoury, P. Z.; Zhang, L.; Li, Q.; Xu, K.; Wang, C.; Zhang, J.-G.; Xu, W. Polymer-in-“Quasi-Ionic Liquid” Electrolytes for High-Voltage Lithium Metal Batteries. *Adv. Energy Mater.* **2019**, *9*, 1902108.
- (25) Mirsakiyeva, A.; Ebadi, M.; Araujo, C. M.; Brandell, D.; Broqvist, P.; Kullgren, J. Initial Steps in PEO Decomposition on a Li Metal Electrode. *J. Phys. Chem. C* **2019**, *123*, 22851–22857.
- (26) Wang, C.; Zhang, H.; Li, J.; Chai, J.; Dong, S.; Cui, G. The interfacial evolution between polycarbonate-based polymer electrolyte and Li-metal anode. *J. Power Sources* **2018**, *397*, 157–161.
- (27) Riphaut, N.; Stiaszny, B.; Beyer, H.; Indris, S.; Gasteiger, H. A.; Sedlmaier, S. J. Understanding Chemical Stability Issues between Different Solid Electrolytes in All-Solid-State Batteries. *J. Electrochem. Soc.* **2019**, *166*, A975–A983.
- (28) Peljo, P.; Girault, H. H. Electrochemical potential window of battery electrolytes: the HOMO–LUMO misconception. *Energy Environ. Sci.* **2018**, *11*, 2306–2309.
- (29) He, T.-t.; Jing, M.-x.; Yang, H.; Chen, H.; Hua, S.; Ju, B.-w.; Zhou, Q.; Tu, F.-y.; Shen, X.-q.; Qin, S.-b. Effects of gelation behavior of PPC-based electrolyte on electrochemical performance of solid state lithium battery. *SN Applied Sciences* **2019**, *1*, 205.
- (30) Sun, B.; Xu, C.; Mindemark, J.; Gustafsson, T.; Edström, K.; Brandell, D. At the polymer electrolyte interfaces: the role of the polymer host in interphase layer formation in Li-batteries. *J. Mater. Chem. A* **2015**, *3*, 13994–14000.
- (31) Zhou, Q.; Ma, J.; Dong, S.; Li, X.; Cui, G. Intermolecular Chemistry in Solid Polymer Electrolytes for High-Energy-Density Lithium Batteries. *Adv. Mater.* **2019**, *31*, 1902029.
- (32) Zhang, H.; Li, C.; Piszcz, M.; Coysa, E.; Rojo, T.; Rodriguez-Martinez, L. M.; Armand, M.; Zhou, Z. Single lithium-ion conducting solid polymer electrolytes: advances and perspectives. *Chem. Soc. Rev.* **2017**, *46*, 797–815.
- (33) Homann, G.; Stolz, L.; Nair, J.; Laskovic, I. C.; Winter, M.; Kasnatscheew, J. Poly(Ethylene Oxide)-based Electrolyte for Solid-State-Lithium-Batteries with High Voltage Positive Electrodes: Evaluating the Role of Electrolyte Oxidation in Rapid Cell Failure. *Sci. Rep.* **2020**, *10*, 4390.
- (34) Balo, L.; Shalu; Gupta, H.; Kumar Singh, V.; Kumar Singh, R. Flexible gel polymer electrolyte based on ionic liquid EMIMTFSI for rechargeable battery application. *Electrochim. Acta* **2017**, *230*, 123–131.
- (35) Li, Z.; Li, A.; Zhang, H.; Lin, R.; Jin, T.; Cheng, Q.; Xiao, X.; Lee, W.-K.; Ge, M.; Zhang, H.; Zangiabadi, A.; Waluyo, I.; Hunt, A.; Zhai, H.; Borovilas, J. J.; Wang, P.; Yang, X.-Q.; Chuan, X.; Yang, Y. Interfacial engineering for stabilizing polymer electrolytes with 4V cathodes in lithium metal batteries at elevated temperature. *Nano Energy* **2020**, *72*, 104655.
- (36) Kosova, N. V.; Devyatkina, E. T. Comparative study of LiCoO₂ surface modified with different oxides. *J. Power Sources* **2007**, *174*, 959–964.
- (37) Liu, L.; Chen, L.; Huang, X.; Yang, X.-Q.; Yoon, W.-S.; Lee, H. S.; McBreen, J. Electrochemical and In Situ Synchrotron XRD Studies on Al[sub 2]O[sub 3]-Coated LiCoO[sub 2] Cathode Material. *J. Electrochem. Soc.* **2004**, *151*, A1344.
- (38) Yang, X.; Jiang, M.; Gao, X.; Bao, D.; Sun, Q.; Holmes, N.; Duan, H.; Mukherjee, S.; Adair, K.; Zhao, C.; Liang, J.; Li, W.; Li, J.; Liu, Y.; Huang, H.; Zhang, L.; Lu, S.; Lu, Q.; Li, R.; Singh, C. V.; Sun, X. Determining the limiting factor of the electrochemical stability window for PEO-based solid polymer electrolytes: main chain or terminal – OH group? *Energy Environ. Sci.* **2020**, *13*, 1318–1325.
- (39) Koerver, R.; Zhang, W.; de Biasi, L.; Schweidler, S.; Kondrakov, A. O.; Kolling, S.; Brezesinski, T.; Hartmann, P.; Zeier, W. G.; Janek, J. Chemo-mechanical expansion of lithium electrode materials – on the route to mechanically optimized all-solid-state batteries. *Energy Environ. Sci.* **2018**, *11*, 2142–2158.
- (40) Nakayama, M.; Wada, S.; Kuroki, S.; Nogami, M. Factors affecting cyclic durability of all-solid-state lithium polymer batteries using poly(ethylene oxide)-based solid polymer electrolytes. *Energy Environ. Sci.* **2010**, *3*, 1995–2002.
- (41) Wang, X.; Hao, X.; Xia, Y.; Liang, Y.; Xia, X.; Tu, J. A polyacrylonitrile (PAN)-based double-layer multifunctional gel polymer electrolyte for lithium-sulfur batteries. *J. Membr. Sci.* **2019**, *582*, 37–47.
- (42) Hsu, C.-Y.; Liu, R.-J.; Hsu, C.-H.; Kuo, P.-L. High thermal and electrochemical stability of PVDF-graft-PAN copolymer hybrid PEO membrane for safety reinforced lithium-ion battery. *RSC Adv.* **2016**, *6*, 18082–18088.
- (43) Liang, J.; Sun, Y.; Zhao, Y.; Sun, Q.; Luo, J.; Zhao, F.; Lin, X.; Li, X.; Li, R.; Zhang, L.; Lu, S.; Huang, H.; Sun, X. Engineering the conductive carbon/PEO interface to stabilize solid polymer electrolytes for all-solid-state high voltage LiCoO₂ batteries. *J. Mater. Chem. A* **2020**, *8*, 2769–2776.
- (44) Zhai, H.; Gong, T.; Xu, B.; Cheng, Q.; Paley, D.; Qie, B.; Jin, T.; Fu, Z.; Tan, L.; Lin, Y.-H.; Nan, C.-W.; Yang, Y. Stabilizing Polyether Electrolyte with a 4 V Metal Oxide Cathode by Nanoscale Interfacial Coating. *ACS Appl. Mater. Interfaces* **2019**, *11*, 28774–28780.
- (45) Choudhury, S.; Tu, Z.; Nijamudheen, A.; Zachman, M. J.; Stalin, S.; Deng, Y.; Zhao, Q.; Vu, D.; Kourkoutis, L. F.; Mendoza-Cortes, J. L.; Archer, L. A. Stabilizing polymer electrolytes in high-voltage lithium batteries. *Nat. Commun.* **2019**, *10*, 3091.
- (46) Zhao, Q.; Liu, X.; Stalin, S.; Khan, K.; Archer, L. A. Solid-state polymer electrolytes with in-built fast interfacial transport for secondary lithium batteries. *Nature Energy* **2019**, *4*, 365–373.
- (47) Li, Q.; Sun, H. Y.; Takeda, Y.; Imanishi, N.; Yang, J.; Yamamoto, O. Interface properties between a lithium metal electrode and a poly(ethylene oxide) based composite polymer electrolyte. *J. Power Sources* **2001**, *94*, 201–205.
- (48) Zhou, W.; Gao, H.; Goodenough, J. B. Low-Cost Hollow Mesoporous Polymer Spheres and All-Solid-State Lithium, Sodium Batteries. *Adv. Energy Mater.* **2016**, *6*, 1501802.
- (49) Shen, F.; Wang, K.; Yin, Y.; Shi, L.; Zeng, D.; Han, X. PAN/PI functional double-layer coating for dendrite-free lithium metal anodes. *J. Mater. Chem. A* **2020**, *8*, 6183–6189.
- (50) Harry, K. J.; Hallinan, D. T.; Parkinson, D. Y.; MacDowell, A. A.; Balsara, N. P. Detection of subsurface structures underneath dendrites formed on cycled lithium metal electrodes. *Nat. Mater.* **2014**, *13*, 69–73.
- (51) Monroe, C.; Newman, J. The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces. *J. Electrochem. Soc.* **2005**, *152*, A396.
- (52) Klongkan, S.; Pumchusak, J. Effects of Nano Alumina and Plasticizers on Morphology, Ionic Conductivity, Thermal and Mechanical Properties of PEO-LiCF₃SO₃ Solid Polymer Electrolyte. *Electrochim. Acta* **2015**, *161*, 171–176.
- (53) Ramesh, S.; Winie, T.; Arof, A. K. Mechanical studies on poly(vinyl chloride)–poly(methyl methacrylate)-based polymer electrolytes. *J. Mater. Sci.* **2010**, *45*, 1280–1283.
- (54) Chen, L.; Li, Y.; Li, S.-P.; Fan, L.-Z.; Nan, C.-W.; Goodenough, J. B. PEO/garnet composite electrolytes for solid-state lithium batteries: From “ceramic-in-polymer” to “polymer-in-ceramic. *Nano Energy* **2018**, *46*, 176–184.
- (55) Wan, Z.; Lei, D.; Yang, W.; Liu, C.; Shi, K.; Hao, X.; Shen, L.; Lv, W.; Li, B.; Yang, Q.-H.; Kang, F.; He, Y.-B. Low Resistance–Integrated All-Solid-State Battery Achieved by Li₇La₃Zr₂O₁₂ Nanowire Upgrading Polyethylene Oxide (PEO) Composite Electrolyte and PEO Cathode Binder. *Adv. Funct. Mater.* **2019**, *29*, 1805301.
- (56) Zhang, X.; Wang, S.; Xue, C.; Xin, C.; Lin, Y.; Shen, Y.; Li, L.; Nan, C.-W. Self-Suppression of Lithium Dendrite in All-Solid-State Lithium Metal Batteries with Poly(vinylidene difluoride)-Based Solid Electrolytes. *Adv. Mater.* **2019**, *31*, 1806082.
- (57) Wang, C.; Bai, G.; Yang, Y.; Liu, X.; Shao, H. Dendrite-free all-solid-state lithium batteries with lithium phosphorous oxynitride-modified lithium metal anode and composite solid electrolytes. *Nano Res.* **2019**, *12*, 217–223.
- (58) Yan, M.; Liang, J.-Y.; Zuo, T.-T.; Yin, Y.-X.; Xin, S.; Tan, S.-J.; Guo, Y.-G.; Wan, L.-J. Stabilizing Polymer–Lithium Interface in a Rechargeable Solid Battery. *Adv. Funct. Mater.* **2020**, *30*, 1908047.

(59) Zou, Z.; Li, Y.; Lu, Z.; Wang, D.; Cui, Y.; Guo, B.; Li, Y.; Liang, X.; Feng, J.; Li, H.; Nan, C.-W.; Armand, M.; Chen, L.; Xu, K.; Shi, S. Mobile Ions in Composite Solids. *Chem. Rev.* **2020**, *120*, 4169–4221.

(60) Brogioli, D.; Langer, F.; Kun, R.; La Mantia, F. Space-Charge Effects at the Li₇La₃Zr₂O₁₂/Poly(ethylene oxide) Interface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 11999–12007.

(61) Langer, F.; Palagonia, M. S.; Bardenhagen, I.; Glenneberg, J.; La Mantia, F.; Kun, R. Impedance Spectroscopy Analysis of the Lithium Ion Transport through the Li₇La₃Zr₂O₁₂/P(EO)₂₀Li Interface. *J. Electrochem. Soc.* **2017**, *164*, A2298–A2303.

(62) Chen, X. C.; Liu, X.; Samuthira Pandian, A.; Lou, K.; Delnick, F. M.; Dudney, N. J. Determining and Minimizing Resistance for Ion Transport at the Polymer/Ceramic Electrolyte Interface. *ACS Energy Letters* **2019**, *4*, 1080–1085.

(63) Xia, W.; Xu, B.; Duan, H.; Tang, X.; Guo, Y.; Kang, H.; Li, H.; Liu, H. Reaction mechanisms of lithium garnet pellets in ambient air: The effect of humidity and CO₂. *J. Am. Ceram. Soc.* **2017**, *100*, 2832–2839.

(64) Huo, H.; Li, X.; Sun, Y.; Lin, X.; Doyle-Davis, K.; Liang, J.; Gao, X.; Li, R.; Huang, H.; Guo, X.; Sun, X. Li₂CO₃ effects: New insights into polymer/garnet electrolytes for dendrite-free solid lithium batteries. *Nano Energy* **2020**, *73*, 104836.

(65) Gao, Y.; Yan, Z.; Gray, J. L.; He, X.; Wang, D.; Chen, T.; Huang, Q.; Li, Y. C.; Wang, H.; Kim, S. H.; Mallouk, T. E.; Wang, D. Polymer–inorganic solid–electrolyte interphase for stable lithium metal batteries under lean electrolyte conditions. *Nat. Mater.* **2019**, *18*, 384–389.

(66) Chusid, O.; Gofer, Y.; Aurbach, D.; Watanabe, M.; Momma, T.; Osaka, T. Studies of the interface between lithium electrodes and polymeric electrolyte systems using in situ FTIR spectroscopy. *J. Power Sources* **2001**, *97–98*, 632–636.

(67) Yang, N.-H.; Song, Y.-F.; Liu, R.-S. In Operando Transmission X-ray Microscopy Illuminated by Synchrotron Radiation for Li-Ion Batteries. *ACS Energy Letters* **2018**, *3*, 1911–1928.

(68) Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C.-L.; Joubert, L.-M.; Chin, R.; Koh, A. L.; Yu, Y.; Perrino, J.; Butz, B.; Chu, S.; Cui, Y. Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy. *Science* **2017**, *358*, 506.

(69) Wang, X.; Li, Y.; Meng, Y. S. Cryogenic Electron Microscopy for Characterizing and Diagnosing Batteries. *Joule* **2018**, *2*, 2225–2234.

(70) Ebadi, M.; Costa, L. T.; Araujo, C. M.; Brandell, D. Modelling the Polymer Electrolyte/Li-Metal Interface by Molecular Dynamics simulations. *Electrochim. Acta* **2017**, *234*, 43–51.

(71) Wang, J.; Huang, W.; Pei, A.; Li, Y.; Shi, F.; Yu, X.; Cui, Y. Improving cyclability of Li metal batteries at elevated temperatures and its origin revealed by cryo-electron microscopy. *Nature Energy* **2019**, *4*, 664–670.