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Overcoming misconceptions in lithium metal polymer electrolyte batteries

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Lithium metal is the holy grail of anodes due to its 10-fold higher gravimetric capacity than graphite. All-solid-state lithium polymer electrolyte batteries are receiving significant attention due to their increased flexibility compared to inorganic solid-state electrolytes, which enhances processability, accommodates cell swelling, and enables more homogeneous interphases. However, prototype solid-state lithium polymer electrolyte batteries have been limited in their usage due to the low ionic conductivity of the electrolyte, which limits their ability to cycle lithium metal at high rates. In this opinion, we provide alternative interpretations of high-rate capability lithium metal polymer electrolytes and breakthroughs in highly ionically conductive all-solid-state polymer electrolytes. In addition, we provide guidance on how to characterize and evaluate polymer electrolytes in lithium metal batteries.

Broader context

Electrochemical energy storage is one of the key solutions that must be enabled as society trends toward carbon net-zero. Applications critical to electrification, such as electric vehicles, grid-scale storage, and electric flight, necessitate the development of higher energy batteries to further expand their ranges and storage capacity. However, one of the ways current lithium-ion batteries (LIBs) are limited in their maximum energy density is the graphite anode's low maximum theoretical capacity. Lithium metal is the holy grail of anodes due to its 10-fold increase in capacity over graphite. Significant attention has been paid to the research and development (R&D) of all-solid-state lithium metal batteries. The goal is simple: to replace a liquid electrolyte with a solid-state electrolyte. These solid-state electrolytes can potentially improve the cell's overall safety and reduce the need for external thermal management. This increases the energy density of the pack by reducing overall mass and volume. Solid polymer electrolytes offer great potential for solid-state batteries due to their increased mechanical flexibility, which enhances processability, accommodates cell swelling, and enables more homogeneous interphases. In this opinion, we discuss the challenges facing lithium metal polymer batteries and possible paths forward, including encouraging deep collaboration between polymer chemists and electrochemists.

Introduction

The demand for energy storage is rapidly increasing as society trends towards electrification in an effort to achieve carbon net-zero. Applications critical to electrification, such as electric vehicles, grid-scale storage, and electric flight, necessitate the development of higher energy batteries to further expand their

ranges and storage capacity. However, current lithium-ion batteries (LIBs) are limited in their maximum energy density in part due to the graphite anode's maximum theoretical capacity of 372 mAh g⁻¹. Lithium metal is the holy grail of anodes due to its 10-fold increase in gravimetric energy density over graphite (3860 mAh g⁻¹), lowest electrochemical potential (−3.04 V), and low density (0.53 g cm⁻³).^{1–4} Two sets of challenges are associated with using lithium metal: the growth of penetrative dendrites and the continuous consumption of lithium and liquid electrolyte.⁵ Dendrite formation is exacerbated by higher current densities, thus limiting the lithium metal deposition rate.³ One way to mask the challenges associated with lithium metal is to use excess lithium inventory and liquid electrolyte, making the cell appear to have excellent cycle life at the expense of cell energy density.⁶ Significant attention and debate have been focused on this issue in the literature, with many studies claiming long cycle lives of lithium metal cells.

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Productive debate and discussion throughout the literature has culminated in the establishment of excellent guidelines concerning cell composition and testing to mediate the standards in the field and ensure fair comparison across studies.⁷ These guidelines have been successful, with some studies leading to significant achievements, such as Jie *et al.* demonstrating a 19 Ah, >500 Wh kg⁻¹ cell that retains 91% capacity after 130 cycles.⁸ It is worth noting that the cells in this study could charge/discharge >4 mAh cm⁻² of lithium with a charging rate of C/10 (~0.4 mA cm⁻²). Since lithium is plated and dendrites can form during charging, the charging rates must be held to the low current density of ~0.4 mA cm⁻² to mitigate dendritic growth.

Recently, numerous excellent reviews and perspectives have been written on polymer electrolytes.^{9–12} However, some clarifications are needed to ensure consistency across the field. This opinion focuses on some key issues in polymer electrolyte lithium metal batteries and will propose some considerations that will be useful to the broader research community that seeks to advance the field of polymer electrolyte.

Significant research and development (R&D) attention has been paid to all-solid-state lithium metal batteries.^{1,11,13–16} The goal is simple: to replace a liquid electrolyte with a solid-state electrolyte. These solid-state electrolytes typically feature high mechanical strength and high thermal stability, improving the overall safety of the cell and reducing the need for external thermal management. This increases the energy density of the pack by reducing overall mass and volume. Additionally, solid-state electrolytes do not suffer from electrolyte leakage, allowing for increased safety and bipolar stacking of the cells to cut down on non-active materials and further increase energy density of the pack. There are two broad classes of solid-state electrolytes: inorganic and polymeric. Solid polymer electrolytes (SPEs), or an electrolyte containing a polymer and a salt, have increased flexibility relative to inorganic solid-state electrolytes, enhancing processability, accommodating cell swelling, and enabling more homogeneous interphases.¹² The first SPE to gain attention for use in batteries was based on poly(ethylene oxide) (PEO) complexed with high wt% of lithium salts, coined a “polymer-in-salt” electrolyte. However, PEO-based electrolytes are plagued by low ionic conductivity. They must be heated above PEO’s melting point of ~60 °C to achieve appreciable ionic conductivity (~1 × 10⁻⁴ S cm⁻¹), at the expense of mechanical strength.^{12,17} These polymer-in-salt electrolytes also suffer from low electrochemical stability, which limits their usage with high-voltage cathodes. Additionally, PEO-based polymer-in-salt electrolytes’ cation transport number (*t*⁺), the fraction of current used to move lithium cations, is quite low at ~0.2.^{17,18} In contrast, traditional liquid electrolytes exhibit *t*⁺ < 0.5 with higher ionic conductivities (>1 × 10⁻³ S cm⁻¹). It is worth noting that the cation transport number of inorganic solid-state electrolytes is ~1.0.¹⁰ A high transport number is critical to mitigating ion concentration gradients, which drive dendrite formation, ensuring uniform lithium deposits at increased charging rates. For a more detailed discussion on the importance of high transport numbers, we recommend the excellent review by Shan *et al.*¹⁰ Efforts to increase

the ionic conductivity and cation transport number of these polymer electrolytes led to the R&D of a class of electrolytes called single-ion conducting solid polymer electrolytes.¹⁹ The main benefit of anchoring the anion to the polymer backbone and restricting anion mobility is achieving high cation transport numbers, with many single-ion conducting polymer electrolytes achieving >0.9 *t*⁺. While the cation transport number is enhanced, the room temperature ionic conductivity of these single-ion conducting polymer electrolytes remains low (~1 × 10⁻⁵ S cm⁻¹).¹⁰

To achieve ionic conductivities comparable to inorganic solid electrolytes or liquid electrolytes, it is necessary to include conductivity-enhancing additives, often called plasticizers, to form gel polymer electrolytes (GPEs).^{9,20} From our viewpoint, we would argue that the term plasticizer is not appropriate to describe the function and intent of these additives. The primary function of a plasticizer is to separate polymer chains to lower the glass transition temperature, increase free volume, and reduce intermolecular forces. However, if the additive has the effect of supporting alternative pathways for ion conduction, other than polymer chain segmental motion, it should be classified as a multifunctional additive due to its dual role as a plasticizer and solvent for salt dissociation. One could assume that ion transport in polymer electrolytes containing multifunctional additives is analogous to ion transport in a polymer separator soaked with a liquid electrolyte. The addition of multifunctional additives has resulted in gel polymer electrolytes with ionic conductivities of ~1 × 10⁻³ S cm⁻¹, 2–3 orders of magnitude higher than dry solid polymer electrolytes.²¹ However, including these additives removes the benefits of using a solid-state electrolyte; thus, the advantage of a GPE over a liquid-soaked porous separator must be demonstrated. Recently, numerous studies and reviews have focused on *in situ* polymerization of monomers in the presence of initiators and conductivity-enhancing additives to generate an *in situ* formed gel polymer electrolyte.^{9,22–24} These *in situ* formed polymer electrolytes, coined with the new term quasi-solid-state polymer electrolytes (QSSPE), have the supposed advantages of simplified processing and formation of homogeneous interphases with the electrodes, compared to the comparable *ex situ* formed polymer electrolyte films. One of the significant advantages we observed in employing an *in situ* synthesized polymer electrolyte *versus* an *ex situ* formed polymer electrolyte film of the same composition was an increase in ionic conductivity with no detrimental effect on oxidative stability. For example, we synthesized a polymer electrolyte formed *via* the free radical polymerization of trimethylolpropane propoxylate triacrylate (TPPTA) initiated by azobisisobutyronitrile (AIBN) in the presence of LiTFSI salt and additives such as thietane-1,1-dioxide and sulfolane. The *ex situ*, free-standing polymer electrolyte film exhibited an ionic conductivity of 0.33 mS cm⁻¹ at RT and an oxidative stability of 4.5 V. When injected into a separator and polymerized *in situ*, the polymer electrolyte exhibited 0.98 mS cm⁻¹ ion conductivity at RT, a 3-times increase, and maintained an oxidative stability of 4.5 V. For more detailed exploration of this class of materials, we recommend the excellent review by Vijayajumar *et al.*,

who describe in-depth the syntheses, compositions, and performances of *in situ* formed polymer electrolytes.⁹ We agree with Vijayakumar *et al.*'s definitions of GPEs, quasi-solid-state polymer electrolytes, and plasticized polymer electrolytes, and sympathize with the dilemma of having several terms to describe a class of materials. Thus, we propose the unifying term “polyquid” for an *in situ* formed polymer electrolyte containing a polymer and an ionic conductivity-enhancing additive in the presence of a salt.

Compositional confusion in polymer electrolytes

The preeminent mission of polymer electrolyte research is to rival the ionic conductivity of inorganic solid-state and liquid electrolytes. In pursuit of this effort, numerous reports have been published recently purporting high ionic conductivity polymer electrolytes prepared *via* the free radical co-polymerization of vinyl ethylene carbonate (VEC).^{10,25–27} In one such case, Shan *et al.* reported a highly ionically conductive single-lithium-ion conducting polymer electrolyte with ionic conductivity of 1.6 mS cm^{-1} at 20°C (Fig. 2(a)).²⁵ Another example worth highlighting is a study by Tang *et al.*, who report the co-polymerization of VEC with a polymerizable ionic liquid (1-allyl-1-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide) and a perfluorinated crosslinker (2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol diacrylate).²⁷ They report an ionic conductivity of 1.37 mS cm^{-1} at 25°C for a polymer electrolyte comprised of

VEC: ionic liquid: crosslinker in a 3:8.5:2 molar ratio, equating to $\sim 7.5 \text{ wt\%}$ VEC, $\sim 76 \text{ wt\%}$ ionic liquid, and $\sim 16 \text{ wt\%}$ crosslinker. It is worth noting that a polymer electrolyte comprised of the ionic liquid and crosslinker without VEC obtains an ionic conductivity 10 times lower than the polymer electrolyte containing VEC. In our opinion, these are remarkable ionic conductivities to achieve at room temperature, considering that a typical single-ion conducting polymer electrolyte has ionic conductivity of $\sim 0.001 \text{ mS cm}^{-1}$, constituting a 1600 times improvement.¹⁰

This 1600-fold improvement in ionic conductivity reported by Shan *et al.* warranted a deeper exploration to understand the origin and veracity of this observation. Shan *et al.*'s single-ion conducting polymer electrolyte was prepared *via* the *in situ* free radical co-polymerization of vinyl ethylene carbonate (VEC) and lithium (4-styrenesulfonyl)(trifluoromethanesulfonyl)imide (LiSTFSI) monomer with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt and AIBN initiator in a 10:1:1:0.1 molar ratio (VEC:LiSTFSI:LiTFSI:AIBN), respectively, to form the polymer electrolyte poly(VEC-*r*-LiSTFSI) (Fig. 1(a)). However, VEC is an allylic monomer, and it has been widely reported that allylic monomers ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{R}$) do not readily polymerize by free radical polymerization.²⁶ Attempts to polymerize allyl acetate, an allylic monomer analogous to VEC, by free radical polymerization date back to Bartlett *et al.* in 1945; but only low molecular weight oligomers of allyl acetate were formed.²⁸ VEC was reacted with 1 mol% AIBN at 80°C for 10 hours. The reaction products were analyzed by ^1H NMR, confirming 12% monomer conversion to low molecular weight oligomers. This is consistent with Bartlett *et al.*'s finding that the

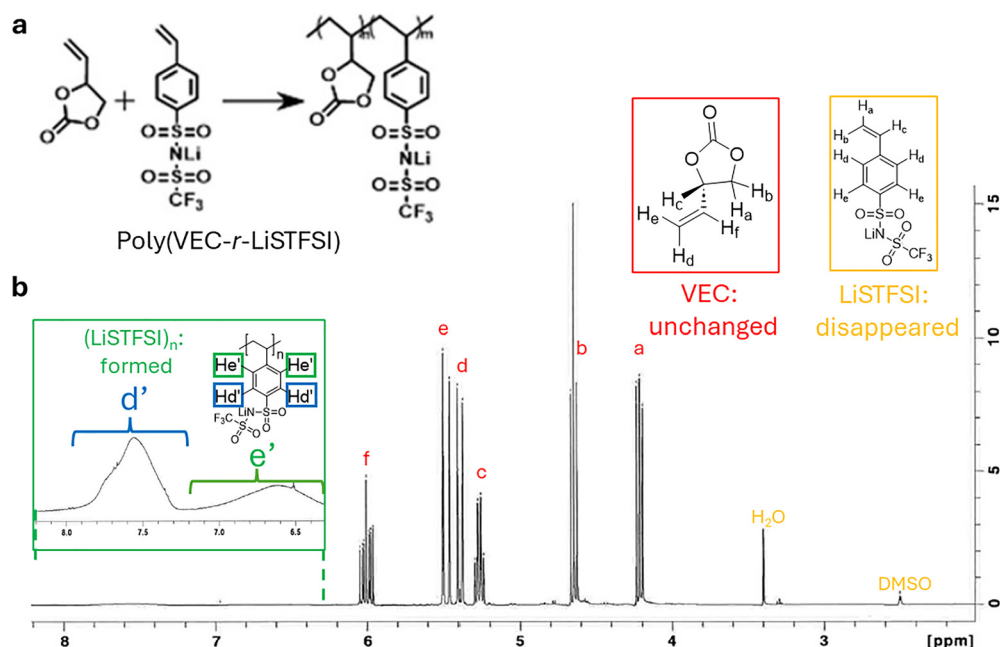


Fig. 1 (a) Synthesis of the single-ion polymer electrolyte poly(VEC-*r*-LiSTFSI). Adapted with permission from ref. 25, Copyright 2022, American Chemical Society. (b) ^1H NMR spectrum of the attempted co-polymerization of VEC and LiSTFSI dissolved in d_6 -DMSO at 400 MHz. The presence of the unreacted VEC is indicated by the peaks (a–f). Inset: Magnified 6.5 to 8.0 ppm region. The broadness of the peaks in the aromatic region and the absence of the allylic protons (^1H NMR [d_6 -DMSO] δ : 5.21 ppm [H_a], 5.95 ppm [H_b], 6.79 ppm [H_c]) is indicative of polymerization of LiSTFSI. In our opinion, this NMR analysis does not support the formation of the single-ion polymer electrolyte poly(VEC-*r*-LiSTFSI).

attempted polymerization of an allylic monomer with the same concentration of AIBN (0.1 mol L^{-1}) at 80°C yielded $\sim 10\%$ monomer conversion. Bartlett *et al.* found, and Matsumoto *et al.* confirmed, that ~ 100 -fold quantities of initiator, relative to traditional free-radical polymerizations, were required to promote monomer conversion.^{28,29} Additionally, the rate of monomer consumption is directly proportional to the rate of initiator consumption, indicating the reaction is self-limiting, or autoinhibited.³⁰ The absence of propagation is due to degradative chain transfer. In this process, the active propagating radical abstracts allylic hydrogen from another monomer to terminate chain growth, forming a new allylic radical. The produced allylic radicals are too stable to re-initiate polymerization due to the resonance stability; instead, they undergo radical–radical termination.³¹ High propagation activation energy of allylic monomers ($24\text{--}27 \text{ kcal mol}^{-1}$) further causes formation of short-chain oligomers instead of the desired high molecular weight polymers.³² While we would argue that free radical polymerization of VEC is infeasible, there is still the question of whether VEC, an allylic monomer, can co-polymerize with LiTFSI, a vinyl monomer. Bevington *et al.* reported an analogous attempt at co-polymerization using allyl ethers, an allylic monomer, with methacrylate and styrene, vinyl monomers.³³ The incorporation of allyl ethers was minimal, with only 8–30 units in copolymers of 50–100 kDa molecular weight. Furthermore, it was suggested that the allyl ether monomers present in the bulk free radical polymerization of methyl methacrylate (MMA) only started reacting noticeably after the MMA had been consumed.³⁴ The propagating poly-MMA radical prefers to react with MMA monomers, rather than an allylic monomer such as allyl ether. The vinyl monomers (*e.g.*, MMA and styrene) are far more reactive than the allylic monomer (*e.g.*, allyl ether). This is evidenced by the large gap between the propagating activation energy of allylic monomers ($24\text{--}27 \text{ kcal mol}^{-1}$) and vinyl monomers such as styrene ($18.9 \text{ kcal mol}^{-1}$).^{32,35}

Shan *et al.* report 85% VEC monomer conversion in the free radical co-polymerization of LiTFSI and VEC in the presence of LiTFSI and AIBN.²⁵ This result is not surprising considering the polymerization reaction was performed under vacuum and the conversion was calculated based on the ^1H NMR of the residue. We performed a similar reaction under reduced pressure at 80°C in a Buchi vacuum oven. Afterwards, we collected a liquid that condensed in a round-bottom collection flask attached to the Buchi, which was found to be unreacted VEC by ^1H NMR analysis, leading to the conclusion that VEC readily evaporates under vacuum at 80°C . The quantity of VEC lost to evaporation is highly dependent on the applied pressure of the vacuum oven. Shan *et al.* do not report the vacuum pressure of their reaction. Assuming the boiling point of VEC follows the Clausius–Clapeyron relation, its boiling point would be 146°C at 35 Torr of pressure and 102°C at 5 Torr of pressure, significantly reduced from its boiling point at atmospheric pressure (237°C). This leads to significant VEC evaporation over the 10 hours of prescribed reaction time. Shan *et al.* attributed the disappearance of VEC to monomer conversion, when most it was likely due to VEC

evaporation under reduced pressure. To confirm the low degree of VEC monomer conversion, the free radical co-polymerization of VEC and LiTFSI with LiTFSI and AIBN initiator was conducted at 80°C for 10 hours in a closed vial under argon. The product was a viscoelastic material, suggesting a degree of polymerization. The ^1H NMR spectra of the reaction product show unreacted VEC (peaks a–f), as shown in Fig. 1(b), while the vinylic protons present in the LiTFSI monomer disappear and the aromatic peaks convert into broad peaks (Fig. 1(b) inset). This implies the LiTFSI polymerized, but the VEC remained largely unreacted. The molecular weight of the poly(LiTFSI) was determined *via* gel permeation chromatography (GPC) using a Shodex OHpak SB-804 HQ column. The column was calibrated using polyethylene glycol (PEG) standards with a mobile phase of 0.1 M sodium azide. The average molecular weight of the poly(LiTFSI) was $\sim 600 \text{ kDa}$ with a polydispersity of ~ 3.6 . This result is consistent with the previously described result of the failed co-polymerization of allyl ethers with methyl methacrylate and styrene. Therefore, we ascribe the high ionic conductivity of the resulting poly(VEC10-*r*-LiTFSI) material to the VEC acting as a liquid, conductivity-enhancing additive in a polymeric matrix of poly(LiTFSI).

The differing interpretations found in studies of single-ion conductors can be extended to other “dry” polymer electrolytes, such as polymer-in-salt electrolytes, further highlighting the importance of understanding a polymer electrolyte’s composition. In one such case, a specific polymer-in-salt electrolyte drew significant attention due to its impressive ionic conductivity of $>1 \text{ mS cm}^{-1}$ at room temperature. This polymer electrolyte was based on a thermoplastic polymer, poly(phenylene sulfide) (PPS), reacted with an electron acceptor (*e.g.*, tetrafluoro-1,4-benzoquinone, TFBQ), resulting in a “charge-transfer-complex” polymer, or CTC (Fig. 2(a)).³⁶ The CTC is mixed with a lithium salt to yield a polymer-in-salt electrolyte. It was claimed that the electrolyte’s high ionic conductivity is due to a novel mechanism of Li^+ conduction that is not based on chain segmental motion. However, insight into the mechanism was limited, which drove our interest in understanding the origin of this exceptional performance. Numerous studies on these materials have proved that the formation of a CTC with salt does not support significant increases in ionic conductivity. Hatakeyama-Sato *et al.* reported ionic conductivities of $\sim 1 \times 10^{-6} \text{ S cm}^{-1}$ for a 70% CTC, 30% LiTFSI electrolyte, on par with PEO-based polymer-in-salt electrolytes.³⁷ Yang and Schaefer obtained similar results, reporting that a CTC-based electrolyte exhibits low ionic conductivity and that additives are necessary to achieve high ionic conductivity.³⁸ Upon deeper exploration, our experimental results and molecular dynamics modeling support the conclusion that CTC polymer and salt electrolytes do not exhibit high ionic conductivity at room temperature, and that polar additives are necessary to promote dissociation of the lithium salt and obtain high ionic conductivity.³⁹ Similar to gel polymer electrolytes, the additive can dramatically affect the electrolyte’s ionic conductivity and oxidative stability (Fig. 2(b) and (c)). Interestingly, we found that the CTC’s primary benefit was in forming a surface layer on the PPS particles, confirmed by cross-sectional scanning electron

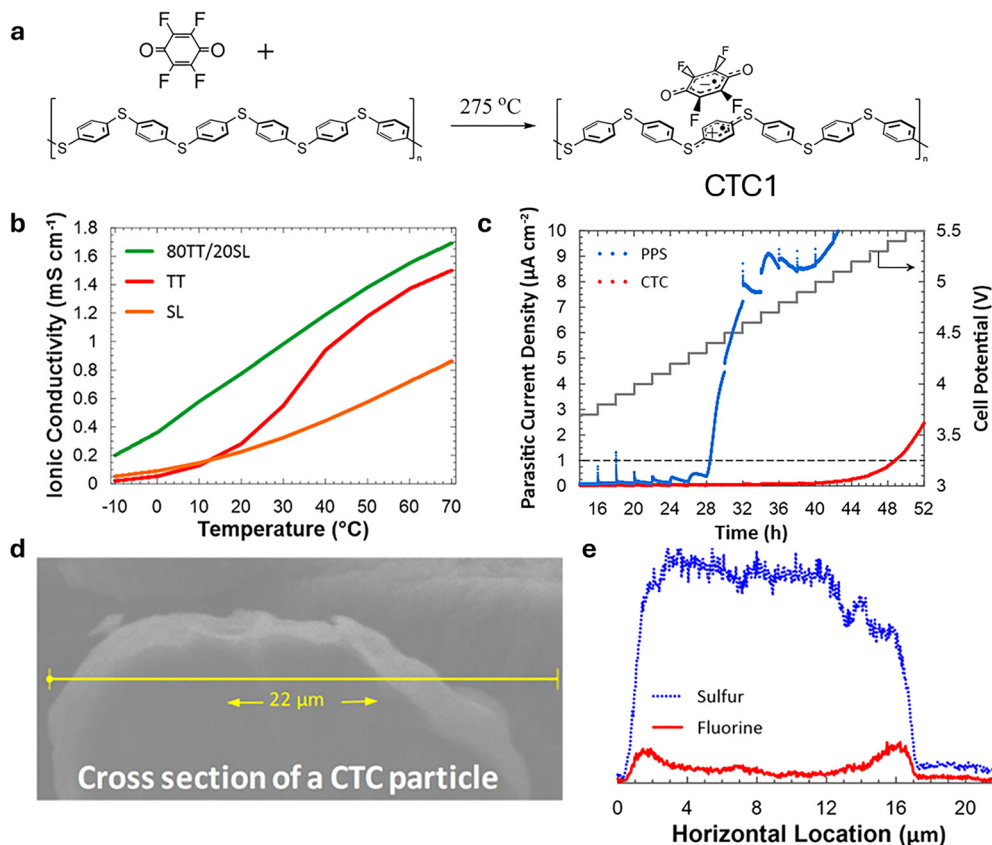


Fig. 2 (a) Oxidation of PPS by TFBQ to yield the charge-transfer-complex (CTC1). (b) Ionic conductivity of polymer electrolytes comprised of CTC1, an additive such as thietane-1,1-dioxide (TT), sulfolane (SL), or a combination of the two, and a lithium salt (LiTFSI). Each polymer electrolyte is comprised of 56 wt% CTC1, 30 wt% additive, and 14 wt% LiTFSI salt. CTC1-(TT)-LiTFSI (red), CTC1-[sulfolane (SL)]-LiTFSI (orange), and CTC1-[80 wt% TT/20 wt% SL]-LiTFSI (green). (c) Oxidative stability of polymer electrolytes comprised of a polymer (such as poly(phenylene sulfide) (PPS in blue) or CTC1 (in red), an additive thietane-1,1-dioxide (TT), and LiTFSI salt in a 56 : 30 : 14 weight ratio. (d) SEM image of a cross-section of a CTC particle. (e) EDS signal from the line scan in (d) reveals the relative intensities of sulfur (dotted blue line) and fluorine (red line) across the particle. Reproduced with permission from ref. 39. Copyright 2023, American Chemical Society.

microscopy (SEM) paired with energy dispersive spectroscopy line scans (EDS) (Fig. 2(d) and (e)) that reveal fluorine signatures associated with CTC formation only on the surface of the PPS particles. This layer significantly improves the oxidative stability of the electrolyte, from 4.4 V for a PPS-based electrolyte to 5.4 V for a CTC-based electrolyte (Fig. 2(c)). These CTC-based electrolytes can open the possibility of utilizing high-voltage cathodes. In our opinion, it is imperative for future studies to fully elucidate the actual composition of a polymer electrolyte to avoid misinterpretations about potential breakthroughs in dry polymer electrolytes with exorbitant ionic conductivities. In our opinion, if you observe a dry polymer electrolyte with extraordinary ionic conductivity, you should be concerned that the high ionic conductivity is due to the presence of a multifunctional additive.

Accurately interpreting high-rate lithium metal cycling

Claims of electrolytes that can withstand ultra-high-rate lithium metal cycling are rampant throughout the literature.^{22,25,40,41}

However, many of these studies do not experimentally validate these claims properly, which we suggest leads to potential misconceptions about the capability of their electrolytes. Li-Li symmetric cells, or cells containing lithium metal for both electrodes, are most commonly used to evaluate the stability of these electrolytes. In this experiment, cells cycle at a given areal current density (mA cm^{-2}) and areal capacity (mAh cm^{-2}) until failure occurs through short circuiting. Shan *et al.* report Li-Li cycling performance of their polymer electrolyte, claiming stable cycling for 3000 cycles at 3 mA cm^{-2} current density and 3 mAh cm^{-2} areal capacity, and stable cycling for 1000 cycles at 10 mA cm^{-2} current density and 10 mAh cm^{-2} areal capacity (Fig. 3(a) and (b)).^{10,25} A snapshot of the voltage profiles of Li-Li cycling at 10 mA cm^{-2} reveals perfectly flat voltage profiles (Fig. 3(b) inset). In our opinion, Li-Li cycling can be deceptive without supplemental experiments to validate the result.⁴⁰ In 2022, Lee *et al.* reported stable Li-Li cycling of an *in situ* polymerized, elastomeric solid-state electrolyte consisting of butyl acrylate (BA) with an interconnected plastic crystal phase (succinonitrile mixed with LiTFSI salt) polymerized *in situ* via free radical polymerization initiated by azobisisobutyronitrile

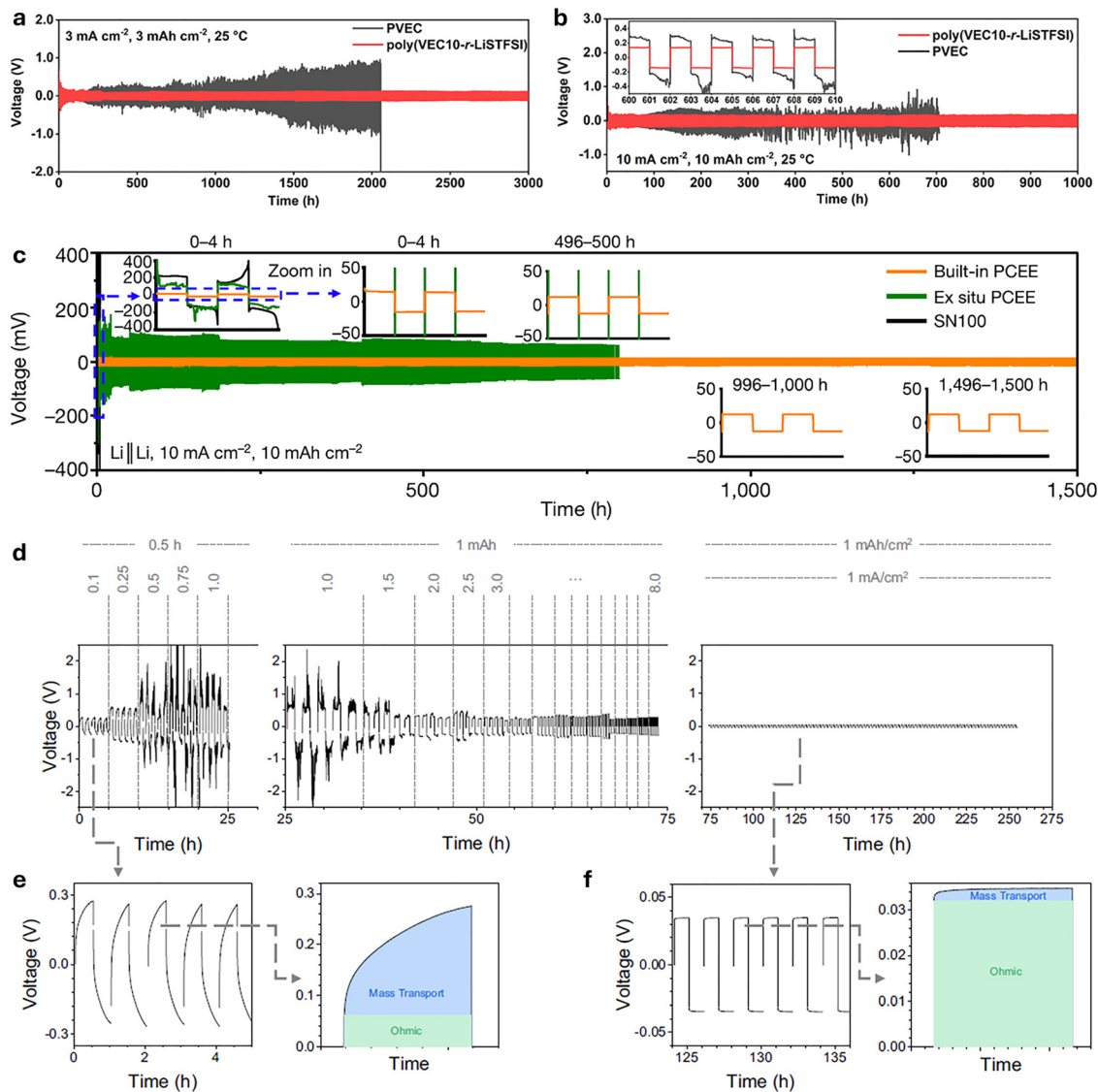


Fig. 3 Stripping/plating profiles of Li/poly(VEC10-r-LiTFSI)/Li and Li/PVEC/Li cells at (a) 3 mA cm⁻² and (b) 10 mA cm⁻² at 25 °C. Reproduced with permission from ref. 25. Copyright 2022, American Chemical Society. (c) Li-Li symmetric cell cycling at 10 mA cm⁻² current density and 10 mAh cm⁻² areal capacity of the built-in plastic crystal elastomeric electrolyte (built-in PCEE), which consists of butyl acrylate interconnected with a plastic crystal phase (succinonitrile mixed with LiTFSI salt) polymerized *in situ* via free radical polymerization initiated by azobisisobutyronitrile (AIBN). Insets: Enlarged voltage profiles for different times. Reproduced with permission from ref. 22, Copyright 2022, Springer Nature. (d) Galvanostatic cycling of a 50 wt% LLZO in PEO-LiTFSI composite electrolyte in a Li||Li symmetric cell at 60 °C. The current densities and plating times/areal capacities are noted for each set of cycles. (e) Early lifetime voltage data show the expected profile with Ohmic and mass transport-related polarizations. (f) Voltage profiles after high-current cycling show mainly Ohmic polarization with a small proportion of mass transport polarization, indicating that the cell resistance has decreased dramatically but is not hard-shortened. Reproduced with permission from ref. 44. Copyright 2024, Elsevier. This profile is also seen in the insets of (b) and (c).

(AIBN), named a Built-in PCEE (plastic crystal elastomeric electrolyte).²² Lee *et al.* claim this electrolyte stably cycles in Li-Li cells at a current density of 10 mA cm⁻² and 10 mAh cm⁻² areal capacity for 1500 cycles with low polarization potentials of 13 mV and perfectly flat voltage profiles (Fig. 3(c)).

Apparent stability of Li-Li symmetric cells with perfectly flat voltage profiles has been raised as a cause of concern.^{42,43} Perfectly flat voltage profiles at elevated current density can indicate exclusively ohmic contributions, instead of mass transport, due to soft-shortening caused by dendrite formation.

Recently, Counihan *et al.* demonstrated a Li-Li symmetric cell with a solid-state composite electrolyte (LLZO in PEO-LiTFSI) that was intentionally soft-shortened by gradually increasing the cycling capacity and current density until cell failure, with the voltage profiles shown in Fig. 3(d).⁴⁴ The voltage profiles feature an initial ohmic polarization followed by a slope due to mass transport contributions, indicating ionic current in an un-shortened cell (Fig. 3(e)). As the current density and capacity increase, the voltage becomes erratic before dropping in magnitude and exhibiting flat voltage profiles. These flat voltage

profiles are comprised of primarily ohmic contributions, with only minor mass transport contributions (Fig. 3(f)). This indicates the cell is soft-shorted due to dendrites reducing the electronic resistance of the cell. It is concluded here that the seemingly stable, high-rate, and high-capacity Li–Li cycling of these discussed polymer electrolytes is potentially due to soft-shortening of the cells, which is attributed to stable cycling instead.

Electrochemical impedance spectroscopy (EIS) is an effective technique for diagnosing cell shorting behavior. Electronic resistance decreases in cells that experience soft-shortening, and the EIS spectrum changes dramatically. This effect is described by Counihan *et al.*, wherein they simulated an electrochemical cell, with an equivalent circuit shown in Fig. 4(a), and reduced the electronic resistance stepwise to generate and evaluate a series of Nyquist plots, shown in Fig. 4(b).⁴⁴ The two most notable changes in the spectra are a significant decrease in the charge transfer resistance and an apparent loss of the Warburg element. The loss of the Warburg element implies a loss of ion diffusion, indicating that electronic processes overtake faradaic processes as the cell becomes increasingly shorted. Counihan *et al.* experimentally validated this simulated result by conducting EIS on the cycled cells discussed previously (Fig. 3(d)), with the resulting Nyquist plots shown in Fig. 4(c). The EIS spectrum of the as-prepared cell exhibits the expected semicircle and

low-frequency element. After cycling, the charge-transfer resistance decreases dramatically, and there is no apparent Warburg element due to severe soft-shortening of the cell. Other studies have also demonstrated this behavior when a cell shorts due to dendrite formation.^{42,43} This phenomenon is visible in Lee *et al.*'s EIS results after various amounts of Li–Li cycling compared to cells that have not been cycled (Fig. 4(d)).²² The EIS spectra exhibit charge-transfer resistances (R_{ct}) of $\sim 200\ \Omega$ in the cells before cycling. After 25 cycles in Li–Li cells, the R_{ct} drops to $\sim 29\ \Omega$, and after 100 cycles, it drops to $\sim 10\ \Omega$ with a significantly reduced Warburg impedance. This implies that the cell has become increasingly soft-shorted to the point of failure, despite contradictory claims that this electrolyte could withstand $10\ \text{mA cm}^{-2}$ current density and $10\ \text{mAh cm}^{-2}$ areal capacity during Li–Li cycling.

The existence of soft-shorts in high-rate Li–Li cell cycling is further reflected by Lee *et al.*'s coulombic efficiency measurements.²² Coulombic efficiency (CE) reflects a cell's reversibility and is defined as the ratio of cell discharge capacity over charge capacity. A perfectly ideal system would feature 100% CE. However, this is realistically impossible due to the electronic isolation of "dead" lithium and side reactions such as SEI formation. The highest-performing lithium metal electrolytes achieve coulombic efficiencies of $\sim 99.5\%$.⁴ Traditional

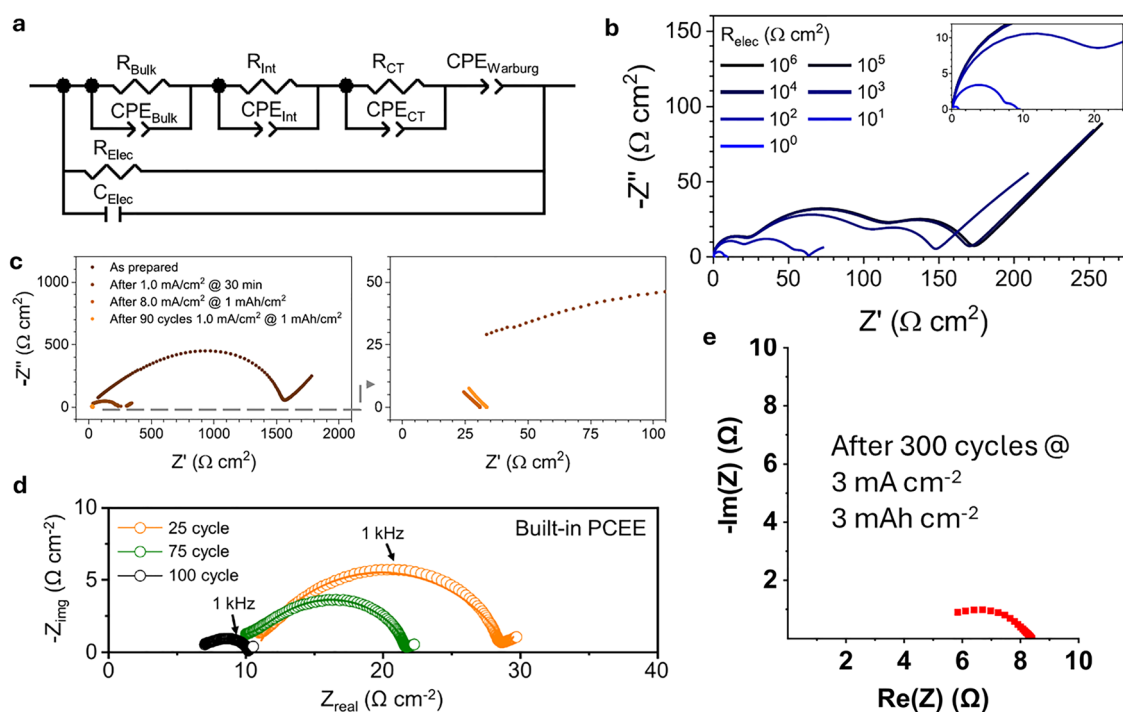


Fig. 4 (a) Equivalent circuit for Nyquist plots shown in (b), where the top elements in series represent the ionic processes and the lower elements in parallel represent the electronic pathways. (b) Simulated Nyquist plots of a hypothetical cell with various R_{elec} values. As the electronic resistance decreases, the low-frequency Warburg element is lost. (c) Select Nyquist plots from electrochemical impedance spectroscopy performed during the cycling of the system shown in Fig. 3(d). Reproduced with permission from ref. 44. Copyright 2024, Elsevier. (d) Nyquist plots obtained by EIS after 25, 75, and 100 cycles of the symmetric Li cells configured with built-in PCEE (plastic crystal elastomeric electrolyte), which consists of butyl acrylate polymerized *in situ* with a plastic crystal phase (succinonitrile mixed with LiTFSI salt), initiated by azobisisobutyronitrile (AIBN). Reproduced with permission from ref. 22 Copyright 2020, Springer Nature. (e) Electrochemical impedance spectrum (5 mV amplitude, 100 mHz–1000 kHz frequency) of a Li–Li symmetric cell containing poly(VEC10-*r*-LiSTFSI) after 300 cycles at $3\ \text{mAh cm}^{-2}$ areal capacity and $3\ \text{mA cm}^{-2}$ current density. The absence of a low-frequency Warburg element indicates loss of ion transport due to soft-shortening.

lithium-ion cells with graphite anodes achieve very high CEs ($>99.9\%$), but even these cells cannot reach the theoretical maximum of 100.0% . Lee *et al.* report 100.0% CE for their polymer electrolyte cycled at 2 mA cm^{-2} current density and 4 mAh cm^{-2} areal capacity, and 100.0% CE when cycled at 5 mA cm^{-2} current density and 10 mAh cm^{-2} areal capacity. It is more likely that these cells became severely soft-shortened at such current densities and capacities, and the current measured was due to electronic conduction across the electrolyte.

To further investigate the high-rate behavior of Shan *et al.*'s polymer electrolyte, the *in situ* formed poly(VEC10-*r*-LiTFSI) polymer electrolyte was recreated and cycled in Li–Li cells at 3 mA cm^{-2} current density and 3 mAh cm^{-2} areal capacity. After 300 cycles, the Nyquist plot obtained *via* EIS of the Li–Li cell exhibited low charge transfer resistance and a complete loss of the low-frequency Warburg element (Fig. 4(e)). As discussed previously, this indicates a dramatic decrease in the electronic resistance of the cell due to soft-shortening during Li–Li cycling at such high current densities and capacities.

Interestingly, Shan *et al.* and Lee *et al.* report modest current densities and areal capacities when employing their polymer electrolytes in full cell configurations, or cells consisting of a lithium metal anode and a conventional cathode such as NMC or LFP. For example, Shan *et al.* report a Li/LFP cell that cycled >1000 times at a current density of 0.35 mA cm^{-2} and an areal

capacity of 0.35 mAh cm^{-2} .²⁵ Lee *et al.* utilized their polymer electrolyte in a Li/NMC-83 cell with a maximum areal capacity of 2.1 mAh cm^{-2} .²² This cell utilizes its maximum capacity of 2.1 mAh cm^{-2} at low current density (0.1 mA cm^{-2}), but loses nearly half of its areal capacity, down to 1.1 mAh cm^{-2} , when cycled at 0.5 mA cm^{-2} . This begs the question of why these cells seemingly cannot cycle close to the previously shown current densities of 10 mA cm^{-2} and areal capacities of 10 mAh cm^{-2} . Lee *et al.* also display the capacity *vs.* potential of their Li/NMC-83 full cell at various current densities. At current densities of 3 mA cm^{-2} , less than a third of the current density at which their Li–Li cells were cycled, the cell maintains less than 20% of its original areal capacity, with an apparent increase in overpotential of $\sim 1 \text{ V}$ relative to low current density operation. However, this seems incongruent with their Li–Li cell cycling performance that exhibits 13 mV polarization potential at 10 mA cm^{-2} current density. These inconsistencies in performance support the conclusion that the observed stability of lithium plating/stripping at high current densities and capacities is due to soft-shortening of the cell, which is attributed to stable cycling. It is worth noting that many factors can influence the performance and rate capability of full cells, such as the kinetics of cathode materials and interfacial contact resistances between the electrode and polymer. It is advisable to fully understand the performance of the polymer electrolyte in Li–Li cells before considering full cell testing.

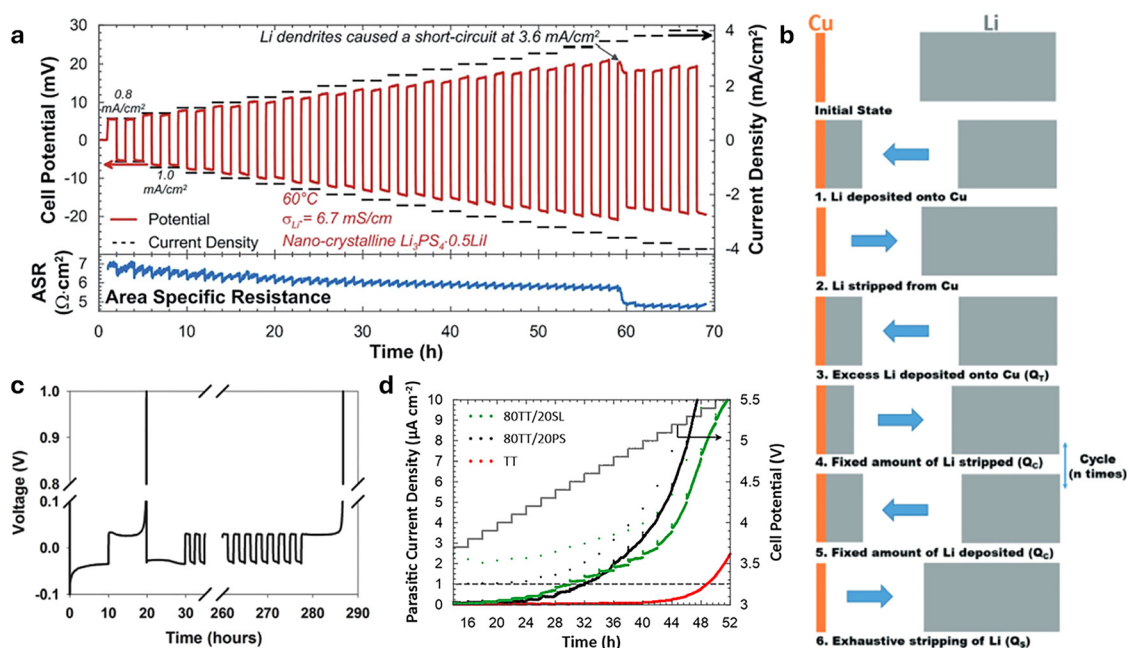


Fig. 5 (a) Critical current density (CCD) test of a Li/nano-crystalline $\text{Li}_3\text{PS}_4\text{-}\frac{1}{2}\text{LiI/Li}$ cell at 60°C . The current is held constant for two cycles at each current, starting at 0.8 mA cm^{-2} and rising to 4.0 mA cm^{-2} in 0.2 mA cm^{-2} steps. Reproduced with permission from ref. 45. Copyright 2019 Royal Society of Chemistry. (b) The schematic diagram of cycling Li||Cu cells using the modified Aurbach method. (c) The measured voltage *versus* time plot for a modified Aurbach procedure. Reproduced with permission from ref. 47. Copyright, 2017 John Wiley and Sons. (d) Oxidative stability of CTC1-thietane-1,1-dioxide (TT)-LiTFSI (red), CTC1-[80 wt% TT/20 wt% PS]-LiTFSI (black), and CTC1-[80 wt% TT/20 wt% sulfolane (SL)]-LiTFSI (green) polymer electrolytes in a cell containing an aluminum foil cathode and lithium metal anode. Each polymer electrolyte is comprised of 56 wt% CTC1, 30 wt% additive, and 14 wt% LiTFSI salt. The additive has a significant influence on the oxidative stability of the polymer electrolyte. Oxidative stability was defined as the potential (gray solid line) at which the parasitic current (green, blue, or red) exceeded $1 \mu\text{A cm}^{-2}$ (gray dashed line). Reproduced with permission from ref. 39. Copyright 2024, American Chemical Society.

Lithium metal testing

A series of experiments is required to fully evaluate lithium metal polymer electrolytes. Lithium metal batteries operated at high current densities are more likely to grow dendrites and experience short-circuiting. The critical current density (CCD) is the maximum allowable current density before shorting of the cell, and is an approximate threshold for reasonable cycling current densities.⁴³ This value is linked to the ionic conductivity of the electrolyte, with higher ionic conductivity electrolytes supporting higher CCDs.⁴⁵ The CCD is determined *via* constant current cycling of a Li–Li symmetric cell. The current is increased stepwise until a voltage drop is measured, indicating a short-circuit, as shown in Fig. 5(a). Once the CCD is determined for a given electrolyte, it can be deduced that cycling above that current density will lead to instability and expedited short-circuiting.

One of the most critical evaluation metrics of a lithium metal electrolyte is the coulombic efficiency (CE) because it is directly related to the cycle life of the cell.^{47,46} The measured CE of an electrolyte is heavily dependent on the testing conditions, such as current density, capacity, electrolyte volume, and excess lithium content. Therefore, important parameters such as the electrolyte content and lithium metal excess should be reported. Half cells of Li–Cu are required to evaluate electrolyte CE accurately, which is otherwise not defined for lithium–lithium cells with excess lithium inventory that is never fully accessed. In half-cell CE experiments, the commonly used Modified Aurbach procedure is recommended (Fig. 5(b) and (c)).⁴⁷ In this procedure, a lithium reservoir (4–5 mAh cm^{−2}) is deposited and then stripped at a current density of 0.5–1.0 mA cm^{−2}. Then, the reservoir is re-deposited, followed by smaller capacity stripping and deposition (~1 mAh cm^{−2}) at current densities of 0.5–1 mA cm^{−2} for

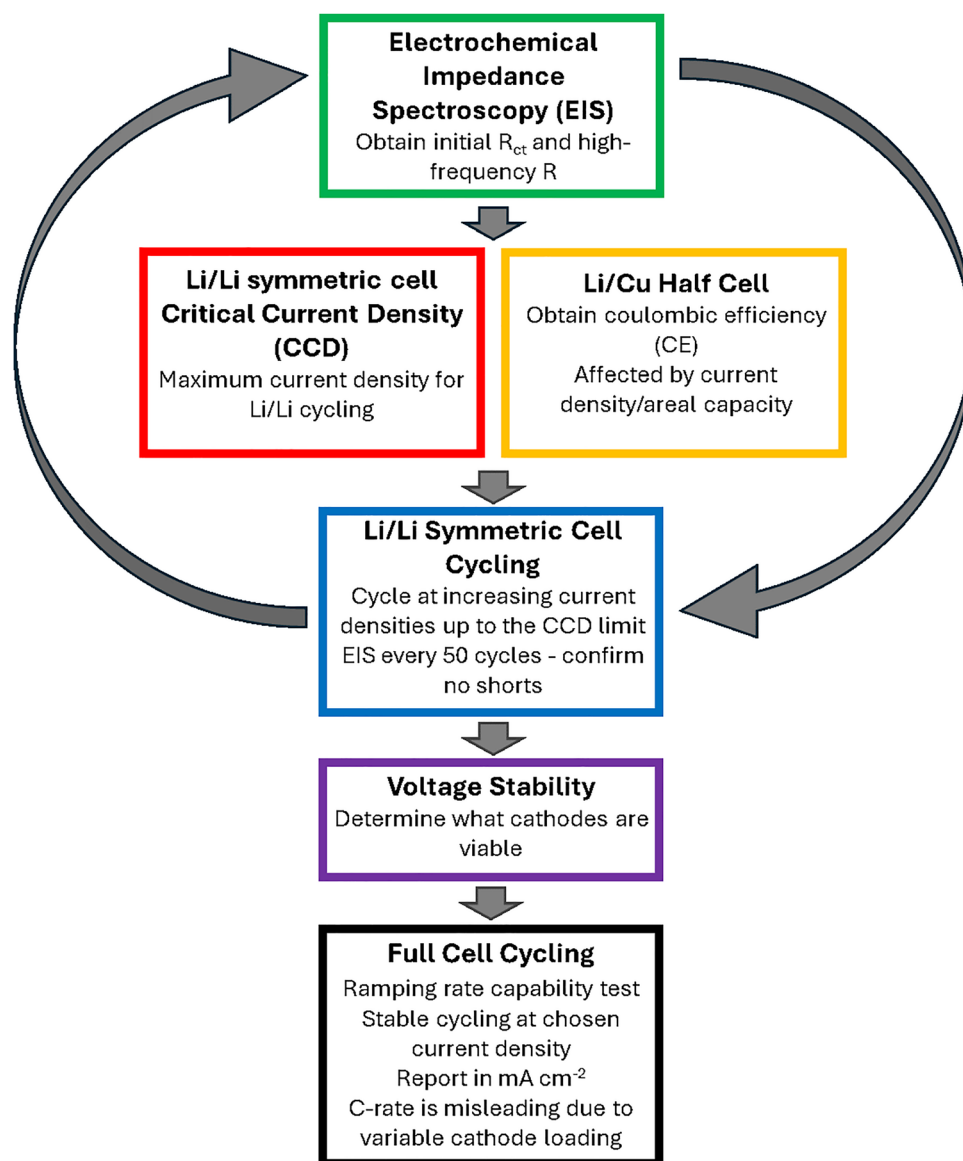


Fig. 6 Experimental flowchart for the electrochemical evaluation of lithium metal batteries.

10–20 cycles. Finally, the entire reservoir of lithium is stripped off, and the final recovered capacity is measured to yield the average CE of the system *via* the following equation:

$$\text{CE}_{\text{avg}} = \frac{nQ_{\text{c}} + Q_{\text{s}}}{nQ_{\text{c}} + Q_{\text{t}}}$$

where n is the number of small stripping/plating cycles, Q_{c} is the capacity of the small stripping/plating cycles, Q_{t} is the capacity of the initial plated reservoir, and Q_{s} is the capacity of the final stripping. This procedure is the most commonly used in lithium metal literature, providing a uniform protocol that can easily be compared across studies.^{48–51} Conventional constant-capacity cycling protocols are also widely used to charge and discharge the cell repeatedly, obtaining CE of each cycle, which can then be averaged.

The energy density of a cell can be increased significantly by utilizing a high-voltage cathode. The oxidative stability of an electrolyte must be evaluated to determine its compatibility with these high-voltage cathodes. Oxidative stability is typically measured by slowly raising the potential of a cell while measuring the current. The potential at which the current reaches an unsatisfactory level is designated as the oxidative stability of the electrolyte. Most studies use linear sweep voltammetry (LSV) at rates of 0.1–1 mV s^{−1} to measure oxidative stability.^{52,53} However, this technique is often too forgiving in its outcome, yielding oxidative stabilities higher than if the electrolyte were held at each potential for some time. Linear sweep voltammetry has the advantage of enabling quick screening of voltage stability. However, linear sweep voltammetry scans are brief relative to the time a full cell spends at high potential during charge. Moreover, it is common practice to hold full cells at a constant potential at the top of charge to ensure the cell charges fully. In a chronoamperometry experiment, the system can reach a steady state parasitic current by measuring the current at a static potential. Therefore, in our opinion, setting the potential to measure parasitic current density for an extended period in a chronoamperometric experiment reflects the conditions in a full cell better than a linear sweep. In this experiment, the voltage is raised stepwise and held for a certain amount of time before being raised again, as shown in Fig. 5(d).³⁹ A current density of 1 μA cm^{−2} is recommended as the cut-off for determining the maximum oxidative stability of the electrolyte. This technique can be expanded to full cell configurations using real cathodes by holding the cell at selected voltages to probe the leakage current.⁵⁴ It can help determine the stability of the electrolyte at specific voltages where anodic stability may be an issue, such as the cell's maximum charged voltage.

With numerous tests and conditions to consider, it can be overwhelming to determine how to analyze polymer electrolyte lithium metal batteries properly. Our proposed workflow for thoroughly analyzing the electrochemical performance of these batteries is presented in Fig. 6. To summarize, beginning with EIS allows for an initial estimation of the cell's R_{ct} and high-frequency resistance. This affords a baseline in which to compare future EIS experiments. Next, the electrolytes CCD and

CE should be determined through the aforementioned methods. The CCD value obtained can provide reasonable current densities for subsequent Li–Li symmetric cell cycling to evaluate stability with lithium metal. It is recommended that EIS be performed after every 50 cycles of Li–Li symmetric cell cycling to ensure the cell is operating properly and is not soft-shortened. Before transitioning to full cell testing, the voltage stability of the electrolyte should be evaluated to determine what cathodes are appropriate. Lastly, full cells should be tested to assess both rate capability, by increasing the current density stepwise, and long-term cycling stability, by galvanostatic cycling at chosen current densities. The cycling current density should be provided (mA cm^{−2}) when discussing full cell performance to avoid the obfuscating effects of low cathode loading on seemingly high C-rates.

Conclusions

Unfortunately, the ionic conductivity of a single-ion conducting or polymer-in-salt polymer electrolyte is limited to $\sim 1 \times 10^{-5}$ S cm^{−1} at room temperature. In our opinion, it is difficult to foresee a dry polymer electrolyte (without ionic conductivity-enhancing additives) that relies upon chain segmental motion for ion conduction being competitive with the ionic conductivity of liquid electrolytes or inorganic solid-state electrolytes. While we emphasize the difficulty of this quest, we believe it is the holy grail of polymer electrolytes to have a dry polymer electrolyte with performance comparable to that of liquid electrolytes. To this end, it is essential to describe in detail the composition of the electrolyte such that there is no misunderstanding about the classification of the electrolyte, *i.e.*, a dry polymer electrolyte, single-ion conductor, gel polymer electrolyte, or polyquid. A lack of information about composition is the prime driver for confusion in the field. Thus, experimental protocols describing the preparation of the polymer electrolyte should be highly detailed. Analytical techniques recommended to characterize polymer electrolytes quantitatively include thermogravimetric analysis (TGA), gel permeation chromatography (GPC), NMR, dynamic scanning calorimetry (DSC), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS).

Understanding the compatibility of polymer electrolytes with lithium metal is essential. Based upon our understanding, there are many differing interpretations of the rate capability of polymer electrolytes in lithium metal cells. It is critical to perform a detailed electrochemical evaluation to dispel concerns about interpreting soft-shorts as stable lithium cycling at high current density. When utilizing lithium metal, whether it be with a liquid, inorganic, or polymeric electrolyte, it is crucial to conduct critical current density (CCD), electrochemical impedance spectroscopy (EIS), and coulombic efficiency (CE) measurements to properly evaluate the electrolyte and avoid any misconceptions concerning electrolyte performance. Most of the R&D on polymer electrolytes utilizes cathodes with low areal capacities, operating at low current densities. It remains

an eminent goal to develop polymer electrolytes with ionic conductivities that enable use of cathode loadings $>1 \text{ mAh cm}^{-2}$, ideally up to 4 mAh cm^{-2} , at current densities competitive with lithium-ion cells.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

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