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RECENT ADVANCES IN POLYMER–INORGANIC COMPOSITE ELECTROLYTES FOR SOLID-STATE LITHIUM/SODIUM BATTERIES

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Abstract
Solid-state batteries are widely regarded as a route to safer and more energy-dense electrochemical storage, yet no single class of solid electrolyte currently satisfies the simultaneous demands of high ionic conductivity, mechanical compliance, wide electrochemical stability and manufacturability. Polymer–inorganic composite electrolytes have emerged as a pragmatic strategy to combine the processability and interfacial contact of polymers with the high conductivity and rigidity of inorganic ion conductors. This review surveys progress in this field over roughly the last decade for both lithium- and sodium-based systems. We first summarise the fundamentals of ion transport in polymers and ceramics and define the metrics used to benchmark electrolytes. We then examine polymer hosts (poly(ethylene oxide), fluorinated polymers, polynitriles, polycarbonates and single-ion conductors) and inorganic fillers (inert oxides, garnets, NASICON phases, perovskites, sulfides and halides), before discussing design strategies that govern ion pathways: random dispersion, aligned and three-dimensional fillers, in situ polymerisation, interfacial functionalisation and multilayer architectures. A dedicated section compares lithium and sodium composites and highlights the comparatively early stage of the sodium field. Interfacial phenomena at the metal anode, at the cathode and between the two phases of the composite are analysed, followed by a critical discussion of scale-up challenges and research gaps, including thin-film fabrication, moisture stability, standardised testing and data-driven design. We conclude by outlining priorities for translating laboratory composites into practical cells.

1. INTRODUCTION

The transition towards electrified transport and renewable-dominated power grids has placed rechargeable batteries at the centre of energy technology. Since their commercialisation in the early 1990s, lithium-ion batteries (LIBs) have improved steadily in energy density and cost, but their reliance on flammable organic carbonate electrolytes imposes intrinsic limits on both safety and attainable energy density [1,2]. Volatile solvents, the limited thermal stability of common lithium salts and the exothermic reactions between charged electrodes and the electrolyte can combine to produce thermal runaway, with well-documented consequences for consumer electronics and electric vehicles [3,4]. As the field pursues cells with specific energies well beyond 300 Wh kg^{-1}, replacing graphite with lithium metal becomes almost unavoidable. Lithium metal, however, is poorly compatible with liquid electrolytes: dendritic deposition, continuous formation of a fragile solid–electrolyte interphase and low Coulombic efficiency all shorten cycle life and raise safety concerns [5].

Solid electrolytes (SEs) offer an attractive way to address these problems simultaneously. In

principle, a dense, non-flammable ion conductor can act as both separator and electrolyte, physically obstruct dendrite growth, enable bipolar cell stacking and widen the operating temperature window [6–8]. Sodium-based batteries have attracted parallel attention. Sodium is far more abundant than lithium and is widely distributed geographically, and sodium-ion cells can use aluminium rather than copper current collectors at the anode. The larger ionic radius of Na^+ (1.02 Å versus 0.76 Å for Li^+) and the higher standard potential of the Na/Na^+ couple (−2.71 V versus −3.04 V vs. the standard hydrogen electrode) reduce attainable energy density, but sodium systems are considered well suited to grid-scale storage, where cost and resource security outweigh gravimetric performance [9–13]. Solid-state architectures are therefore being explored for sodium as well, building on decades of experience with high-temperature Na–S and related technologies [14,15].

Two broad families of solid electrolytes have dominated research. Inorganic ceramics and glasses oxides such as garnet $Li_7La_3Zr_2O_{12}$ (LLZO) and NASICON-type phosphates, sulfides such as $Li_{10}GeP_2S_{12}$ (LGPS) and the argyrodites, and more recently halides offer room-temperature conductivities from about 10^{-4} to above 10^{-2} S cm^{-1}, high cation transference numbers and, in the case of oxides, good thermal stability [16–18]. They are, however, intrinsically brittle, usually require high-temperature or high-pressure processing, and frequently form poor solid–solid contacts with electrodes, which leads to high interfacial resistance and mechanical failure during cycling [18,19]. Sulfides are moisture-sensitive and can release toxic H_2S, while oxides containing reducible cations such as Ti^{4+} and Ge^{4+} are unstable against lithium metal [20].

Solid polymer electrolytes (SPEs), in contrast, are soft, can be processed by scalable film-forming techniques, and make intimate contact with rough electrode surfaces. Since the discovery of ion conduction in poly(ethylene oxide) (PEO)–alkali salt complexes [21] and the subsequent recognition of their battery potential [22], polymer electrolytes have been studied intensively [23,24]. Their central limitation is a low ionic conductivity at ambient temperature typically 10^{-8}–10^{-6} S cm^{-1} for PEO-based systems accompanied by low cation transference numbers, limited oxidative stability and a mechanical softness that offers little resistance to dendrite penetration [23–25].

Polymer–inorganic composite electrolytes (CEs) aim to combine the advantages of both families. The concept is not new: inert ceramic fillers were introduced into PEO-lithium salt films in the early 1980s to improve mechanical stability [26], and the systematic study of composite polymer electrolytes followed [27]. A turning point came with the demonstration that nanoscale TiO_2 and Al_2O_3 particles enhance both conductivity and interfacial stability of PEO-based electrolytes [28]. Over the past decade, attention has shifted towards "active" fillers that conduct ions themselves, towards high-aspect-ratio and three-dimensional filler architectures, and towards sodium analogues [29–31]. A number of reviews now cover composite electrolytes in general [32–35].

Despite this progress, several questions remain contested: whether ions move predominantly through the polymer, the filler or their interface; what filler loading regime is optimal; how sodium composites differ from lithium ones; and how laboratory metrics translate to practical cells. Most existing reviews focus on lithium systems or on a single filler family. The present review takes a broader view. It covers the fundamentals of ion transport and benchmarking metrics (Section 2), polymer matrices (Section 3), inorganic fillers (Section 4), design strategies for composites (Section 5), sodium-based composites and a comparison with lithium systems (Section 6), interfacial challenges (Section 7), and outstanding challenges and future directions (Section 8). The emphasis throughout is on mechanistic understanding and on the critical evaluation of reported performance, rather than on cataloguing conductivity values.

2. Fundamentals of Ion Transport and Benchmarking Metrics

2.1 Ion transport in polymer electrolytes

In most polymer electrolytes, a salt is dissolved in a polar host whose heteroatoms (ether oxygen in PEO, carbonyl oxygen in polyesters and polycarbonates, nitrile nitrogen in polyacrylonitrile) coordinate the cation. In PEO, Li^+ is typically coordinated by five to six ether oxygens, often supplied by one or two chains, forming transient physical cross-links. Transport

occurs mainly in the amorphous phase, where local segmental motion of the chains continuously breaks and re-forms coordination bonds, allowing cations to migrate along and between chains [23,36,37]. Because segmental motion is thermally activated, conductivity above the glass-transition temperature is commonly described by the Vogel–Fulcher–Tammann (VFT) relation, $\sigma(T) = A\,T^{-1/2}\exp[-B/(T - T_0)]$, in which T_0 lies typically 30–50 K below the glass-transition temperature (T_g) and B is a pseudo-activation energy.

Crystalline PEO was long considered insulating, but Gadjourova and co-workers showed that ordered crystalline PEO:$LiXF_6$ complexes can conduct through cation motion along helical tunnels [38]. Nevertheless, practical high conductivity in PEO electrolytes still requires suppression of crystallinity (the melting temperature is about 60–65 °C), which is why most PEO-based cells are operated at 60–80 °C [23,39]. A second defining feature is that, in salt-in-polymer systems, anions are usually more mobile than cations. Because Li^+ is strongly coordinated, the Li^+ transference number (t_{Li+}) of PEO–LiTFSI is often only 0.1–0.3 [39]. Under DC polarisation, anion migration produces salt-concentration gradients that limit the usable current density and contribute to non-uniform lithium deposition.

2.2 Ion transport in inorganic conductors

In crystalline inorganic conductors, ion transport proceeds by discrete hops between crystallographic sites through vacancy or interstitial mechanisms. High conductivity requires a suitable framework: continuous low-barrier pathways, a high concentration of mobile ions coexisting with vacant sites, and a polarisable, weakly binding anion sublattice [16,17]. Computational and experimental studies indicate that a body-centred-cubic anion sublattice provides particularly low migration barriers for Li^+, which partly explains the very high conductivity of thiophosphates such as LGPS [40,41]. In polycrystalline pellets, the measured total conductivity includes grain-boundary contributions that can be orders of magnitude more resistive than the bulk, notably in perovskite $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) [16,42]. When such ceramics are embedded in a polymer, additional interfaces arise that can either promote or hinder transport, a point taken up in Section 5.

2.3 Benchmarking metrics

Comparing electrolytes requires a shared vocabulary of metrics, and inconsistent reporting has been a persistent source of confusion in the literature [43]. The first metric is the total ionic conductivity, normally obtained from electrochemical impedance spectroscopy (EIS) with ion-blocking electrodes. Values should be reported together with film thickness, temperature, the pressure applied to the sample and whether residual solvent is present. For technologically relevant thin separators, a conductivity of about 10^{-4} S cm^{-1} at ambient temperature is often quoted as a practical target, although the relevant quantity inside a cell is the area-specific resistance, which also depends on thickness [6,8].

The second metric is the cation transference number. The steady-state current method of Bruce and Vincent, which combines DC polarisation with impedance measurements before and after polarisation of a symmetric cell, remains the most widely used technique [44,45]. It assumes ideal dilute-solution behaviour, however, and can be unreliable for concentrated or strongly associated systems. Composite electrolytes containing anion-trapping fillers, or single-ion polymer matrices, can drive t_{Li+} towards unity and thereby mitigate concentration polarisation [46,47].

Third, the electrochemical stability window (ESW) is usually estimated by linear sweep or cyclic voltammetry. Measurements on inert electrodes at slow sweep rates tend to overestimate the practical window because decomposition kinetics are sluggish and the electrolyte/electrode contact area is small, so voltammetry should be complemented by full-cell cycling and post-mortem spectroscopy. For PEO, an oxidation onset near 3.8–4.0 V versus Li/Li^+ is often quoted, although recent work suggests that terminal hydroxyl groups, rather than the ether backbone, may govern this limit [48].

Fourth, mechanical properties matter. The classic analysis of Monroe and Newman suggested that a separator with a shear modulus about twice that of lithium could suppress dendrite growth through pressure effects at the interface [49]. Experiments on stiff ceramics later showed that

lithium filaments can nevertheless propagate along grain boundaries and through pores and defects in garnets, so modulus alone is an insufficient design criterion [50,51]. Composite electrolytes should therefore be characterised for elastic modulus, fracture behaviour and performance under realistic stack pressure.

Finally, the critical current density (CCD), interfacial resistance and cycling stability in symmetric and full cells provide the most application-relevant evidence. Reports should specify stack pressure, temperature, areal capacity per cycle and cathode loading; without these details, comparisons between studies are of limited value [43,52].

2.4 Conduction pathways in composites

In a composite, three pathways can in principle carry ions: the bulk polymer with its dissolved salt, the inorganic filler, and the polymer/filler interfacial region. The total conductivity depends on which of these dominate and how they are connected in series and in parallel. Continuum descriptions borrowed from heterogeneous-media theory, such as effective-medium and percolation models, capture the dependence on volume fraction, aspect ratio and connectivity, but they generally treat the interface as a sharp boundary and therefore miss effects that are frequently the most important [30,53]. Isotope-labelling solid-state NMR, in which one electrode or the filler is enriched in ^{6}Li and the migration of the isotope into the other phases is tracked, has made it possible to identify which phase ions actually traverse [30].

Three limiting scenarios are commonly distinguished. In the first, the polymer dominates and the filler is essentially passive: the benefits arise from suppression of crystallinity and enhanced salt dissociation, so conductivity rises modestly with loading and then declines as agglomeration sets in [28,54]. In the second, the interface dominates: a modified polymer layer or space-charge region adjacent to the filler surface, with higher carrier concentration or mobility, forms a conducting shell, and percolation of these shells can produce a sharp increase in conductivity [53,55]. In the third, the ceramic dominates: at high loading or with continuous ceramic scaffolds, ions travel through the ceramic network and the polymer acts largely as a binder, so conductivity approaches ceramic values but is limited by particle-contact and grain-boundary resistance [29,56].

Real materials often combine these behaviours, and the balance shifts with filler loading, temperature and salt content. This multiplicity helps explain the apparently conflicting reports on whether “active” fillers outperform “passive” ones [30,57]. It also implies that activation energies extracted from Arrhenius plots must be interpreted with care: a change of slope near the polymer melting temperature reflects a phase transition in the matrix and not necessarily a switch in the ion-conduction mechanism [23]. Mechanistic claims about filler function are therefore most convincing when supported by direct probes of ion pathways rather than by conductivity trends alone.

3. Polymer Matrices

The host polymer determines the baseline conductivity, electrochemical window and mechanical character of a composite, and it often dominates overall ion transport even when highly conductive ceramic fillers are added. Selection criteria include a high concentration of polar coordinating groups, a low glass-transition temperature, sufficient dielectric constant to dissociate the salt, and chemical compatibility with the electrodes [23,25,58]. The principal hosts are summarised in Table 1 and discussed below.

3.1 Poly(ethylene oxide)

PEO remains the benchmark polymer host because its ether oxygens coordinate alkali cations effectively, its low T_g (about −60 °C) supports segmental mobility, and it dissolves large quantities of salts such as LiTFSI, LiFSI and $LiClO_4$. It is also chemically compatible with lithium metal and inexpensive [21,22,24]. Its shortcomings are equally well known: semi-crystalline behaviour at room temperature, a low t_{Li+}, limited oxidative stability and mechanical softness above its melting point. Salt concentration influences performance non-monotonically. Conductivity initially rises with charge-carrier concentration but eventually falls as ion association and an increasing T_g restrict segmental motion [54,59].

Ceramic fillers modify this balance by disrupting crystallisation and by providing additional interfacial pathways, and PEO remains the

matrix in the majority of published composites [32,35]. Copolymerisation, cross-linking, branching and the use of low-molecular-weight PEO plasticisers can further suppress crystallinity, albeit usually at the cost of mechanical strength [24,58]. In this sense, PEO functions best as a well-understood model system in which the influence of a filler can be isolated, and many mechanistic insights into composites have been obtained in PEO-based materials.

3.2 Fluorinated polymers

Poly(vinylidene fluoride) (PVDF) and its copolymer with hexafluoropropylene (PVDF-HFP) offer a very different profile. The strongly electron-withdrawing C–F groups give a high dielectric constant that assists salt dissociation, and the polymers show good oxidative stability, mechanical robustness and thermal resistance. However, the chains lack strongly coordinating groups, so ion transport relies on polar interactions, and the room-temperature conductivity of truly dry films is low. Practical PVDF-based electrolytes often retain high-boiling solvents such as N,N-dimethylformamide (DMF), or contain deliberate plasticisers, and these can dominate the observed conductivity and undermine stability against lithium metal. Where such films are described as "solid," the residual solvent content should be reported explicitly [25,33]. Interactions between PVDF and basic garnet surfaces have been reported to induce dehydrofluorination and to alter the polymer's crystallinity and local dielectric environment, which can modify ion transport and interfacial behaviour [60].

3.3 Polynitriles, acrylates, polyesters and polycarbonates

Polyacrylonitrile (PAN) exhibits strong oxidation resistance because of its nitrile groups but is unstable against lithium metal, so it is used mostly in gel electrolytes or in combination with protective layers. Poly(methyl methacrylate) (PMMA) is amorphous and forms dimensionally stable gels, but has weak mechanical properties in the absence of cross-linking. Aliphatic polyesters such as poly(ε-caprolactone) (PCL) and polycarbonates such as poly(ethylene carbonate) (PEC) and poly(propylene carbonate) (PPC) coordinate Li^+ more weakly than ethers, which can allow higher t_{Li+}, and they display better oxidation stability, making them attractive for high-voltage cathodes [25,58]. Their drawbacks—lower conductivity in dilute-salt regimes and, for polycarbonates, susceptibility to reduction at lithium or sodium metal—call for careful interface design or for use as cathode-side layers in multilayer architectures [25,61].

3.4 Single-ion conductors, salts and anion management

In single-ion conducting polymers, anions are covalently tethered to the polymer backbone so that only the cation is mobile. Block copolymers combining a PEO central block with lithium poly(styrene-sulfonylimide) end blocks have demonstrated t_{Li+} close to unity and improved behaviour at lithium electrodes [46,47]. The price is generally a lower conductivity, because dissociation of the tethered anion is limited, but combining single-ion polymers with ceramic fillers is a promising route to reconciling high transference number with adequate conduction. Anion-immobilising fillers and composites can similarly raise the effective transference number without covalent tethering, and thereby help homogenise lithium flux [62,63].

The choice of salt is also important. Bulky, charge-delocalised anions such as $TFSI^-$ and FSI^- plasticise the polymer and promote dissociation compared with ClO_4^- or $CF_3SO_3^-$, whereas smaller anions can give higher t_{Li+} in some hosts but poorer dissociation [24,59]. In composites, the salt and the filler surface must be considered together, since surface Lewis-acid sites interact strongly with the anion, and this interaction underlies many of the beneficial effects attributed to fillers.

3.5 Polymer design for compatibility with fillers

Composite electrolytes place additional demands on the polymer beyond those in neat SPEs. The matrix must wet the filler surface, tolerate its acidity or basicity, and retain mechanical integrity at high filler loading. Several design strategies address these requirements. Block and graft copolymers that combine an ion-conducting block, typically PEO, with a rigid or oxidation-stable block can form nanoscale phase-separated structures that decouple mechanical strength from ion transport [47,58]. Polymer chains grafted onto filler surfaces entangle with the matrix and improve dispersion, and in some systems allow the interfacial region to be

engineered independently of the bulk. Polymers carrying functional groups able to hydrogen-bond or coordinate to the ceramic surface can strengthen polymer–filler adhesion and reduce interfacial voids.

Low-molecular-weight additives are also widely used. Short-chain PEO, organic plastic crystals such as succinonitrile and small amounts of ionic liquids plasticise the matrix and raise conductivity, but at the cost of reduced electrochemical stability and, in some cases, poor compatibility with lithium or sodium metal [24,25]. It is therefore important to classify such materials honestly: a membrane containing a substantial fraction of liquid or plasticiser is better described as a quasi-solid or gel-type composite, and its properties should not be compared directly with those of dry systems [33,34].

Table 1. Representative polymer hosts for composite electrolytes.

Polymer	Coordinating groups / key features	Advantages	Main limitations	Refs.
PEO	Ether oxygens; $T_g \approx -60$ °C; semi-crystalline	High salt solubility; stable against Li metal; low cost; well studied	Low RT conductivity; low t_{Li^+}; oxidation onset near 4 V; soft	[21,24,48]
PVDF / PVDF-HFP	C–F dipoles; high dielectric constant	Oxidative stability; mechanical strength; thermal stability	Weak cation coordination; residual solvent; reactive with basic fillers	[25,60]
PAN	Nitrile groups	Oxidation resistant; good mechanical properties	Unstable against Li metal; mainly used in gel form	[25,64]
PMMA	Carbonyl groups; amorphous	Good gel formation; amorphous	Weak mechanics without cross-linking	[25]
PCL and other polyesters	Ester carbonyls	Better oxidative stability than PEO; biodegradable options	Low conductivity at low salt; reactivity with Li metal	[25,58]
PEC / PPC (polycarbonates)	Carbonate groups	High salt loading; higher t_{Li^+}; oxidative stability	Reduction at Li/Na metal; moderate mechanics	[25,61]
Single-ion polymers	Tethered anions (e.g. sulfonylimide)	t_{Li^+} approaching 1; reduced polarisation	Lower conductivity; complex synthesis	[46,47]

4. Inorganic Fillers

Inorganic fillers are commonly divided into passive (inert) and active (ion-conducting) types, although, as discussed below, this distinction blurs in practice. Representative fillers are listed in Table 2 together with their typical conductivities and principal advantages and drawbacks.

4.1 Passive oxide fillers

Nanoparticulate oxides such as SiO_2, Al_2O_3, TiO_2 and ZrO_2 were the first fillers studied. Their beneficial effects are attributed to several mechanisms: disruption of polymer chain packing and hence lower crystallinity and melting temperature; Lewis acid–base interactions between surface groups and both the polymer's ether oxygens and the salt anions, which promote salt dissociation and liberate additional cations; and scavenging of trace impurities at the lithium interface, which improves interfacial stability [27,28,63,65]. Croce and co-workers showed that nano-sized TiO_2 and Al_2O_3 raise conductivity at moderate temperatures and, importantly, greatly improve the time evolution of the lithium/electrolyte interfacial resistance [28].

Uniform dispersion is a decisive factor. SiO_2 nanospheres generated in situ by hydrolysis of precursors within a PEO matrix achieve far more homogeneous distribution than blended particles and raise both conductivity and transference numbers [66]. The effects are size- and loading-dependent: at high loading, agglomeration and blocking of conduction pathways reduce conductivity [54,65]. Comparative studies of active versus passive nanoparticles in PEO matrices found that the intrinsic conductivity of the filler is not always the decisive parameter, implying that surface chemistry and the interaction with polymer and salt can be equally important [57].

4.2 Garnet-type oxides

Garnet-type LLZO is the most widely studied active oxide filler because of its high bulk conductivity in the cubic phase, its wide electrochemical window and, crucially, its apparent chemical stability against lithium metal [20,67,68]. The cubic phase, stabilised by aliovalent doping with Al, Ga or Ta, conducts at roughly 10^{-4}–10^{-3} S cm^{-1} at room temperature in dense ceramics. In composites, LLZO nanoparticles, nanowires and fibres are dispersed in PEO or PVDF matrices [60,69,70]. A limitation is surface reactivity in air. LLZO undergoes Li^+/H^+ exchange with moisture and forms Li_2CO_3 and LiOH layers that raise interfacial resistance [68,71].

Perhaps the most important mechanistic insight came from isotope-labelling solid-state NMR of PEO–$LiClO_4$/LLZO composites. Zheng and co-workers found that, in the composites studied, Li^+ ions travel preferentially through the polymer phase and the polymer/ceramic interface rather than through the LLZO particles, an outcome attributed to high resistance for Li^+ transfer across the polymer/ceramic boundary [30]. This result cautions against assuming that adding a highly conductive ceramic necessarily creates ceramic-mediated pathways, and it motivates the design strategies discussed in Section 5.

4.3 NASICON-type phosphates and perovskites

NASICON-type phosphates, exemplified by $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) and $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP), are air-stable and inexpensive, with conductivities around 10^{-4}–10^{-3} S cm^{-1} [16,72]. Their major flaw is the reducibility of Ti^{4+} (and Ge^{4+}) on contact with lithium metal, which requires that they be shielded from the anode by a polymer or interlayer [16,20]. The sodium analogue, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, was introduced in the 1970s and remains the leading oxide Na^+ conductor [73,74].

The perovskite LLTO exhibits high bulk conductivity (of order 10^{-3} S cm^{-1}), but grain-boundary resistance and Ti^{4+} reducibility limit its use as a bulk electrolyte. As one-dimensional nanowires, however, it has proven an extremely effective filler, because the wires provide continuous, grain-boundary-free conduction paths that extend through the polymer [64,75].

4.4 Sulfides and halides

Sulfide electrolytes such as LGPS and the argyrodite Li_6PS_5Cl reach 10^{-3}–10^{-2} S cm^{-1} and are soft enough to be cold-pressed into dense layers [41,76,77]. Incorporating them into PEO can create composites with improved conductivity and interfacial contact, but the moisture sensitivity and narrow electrochemical window of sulfides, and their potential to react with polymers or salts during solvent processing, constrain the compatible polymers and processing conditions [16,78]. Sodium analogues such as Na_3PS_4 and $Na_{11}Sn_2PS_{12}$ reach conductivities of about 10^{-4} and several 10^{-3} S cm^{-1}, respectively [79,80].

Halide electrolytes based on Li_3YCl_6, Li_3InCl_6 and related compositions combine millisiemens-per-centimetre conductivity with deformability and better oxidative stability than sulfides [81,82]. They have only begun to be explored in polymer composites, and their reduction at low potentials means that direct contact with lithium metal must be avoided.

4.5 Emerging fillers and selection principles

Beyond these families, metal–organic frameworks (MOFs), zeolites, clays and covalent organic frameworks have been examined as fillers whose tunable pores can host anions or solvate cations [33,83]. Design principles emerging from the literature include (i) chemical compatibility with polymer, salt and electrodes; (ii) small particle size and controllable surface chemistry; (iii) high aspect ratio if continuity of conduction paths is desired; and (iv) tolerance of the processing environment, particularly moisture [32,33].

Because no single filler meets all criteria, hybrid or core–shell fillers and multi-filler systems are increasingly reported.

4.6 Filler stability and long-term compatibility

Fillers must remain chemically and physically stable in contact with the polymer, salt and electrodes over the lifetime of a cell. Thermodynamic analyses show that many oxide and sulfide electrolytes are stable only within limited potential windows, and that apparent kinetic stability can mask slow interfacial decomposition during extended cycling [16,20]. Interaction with the salt is a further consideration: strongly Lewis-acidic or basic filler surfaces can react with anions such as $TFSI^-$ or with residual solvents, altering both the filler surface and the polymer environment [60,63]. Surface contamination layers on garnets can catalyse polymer degradation and increase interfacial resistance [68,71]. Physical ageing—settling, agglomeration or migration of filler particles during storage and cycling—can gradually degrade the uniformity of the composite, yet long-term studies of filler distribution are rare. Systematic ageing tests, together with post-mortem analysis of the filler surface, should become standard practice in composite development.

Table 2. Representative inorganic fillers and typical room-temperature ionic conductivities of the neat materials.

Filler	Class	Typical conductivity (S cm^{-1})	Strengths	Limitations	Refs.
SiO_2, Al_2O_3, TiO_2	Passive oxides	Insulating	Low cost; anion interaction; suppress crystallinity	No intrinsic conduction; agglomeration	[28,66]
Doped LLZO	Garnet	≈ 10^{-4}–10^{-3}	Stable against Li; wide window	Surface Li_2CO_3; high-temperature synthesis	[67,68]
LATP / LAGP	NASICON (Li)	≈ 10^{-4}–10^{-3}	Air-stable; low cost	Reduced by Li metal (Ti^{4+}, Ge^{4+})	[16,72]
LLTO	Perovskite	Bulk ≈ 10^{-3}; total lower	Excellent as nanowires	Grain boundaries; Ti^{4+} reduction	[64,75]
LGPS	Sulfide	Up to ≈ 10^{-2}	Very high conductivity; soft	Moisture-sensitive; narrow window; Ge cost	[41,76]
Li_6PS_5Cl	Sulfide (argyrodite)	≈ 10^{-3}	High conductivity; scalable	H_2S release; limited window	[77]
Li_3InCl_6 / Li_3YCl_6	Halide	≈ 10^{-3}	Oxidative stability; deformable	Reduced by Li metal; cost of In/Y	[81,82]
$Na_3Zr_2Si_2PO_{12}$	NASICON (Na)	≈ 10^{-4}–10^{-3} (optimised)	Leading oxide Na conductor; stable	High sintering temperature; grain boundaries	[73,74,84]
Na_3PS_4 / $Na_{11}Sn_2PS_{12}$	Sulfide (Na)	≈ 10^{-4} / several 10^{-3}	Room-temperature Na conduction; soft	Moisture sensitivity	[79,80]
MOFs, zeolites, COFs	Porous	Variable	Tunable pores; anion trapping	Poorly understood; scalability	[33,83]

5. Design Strategies for Composite Electrolytes

The performance of a composite depends less on the identity of its components than on how they are arranged. Over the past decade, research has moved from simple blending of particles in a polymer towards deliberately engineered architectures in which ion pathways, interfaces and mechanical properties are controlled at the nanoscale. This section discusses the principal design strategies.

5.1 Filler content, percolation and composition regimes

Composite architectures are often classified by composition. In ceramic-in-polymer ("polymer-rich") electrolytes, a small fraction of filler (typically below about 20 wt%) is dispersed in a continuous polymer matrix; conduction is dominated by the polymer and by polymer/filler interfaces, and the composite remains flexible. In polymer-in-ceramic ("ceramic-rich") electrolytes, the ceramic fraction is high and forms a near-percolating network, while a minor polymer fraction acts as binder and wetting agent. Chen and co-workers examined the transition between these regimes in PEO/garnet composites [29]. In general, ceramic-rich compositions offer higher stiffness and thermal stability but need effective particle–particle contact to realise their conductivity, whereas polymer-rich compositions offer flexibility and easier processing but inherit the temperature dependence of the polymer.

Conductivity as a function of filler content is rarely monotonic. At low loading, the filler disrupts polymer crystallinity and creates interfacial pathways; beyond an optimum, agglomeration, filler–filler contact resistance and dilution of the conducting polymer phase reduce conductivity [53,65]. The systematic study of Zheng and Hu on PEO–$LiClO_4$–LLZO composites underlined that the polymer/ceramic interface plays a key role and that the observed conductivity reflects an interplay between salt concentration and filler content rather than filler content alone [53]. It follows that conductivity values reported for a single salt concentration and a single loading are poor guides to the achievable optimum.

5.2 Filler morphology and alignment

Randomly dispersed spherical particles require high loadings to form connected pathways, at which point mechanical properties and processability suffer. One-dimensional fillers are therefore attractive, since their high aspect ratio allows percolation at low volume fractions. Liu and co-workers embedded LLTO nanowires in PEO–LiTFSI and reported room-temperature conductivities of the order of 10^{-4} S cm^{-1} at a nanowire loading of 15 wt%, higher than that of particle-filled controls, and they highlighted the contribution of the nanowire surface to the conductivity [75]. In a later study, aligned LLTO nanowires oriented across the thickness of a PAN-based membrane gave a room-temperature conductivity significantly higher than that of randomly oriented analogues [64]. Analogous benefits have been reported for LLZO nanowires, where both doping level and morphology influence the conductivity enhancement [85]. Constructing vertically aligned, continuous ceramic–polymer interfaces has likewise been reported to enhance ionic conductivity relative to random dispersions [55].

A further step is the use of continuous three-dimensional ceramic networks. Fu and co-workers infiltrated PEO into an electrospun garnet nanofibre network and obtained a flexible membrane whose conductivity was of the order of 10^{-4} S cm^{-1} at room temperature, with the interconnected fibres providing uninterrupted ceramic paths [56]. Related approaches use templated or hydrogel-derived garnet frameworks [86] and elastic, aligned LLZO nanofibres [87]. The attraction of these architectures is that they decouple mechanics and conduction—the continuous ceramic scaffold provides stiffness and fast conduction, and the polymer provides flexibility and interfacial contact. Their drawbacks are the multi-step fabrication and the challenge of maintaining fibre continuity and alignment at scale.

5.3 Ultrathin films and host scaffolds

Cell-level energy density requires electrolyte layers that are as thin as possible; free-standing electrolytes often exceed 100 µm, which negates much of the gravimetric advantage of solid-state designs [88,89]. An effective strategy is to fill a mechanically robust, porous scaffold with the polymer electrolyte. Wan and co-workers used a vertically aligned nanoporous polyimide film filled with PEO/LiTFSI to obtain a membrane less than 10 µm thick with high mechanical

strength and ionic conductivity on the order of 10^{-4} S cm^{-1} at near-ambient temperature, and demonstrated cycling in full cells [90]. The scaffold approach separates the mechanical function from the ion-conducting function, allowing the conducting phase to be optimised for transport. Combining ceramic fillers with such scaffolds is a logical extension, although few systematic studies exist.

5.4 In situ polymerisation and cross-linking

A persistent difficulty of solid-state cells is the poor physical contact between electrolyte and electrode particles, particularly in thick composite cathodes. In situ polymerisation—infiltrating monomers, initiators and salts into a pre-assembled cell and then curing thermally or by irradiation—fills voids and yields an intimate, conformal interface. Ring-opening polymerisation of cyclic ethers and radical polymerisation of acrylates are the most common routes [33,34]. In situ approaches can also be applied to the filler itself: the in situ synthesis of monodisperse SiO_2 nanospheres within PEO is an instructive example that avoids the agglomeration typical of blending [66]. The limitations concern incomplete conversion, residual monomer or initiator by-products, and the limited oxidative stability of some ring-opened polymers, all of which may compromise long-term performance and must be assessed by post-mortem analysis.

Cross-linking more generally improves dimensional stability and suppresses crystallinity, but reduces chain mobility and may hinder recycling at end of life. Dynamic or reversible cross-links, which combine mechanical robustness with the capacity for reprocessing, represent an interesting direction that has been little explored in composites [58].

5.5 Filler surface engineering

The filler surface controls dispersion, ion coordination and interfacial transfer. Grafting silane coupling agents or polymer brushes onto ceramic surfaces improves compatibility with the matrix and reduces agglomeration, while washing or thermal treatment can remove the Li_2CO_3/LiOH layers that form on garnet surfaces [68,71]. Fillers bearing Lewis-acid sites that bind anions can raise the effective Li^+ transference number and thereby reduce polarisation [62,63]. Anchoring ion-conducting groups or ionic liquids to the filler surface can generate "ionic bridges" across the polymer/ceramic boundary, aiming to lower the interfacial barrier identified as limiting in garnet/PEO composites [30,32]. Such functionalisation must be evaluated carefully, because organic surface layers may introduce their own electrochemical instabilities.

5.6 Multilayer and gradient architectures

Different regions of a cell impose different demands: the anode side requires stability against a strongly reducing metal, while the cathode side requires stability at high potential. Layered architectures therefore combine materials with complementary properties. Zhou and co-workers sandwiched a ceramic membrane between polymer layers, so that the polymer contacts the lithium anode and cathode while the ceramic core provides mechanical strength and suppresses dendrite propagation [91]. A double-layer design pairs a reduction-stable layer at the anode with an oxidation-stable layer at the cathode, enabling operation with high-voltage cathodes that PEO alone cannot support [61]. Gradient composites, in which filler type or loading varies through the thickness, extend this concept; they are attractive, but interlayer resistance and delamination under cycling remain open concerns.

5.7 Fabrication routes

Solution casting followed by drying and hot pressing is the most common laboratory method; it is simple and flexible, but residual solvent can strongly affect the measured properties, and solvents such as acetonitrile, DMF and N-methyl-2-pyrrolidone raise toxicity and cost concerns at scale. Electrospinning enables nanofibre scaffolds and aligned architectures [56,87]. Tape casting, extrusion and hot-melt routes are solvent-free or solvent-lean alternatives that are more compatible with roll-to-roll manufacturing, but demand polymers and fillers that tolerate shear and elevated temperature [92]. Additive manufacturing has been demonstrated for electrode and electrolyte structures, although industrial relevance remains to be shown. Whatever the route, reporting the drying protocol, residual solvent content and thickness uniformity is essential for reproducibility [33,43].

5.8 Mechanical and thermal behaviour of composites

Mechanical and thermal properties are often treated as secondary to conductivity, but they determine whether a composite can be handled, assembled into cells and operated safely. Neat PEO films are soft, with moduli in the megapascal range, and flow above their melting temperature, whereas ceramic-rich composites can reach the gigapascal range but are brittle. The early studies on inert fillers already demonstrated that ceramic particles improve the dimensional stability of PEO-based films at elevated temperature by acting as physical cross-links that limit creep [26]. Fluorinated matrices coupled with garnet fillers have been reported to show enhanced mechanical strength and thermal stability relative to the neat polymer [60], and scaffold-based designs decouple these properties from the polymer entirely [90].

Thermal behaviour is equally important for safety. The polymer component sets the upper temperature limit and governs the response to abuse conditions, while the ceramic component can improve thermal stability and reduce shrinkage. However, few studies quantify heat release, gas evolution or short-circuit behaviour of composite electrolytes at the cell level, which limits the strength of the safety claims that can be made [4,8]. A balanced approach measures modulus, elongation at break, thermal shrinkage and, where possible, puncture resistance alongside conductivity, so that trade-offs are visible [29,32].

5.9 Comparison of design strategies

Table 3 summarises the strategies described above. No approach dominates on every criterion. Random dispersion of nanoparticles is the simplest and most scalable route but yields modest gains; aligned and three-dimensional architectures deliver higher conductivity at lower ceramic content but require complex fabrication; scaffold-based thin films offer the best route to thin, mechanically robust membranes; in situ polymerisation provides the best interfacial contact; and multilayer designs decouple the conflicting requirements of anode and cathode at the price of additional interfaces. In practice, the most promising systems are likely to combine several of these elements—for example, a surface-functionalised ceramic scaffold infiltrated in situ with a polymer electrolyte and coupled with a stable cathode-side layer. The corresponding challenge is to keep such hybrid designs simple enough to be manufactured at scale.

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Table 3. Summary of design strategies for polymer–inorganic composite electrolytes.

Strategy	Main benefit	Main challenge	Maturity	Refs.
Random nanoparticle dispersion	Simple and scalable; reduced polymer crystallinity	Agglomeration; modest conductivity gain	High	[28,66]
Aligned nanowires / vertical interfaces	Percolation at low loading; enhanced conductivity	Alignment at scale; filler cost	Medium	[55,64]
Three-dimensional ceramic scaffolds	Continuous ceramic paths; mechanical strength	Multi-step fabrication; brittleness	Medium	[56,86,87]
Porous host scaffold (e.g. polyimide)	Ultrathin, strong membranes	Complete filling; limited ceramic integration	Emerging	[90]
In situ polymerisation	Conformal contact; void filling	Incomplete conversion; by-products	Medium	[34,66]
Filler surface functionalisation	Dispersion; anion trapping; lower interfacial barrier	Added complexity; stability of organic layers	Medium	[62,63]
Multilayer / gradient designs	Separates anode and cathode requirements	Interlayer resistance; delamination	Medium	[61,91]

6. Sodium-Based Composite Electrolytes and Comparison with Lithium Systems

6.1 How sodium differs from lithium

Sodium composites follow the same design logic as lithium systems, but with important differences arising from the physical chemistry of Na^+. The larger ionic radius and lower charge density of Na^+ weaken its interaction with coordinating groups, which can facilitate dissociation of sodium salts in polymer hosts. In rigid lattices, the same properties imply that the migration pathways must be wide enough to accommodate the larger ion; the NASICON framework, whose bottlenecks are well suited to Na^+, is a prime example and explains its status as the leading oxide sodium conductor [14,73,74]. Studies of PEO–NaTFSI and PEO–NaFSI electrolytes have reported ionic conductivities broadly comparable to those of lithium analogues, with thermal and phase behaviour that depends strongly on the anion and salt concentration [93].

A further consideration is that many sodium cathodes operate at lower average voltages than their lithium counterparts, for example phosphates and Prussian-blue analogues at about 3–3.5 V [11,13]. This eases the oxidative demand on the electrolyte and could make polymers such as PEO, whose oxidative stability is limited, more compatible with sodium cathodes than with high-voltage lithium ones. Conversely, sodium metal is more reactive than lithium and melts at only 97.8 °C, which restricts thermal operating windows and safety margins, particularly for polymers that require elevated temperatures for adequate conduction [14,94].

6.2 Reported sodium composite electrolytes

Fewer studies have addressed sodium polymer–ceramic composites than lithium ones. The addition of TiO_2 nanoparticles to PEO–$NaClO_4$ has been shown to improve ionic conductivity and interfacial behaviour in sodium cells, mirroring the classic passive-filler effect in lithium systems [95]. Composite electrolytes incorporating NASICON-type ceramics within a PEO-based matrix have been reported to combine the wide electrochemical window and Na^+ conduction of the ceramic with the flexibility of the polymer [31]. Dense NASICON electrolytes with tailored doping have also been used directly in monolithic solid-state sodium batteries, illustrating the potential of the oxide route [84]. Sulfide sodium conductors such as Na_3PS_4 and $Na_{11}Sn_2PS_{12}$ offer the highest room-temperature conductivities among sodium solid electrolytes [79,80], but their combination with polymers is still largely unexplored. Broad reviews of sodium solid electrolytes and interphases identify composite systems as a promising but immature area [15,94].

6.3 Comparative assessment

Table 4 summarises the main physical and technological differences between lithium and sodium composite electrolytes. Two observations are worth emphasising. First, the maturity gap is large: the majority of mechanistic insights on ion pathways, filler effects and interface chemistry have been obtained in lithium systems, and it is not yet clear to what extent they carry over to sodium. Second, the sodium systems' lower cost and material abundance shift the optimisation targets. For stationary storage, an electrolyte that is modestly less conductive but far cheaper and made from abundant elements—for instance a NASICON-polymer composite—may be preferable to a high-performance lithium composite based on tantalum-doped garnet or germanium sulfide [9,11].

Table 4. Comparison of lithium- and sodium-based composite electrolyte systems.

Property / aspect	Lithium systems	Sodium systems
Ionic radius of cation (Å)	0.76	1.02
Standard potential (V vs. SHE)	−3.04	−2.71
Theoretical capacity of metal anode (mAh g^{-1})	≈ 3860	≈ 1166
Melting point of metal (°C)	180.5	97.8

Property / aspect	Lithium systems	Sodium systems
Natural abundance	Low (tens of ppm in the crust)	High (percent level in the crust)
Typical polymer hosts	PEO, PVDF-HFP, PAN, polycarbonates, single-ion polymers	PEO, PVDF-HFP, PAN (fewer studies)
Typical inorganic fillers	LLZO, LATP/LAGP, LLTO, LGPS, argyrodites, halides	NASICON ($Na_3Zr_2Si_2PO_{12}$), β-alumina, Na_3PS_4, TiO_2
Literature maturity	Extensive; mechanistic understanding advancing	Limited; mostly early-stage demonstrations
Main open issues	Interfacial resistance; dendrites; high-voltage stability; cost of Ta/Ga/Ge	Na metal reactivity and low melting point; interphase control; limited mechanistic data
Refs.	[6,29,33]	[14,15,94]

6.4 Cross-learning and outlook for sodium composites

Lessons from lithium can be transferred to sodium, but with caveats. Passive-filler effects on crystallinity and salt dissociation are largely independent of the identity of the alkali cation and are already visible in sodium systems [95]. Aligned and three-dimensional NASICON architectures are natural analogues of the garnet nanofibre networks developed for lithium, yet they have been comparatively little studied. Multilayer designs may prove especially valuable for sodium, because the greater reactivity of the metal makes the anode-side layer a critical design element [94].

On the other hand, some lithium lessons may not carry over. The interfacial resistance between polymer and ceramic is likely to differ for Na^+, and the relative contributions of interfacial and bulk pathways cannot be assumed to match those established for garnet/PEO composites. Crucially, the lower cost and abundance of sodium may justify designs, such as thick, ceramic-rich composites with moderate conductivity, that would not be competitive in lithium systems but would be attractive for stationary storage. Rapid progress would be helped by open reporting practices, including the publication of raw impedance data and negative results, and by adopting the benchmarking standards proposed for lithium cells [43].

7. Interfacial Challenges

Interfaces, rather than bulk conductivity, most often limit the performance of solid-state cells [7,51]. In composite electrolytes, three families of interfaces coexist: those between the electrolyte and the metal anode, those between the electrolyte and the cathode, and those internal to the composite between polymer, filler and salt. Each is discussed in turn.

7.1 The metal anode interface

At the anode, three issues are intertwined: physical contact, chemical stability and dendrite formation. PEO is chemically compatible with lithium metal, forms a relatively stable passivation layer, and is soft enough to conform to the metal surface. The ceramic component, however, may not be compatible. Ti- and Ge-containing NASICON and perovskite fillers are reduced by lithium, forming electronically conducting interphases that permit continued decomposition, and sulfides such as LGPS decompose into Li_2S, Li_3P and lithium–germanium alloys on contact with lithium metal [16,20]. Garnets are the most stable but are poorly wetted by lithium because of surface carbonate layers, giving high interfacial resistance; removal of contaminants and the introduction of thin lithiophilic interlayers has been shown to reduce this resistance dramatically [71]. Composites in which the polymer forms the outermost layer avoid direct ceramic–metal contact and thereby delay these problems, but expose the polymer to the anode and depend on its stability there [51,91].

Despite the mechanical rationale for solid electrolytes, dendrite-like lithium deposition has been observed even in dense garnets, propagating along grain boundaries and through pores at high current densities [50]. In addition, voids

that form during stripping at low stack pressure increase the local current density and seed filament growth [51,52]. In polymer-rich composites, a dominant mechanism is the inhomogeneous Li^+ flux caused by a low transference number and salt depletion at the interface, which explains the emphasis on anion immobilisation and single-ion architectures [39,62]. Design principles that link electrolyte modulus, interfacial energy and transport properties to the stability of lithium deposition have been proposed and provide a useful framework for composite design, although they need experimental validation in composite systems specifically [96].

For sodium metal, the same categories of problems apply, and are aggravated by higher reactivity and lower melting point. Sodium forms a less stable interphase with many organic components than lithium, wetting of NASICON ceramics by sodium is often poor, and sodium filaments can propagate at grain boundaries in oxide electrolytes. The available data are far more limited than for lithium [14,94], which is one of the most significant knowledge gaps in the field.

7.2 Internal interfaces in the composite

The polymer/filler boundary is both the source of many of the benefits of composites and one of their principal uncertainties. Lewis-acid–base interactions at the filler surface can lower crystallinity, promote salt dissociation and generate an interfacial layer with altered transport properties [63,65]. Conversely, the NMR results on PEO/LLZO show that ion transfer across the polymer/ceramic boundary can be difficult and that the ceramic can be bypassed by ions travelling through the polymer or along the interface [30]. Which of these behaviours prevails depends on the surface chemistry of the filler, the presence of contamination layers, the salt and its concentration, and the processing history. Chemical reactions between components are a further concern: the reaction of PVDF with basic garnet surfaces [60], the reduction of polycarbonates at low potential [25], and the decomposition of sulfides in polar solvents [16] are examples in which the assumed “inert” interface is in fact reactive.

7.3 The cathode interface

At the cathode, the electrolyte must be stable at high potential, must accommodate the volume changes of the active material during cycling, and must maintain ionic contact throughout the composite cathode. The limited oxidative stability of ether-based polymers restricts PEO-based cells mainly to lower-voltage cathodes such as $LiFePO_4$; operating with high-voltage layered oxides requires either a catholyte based on an oxidatively stable polymer or an interfacial coating [48,61]. Layered oxides expand and contract during cycling, and in rigid ceramic electrolytes this chemo-mechanical strain causes loss of contact and progressive capacity fade [97]. Polymer components, by virtue of their compliance, accommodate such strain better, which is a primary reason for the use of composites in the cathode layer. The catholyte's composition, the ionic and electronic percolation within the cathode, and the interphases formed between active material and electrolyte each affect rate capability and cycle life [34,89].

7.4 Characterisation of interfaces

Progress depends on techniques capable of resolving ion transport and chemistry at buried interfaces. Isotope-labelling solid-state NMR, as used to trace lithium pathways in PEO/LLZO composites, provides direct information on which phase carries the current [30]. Operando X-ray tomography and diffraction, cryogenic electron microscopy, depth-resolved X-ray photoelectron spectroscopy and time-of-flight secondary-ion mass spectrometry have been used to characterise interphase formation and void evolution in solid-state cells [51,52]. Correlating such measurements with electrochemical data from symmetric and full cells under controlled pressure and temperature is essential to move from empirical optimisation to rational design.

7.5 Stack pressure and interfacial mechanics

Mechanics play a central role at solid–solid interfaces. Lithium and sodium creep under pressure, and maintaining contact during stripping requires that metal be supplied to the interface at a rate matching its removal. If it is not, voids form and the effective contact area decreases, which raises local current density and accelerates failure [51,52]. Rigid ceramic electrolytes generally require substantial stack

pressure to sustain contact, which is difficult to apply in practical cell formats, whereas compliant polymer layers relax this requirement and can accommodate moderate volume changes [89,97]. This is a compelling practical argument for composites: even a thin polymer-rich interlayer between a ceramic and the electrodes can reduce the pressure needed to keep the interface intact. Reporting the pressure used in every experiment is essential, since results obtained at several megapascals may not transfer to cells operating near ambient pressure [43]. Continuum models such as that of Monroe and Newman provide qualitative guidance on how mechanical properties influence deposition stability [49], but a quantitative description that accounts for plastic flow of the metal, heterogeneous electrolyte structure and electrochemically induced stress is still lacking.

8. Challenges and Future Perspectives

8.1 Conductivity, thickness and operating temperature

Most high-performing PEO-based composites still require operating temperatures of 50–70 °C, which imposes system-level costs for thermal management and reduces appeal for consumer applications. Achieving conductivity of the order of 10^{-3} S cm^{-1} at room temperature without sacrificing electrochemical or mechanical stability remains an unresolved challenge for dry polymer-rich systems [6,39]. Two paths are pursued. One is to shift transport away from the polymer towards continuous ceramic pathways (ceramic-rich composites, three-dimensional scaffolds), which trades flexibility for conductivity [29,56]. The other is to improve the polymer itself through chemistry that decouples ion motion from segmental dynamics, such as new coordinating groups, high-salt or "polymer-in-salt" concepts, and single-ion architectures [46,58]. Likely outcomes combine both, with thin composite layers supported on mechanically robust scaffolds [90].

Thickness is closely tied to the system's practical energy density. The energy densities frequently projected for solid-state cells assume separators of a few tens of micrometres, whereas many reported composites are considerably thicker [88,89]. Studies of solid-state cells at realistic scale show that cell-level metrics depend strongly on electrolyte thickness, cathode loading and the proportion of inactive material [43]. Consequently, ultrathin, defect-free composites with high mechanical strength should be a central research priority.

8.2 Processing, moisture and scale-up

Laboratory methods do not necessarily translate into scalable manufacturing. Garnets require high-temperature synthesis and doping with elements such as Ta or Ga, which raises cost, while their sensitivity to CO_2 and moisture demands controlled atmospheres during storage and processing [68,71]. Sulfides pose greater difficulties because of H_2S evolution, and halides show sensitivity to moisture, although less severe [16,82]. Roll-to-roll compatible processes—solvent-free extrusion, dry film calendering, tape casting—must be adapted for composites with homogeneous filler dispersion at high throughput [92]. Solvent selection is another concern: solvents commonly used in polymer processing are toxic or costly, and their residues can influence measured properties, so solvent-free or aqueous routes are desirable where compatible with the chemistry [33,92]. Techno-economic analyses that include raw material and processing costs, still scarce for composite electrolytes, should be integrated into materials development from an early stage.

8.3 Standardised testing and reporting

A persistent obstacle to progress is the inconsistent reporting of test conditions. Conductivity values are reported at different temperatures, with and without residual solvent, and with widely varying sample thickness; cycling data use different current densities, areal capacities and stack pressures; and stability windows are estimated in incompatible ways [43,52]. Community adoption of minimum reporting standards—covering composition (including any solvent and plasticiser content), thickness, temperature, pressure, cathode loading, N/P ratio and cell format—would greatly improve comparability. For transference numbers, the limitations of the steady-state method mean that alternative or complementary approaches, such as electrophoretic NMR and concentrated-solution analysis, should be considered where appropriate [39,44].

8.4 Computation and data-driven design

The parameter space of composite electrolytes—polymer chemistry, salt, filler composition, morphology, surface chemistry and loading—is far too large to explore by trial and error. High-throughput computational screening has been applied to identify candidate lithium-ion conductors from tens of thousands of structures [98], and design principles derived from first-principles calculations have guided the search for fast conductors and stable interfaces [20,40]. Extending such approaches to composites requires models that capture polymer dynamics, interfacial ion transfer and space-charge effects, together with machine-learning potentials able to treat systems at the necessary length and time scales. Coupling automated synthesis with rapid characterisation and active learning could accelerate optimisation, but relies on the standardised, high-quality datasets discussed above.

8.5 Safety, sustainability and end-of-life

Solid-state does not automatically mean safe. Lithium metal remains highly reactive, sulfides can release toxic gases, and mechanical failure can create internal short circuits; safety claims should be supported by abuse testing on practical cell formats [4,8]. Sustainability considerations should extend beyond the operating phase. Composite electrolytes contain critical or geographically concentrated elements (La, Ta, Ge, In, Y), fluorinated polymers and, in cross-linked systems, matrices that resist recycling. Designing for recyclability—using abundant elements, recoverable polymers, reversible cross-links and separable components—would align solid-state technology with broader sustainability goals for batteries [9]. Sodium systems, by using abundant elements, offer a natural platform for sustainability-driven design.

8.6 Priorities for sodium composites

For sodium, the immediate needs are basic: systematic studies of polymer–salt–filler combinations under standardised conditions, interfacial characterisation at the sodium metal anode, and evaluation against practical cathodes. NASICON-polymer composites, sulfide-polymer composites and hybrid multilayer architectures appear the most promising near-term targets [31,80,84]. Mechanistic studies analogous to isotope-labelling NMR in lithium systems would help establish whether ions in sodium composites also travel predominantly through polymer and interfacial regions [30].

8.7 Full-cell demonstrations and benchmarking

Lithium-metal-polymer cells based on PEO electrolytes and $LiFePO_4$ cathodes, operating at elevated temperature, have long been demonstrated beyond the laboratory scale, and they set a useful baseline against which composite electrolytes should be assessed. Many academic reports of composite electrolytes, however, use cathodes with low active-material loading (often below about 2 mg cm^{-2}), thick lithium foil in large excess, low C-rates and elevated temperature. Such conditions flatter the performance of the electrolyte and hide limitations that appear at practical loadings, where ion transport within the thick composite cathode becomes rate limiting [43,89].

More realistic evaluations use areal capacities of several mAh cm^{-2}, limited lithium excess (low negative-to-positive capacity ratio), controlled stack pressure and temperatures closer to ambient. They should also report cell-level metrics, including the mass and volume fraction of the electrolyte and the resulting gravimetric and volumetric energy density, so that claims of superiority over lithium-ion cells can be tested [43,88]. Pairing composite electrolytes with high-voltage cathodes, silicon-containing or lithium-metal anodes and, for sodium, with practical polyanionic or layered oxide cathodes, will be the true test of the strategies reviewed here [15,61].

8.8 Summary of research priorities

- Ultrathin (below ~20 µm), mechanically robust composite membranes with room-temperature conductivity approaching 10^{-3} S cm^{-1} and t_{Li^+} or t_{Na^+} well above the values of conventional PEO systems.
- Direct mechanistic evidence, for each polymer/filler/salt system, of the dominant ion-conduction pathway, obtained with isotope-labelling NMR and complementary techniques.
- Stable, low-resistance interfaces to lithium and sodium metal and to high-voltage cathodes, using multilayer or gradient designs and rationally chosen interlayers.

• Scalable, solvent-free and moisture-tolerant processing routes, supported by techno-economic and life-cycle assessments.
• Community standards for measurement and reporting, so that performance claims are comparable and reproducible.
• Data-driven design tools that integrate polymer dynamics, interfacial transport and stability, and design for recycling from the outset.

9. Conclusions

Polymer–inorganic composite electrolytes occupy a pragmatic position between the flexibility of polymers and the high conductivity of ceramics. Over four decades the field has progressed from the observation that inert fillers modify PEO to sophisticated architectures with aligned nanowires, three-dimensional scaffolds, multilayers and in situ-formed networks. Three lessons emerge from this body of work. First, ion transport in composites cannot be understood by simple mixing rules: the polymer, the filler surface and the interface between them all contribute, and in some systems ions bypass the nominally highly conductive ceramic almost entirely [30]. Design should therefore address interfaces and connectivity as much as intrinsic filler conductivity. Second, interfacial stability with electrodes, rather than bulk conductivity, often determines cell performance, and it is here that composites can offer real advantages through layered and compliant architectures [61,91]. Third, the maturity of the field is uneven: lithium-based composites are studied extensively, whereas sodium-based analogues, arguably more relevant to low-cost stationary storage, are at an early stage.

For practitioners, the evidence reviewed here suggests a set of practical guidelines. Begin with a well-characterised polymer–salt baseline and measure it under the same conditions as the composite. Choose fillers on the basis of chemical compatibility with the polymer, the salt and both electrodes, not on bulk conductivity alone. Verify the dominant ion pathway directly instead of inferring it from conductivity trends. Evaluate the composite in cells with realistic loading, lithium or sodium excess, pressure and temperature. Finally, report every parameter needed for others to reproduce the result, including thickness, residual solvent and processing history [33,43].

Substantial challenges remain before composite electrolytes can support commercial solid-state batteries: room-temperature conductivity in ultrathin films, stable interfaces with alkali metal anodes and high-voltage cathodes, moisture-tolerant and scalable processing, and standardised evaluation. Addressing them will require closer integration of synthesis, advanced characterisation, computation and manufacturing science. If these efforts succeed, polymer–inorganic composites are well placed to bridge the gap between promising laboratory results and practical lithium and sodium solid-state batteries.

REFERENCES

[1] J.B. Goodenough, Y. Kim, Challenges for rechargeable Li batteries, Chem. Mater. 22 (2010) 587.
[2] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, Chem. Rev. 104 (2004) 4303.
[3] Q. Wang, P. Ping, X. Zhao, et al., Thermal runaway caused fire and explosion of lithium ion battery, J. Power Sources 208 (2012) 210.
[4] J. Kalhoff, G.G. Eshetu, D. Bresser, S. Passerini, Safer electrolytes for lithium-ion batteries: state of the art and perspectives, ChemSusChem 8 (2015) 2154.
[5] X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, Toward safe lithium metal anode in rechargeable batteries: a review, Chem. Rev. 117 (2017) 10403.
[6] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, Nat. Rev. Mater. 2 (2017) 16103.
[7] J. Janek, W.G. Zeier, A solid future for battery development, Nat. Energy 1 (2016) 16141.
[8] Q. Zhao, S. Stalin, C.-Z. Zhao, L.A. Archer, Designing solid-state electrolytes for safe, energy-dense batteries, Nat. Rev. Mater. 5 (2020) 229.
[9] D. Larcher, J.-M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, Nat. Chem. 7 (2015) 19.

[10] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, Chem. Rev. 114 (2014) 11636.
[11] J.-Y. Hwang, S.-T. Myung, Y.-K. Sun, Sodium-ion batteries: present and future, Chem. Soc. Rev. 46 (2017) 3529.
[12] H. Pan, Y.-S. Hu, L. Chen, Room-temperature stationary sodium-ion batteries for large-scale electric energy storage, Energy Environ. Sci. 6 (2013) 2338.
[13] D. Kundu, E. Talaie, V. Duffort, L.F. Nazar, The emerging chemistry of sodium ion batteries for electrochemical energy storage, Angew. Chem. Int. Ed. 54 (2015) 3431.
[14] K.B. Hueso, M. Armand, T. Rojo, High temperature sodium batteries: status, challenges and future trends, Energy Environ. Sci. 6 (2013) 734.
[15] C. Zhao, L. Liu, X. Qi, et al., Solid-state sodium batteries, Adv. Energy Mater. 8 (2018) 1703012.
[16] J.C. Bachman, S. Muy, A. Grimaud, et al., Inorganic solid-state electrolytes for lithium batteries: mechanisms and properties governing ion conduction, Chem. Rev. 116 (2016) 140.
[17] T. Famprikis, P. Canepa, J.A. Dawson, M.S. Islam, C. Masquelier, Fundamentals of inorganic solid-state electrolytes for batteries, Nat. Mater. 18 (2019) 1278.
[18] Z. Gao, H. Sun, L. Fu, et al., Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries, Adv. Mater. 30 (2018) 1705702.
[19] J.W. Fergus, Ceramic and polymeric solid electrolytes for lithium-ion batteries, J. Power Sources 195 (2010) 4554.
[20] Y. Zhu, X. He, Y. Mo, Origin of outstanding stability in the lithium solid electrolyte materials: insights from thermodynamic analyses based on first-principles calculations, ACS Appl. Mater. Interfaces 7 (2015) 23685.
[21] D.E. Fenton, J.M. Parker, P.V. Wright, Complexes of alkali metal ions with poly(ethylene oxide), Polymer 14 (1973) 589.
[22] M. Armand, Polymer solid electrolytes – an overview, Solid State Ionics 9–10 (1983) 745.
[23] W.H. Meyer, Polymer electrolytes for lithium-ion batteries, Adv. Mater. 10 (1998) 439.
[24] L. Long, S. Wang, M. Xiao, Y. Meng, Polymer electrolytes for lithium polymer batteries, J. Mater. Chem. A 4 (2016) 10038.
[25] J. Mindemark, M.J. Lacey, T. Bowden, D. Brandell, Beyond PEO—alternative host materials for Li^+-conducting solid polymer electrolytes, Prog. Polym. Sci. 81 (2018) 114.
[26] J.E. Weston, B.C.H. Steele, Effects of inert fillers on the mechanical and electrochemical properties of lithium salt–poly(ethylene oxide) polymer electrolytes, Solid State Ionics 7 (1982) 75.
[27] F. Capuano, F. Croce, B. Scrosati, Composite polymer electrolytes, J. Electrochem. Soc. 138 (1991) 1918.
[28] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nanocomposite polymer electrolytes for lithium batteries, Nature 394 (1998) 456.
[29] L. Chen, Y. Li, S.-P. Li, L.-Z. Fan, C.-W. Nan, J.B. Goodenough, PEO/garnet composite electrolytes for solid-state lithium batteries: from "ceramic-in-polymer" to "polymer-in-ceramic", Nano Energy 46 (2018) 176.
[30] J. Zheng, M. Tang, Y.-Y. Hu, Lithium ion pathway within $Li_7La_3Zr_2O_{12}$-polyethylene oxide composite electrolytes, Angew. Chem. Int. Ed. 55 (2016) 12538.
[31] Z. Zhang, Q. Zhang, C. Ren, et al., A ceramic/polymer composite solid electrolyte for sodium batteries, J. Mater. Chem. A 4 (2016) 15823.
[32] M. Dirican, C. Yan, P. Zhu, X. Zhang, Composite solid electrolytes for all-solid-state lithium batteries, Mater. Sci. Eng. R 136 (2019) 27.
[33] Y. Zheng, Y. Yao, J. Ou, et al., A review of composite solid-state electrolytes for lithium batteries: fundamentals, key materials and advanced structures, Chem. Soc. Rev. 49 (2020) 8790.

[34] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, G. Wang, Polymer electrolytes for lithium-based batteries: advances and prospects, Chem 5 (2019) 2326.
[35] Q. Zhang, K. Liu, F. Ding, X. Liu, Recent advances in solid polymer electrolytes for lithium batteries, Nano Res. 10 (2017) 4139.
[36] M.A. Ratner, D.F. Shriver, Ion transport in solvent-free polymers, Chem. Rev. 88 (1988) 109.
[37] D. Diddens, A. Heuer, O. Borodin, Understanding the lithium transport within a Rouse-based model for a PEO/LiTFSI polymer electrolyte, Macromolecules 43 (2010) 2028.
[38] Z. Gadjourova, Y.G. Andreev, D.P. Tunstall, P.G. Bruce, Ionic conductivity in crystalline polymer electrolytes, Nature 412 (2001) 520.
[39] V. Bocharova, A.P. Sokolov, Perspectives for polymer electrolytes: a view from fundamentals of ionic conductivity, Macromolecules 53 (2020) 4141.
[40] Y. Wang, W.D. Richards, S.P. Ong, et al., Design principles for solid-state lithium superionic conductors, Nat. Mater. 14 (2015) 1026.
[41] N. Kamaya, K. Homma, Y. Yamakawa, et al., A lithium superionic conductor, Nat. Mater. 10 (2011) 682.
[42] B. Zhang, R. Tan, L. Yang, et al., Mechanisms and properties of ion-transport in inorganic solid electrolytes, Energy Storage Mater. 10 (2018) 139.
[43] S. Randau, D.A. Weber, O. Kötz, et al., Benchmarking the performance of all-solid-state lithium batteries, Nat. Energy 5 (2020) 259.
[44] P.G. Bruce, C.A. Vincent, Steady state current flow in solid binary electrolyte cells, J. Electroanal. Chem. 225 (1987) 1.
[45] J. Evans, C.A. Vincent, P.G. Bruce, Electrochemical measurement of transference numbers in polymer electrolytes, Polymer 28 (1987) 2324.
[46] H. Zhang, C. Li, M. Piszcz, et al., Single lithium-ion conducting solid polymer electrolytes: advances and perspectives, Chem. Soc. Rev. 46 (2017) 797.
[47] R. Bouchet, S. Maria, R. Meziane, et al., Single-ion BAB triblock copolymers as highly efficient electrolytes for lithium-metal batteries, Nat. Mater. 12 (2013) 452.
[48] X. Yang, M. Jiang, X. Gao, et al., Determining the limiting factor of the electrochemical stability window for PEO-based solid polymer electrolytes: main chain or terminal —OH group?, Energy Environ. Sci. 13 (2020) 1318.
[49] C. Monroe, J. Newman, The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces, J. Electrochem. Soc. 152 (2005) A396.
[50] Y. Ren, Y. Shen, Y. Lin, C.-W. Nan, Direct observation of lithium dendrites inside garnet-type lithium-ion solid electrolyte, Electrochem. Commun. 57 (2015) 27.
[51] T. Krauskopf, F.H. Richter, W.G. Zeier, J. Janek, Physicochemical concepts of the lithium metal anode in solid-state batteries, Chem. Rev. 120 (2020) 7745.
[52] K.B. Hatzell, X.C. Chen, C.L. Cobb, et al., Challenges in lithium metal anodes for solid-state batteries, ACS Energy Lett. 5 (2020) 922.
[53] J. Zheng, Y.-Y. Hu, New insights into the compositional dependence of Li-ion transport in polymer–ceramic composite electrolytes, ACS Appl. Mater. Interfaces 10 (2018) 4113.
[54] W. Wieczorek, D. Raducha, A. Zalewska, J.R. Stevens, Effect of salt concentration on the conductivity of PEO-based composite polymeric electrolytes, J. Phys. Chem. B 102 (1998) 8725.
[55] X. Zhang, J. Xie, F. Shi, et al., Vertically aligned and continuous nanoscale ceramic–polymer interfaces in composite solid polymer electrolytes for enhanced ionic conductivity, Nano Lett. 18 (2018) 3829.
[56] K. Fu, Y. Gong, J. Dai, et al., Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries, Proc. Natl. Acad. Sci. U.S.A. 113 (2016) 7094.

[57] W. Wang, E. Yi, A.J. Fici, R.M. Laine, J. Kieffer, Lithium ion conducting poly(ethylene oxide)-based solid electrolytes containing active or passive ceramic nanoparticles, J. Phys. Chem. C 121 (2017) 2563.

[58] J. Lopez, D.G. Mackanic, Y. Cui, Z. Bao, Designing polymers for advanced battery chemistries, Nat. Rev. Mater. 4 (2019) 312.

[59] A. Arya, A.L. Sharma, Polymer electrolytes for lithium ion batteries: a critical study, Ionics 23 (2017) 497.

[60] X. Zhang, T. Liu, S. Zhang, et al., Synergistic coupling between $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ and poly(vinylidene fluoride) induces high ionic conductivity, mechanical strength, and thermal stability of solid composite electrolytes, J. Am. Chem. Soc. 139 (2017) 13779.

[61] W. Zhou, Z. Wang, Y. Pu, et al., Double-layer polymer electrolyte for high-voltage all-solid-state rechargeable batteries, Adv. Mater. 31 (2019) 1805574.

[62] C.-Z. Zhao, X.-Q. Zhang, X.-B. Cheng, et al., An anion-immobilized composite electrolyte for dendrite-free lithium metal anodes, Proc. Natl. Acad. Sci. U.S.A. 114 (2017) 11069.

[63] F. Croce, L. Persi, B. Scrosati, et al., Role of the ceramic fillers in enhancing the transport properties of composite polymer electrolytes, Electrochim. Acta 46 (2001) 2457.

[64] W. Liu, S.W. Lee, D. Lin, et al., Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires, Nat. Energy 2 (2017) 17035.

[65] W. Wieczorek, Z. Florjanczyk, J.R. Stevens, Composite polyether based solid electrolytes, Electrochim. Acta 40 (1995) 2251.

[66] D. Lin, W. Liu, Y. Liu, et al., High ionic conductivity of composite solid polymer electrolyte via in situ synthesis of monodispersed SiO_2 nanospheres in poly(ethylene oxide), Nano Lett. 16 (2016) 459.

[67] R. Murugan, V. Thangadurai, W. Weppner, Fast lithium ion conduction in garnet-type $Li_7La_3Zr_2O_{12}$, Angew. Chem. Int. Ed. 46 (2007) 7778.

[68] S. Ramakumar, C. Deviannapoorani, L. Dhivya, L.S. Shankar, R. Murugan, Lithium garnets: synthesis, structure, Li^+ conductivity, Li^+ dynamics and applications, Prog. Mater. Sci. 88 (2017) 325.

[69] J.-H. Choi, C.-H. Lee, J.-H. Yu, C.-H. Doh, S.-M. Lee, Enhancement of ionic conductivity of composite membranes for all-solid-state lithium rechargeable batteries incorporating tetragonal $Li_7La_3Zr_2O_{12}$ into a polyethylene oxide matrix, J. Power Sources 274 (2015) 458.

[70] J. Zhang, N. Zhao, M. Zhang, et al., Flexible and ion-conducting membrane electrolytes for solid-state lithium batteries: dispersion of garnet nanoparticles in insulating polyethylene oxide, Nano Energy 28 (2016) 447.

[71] X. Han, Y. Gong, K. Fu, et al., Negating interfacial impedance in garnet-based solid-state Li metal batteries, Nat. Mater. 16 (2017) 572.

[72] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, Ionic conductivity of solid electrolytes based on lithium titanium phosphate, J. Electrochem. Soc. 137 (1990) 1023.

[73] H.Y-P. Hong, Crystal structures and crystal chemistry in the system $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, Mater. Res. Bull. 11 (1976) 173.

[74] J.B. Goodenough, H.Y-P. Hong, J.A. Kafalas, Fast Na^+-ion transport in skeleton structures, Mater. Res. Bull. 11 (1976) 203.

[75] W. Liu, N. Liu, J. Sun, et al., Ionic conductivity enhancement of polymer electrolytes with ceramic nanowire fillers, Nano Lett. 15 (2015) 2740.

[76] Y. Kato, S. Hori, T. Saito, et al., High-power all-solid-state batteries using sulfide superionic conductors, Nat. Energy 1 (2016) 16030.

[77] H.-J. Deiseroth, S.-T. Kong, H. Eckert, et al., Li_6PS_5X: a class of crystalline Li-rich solids with an unusually high Li^+ mobility, Angew. Chem. Int. Ed. 47 (2008) 755.

[78] Y. Zhao, C. Wu, G. Peng, et al., A new solid polymer electrolyte incorporating $Li_{10}GeP_2S_{12}$ into a polyethylene oxide matrix for all-solid-state lithium batteries, J. Power Sources 301 (2016) 47.

[79] A. Hayashi, K. Noi, A. Sakuda, M. Tatsumisago, Superionic glass-ceramic electrolytes for room-temperature rechargeable sodium batteries, Nat. Commun. 3 (2012) 856.
[80] A. Hayashi, N. Masuzawa, S. Yubuchi, et al., A sodium-ion sulfide solid electrolyte with unprecedented conductivity at room temperature, Nat. Commun. 10 (2019) 5266.
[81] T. Asano, A. Sakai, S. Ouchi, et al., Solid halide electrolytes with high lithium-ion conductivity for application in 4 V class bulk-type all-solid-state batteries, Adv. Mater. 30 (2018) 1803075.
[82] X. Li, J. Liang, J. Luo, et al., Air-stable Li_3InCl_6 electrolyte with high voltage compatibility for all-solid-state batteries, Energy Environ. Sci. 12 (2019) 2665.
[83] C. Yuan, J. Li, P. Han, et al., Enhanced electrochemical performance of poly(ethylene oxide) based composite polymer electrolyte by incorporating nano-sized metal-organic framework, J. Power Sources 240 (2013) 653.
[84] Y. Lu, J.A. Alonso, Q. Yi, et al., A high-performance monolithic solid-state sodium battery with Ca^{2+} doped $Na_3Zr_2Si_2PO_{12}$ electrolyte, Adv. Energy Mater. 9 (2019) 1901205.
[85] T. Yang, J. Zheng, Q. Cheng, Y.-Y. Hu, C.K. Chan, Composite polymer electrolytes with $Li_7La_3Zr_2O_{12}$ garnet-type nanowires as ceramic fillers: mechanism of conductivity enhancement and role of doping and morphology, ACS Appl. Mater. Interfaces 9 (2017) 21773.
[86] J. Bae, Y. Li, J. Zhang, et al., A 3D nanostructured hydrogel-framework-derived high-performance composite polymer lithium-ion electrolyte, Angew. Chem. Int. Ed. 57 (2018) 2096.
[87] Y. Zhao, J. Yan, W. Cai, et al., Elastic and well-aligned ceramic LLZO nanofiber based electrolytes for solid-state lithium batteries, Energy Storage Mater. 23 (2019) 306.
[88] Y.-K. Sun, Promising all-solid-state batteries for future electric vehicles, ACS Energy Lett. 5 (2020) 3221.
[89] S. Xia, X. Wu, Z. Zhang, Y. Cui, W. Liu, Practical challenges and future perspectives of all-solid-state lithium-metal batteries, Chem 5 (2019) 753.
[90] J. Wan, J. Xie, X. Kong, et al., Ultrathin, flexible, solid polymer composite electrolyte enabled with aligned nanoporous host for lithium batteries, Nat. Nanotechnol. 14 (2019) 705.
[91] W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram, J.B. Goodenough, Plating a dendrite-free lithium anode with a polymer/ceramic/polymer sandwich electrolyte, J. Am. Chem. Soc. 138 (2016) 9385.
[92] J. Schnell, T. Günther, T. Knoche, et al., All-solid-state lithium-ion and lithium metal batteries – paving the way to large-scale production, J. Power Sources 382 (2018) 160.
[93] A. Boschin, P. Johansson, Characterization of NaX (X: TFSI, FSI) – PEO based solid polymer electrolytes for sodium batteries, Electrochim. Acta 175 (2015) 124.
[94] G.G. Eshetu, G.A. Elia, M. Armand, et al., Electrolytes and interphases in sodium-based rechargeable batteries: recent advances and perspectives, Adv. Energy Mater. 10 (2020) 2000093.
[95] Y.L. Ni'mah, M.-Y. Cheng, J.H. Cheng, J. Rick, B.-J. Hwang, Solid-state polymer nanocomposite electrolyte of TiO_2/PEO/$NaClO_4$ for sodium ion batteries, J. Power Sources 278 (2015) 375.
[96] M.D. Tikekar, S. Choudhury, Z. Tu, L.A. Archer, Design principles for electrolytes and interfaces for stable lithium-metal batteries, Nat. Energy 1 (2016) 16114.
[97] R. Koerver, W. Zhang, L. de Biasi, et al., Chemo-mechanical expansion of lithium electrode materials – on the route to mechanically optimized all-solid-state batteries, Energy Environ. Sci. 11 (2018) 2142.
[98] A.D. Sendek, Q. Yang, E.D. Cubuk, et al., Holistic computational structure screening of more than 12000 candidates for solid lithium-ion conductor materials, Energy Environ. Sci. 10 (2017