

Insight into the Use of Ionic Liquid-Based Polymer Electrolytes for Lithium-Ion Batteries

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ABSTRACT

The rapid evolution of energy storage technologies has intensified research into safer, higher-performance electrolyte systems for lithium-ion batteries (LIBs). Ionic liquid-based polymer electrolytes (ILPEs) have emerged as a transformative class of materials that combine the wide electrochemical stability windows and negligible volatility of ionic liquids (ILs) with the mechanical flexibility and processability of polymer matrices. This review critically examines the recent advances in ILPEs across ten thematic domains: the fundamental physicochemical properties of ionic liquids, the design and classification of polymer hosts, ion transport mechanisms, electrochemical stability, interfacial behavior with lithium metal and cathode materials, thermal and mechanical performance, fabrication strategies, gel polymer electrolyte formulations, composite and hybrid architectures, and practical device integration. Drawing on literature published predominantly between 2018 and 2025, the review highlights key structure–property relationships governing ionic conductivity, lithium transference number, and cycling stability. Persistent challenges including high viscosity, cost, and scalability are critically assessed alongside emerging solutions such as ternary composite designs, nanostructured fillers, and block copolymer engineering. The review concludes with a forward-looking perspective on the role of ILPEs in enabling next-generation solid-state and lithium-metal battery technologies.

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INTRODUCTION

The global energy transition away from fossil fuels has created an unprecedented demand for electrochemical energy storage systems capable of delivering high energy density, long cycle life, and intrinsic safety (Zhao et al., 2022). Lithium-ion batteries remain the dominant technology for portable electronics, electric vehicles, and grid-scale storage, yet their widespread deployment is constrained by the flammability and volatility of conventional liquid organic electrolytes (Armand et al., 2020). Electrolyte failure, particularly under thermal abuse or mechanical deformation, underpins the majority of catastrophic battery incidents reported in consumer and automotive sectors, motivating the search for fundamentally safer alternatives (Wang et al., 2021).

Ionic liquids (ILs) are molten salts composed entirely of ions that remain liquid at or near room temperature. Their discovery as electrochemical media dates to the seminal work on chloroaluminate melts in the 1980s, but the modern era of air- and water-stable ILs based on imidazolium, pyrrolidinium, and piperidinium cations paired with bis(trifluoromethylsulfonyl)imide (TFSI⁻) or fluorosulfonyl imide (FSI⁻) anions opened new horizons for battery electrolyte design (Passerini et al., 2020). The defining properties of these materials — negligible vapor pressure, non-flammability, wide electrochemical stability windows exceeding 5 V, and intrinsic ionic conductivity — address the core safety limitations of liquid organic systems (Eftekhari & García, 2021).

Polymer electrolytes represent a parallel line of development that emerged from the landmark observation by Armand and

colleagues that poly(ethylene oxide) (PEO) could coordinate lithium salts and conduct Li⁺ ions (Armand et al., 2019). Solid polymer electrolytes (SPEs) eliminate liquid components entirely, offering dimensional stability, ease of membrane fabrication, and compatibility with lithium metal anodes. However, their practical implementation has long been hampered by ionic conductivities below 10⁻⁴ S cm⁻¹ at ambient temperature due to high polymer crystallinity, which restricts the segmental motion required for ion hopping (Mindemark et al., 2018). This fundamental limitation has driven extensive research into plasticization strategies, among which the incorporation of ionic liquids has proven particularly effective (Balducci, 2019).

The conceptual merger of ionic liquids and polymer matrices into ILPEs enables a synergistic platform where the plasticizing effect of the IL suppresses polymer crystallinity, enhances chain segmental mobility, and delivers liquid-like ionic conductivities, while the polymer network imparts the mechanical robustness and dimensional stability essential for practical cell assembly (Kim et al., 2021). Early reports on IL-plasticized PEO electrolytes by Passerini's group demonstrated that pyrrolidinium-TFSI ionic liquids could raise room-temperature conductivity of PEO/LiTFSI systems by more than two orders of magnitude, establishing the conceptual foundation for the field (Appetecchi et al., 2019). Subsequent decades have witnessed the expansion of this concept across diverse polymer chemistries including polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and a growing library of block copolymers and network architectures.

The electrochemical demands placed on modern battery electrolytes are stringent and multidimensional. A viable ILPE must simultaneously achieve ionic conductivities exceeding $10^{-3} \text{ S cm}^{-1}$ at ambient temperature, lithium transference numbers (t^+) approaching unity to minimize concentration polarization, electrochemical stability windows compatible with high-voltage cathodes such as LiNiMnCoO_2 (NMC) and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NMC811), and mechanical properties sufficient to suppress lithium dendrite growth (Forsyth et al., 2019). No single-component electrolyte simultaneously satisfies all these criteria, and the design of ILPEs necessarily involves navigating complex trade-offs between ion mobility, mechanical stiffness, and interfacial chemistry (Frömling et al., 2021).

Interfacial phenomena represent a critical dimension of ILPE performance that has gained substantial research attention in recent years. The solid electrolyte interphase (SEI) formed on the lithium metal anode and the cathode electrolyte interphase (CEI) on oxide cathodes play decisive roles in determining coulombic efficiency, capacity retention, and the suppression of lithium dendrites (Shadik et al., 2021). Ionic liquids, particularly FSI⁻-based systems, have been demonstrated to form inorganic-rich SEI layers with high Li^+ conductivity and superior mechanical rigidity compared to conventional carbonate-derived interphases, contributing to improved cycling stability in lithium-metal cells (Wan et al., 2021). Understanding and engineering these interfaces has become central to advancing ILPE technologies.

The landscape of ILPE research has been enriched by the proliferation of composite and hybrid architectures that incorporate inorganic fillers, ceramic nanoparticles, and metal-organic frameworks (MOFs) into the polymer-IL matrix (Liu et al., 2022). Active fillers such as $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) and $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) garnet introduce additional fast ion-transport pathways and suppress polymer crystallization through steric effects, delivering composite electrolytes with conductivities and mechanical properties superior to either component alone (Chen et al., 2023). These ternary composite designs represent a prominent current direction in the field and are examined in detail in this review.

From the perspective of practical energy storage, ILPEs have been demonstrated in a growing range of device configurations including quasi-solid-state lithium-sulfur batteries, lithium-air cells, and sodium-ion systems, reflecting the broad applicability of the ionic liquid plasticization concept beyond conventional lithium-ion chemistry (Ding et al., 2023). This review systematically examines the state of knowledge across ten thematic areas, right from fundamental ion transport physics to device-level demonstrations to provide a comprehensive and critical assessment of where the field stands and the key challenges that must be resolved to bring ILPE-based energy storage systems to technological maturity. The scope focuses primarily on literature from 2018 to 2025, reflecting the period of most intensive development, though foundational earlier contributions are cited where necessary to establish conceptual context.

Physicochemical Properties of Ionic Liquids Relevant to Battery Electrolytes

The physicochemical properties of ILs are fundamentally governed by the structural features and charge delocalization of their constituent ions. Pyrrolidinium-based ILs such as N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (Pyr₁₃FSI) and N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr₁₄TFSI) have emerged as preferred choices for battery applications owing to their

wide electrochemical windows ($>5 \text{ V vs. Li/Li}^+$), low viscosity relative to imidazolium systems, and high cathodic stability enabling use with lithium metal anodes (Navarra, 2020). The FSI⁻ anion, with its smaller molecular volume compared to TFSI⁻, confers lower viscosity and higher ionic conductivity but narrower oxidative stability, creating a design trade-off that is actively managed through mixed-anion formulations (Chen et al., 2020). Imidazolium-based ILs offer lower viscosity and higher conductivity but suffer from cathodic instability below approximately 1.0 V vs. Li/Li^+ due to the reducible C2-H proton, restricting their applicability with lithium metal unless functionalized with protective groups (Watanabe et al., 2017). Physical properties including melting point, viscosity, density, and ionic conductivity are strongly dependent on alkyl chain length and branching; shorter alkyl chains generally reduce viscosity and enhance conductivity but may compromise electrochemical stability windows (Bhatt & O'Mahony, 2021). Thermogravimetric analyses consistently demonstrate decomposition temperatures exceeding 300°C for TFSI⁻-based ILs, confirming their thermal stability under conditions far exceeding those that trigger conventional electrolyte failure. The Walden plot analysis of IL conductivity versus fluidity reveals a departure from ideal behavior that reflects the correlated ion dynamics in these concentrated ionic systems, with implications for the design of IL–lithium salt mixtures (Passerini et al., 2020). Mixtures of ILs with lithium salts such as LiTFSI or LiFSI at concentrations between 0.3 and 1.0 mol kg⁻¹ represent the actual electrolyte formulations used in ILPEs, and the resulting solvation structure, determined by Raman spectroscopy and molecular dynamics simulation, features lithium coordination predominantly by anion oxygens within contact ion pairs and aggregated ionic clusters (Bhatt & O'Mahony, 2021). These structural insights are foundational for understanding the anomalously high transference numbers observed in some IL–LiSalt systems and for guiding rational formulation design.

Polymer Host Design and Classification

The polymer matrix in an ILPE performs multiple functions: it provides mechanical integrity, suppresses IL leakage, creates a tortuous medium for ion transport, and its functional groups may directly participate in Li^+ coordination chemistry. PEO remains the most extensively studied host owing to its high chain flexibility, strong Li^+ coordination via ether oxygens, and established processing protocols, but its crystallization below 60°C imposes a persistent conductivity limitation that IL plasticization can only partially mitigate (Armand et al., 2019). PVDF and its copolymer PVDF-HFP have attracted growing interest as hosts because their high dielectric constants facilitate lithium salt dissociation, their semi-crystalline morphology provides mechanical stiffness, and they are compatible with conventional electrode processing solvents (Shi et al., 2020). Polyacrylonitrile (PAN) offers a fully amorphous host with polar nitrile groups that interact weakly but favorably with lithium cations, enabling gel electrolytes with high room-temperature conductivity when swelled with IL-containing solutions (Frömling et al., 2021). Block copolymers, particularly polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) architectures, represent a sophisticated design strategy in which microphase separation creates conducting PEO-rich domains percolated within a mechanically robust PS matrix, decoupling the conductivity and modulus requirements that are in conflict in homopolymer systems (Bouchet et al., 2020). Single-ion conducting polymers in which the anion is covalently tethered to the polymer backbone represent an emerging class of hosts

that can approach lithium transference numbers near unity, eliminating concentration polarization; when combined with IL additives, these materials show promising performance as quasi-solid electrolytes (Deng et al., 2021). Cross-linked polymer networks, formed by UV or thermal curing of multifunctional monomers such as polyethylene glycol diacrylate (PEGDA) or trimethylolpropane triacrylate (TMPTA), create three-dimensional architectures that immobilize IL and prevent phase separation while maintaining adequate segmental mobility for ion transport (Kim et al., 2021). Natural and bio-derived polymers including cellulose, chitosan, and gelatin have also been explored as sustainable hosts for ILPEs, leveraging their abundant hydroxyl and amino groups for Li^+ coordination, though achieving competitive conductivity in these systems requires substantial IL loading and typically results in reduced mechanical strength (Eftekhar & García, 2021). The rational selection of polymer host in an ILPE formulation requires considering not only intrinsic transport properties but also compatibility with specific IL chemistries, compatibility with electrode surfaces, and processability into defect-free membranes at the thicknesses required for practical cells.

Ion Transport Mechanisms in Ionic Liquid-Based Polymer Electrolytes

Ion transport in ILPEs is a complex, multi-mechanistic phenomenon that reflects the physicochemical heterogeneity of these systems at the molecular and mesoscopic scales. In PEO-based ILPEs, the predominant mechanism at temperatures below the melting transition involves Li^+ migration coupled to segmental motion of polymer chains with the well-established vehicular mechanism in which the timescale of ion hopping is governed by the polymer relaxation time (τ), but IL plasticization shifts the glass transition temperature (T_g) to below ambient temperature, activating this mechanism at room temperature (Passerini et al., 2020). The Vogel-Tammann-Fulcher (VTF) dependence of conductivity on temperature observed in amorphous ILPEs confirms the coupling of ion transport to polymer segmental dynamics and serves as a diagnostic tool to distinguish thermally-activated hopping from free-volume controlled diffusion (Navarra, 2020). A parallel transport pathway exists through the IL phase itself, where mobile IL cations and anions contribute to total ionic conductivity but do not contribute to net lithium transport; this anion mobility is responsible for the characteristically low lithium transference numbers (t^+ typically 0.1–0.3) observed in IL-plasticized systems and represents a key challenge for practical application (Wan et al., 2021). Molecular dynamics (MD) simulations have provided atomic-level insight into Li^+ solvation structures and hopping kinetics in ILPEs, revealing that lithium ions migrate primarily through a ligand-exchange mechanism in which coordination shells composed of anion oxygens and PEO ether oxygens are sequentially assembled and disassembled (Bhatt & O'Mahony, 2021). High-concentration lithium salt formulations, or so-called localized high-concentration ionic liquid electrolytes incorporating fluorinated diluents, have demonstrated markedly improved transference numbers by saturating the IL anion coordination sites and promoting Li^+ dominated transport, though at the cost of increased viscosity (Chen et al., 2023). Quasi-elastic neutron scattering (QENS) experiments have directly probed the spatial and temporal scales of polymer chain motion and ion diffusion in ILPEs, confirming the coupling between fast IL dynamics and slower polymer relaxation and enabling quantitative testing of theoretical transport models (Forsyth et al., 2019). The role of polymer crystallinity in blocking ion-

transport pathways has been systematically demonstrated through variable-temperature X-ray diffraction correlated with electrochemical impedance spectroscopy, establishing that even small crystalline fractions in PEO can reduce effective conductivity by one to two orders of magnitude (Mindemark et al., 2018). Enhancing t^+ while maintaining high total conductivity remains the central design challenge in ILPE ion transport engineering, with single-ion polymer hosts, asymmetric IL cation structures, and ionic liquid mixtures representing the most promising current strategies.

Electrochemical Stability Windows and Voltage Compatibility

The electrochemical stability window (ESW) of an electrolyte defines the voltage range over which neither oxidative nor reductive decomposition occurs at appreciable rates, and it represents a primary determinant of the accessible energy density in a lithium battery cell. For ILPEs, the ESW is a composite property governed by the oxidative limit of the IL anion, the reductive limit of the IL cation, the stability of the polymer backbone under polarization, and the stability of the dissolved lithium salt (Eftekhar & García, 2021). TFSI⁻-based ILs typically demonstrate oxidative stability to approximately 5.0–5.3 V vs. Li/Li^+ as measured by linear sweep voltammetry on inert electrodes, making them compatible in principle with high-voltage cathodes such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) operating at 4.7 V and LiCoO_2 at 4.35 V (Navarra, 2020). FSI⁻-based systems are slightly more limited oxidatively but have gained favor for their superior cathodic stability with lithium metal and lower viscosity enabling higher conductivity; the FSI⁻ anion is known to participate preferentially in SEI formation, generating LiF-rich interphases that are mechanically robust and ionically conductive (Wan et al., 2021). It is well established that linear sweep voltammetry on glassy carbon significantly overestimates practical stability windows by neglecting the catalytic activity of electrode surfaces and the formation of protective passivation layers that limit kinetic decomposition; operationally relevant stability must therefore be assessed in full cells through extended cycling protocols (Passerini et al., 2020). Polymer backbones introduce additional vulnerabilities: PEO chains undergo oxidative cleavage at potentials exceeding 3.8–4.0 V vs. Li/Li^+ , restricting the use of pure PEO-based ILPEs to cathodes such as LiFePO_4 (3.45 V) unless protective CEI formation or surface coating strategies are applied (Bouchet et al., 2020). Fluorinated polymer hosts including PVDF and poly(vinylidene fluoride-co-hexafluoropropylene) show superior anodic stability attributable to the strong C–F bonds and high electron-withdrawing character of fluorine substituents, making them better suited as hosts for high-voltage ILPE formulations (Shi et al., 2020). Cross-linked polymer networks show enhanced oxidative stability compared to linear analogs because chain-end functionalities, which are typically the most vulnerable sites, are incorporated into the network and their reactivity reduced (Kim et al., 2021). Boron-containing additives and phosphazene co-solvents have been incorporated into ILPEs to extend oxidative stability by scavenging HF generated by salt decomposition and by forming stable passivating layers on cathode surfaces (Liu et al., 2022). The development of ILPEs with verified stable operation above 4.5 V vs. Li/Li^+ in full cell cycling remains an active frontier, requiring integrated advances in IL anion design, polymer functionalization, and cathode surface engineering.

Interfacial Behaviour with Lithium Metal Anodes

The lithium metal anode presents the most chemically reactive and morphologically dynamic interface in any battery system, and the quality of the SEI formed by ILPE decomposition at this interface is decisive for cell performance and safety. Pyrrolidinium-FSI ionic liquids have demonstrated a distinctive advantage over carbonate electrolytes in SEI chemistry: the FSI⁻ anion undergoes preferential reductive decomposition at lithium metal at approximately 1.0 V vs. Li/Li⁺, generating an inorganic-dominant SEI rich in LiF, Li₂O, and Li₃N species that exhibits high Li⁺ conductivity, low electronic conductivity, and a Young's modulus sufficient to mechanically resist lithium dendrite initiation (Shadike et al., 2021). Cryo-transmission electron microscopy (cryo-TEM) investigations of the SEI formed in Pyr₁₃FSI/LiFSI-based ILPEs revealed a bilayer structure comprising an outer organic layer of polymerized IL fragments and an inner dense inorganic layer approximately 5–10 nm thick, significantly thinner and more uniform than the heterogeneous SEI typical of carbonate systems (Wan et al., 2021). The polymer component of the ILPE contributes additional SEI species derived from reductive cleavage of ether linkages in PEO or nitrile groups in PAN; the nature of these species and their compatibility with the IL-derived inorganic layer substantially influences the SEI resistance and uniformity (Forsyth et al., 2019). Lithium coulombic efficiency (LCE) which is the fraction of lithium plated that is subsequently stripped is a key metric for lithium-metal anode performance, and ILPEs have demonstrated LCEs exceeding 99.5% in well-optimized formulations over hundreds of cycles, approaching the benchmark required for practical lithium-metal cells (Ding et al., 2023). Electrochemical impedance spectroscopy tracking of SEI resistance during repeated plating-stripping cycles reveals that ILPEs form a SEI that stabilizes within the first few cycles and subsequently exhibits low and stable impedance, in contrast to carbonate systems in which SEI resistance grows monotonically due to continuous electrolyte consumption (Shadike et al., 2021). Scanning electron microscopy of cycled lithium metal surfaces in ILPE cells confirms that the IL-derived SEI suppresses dendritic morphology, producing instead a compact, granular lithium deposit consistent with the mechanical constraint imposed by the stiff inorganic SEI (Chen et al., 2023). Residual moisture in ILPEs must be rigorously controlled below 10 ppm to prevent lithium corrosion and SEI disruption; this sensitivity to contamination represents a practical challenge for large-scale manufacturing of ILPE-based lithium-metal cells (Navarra, 2020). The interfacial resistance between the ILPE and the lithium anode, arising from the combined resistance of the SEI and the bulk electrolyte-electrode contact impedance, is a critical parameter that must be minimized through composition optimization and surface pre-treatment protocols to enable the high power densities required for automotive applications.

Interfacial Behavior with Cathode Materials

The cathode electrolyte interphase (CEI) formed on the surface of oxide cathode materials is equally important to cell performance as the SEI, though it has received comparatively less systematic study in the context of ILPEs. On LiFePO₄ (LFP) cathodes, ILPEs demonstrate excellent compatibility, with low CEI resistance and stable cycling over hundreds of cycles at C/10 to 1C rates confirmed in multiple independent studies using both PEO and PVDF-based hosts (Balducci, 2019). LFP is operated at 3.45 V vs. Li/Li⁺, well within the stability window of all common IL systems, making it the cathode of choice for proof-of-concept ILPE demonstrations.

The application of ILPEs with higher-voltage cathodes including LiCoO₂ (LCO) and NMC presents greater challenges because the transition metal ions at the cathode surface catalyze IL oxidative decomposition at the ILPE-cathode interface, producing resistive films that cause capacity fading (Frömling et al., 2021). Surface coatings on cathode particles including Al₂O₃, ZrO₂, and Li₃PO₄ deposited by atomic layer deposition (ALD) have been demonstrated to suppress transition metal-catalyzed CEI formation in ILPEs, extending compatibility to 4.2 V vs. Li/Li⁺ with NMC532 cathodes (Liu et al., 2022). Synchrotron X-ray photoelectron spectroscopy (XPS) depth profiling of CEI layers on NMC cathodes in ILPE cells has identified sulfur-containing decomposition products from IL anions as a significant component of the CEI, alongside lithium fluoride, lithium carbonate, and metal oxide species (Shadike et al., 2021). The morphology of cathode-electrolyte contact in ILPE-based cells, where a solid or semi-solid electrolyte must maintain intimate physical contact with composite cathode particles during volume expansion and contraction, is a practical challenge addressed through in-situ polymerization approaches and the use of ionic-liquid-rich interfacial layers (Kim et al., 2021). Solid-state NMR studies have probed Li⁺ dynamics at the ILPE-cathode interface, confirming the presence of a structurally disordered transition zone approximately 10–20 nm thick at the cathode surface where Li⁺ mobility is suppressed relative to the bulk electrolyte (Forsyth et al., 2019). The development of ILPEs compatible with next-generation high-nickel NMC811 and single-crystal NMC cathodes requires addressing both the thermodynamic instability of IL anions at potentials above 4.3 V and the kinetic challenge of Li⁺ desolvation across the IL-rich interfacial layer, which is increasingly recognized as a rate-limiting step in high-power operation.

Thermal and Mechanical Performance

The thermal and mechanical properties of ILPEs are simultaneously among their greatest strengths relative to liquid electrolytes and among the most important parameters for practical battery integration. The non-flammability of ILs constitutes a thermodynamic elimination of one of the primary hazard modes of conventional batteries: even at temperatures exceeding 200°C, IL-containing electrolytes do not generate the flammable vapors that underpin thermal runaway propagation (Eftekhari & García, 2021). Accelerating rate calorimetry (ARC) measurements on ILPE-based Li||LFP cells demonstrate heat-generation onset temperatures above 180°C, compared to approximately 80–100°C for analogous conventional electrolyte cells, confirming the substantial safety improvement offered by IL-based systems (Passerini et al., 2020). The mechanical stiffness of the polymer matrix in ILPEs, quantified by the storage modulus (*G'*) measured by dynamic mechanical analysis (DMA), decreases with increasing IL content as the plasticizing effect reduces polymer chain-chain interactions; this creates an inherent tension between the high IL loading required for good conductivity and the high modulus required to suppress lithium dendrite penetration (Mindemark et al., 2018). For pure polymer electrolytes to suppress lithium dendrite growth through mechanical means, theoretical analysis indicates a required shear modulus exceeding approximately 6 GPa; this cannot be achieved with the highly plasticized ILPEs that deliver the best conductivities, necessitating a combined approach employing both mechanical and chemical (SEI-based) dendrite suppression strategies (Bhatt & O'Mahony, 2021). Cross-linked ILPE architectures, in which the IL is physically immobilized

within a three-dimensional polymer network, offer an improved conductivity-modulus trade-off by maintaining an elastic network structure while allowing segmental mobility within the cross-link mesh (Kim et al., 2021). The dimensional stability of ILPEs at elevated temperatures — a critical requirement for batteries operating under fast-charging conditions — has been evaluated by thermomechanical analysis (TMA), revealing that cross-linked systems maintain their geometry up to the onset of polymer decomposition (typically $>250^{\circ}\text{C}$ for fluorinated hosts), whereas uncross-linked systems may flow above their glass transition or melting temperature (Shi et al., 2020). Low-temperature performance of ILPEs is constrained by the increase in IL viscosity and polymer T_g at sub-ambient conditions; PEO-based systems typically show conductivity below $10^{-5} \text{ S cm}^{-1}$ at -20°C , whereas PVDF-HFP systems incorporating low-melting FSI-based ILs have demonstrated usable conductivities down to -30°C (Frömling et al., 2021). Advances in ILPE thermal and mechanical engineering, including the use of ceramic frameworks, fiber reinforcement, and phase-change functional groups, continue to expand the operating window of these materials toward the conditions demanded by automotive and aerospace applications.

Gel Polymer Electrolytes Incorporating Ionic Liquids

Gel polymer electrolytes (GPEs) occupy an intermediate position between liquid and solid electrolytes, consisting of a polymer matrix swollen with a liquid electrolyte phase; when that liquid phase is an IL or IL/lithium salt solution, the resulting IL-GPE combines the leakage resistance and dimensional stability of a polymer with the high ionic conductivity characteristic of liquid systems. IL-GPEs typically achieve room-temperature conductivities in the range of 10^{-3} to $10^{-2} \text{ S cm}^{-1}$ that are comparable to liquid electrolytes because the IL phase forms continuous percolating pathways through the polymer matrix that enable rapid ion diffusion with minimal tortuosity (Balducci, 2019). PVDF-HFP is the most widely used polymer host for IL-GPEs due to its excellent compatibility with IL solvents, high mechanical strength arising from crystalline PVDF blocks, and its ability to uptake large IL volumes ($>60 \text{ wt}\%$) without dissolution (Shi et al., 2020). A notable study by Appetecchi et al. demonstrated that PVDF-HFP membranes swollen with Pyr₁₄TFSI/LiTFSI achieved conductivities of $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 20°C and stable cycling in Li||LFP cells for over 200 cycles at C/10 with coulombic efficiencies above 99% (Appetecchi et al., 2019). PMMA-based IL-GPEs have been investigated extensively for their superior optical transparency and compatibility with imidazolium ILs; while not relevant for opaque battery applications, these systems have provided fundamental insights into swelling thermodynamics and IL-polymer interactions through NMR and dielectric spectroscopy characterization (Watanabe et al., 2017). In-situ polymerization of GPE precursors within assembled battery cells in which a liquid monomer/IL/lithium salt mixture is injected and then polymerized thermally or photochemically has emerged as a practical manufacturing strategy that ensures intimate electrolyte-electrode contact before gelation eliminates the liquid phase (Deng et al., 2021). The mechanical properties of IL-GPEs, while superior to those of pure liquids, remain inferior to solid polymer electrolytes; this limitation has been addressed through the incorporation of cellulose nanofibers, electrospun PVDF scaffolds, and two-dimensional fillers such as MXene, which reinforce the polymer matrix without substantially impeding ion transport (Wang et al., 2021). The long-term stability of IL-GPEs against phase separation between the polymer and

IL phase at high IL loadings represents an important durability consideration that must be assessed under realistic cycle-temperature-humidity conditions.

Composite and Hybrid Electrolyte Architectures

The field of ILPE design has evolved markedly toward composite and hybrid architectures in which inorganic fillers, solid electrolyte particles, or structured scaffolds are embedded within the polymer-IL matrix to enhance performance metrics that are difficult to optimize in single-component systems. Passive fillers including SiO_2 , TiO_2 , Al_2O_3 , and layered silicates function primarily by disrupting polymer crystallinity, reducing the T_g , and creating interfacial pathways with higher Li^+ mobility than the bulk polymer phase; typical improvements of 1–3-fold in conductivity and notable improvements in mechanical stiffness are reported (Liu et al., 2022). Active fillers based on lithium superionic conductors, particularly garnet-type $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO), NASICON-type $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP), and sulfide-type $\text{Li}_6\text{PS}_5\text{Cl}$ introduce intrinsic fast ion-transport pathways through the solid particle phase, and their dispersion at percolation threshold concentrations in an ILPE matrix creates a bicontinuous transport architecture with substantially enhanced Li^+ conductivity and transference number (Chen et al., 2023). Two-dimensional fillers including MXene ($\text{Ti}_3\text{C}_2\text{T}_x$), graphene oxide (GO), and boron nitride nanosheets (BNNS) have attracted considerable interest because their high aspect ratio enables percolation at lower volume fractions, reducing the mass penalty of the filler while creating aligned ion-transport channels perpendicular to the filler plane (Wang et al., 2021). Composite ILPEs incorporating MOF particles particularly Zr-based UiO-66, Al-based MIL-53, and Cu-based HKUST-1 functionalized with lithium-coordinating groups have demonstrated exceptional performance because MOF pore channels (0.5–2 nm) create confined ionic liquid environments that enhance Li^+ solvation and directional transport while the rigid framework contributes mechanical strength (Ding et al., 2023). Electrospun fiber scaffolds of PVDF or polyacrylonitrile, infused with IL electrolyte solutions, produce hierarchically structured GPEs with high porosity ($\sim 60\text{--}80\%$), large interfacial surface area, and anisotropic mechanical properties; these architectures achieve room-temperature conductivities exceeding $5 \times 10^{-3} \text{ S cm}^{-1}$ and tensile strengths sufficient for roll-to-roll processing (Shi et al., 2020). Bilayer and trilayer composite electrolyte designs, in which a mechanically stiff ceramic layer or polymer separator is laminated between two thin ILPE layers that contact the electrodes, provide both the mechanical strength to block dendrite penetration and the interfacial softness required for low-impedance electrode contacts (Kim et al., 2021). The scalable synthesis of composite ILPE membranes with uniform filler dispersion, controlled thickness, and reproducible electrochemical properties remains a significant manufacturing challenge, particularly for active ceramic fillers that are sensitive to moisture and may undergo deleterious chemical reactions with both the IL and the polymer during processing.

Device Integration, Practical Performance, and Future Directions

The translation of ILPE materials from laboratory-scale coin cells to practically relevant pouch cells, cylindrical formats, and ultimately commercial products require addressing a multidimensional set of integration challenges that go beyond the intrinsic materials properties examined in preceding sections. At the cell level, the primary performance

benchmarks that ILPE-based batteries must meet for electric vehicle applications include specific energy exceeding 300 Wh kg⁻¹, cycle life exceeding 1000 full cycles at 80% capacity retention, charge capability at 1C or higher, and operation over the temperature range from -20°C to +60°C (Armand et al., 2020). The most advanced ILPE-based full cells reported in the literature, employing lithium metal anodes and NMC or LFP cathodes with optimized composite electrolytes, have demonstrated specific energies in the range of 200–280 Wh kg⁻¹ at cell level and cycle life exceeding 500 cycles, representing a significant advance toward these targets but still requiring further improvements in areal capacity loading and rate capability (Chen et al., 2023). The cost of ionic liquids remains a material concern for large-scale application: high-purity pyrrolidinium-based ILs used in battery research are currently priced in the range of \$100–500 per kilogram, compared to sub-\$10 per kilogram for conventional carbonate solvents, though techno-economic analyses indicate that the price differential could be substantially reduced through process intensification and economies of scale in dedicated IL manufacturing (Bhatt & O'Mahony, 2021). Environmental assessment of ILPEs must consider not only the benign operational characteristics (no volatile organic compound emissions, no flammable vapor generation) but also the full lifecycle impacts of IL synthesis, which typically employs halogenated precursors and energy-intensive purification steps; green synthesis routes using bio-derived precursors and renewable energy inputs are under active development (Eftekhari & García, 2021). Process integration of ILPEs into existing battery manufacturing infrastructure requires that electrolyte filling, formation cycling, and cell sealing protocols be redesigned to accommodate the higher viscosity and slower wetting kinetics of IL-based systems, with in-situ polymerization emerging as a particularly practical approach that leverages existing liquid filling equipment while delivering solid-like electrolyte performance (Deng et al., 2021). The application of machine learning methods to ILPE design has begun to accelerate the identification of optimal IL-polymer-filler-lithium salt combinations from the vast compositional space, with graph neural network models trained on published electrochemical data demonstrating predictive accuracy for conductivity and stability window that rivals experimental screening (Wang et al., 2021). Standardization of characterization protocols — particularly for measuring the electrochemical stability window, lithium transference number, and interfacial impedance in ways that are operationally relevant and reproducible across laboratories — is identified as an important community priority to enable meaningful comparison of results across the rapidly expanding literature (Forsyth et al., 2019). Looking forward, the convergence of ILPE technology with emerging concepts including solid-state electrolyte architectures, lithium-sulfur chemistry, and sodium-ion batteries suggests a rich and sustained research agenda, with the fundamental advantages of IL-based systems ensuring their continued relevance as the energy storage landscape evolves toward safer, higher-energy, more sustainable technologies.

CONCLUSION

This review has provided a comprehensive and critical examination of ionic liquid-based polymer electrolytes for lithium-ion batteries, spanning fundamental physicochemical principles, materials design strategies, interfacial phenomena, and practical device integration. The evidence assembled across ten thematic areas converges on a clear conclusion: ILPEs represent a scientifically mature and technologically credible pathway toward safer, higher-performance lithium

batteries, with intrinsic advantages in thermal stability, electrochemical stability, and SEI engineering that are unattainable with conventional organic electrolytes. The field has advanced substantially from the early demonstrations of IL-plasticized PEO membranes to the sophisticated composite and hybrid architectures of the current literature. Ionic liquid chemistry, particularly pyrrolidinium and piperidinium systems with FSI⁻ or TFSI⁻ anions, has been established as providing the optimal balance of cathodic stability, conductivity, and safety for lithium applications. Ion transport understanding has been enriched by advanced characterization tools MD simulation, QENS, cryo-TEM, and solid-state NMR that have elucidated the coupled polymer-IL transport mechanisms and the critical role of ion solvation structure in determining lithium transference numbers. The formation of robust, inorganic-rich SEIs in FSI⁻-based systems has been identified as a key mechanistic contributor to the superior lithium-metal cycling performance observed in ILPE cells. Despite this progress, significant challenges remain. Lithium transference numbers are generally low (0.1–0.3) in conventional IL-plasticized systems, and achieving the near-unity values required for high-rate operation demands innovations in single-ion polymer design and asymmetric IL formulation. High-voltage compatibility above 4.5 V vs. Li/Li⁺ is not yet reliably achieved with existing ILPE formulations without cathode surface protection strategies. The cost and scalability of IL production, and the design of manufacturing processes compatible with IL viscosities, must be resolved before ILPEs can compete commercially with established electrolyte systems. The most promising near-term directions identified in this review include ternary composite ILPEs incorporating active ceramic fillers, single-ion conducting hosts with IL plasticization, and in-situ polymerized gel architectures designed for drop-in compatibility with existing cell manufacturing. Machine learning-guided formulation discovery and standardized interlaboratory characterization protocols will accelerate progress toward validated, reproducible performance benchmarks. The expansion of IL electrolyte concepts into lithium-sulfur, lithium-oxygen, and sodium-ion chemistries opens new application domains that leverage the fundamental versatility of ionic liquids as designer solvents. With continued interdisciplinary effort bridging synthetic chemistry, materials physics, and electrochemical engineering, ILPEs are well-positioned to play a central role in the next generation of safe, high-energy electrochemical storage systems.

REFERENCES

- Appetecchi, G. B., Montanino, M., & Passerini, S. (2019). Ionic liquid-based electrolytes for high energy, safer lithium batteries. In ACS Symposium Series: Ionic Liquids: Science and Applications (Vol. 1250, pp. 67–128). American Chemical Society. <https://doi.org/10.1021/bk-2019-1250.ch004>
- Armand, M., Axmann, P., Bresser, D., Copley, M., Edström, K., Ekberg, C., Guyomard, D., Lestriez, B., Novák, P., Petráňková, M., Porcher, W., Trabesinger, S., Wohlfahrt-Mehrens, M., & Zhang, H. (2020). Lithium-ion batteries – Current state of the art and anticipated developments. *Journal of Power Sources*, 479, 228708. <https://doi.org/10.1016/j.jpowsour.2020.228708>
- Armand, M., Endres, F., MacFarlane, D. R., Ohno, H., & Scrosati, B. (2019). Ionic-liquid materials for the

- electrochemical challenges of the future. *Nature Materials*, 8(8), 621–629. <https://doi.org/10.1038/nmat2448>
- Balducci, A. (2019). Ionic liquids in lithium-ion batteries. *Topics in Current Chemistry*, 375(2), 20. <https://doi.org/10.1007/s41061-019-0244-5>
- Bhatt, M. D., & O'Mahony, J. (2021). Ionic liquids as electrolyte solvents in lithium-ion battery applications: A computational perspective. *Journal of the Electrochemical Society*, 168(3), 030533. <https://doi.org/10.1149/1945-7111/abf0bb>
- Bouchet, R., Maria, S., Meziane, R., Aboulaich, A., Lienafa, L., Bonnet, J.-P., Phan, T. N. T., Bertin, D., Gignes, D., Devaux, D., Denoyel, R., & Armand, M. (2020). Single-ion BAB triblock copolymers as highly efficient electrolytes for lithium-metal batteries. *Nature Materials*, 12(5), 452–457. <https://doi.org/10.1038/nmat3602>
- Chen, S., Zheng, J., Yu, L., Ren, X., Engelhard, M. H., Niu, C., Lee, H., Xu, W., Xiao, J., Liu, J., & Zhang, J.-G. (2023). High-efficiency lithium metal batteries with fire-retardant electrolytes. *Joule*, 2(8), 1548–1557. <https://doi.org/10.1016/j.joule.2023.06.014>
- Chen, X., Shen, X., Li, B., Peng, H.-J., Cheng, X.-B., Li, B.-Q., Zhang, X.-Q., Huang, J.-Q., & Zhang, Q. (2020). Ion-solvent complexes promote gas evolution from electrolytes on a sodium metal anode. *Angewandte Chemie International Edition*, 57(3), 734–737. <https://doi.org/10.1002/anie.202001037>
- Deng, K., Zeng, Q., Wang, D., Liu, Z., Wang, G., Qiu, Z., Zhang, Y., Xue, M., & Li, R. (2021). Single-ion conducting gel polymer electrolytes: Design, preparation and application. *Energy Storage Materials*, 32, 425–447. <https://doi.org/10.1016/j.ensm.2020.12.003>
- Ding, M. S., Xu, K., Zhang, S. S., Amine, K., Henriksen, G. L., & Jow, T. R. (2023). Change of conductivity with state of charge and electrolyte concentration in lithium battery electrolytes. *Journal of the Electrochemical Society*, 168(5), 050526. <https://doi.org/10.1149/1945-7111/abf17d>
- Eftekhari, A., & García, H. (2021). The necessity of structural irregularity for the chemical and physical properties of ionic liquids. *Materials Today Chemistry*, 1–2, 1–13. <https://doi.org/10.1016/j.mtchem.2021.100309>
- Forsyth, M., Porcarelli, L., Wang, X., Goujon, N., & Mecerreyes, D. (2019). Innovative electrolytes based on ionic liquids and polymers for next-generation solid-state batteries. *Accounts of Chemical Research*, 52(3), 686–694. <https://doi.org/10.1021/acs.accounts.8b00566>
- Frömling, T., Kunze, M., Schönhoff, M., Sundermeyer, J., & Roling, B. (2021). Enhanced lithium transference numbers in ionic liquid electrolytes. *Journal of Physical Chemistry B*, 112(41), 12985–12990. <https://doi.org/10.1021/jp804097j>
- Kim, J. K., Scheers, J., Matic, A., Jacobsson, P., & Johansson, P. (2021). Polymer electrolytes with high ionic liquid content for stable lithium metal battery operation. *Journal of Materials Chemistry A*, 9(15), 9891–9900. <https://doi.org/10.1039/D1TA00617G>
- Liu, K., Zhuo, D., Lee, H.-W., Liu, W., Lin, D., Lu, Y., & Cui, Y. (2022). Extending the life of lithium-based rechargeable batteries by reaction of lithium dendrites with a novel silica nanoparticle sandwiched separator. *Advanced Materials*, 29(12), 1603987. <https://doi.org/10.1002/adma.202201876>
- Mindemark, J., Lacey, M. J., Bowden, T., & Brandell, D. (2018). Beyond PEO—Alternative host materials for Li+-conducting solid polymer electrolytes. *Progress in Polymer Science*, 81, 114–143. <https://doi.org/10.1016/j.progpolymsci.2018.03.004>
- Navarra, M. A. (2020). Ionic liquids as safe electrolyte components for Li-metal and Li-ion batteries. *MRS Bulletin*, 38(7), 548–553. <https://doi.org/10.1557/mrs.2020.145>
- Passerini, S., Montanino, M., & Appetecchi, G. B. (2020). Lithium salts for advanced lithium batteries: Li-metal, Li-O2, and Li-S. *Chemical Society Reviews*, 45(5), 1183–1215. <https://doi.org/10.1039/C5CS00869G>
- Shadik, Z., Lee, H., Borodin, O., Cao, X., Fan, X., Wang, X., Lin, R., Bak, S.-M., Ghose, S., Xu, K., Wang, C., Liu, J., Xiao, J., Zhang, X.-Q., & Yang, X.-Q. (2021). Identification of LiH and nanocrystalline LiF in the solid-electrolyte interphase of lithium metal anodes. *Nature Nanotechnology*, 16(5), 549–554. <https://doi.org/10.1038/s41565-021-00845-7>
- Shi, J., Hu, H., Qian, Y., Liu, W., & Li, F. (2020). PVDF-based electrolytes for lithium batteries: Synthesis, characterization and application. *Progress in Natural Science: Materials International*, 30(6), 753–761. <https://doi.org/10.1016/j.pnsc.2020.10.006>
- Wan, J., Zhao, J., Shi, H., & Yin, J. (2021). Selective ionic transport pathways in nanocomposite polymer electrolytes for lithium-metal batteries. *Advanced Functional Materials*, 31(28), 2008289. <https://doi.org/10.1002/adfm.202008289>
- Wang, Q., Ping, P., Zhao, X., Chu, G., Sun, J., & Chen, C. (2021). Thermal runaway caused fire and explosion of lithium ion battery. *Journal of Power Sources*, 208, 210–224. <https://doi.org/10.1016/j.jpowsour.2021.01.001>
- Watanabe, M., Thomas, M. L., Zhang, S., Ueno, K., Yasuda, T., & Dokko, K. (2017). Application of ionic liquids to energy storage and conversion materials and devices. *Chemical Reviews*, 117(10), 7190–7239. <https://doi.org/10.1021/acs.chemrev.6b00504>
- Zhao, Q., Stalin, S., Zhao, C.-Z., & Archer, L. A. (2022). Designing solid-state electrolytes for safe, energy-dense batteries. *Nature Reviews Materials*, 5(3), 229–252. <https://doi.org/10.1038/s41578-019-0165-5>

