

Decoupled ion transport in polymer electrolytes

Qi Lai, Berkay Erdoğan, Jixu Yang, Wei Wang, Quanquan Pang (✉)

State Key Laboratory of Advanced Waterproof Materials, Beijing Key Laboratory for Theory and Technology of Advanced Battery Materials,
School of Materials Science and Engineering, Peking University, Beijing 100871, China

HIGHLIGHTS

- Li^+ motion in coupled polymer electrolytes follows segmental relaxation.
- Decoupling should be assessed using relaxation, the Walden relation, $\sigma(T_g)$, or Haven metrics.
- Design should control pathway connectivity, hopping barriers, and ion selectivity.
- Mechanical support and ion solvation should be assigned to distinct motifs.
- Battery relevance requires steady-state current and stable electrode contact.

Keywords:

Polymer electrolytes
Decoupled ion transport
Segmental relaxation
Modified Walden analysis
Cation transference number

ABSTRACT

Polymer electrolytes are useful for batteries because they form flexible films and maintain good electrode contact. In most dry systems, however, ion motion still depends on the relaxation of the polymer host. In poly(ethylene oxide) (PEO) and related materials, Li^+ moves by exchanging between coordination sites. As segmental relaxation slows near T_g , ion transport slows correspondingly. This coupling explains why high conductivity and high mechanical strength are difficult to obtain simultaneously in a dry polymer. Here decoupled ion transport is defined as a change in the rate-limiting step, rather than as a synonym for high conductivity. The evidence is assessed using Vogel–Tammann–Fulcher and Arrhenius temperature dependences, the Angell decoupling index, modified Walden analysis, conductivity at T_g , and the Haven ratio. Design routes are then organized around four variables: pathway connectivity, local hopping barriers, mechanical support, and mobile-ion selectivity. The strongest claims link local structure, relaxation, species-specific diffusion, and steady-state cell behavior. For batteries, the relevant question is not only the magnitude of σ , but also which species carries the current, where it moves, and whether that pathway remains intact in thin films and at interfaces.

© The Authors (2026)

1 Introduction

Polymer electrolytes entered battery research because they solve a practical materials problem [1–9]. A polymer can be cast as a thin film, bent without fracture, and pressed into contact with rough electrodes. These traits are difficult to combine in many inorganic solid electrolytes. Early PEO-based electrolytes showed that polymers can dissociate salts and carry ions, but also exposed the main limitation: room-temperature conductivity was too low for most battery operation [10–12]. In PEO and lithium salt complexes, Li^+ is coordinated by ether oxygens. To move, the ion must leave one coordination environment and enter another. This exchange is tied to segmental relaxation of the host. Fast segmental motion opens new coordination sites,

whereas slow segmental motion keeps the ion trapped [13–17]. This mechanism established a clear design rule: lower T_g , suppress crystallinity, and keep the polymer amorphous. This rule is effective in many cases, but it introduces a structural conflict. Lowering T_g usually lowers modulus and weakens the film. Raising the modulus often raises T_g and slows ion motion. The same motion that helps Li^+ move can therefore weaken the mechanical role of the polymer [18–20].

The conflict becomes clear when the transport relations are written out. At the continuum level, diffusion follows Fick's first law

$$J = -D\nabla c, \quad (1)$$

where J is the diffusive flux, D is the diffusion coefficient and c is the concentration. Conservation of mass gives Fick's second law

✉ Corresponding author. E-mail: qq pang@pku.edu.cn (Q. Pang)

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c). \quad (2)$$

Although Fick's laws are standard models for ion transport in many systems, describing how concentration profiles evolve, they do not identify the molecular events that determine the diffusion coefficient D . A random-walk picture makes this explicit. The Einstein–Smoluchowski relation gives the mean-square displacement as

$$\langle x^2 \rangle = 2Dt, \quad (3)$$

for one-dimensional diffusion, or

$$\langle r^2 \rangle = 6Dt, \quad (4)$$

for three-dimensional diffusion. If the ion moves by jumps of a defined length a and mean waiting time τ_j , the same relation gives

$$D = \frac{a^2}{6\tau_j}. \quad (5)$$

Conductivity can therefore increase when the mobile-ion concentration is higher, the jump length is longer, or when the waiting time between jumps is shorter. However, these three levers are not equivalent and should not be treated as a single design strategy.

Charge transport is described by the Nernst–Einstein relation. For a single mobile ion type,

$$\sigma = \frac{cq^2D}{k_B T}, \quad (6)$$

where q is the ion charge and k_B is the Boltzmann constant. For several mobile species, the conductivity is summed over each species, and the relation assumes uncorrelated motion. In concentrated polymer electrolytes, where this assumption often fails, tracer diffusion and conductivity cannot be treated as equivalent measurements.

The next step connects mobility to polymer relaxation. In the Stokes–Einstein picture, ion mobility in a viscous medium is roughly inversely proportional to viscosity,

$$\mu \propto \frac{1}{\eta r}, \quad (7)$$

where η is viscosity and r is an effective hydrodynamic radius. The Maxwell relation connects viscosity with structural relaxation,

$$\eta = G_\infty \tau_\alpha, \quad (8)$$

where G_∞ is the high-frequency modulus and τ_α is the segmental relaxation time. Combining these relations yields the coupled-polymer result

$$\mu \propto \frac{1}{\tau_\alpha}. \quad (9)$$

In words, ion mobility increases when segmental

relaxation becomes faster and decreases when it slows. The Walden relation ($\Lambda\eta \approx \text{constant}$) expresses the same idea for molar conductivity Λ . It is not exact for polymer electrolytes, but it provides a useful reference line for determining whether ion motion follows the polymer host [13,14,21–23].

Recent reviews have framed the need from both battery and polymer-physics viewpoints [8,9,21–23]. This perspective discusses materials designed to escape this coupling. Here, decoupled ion transport means that ion motion is no longer governed mainly by segmental relaxation. The polymer may still provide solvation sites, free volume, or mechanical support, but the ion must have a local route that does not depend on the bulk host relaxing. This distinction is needed because the term “decoupling” is currently used in several ways. Some studies separate conductivity from modulus. Some separate ion diffusion from structural relaxation. Others separate cation motion from anion motion. Although these claims are related, they are not equivalent. Here, decoupling is treated as a measurable change in transport mechanism, and the polymer designs that make this change useful in a cell are discussed.

2 Defining transport decoupling

The coupled baseline is clearest in the temperature dependence of conductivity. In a typical amorphous polymer electrolyte, conductivity follows a Vogel–Tamman–Fulcher (VTF) form,

$$\sigma(T) = \sigma_0 \exp\left[-\frac{B}{T - T_0}\right], \quad (10)$$

where σ_0 is a pre-exponential factor, B is a pseudo-activation parameter, and T_0 is the Vogel temperature, usually below T_g . The curve bends as temperature approaches T_g because the ion must wait for local free volume and coordination sites to open. The barrier is not fixed as it would be in a rigid lattice; it changes with the structural relaxation of the polymer [13,14,21–23].

The decoupled limit has a different signature. If ions hop between sites in a static or slowly changing landscape, conductivity can follow an Arrhenius form,

$$\sigma(T) = A \exp\left[-\frac{E_a}{RT}\right], \quad (11)$$

where E_a is the activation energy for ion hopping and R is the gas constant. The slope of $\log \sigma$ versus $1/T$ then gives a local hopping barrier. The polymer is still present, but its main relaxation no longer sets the ion-motion clock. This physical distinction is summarized in Figs. 1(a) and 1(b). The change from VTF to Arrhenius behavior is the first sign of decoupling, yet not sufficient to establish it.

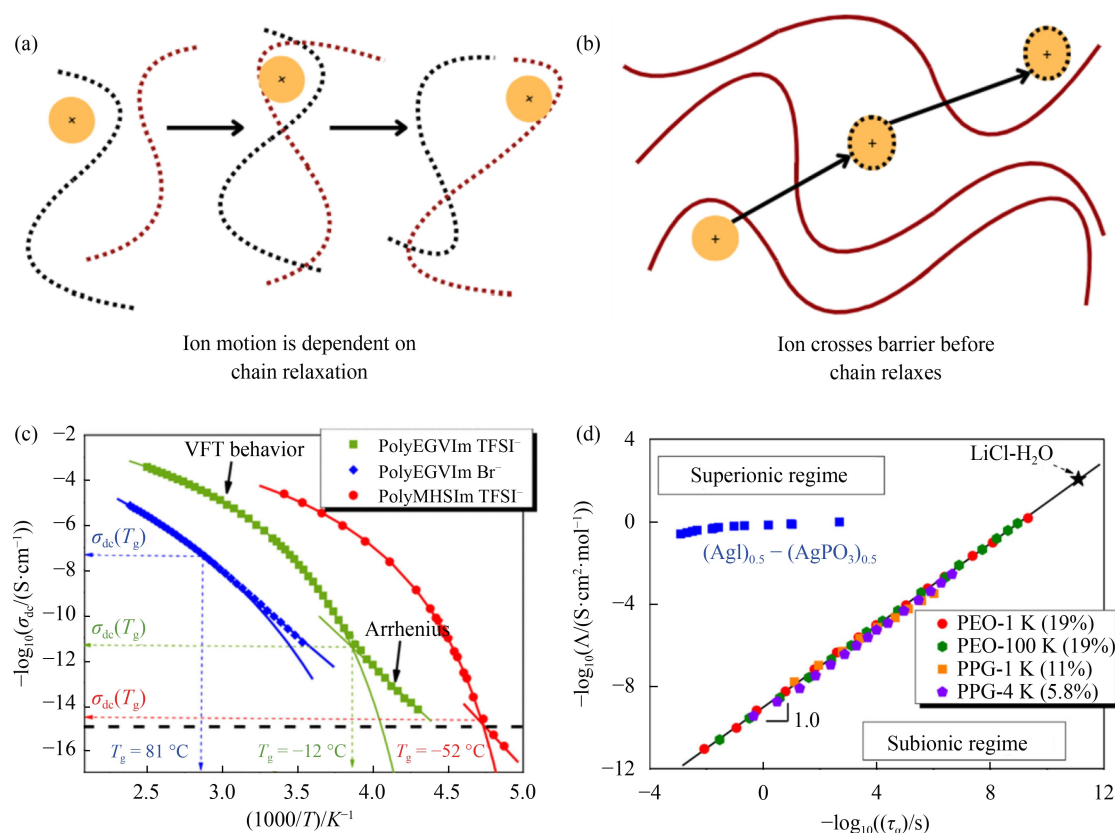


Fig. 1 Coupled and decoupled ion transport.

(a) Coupled transport in a polymer electrolyte, where Li^+ motion is gated by segmental relaxation and follows a VTF-type temperature dependence; (b) decoupled transport, where ions hop through pre-organized or slowly changing local sites and the temperature dependence approaches an Arrhenius limit (Panels (a) and (b) redrawn based on Refs. [14,21]); (c) temperature-dependent conductivity comparing VTF and Arrhenius limits; (d) modified Walden plot showing the ideal coupled line ($\alpha = 1$) and the superionic regime ($\alpha < 1$) (Panels (c) and (d) adapted from Bocharova & Sokolov [14], copyright 2020, American Chemical Society).

A polymer can appear nearly Arrhenius over a narrow temperature window while ion motion is still partly controlled by the host. A more direct test compares the timescale of structural relaxation and ion motion. Broadband dielectric spectroscopy (BDS) can separate these two responses: the segmental α -relaxation of the polymer and the conductivity relaxation of mobile ions.

The first metric is the Angell decoupling index, often written as R_τ . It compares the structural relaxation time τ_α with the conductivity relaxation time τ_σ at T_g

$$R_\tau = \frac{\tau_\alpha(T_g)}{\tau_\sigma(T_g)}. \quad (12)$$

If the two timescale parameters are similar, ion motion freezes with the polymer and R_τ approaches unity. When τ_σ is many orders of magnitude shorter than τ_α , ion motion is decoupled (Fig. 1(b)) [14,21,24–30].

The second metric is the modified Walden plot. In a simple liquid, molar conductivity scales with fluidity,

$$\Lambda \propto \eta^{-1}. \quad (13)$$

For a polymer, the inverse structural relaxation time is commonly used as the practical measure of fluidity

$$\Lambda \propto \left(\frac{1}{\tau_\alpha} \right)^\alpha. \quad (14)$$

The exponent α is close to unity for coupled motion. A value below 1 means that conductivity slows less strongly than structural relaxation. In a modified Walden plot, such systems sit above the ideal coupled line and are often described as superionic relative to the polymer host (Fig. 1(d)) [14,21,24,25,27,31,32]. Polymerized ionic liquids are useful test systems because their chemistry can be varied while dielectric and mechanical measurements track the corresponding dynamics [33–39].

The third metric is conductivity at T_g . A coupled material should have negligible $\sigma(T_g)$ because structural relaxation is slow at the glass transition. Bocharova and Sokolov [14] used this comparison to show that many polymer electrolytes, despite different chemistries,

approach the coupled limit when evaluated at T_g . A material with $\sigma(T_g)$ well above this baseline shows that ion motion has not frozen with the host polymer.

The final metric is the Haven ratio. It indicates whether ions that move microscopically also contribute to net charge current. Conductivity measures collective charge transport, and NMR diffusion measures how fast tracer ions move, even when part of that motion is paired, correlated, or back-and-forth. The Nernst–Einstein relation converts conductivity into an apparent diffusion coefficient, D_σ . NMR gives a tracer diffusion coefficient, often denoted D_{tracer} . The Haven ratio compares these two quantities

$$H_R = \frac{D_\sigma}{D_{\text{tracer}}}. \quad (15)$$

Although some papers give its inverse, if H_R is far below 1, many ions move in correlated pairs or clusters and do not produce the same net current. This distinction matters because decoupling from segmental relaxation does not automatically result in efficient charge transport [29,30,40–42].

These metrics answer different questions. VTF versus Arrhenius behavior shows whether the rate-limiting step resembles segmental friction or local hopping. R_τ shows how far conductivity relaxation is separated from structural relaxation, whereas the Walden exponent shows how conductivity scales with relaxation. $\sigma(T_g)$ screens whether ion motion remains active when segmental relaxation is slow. The Haven ratio tests whether mobile ions carry net charge. A convincing decoupling claim combines these tests rather than relying on one conductivity metric. A room-temperature conductivity, taken alone, does not reveal which species carries the current, where in the material transport occurs, or whether the pathway survives in a real cell.

3 Designing decoupled pathways

Decoupling strategies are clearer when they are treated as design variables rather than as isolated material families. The design task is to combine them without losing processability, contact or selectivity. A useful polymer electrolyte must build a connected pathway for ions, lower the hopping barrier along that pathway, separate mechanical support from the ion-solvating environment, and limit cation–anion correlations.

3.1 Building ion-rich pathways

The first design variable is pathway connectivity. A direct route beyond the coupled PEO picture is to raise the salt content until the material no longer behaves as a

dilute salt-in-polymer electrolyte.

In dilute PEO–Li salt complexes, Li^+ is mainly coordinated by ether oxygens. At high salt loading, there are not enough ether oxygens to coordinate every Li^+ . The anion enters the Li^+ coordination shell, and the material begins to resemble a polymer system dispersed within an ionic network [15,43–45]. Raman spectroscopy gives direct evidence for this transition (Fig. 2(a)). In PEO–LiTFSI, the TFSI[−] band near 740 cm^{-1} changes as salt content increases from EO-rich to ion-rich compositions. The free-anion contribution decreases, while the contact-ion-pair contribution near 746 cm^{-1} increases [43]. This change matters because it shows that part of the Li^+ coordination environment has shifted from ether oxygens toward anion participation. Molecular simulations then connect the coordination change to motion. In PEO–LiTFSI, Li^+ transport involves repeated coordination exchange through a changing solvation shell rather than smooth diffusion through a homogeneous medium. Borodin and Smith revealed that Li^+ motion combines displacement along PEO chains, motion with PEO segments, and intersegmental hops between coordination environments [15]. The coordination-tracking scheme in Fig. 2(b) separates continuous motion, vehicular motion and hopping by following how the Li^+ coordination shell changes with time. For the low-salt PEO:LiTFSI and PCL:LiTFSI systems shown in Fig. 2(c) ($x = 0.08$), the probability map mainly reflects polymer-mediated continuous exchange. At higher salt content, the same study shows a shift toward anion-mediated continuous motion, especially in weakly coordinating PCL [46]. Atomic diffusion studies also demonstrate that salt concentration, temperature, and molecular weight change the local cage and long-range diffusion response [44,47]. Ion-rich pathways can reduce the need for large-scale chain relaxation, but they introduce a second limitation. Dense ionic domains often sustain strong correlations. If cations and anions move together, tracer diffusion can be high while net charge transport remains limited [40,45].

High salt loading should therefore be treated as a way to build a connected ionic pathway, not as a simple carrier-concentration lever. Once the pathway forms, the questions are how long Li^+ stays at one site, how often it exchanges, and how much of the motion is cancelled by the anion.

3.2 Preserving free volume without freezing local motion

The second design variable is the lifetime and connectivity of free volume. Rather than making the polymer more liquid-like, which would weaken its mechanical properties, a better approach is to use rigid and contorted chains that cannot pack efficiently and thus

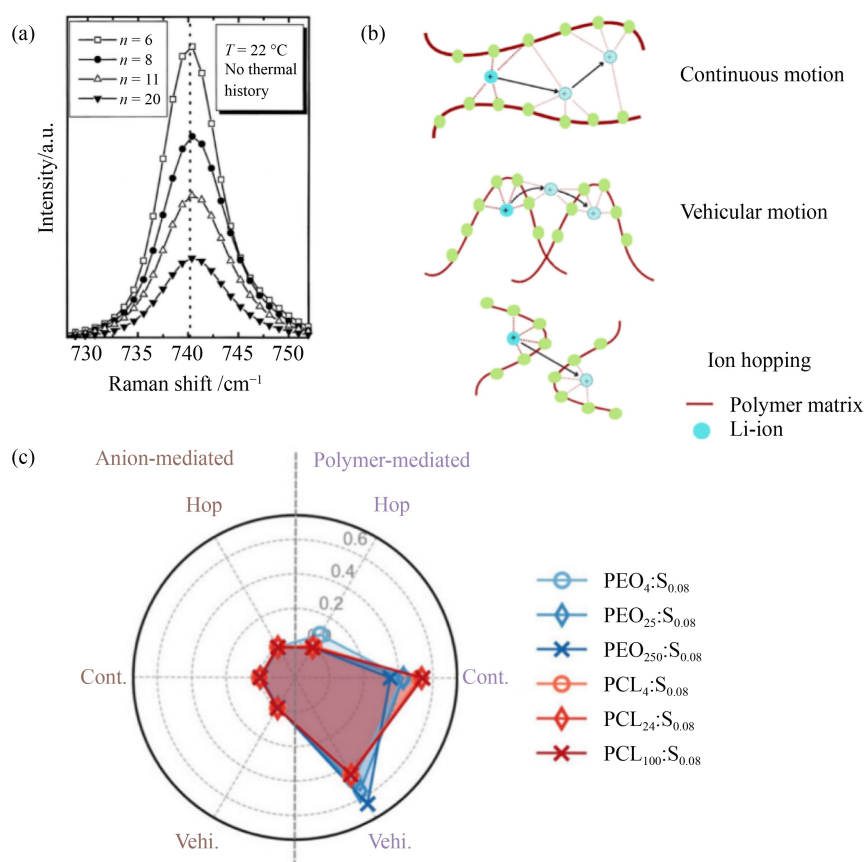


Fig. 2 Coordination exchange in PEO-LiTFSI polymer electrolytes.

(a) Raman spectra of PEO-LiTFSI at different [EO]/[Li] ratios, showing how the TFSI⁻ band near 740 cm⁻¹ changes as the free-anion and coordinated-anion populations shift with salt content (adapted from Edman [43], copyright 2000, American Chemical Society); (b) coordination-tracking schematic defining hopping, continuous motion, and vehicular motion based on changes in the Li⁺ coordination shell (redrawn based on Refs.[15,46]); (c) MD-derived transport-mode probability map for low-salt PEO:LiTFSI and PCL:LiTFSI model electrolytes ($x = 0.08$), comparing anion-mediated and polymer-mediated hopping, continuous, and vehicular contributions (adapted from Gudla et al. [46], copyright 2025, American Chemical Society).

retain permanent free volume.

Polymers of intrinsic microporosity (PIMs) exemplify this strategy by trapping free volume through their backbone geometry (Fig. 3(a)) [48,49]. This free volume is not created by thermal segmental motion in the same way as in PEO. In oxanorbornene dicarboximide polymers with oligomeric ethylene oxide side chains, the rigid backbone supplies shape-persistent free volume, while the side chains supply local Li⁺ solvation sites (Fig. 3(b)) [49]. This architecture can support decoupled transport because it gives the ion space to move while the polymer remains mechanically solid. BDS revealed that conductivity relaxation separates from segmental relaxation. This separation is direct dynamical evidence for decoupling (Fig. 3(c)) [49]. The rigid backbone raises T_g . The same example also shows why decoupling is not sufficient by itself. The side chains are more mobile than the backbone, but they remain attached to a glassy framework. If their local motion is too slow,

room-temperature conductivity remains limited even when R_r is large [49]. A material can therefore be strongly decoupled and still conduct only modestly at 25 °C.

Rigid polymers should therefore not be seen as a simple solution. They solve one part of the problem while creating another. The target is not maximum rigidity, but a semi-static pathway with a low local hopping barrier. PIM-based composites offer one way to seek this balance. Recent PIM-1/PTFE/PEO composite membranes use PIM-1 as a reinforcing and porous component while retaining a softer ion-solvating phase [50]. In that mixed architecture, the rigid component stabilizes the softer PEO matrix instead of becoming the only transport environment. This design enabled Li||Li symmetric cells to cycle for more than 2000 h (Fig. 3(d)).

The broad principle is that free volume should be characterized not only by amount, but also by its lifetime and connectivity. Free volume that collapses near T_g

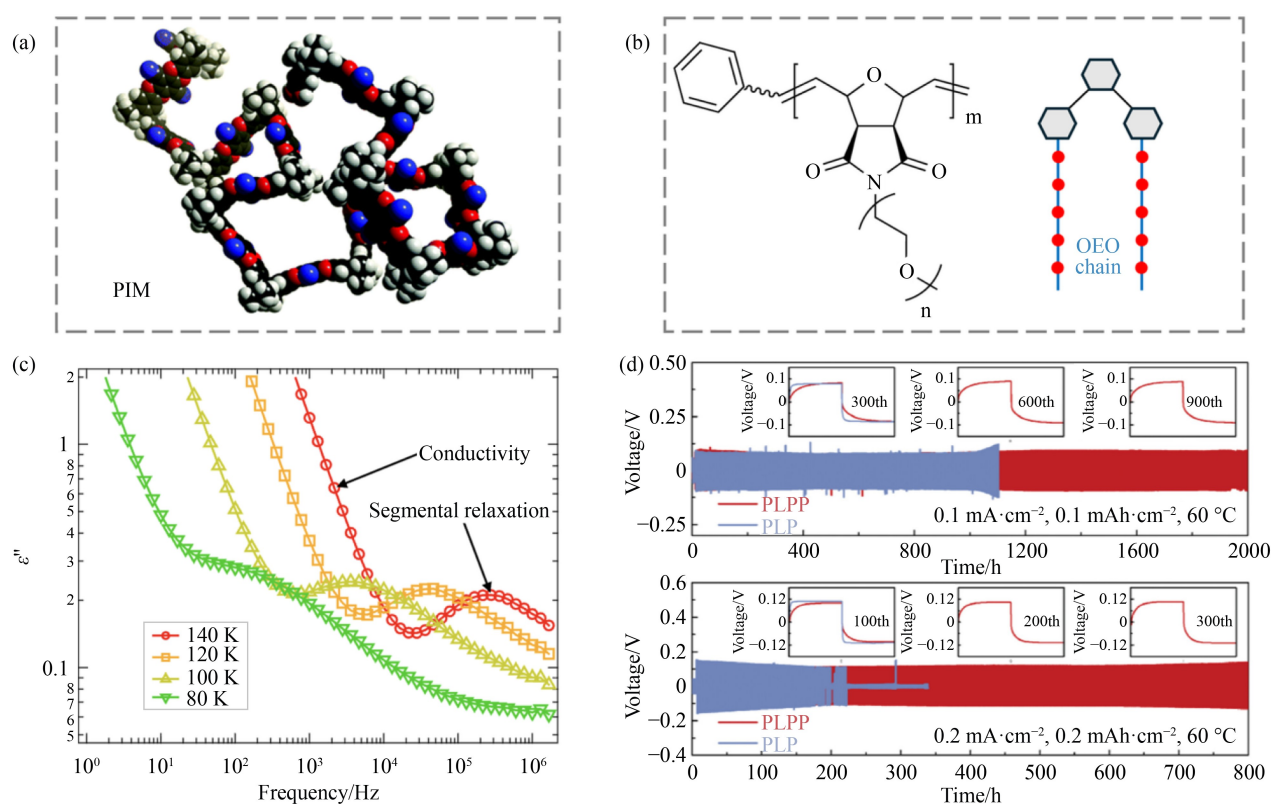


Fig. 3 Free-volume lifetime and rigid-backbone polymer electrolytes.

(a) PIM/free-volume concept, showing how a rigid and contorted backbone can preserve poorly packed void space (adapted from McKeown & Budd [48], copyright 2006, The Royal Society of Chemistry); (b) oxanorbornene dicarboximide polymer with oligomeric ethylene oxide side chains, combining a rigid backbone with local Li^+ -solvating side chains; (c) BDS-derived conductivity relaxation and segmental relaxation, showing a separation between τ_σ and τ_α (Panels (b) and (c) adapted from Adams et al. [49], with an author-drawn inset schematic added in panel (b), copyright 2017, Elsevier); (d) $\text{Li}||\text{Li}$ symmetric-cell cycling of PIM-1/PTFE/PEO composite membranes (adapted from Liang et al. [50], copyright 2024, Wiley-VCH).

remains tied to segmental motion. Free volume built into a rigid backbone may support hopping. Free volume that is disconnected from the polymer chain contributes little. These distinctions determine whether PIM-like polymers support decoupled transport or simply raise glassiness.

3.3 Separating mechanics from solvation

A third design variable is the functional separation of mechanical and ionic roles. This strategy addresses the trade-off between stiffness, toughness, and conductivity. It does not always demonstrate that ion dynamics are fully decoupled from segmental motion, but it shows explicitly which part of the polymer carries stress and which part solvates ions.

The supramolecular lithium-ion conductor (SLIC) illustrates this principle [51]. Its soft polyether-rich segments carry Li^+ , whereas UPy groups form reversible hydrogen-bonded clusters that provide toughness.

Conductivity is governed mainly by the soft segment, whereas mechanical strength is enhanced by the supramolecular bonds (Figs. 4(a) and 4(b)). The reported room-temperature conductivity is about $1.2 \times 10^{-4} \text{ S/cm}$, and the toughness reaches about 29 MJ/m^3 [51]. The design principle is that a polymer electrolyte can be strengthened without rigidifying the ion-solvating environment. Bottlebrush networks encode the same mechanical idea. A bottlebrush chain can deform by unfolding its backbone before the side chains are pulled tight (Fig. 4(c)) [52]. This changes the usual relation between stiffness and extensibility in a single network. Although this bottlebrush polymer is not a battery electrolyte, it demonstrates a useful rule for polymer electrolytes: topology can separate the strand that carries stress from the local environment that governs motion.

For polymer electrolytes, orthogonal designs reduce the pressure on one phase to perform every function. A polar ion-conducting channel can remain percolated if a

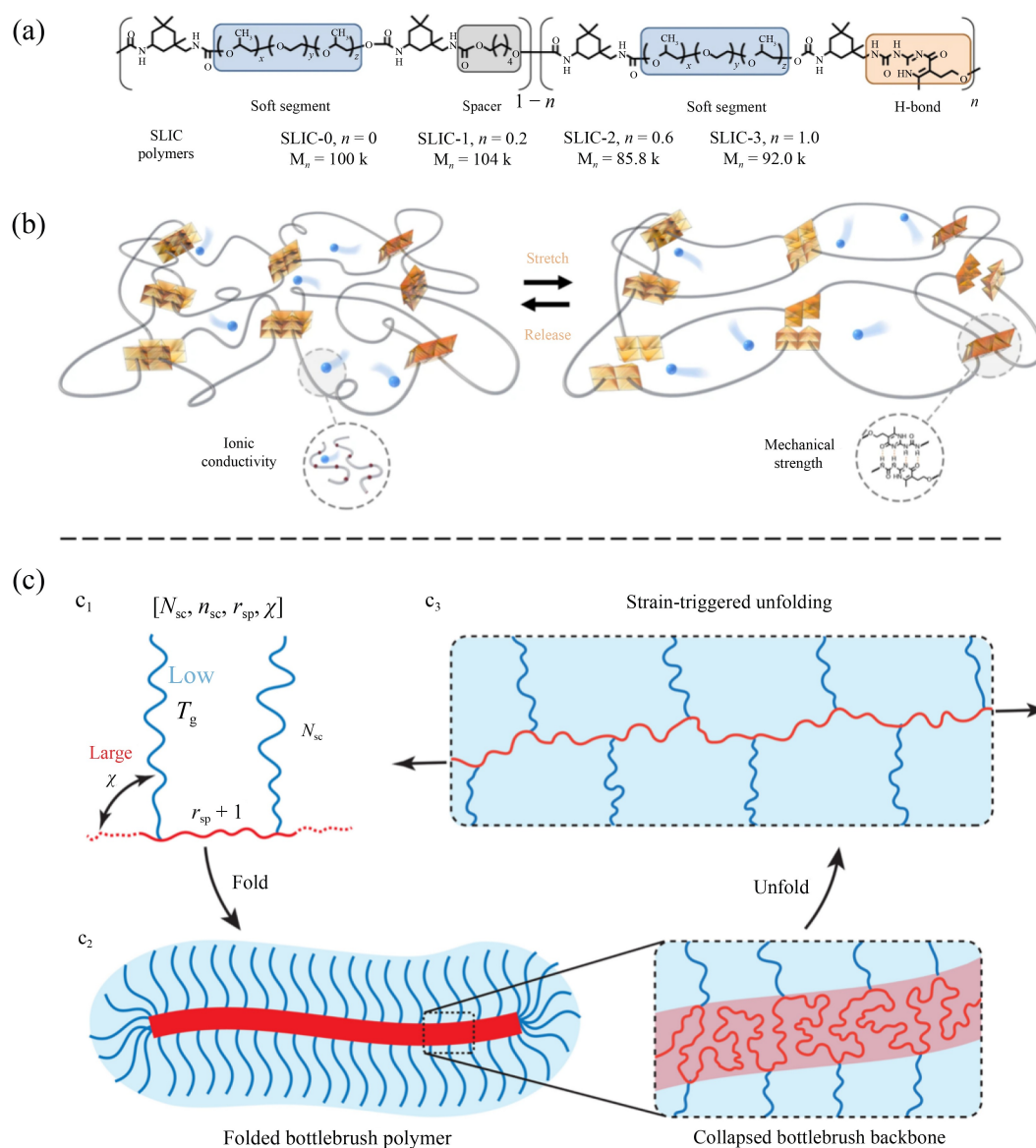


Fig. 4 Separating mechanical support from ion solvation.

(a) Molecular architecture of the supramolecular lithium-ion conductor (SLIC), where soft polyether segments solvate Li⁺ and UPy groups form reversible hydrogen-bonded clusters; (b) SLIC network schematic showing soft ion-solvating domains and reversible mechanical cross-links (Panels (a) and (b) adapted from Mackanic et al. [51], copyright 2019, Springer Nature); (c) bottlebrush network deformation, where backbone unfolding precedes side-chain stretching and separates stiffness from extensibility (adapted from Huang et al. [52], copyright 2024, American Association for the Advancement of Science).

separate scaffold holds the shape. A dynamic bond can help maintain interfacial contact without turning the whole electrolyte into a liquid. A soft polyether can remain soft if a second motif carries stress. This separation also creates a naming problem. Each report should state which coupling has been broken. If conductivity still follows T_g -normalized VTF behavior, the material has separated mechanical strength from conductivity, but ion motion may still be tied to segmental relaxation. If τ_σ is much shorter than τ_α , the

decoupling is dynamical. Both statements are relevant indicators, although they are not the same.

3.4 Using polarity to control ion pairing and selectivity

The fourth design variable is the electrostatic environment around the mobile ion. In standard PEO, Li⁺ binds strongly to ether oxygens and often remains associated with its counter-anion. A high-polarity host can screen these interactions. When local Coulomb

attraction is weaker, the ion can leave one site and enter the next more readily [21,53–57].

Polymeric zwitterions provide this electrostatic environment within each repeat unit (Fig. 5(a)). A zwitterionic repeat unit carries tethered cationic and anionic groups. The polymer has no net charge, but it contains many local dipoles. These dipoles increase the effective polarity of the matrix and promote dissociation of added lithium salt (Fig. 5(b)) [57]. Because the charged groups are tethered to the polymer, they shape the local environment without contributing to long-range ion current. Jones et al. [57] linked this chemical concept to transport data in polymeric zwitterionic ionic liquid electrolytes (Fig. 5(c)). They reported Li^+ conductivity of up to 1.6 mS/cm and cation selectivity values of $t_+ \approx 0.6$ –0.7. Their mechanism is a zwitterionic phase that

creates superionically conductive domains and a more size-selective pathway for Li^+ . Polarity, morphology and ion-pair strength must work together, and salt loading determines whether local domains form a connected Li^+ pathway. Recent dry zwitterionic polymer electrolytes bring the discussion closer to practical cells (Fig. 5(d)) [58]. They demonstrate structural analysis, NMR diffusion, simulations, Walden analysis, and battery tests. This combination matters because it does not rely on conductivity alone. It links aligned ion channels, weak ion binding, and mobile Li^+ populations to the behavior of a dry polymer electrolyte. This evidence advances the field from materials screening toward mechanism-based electrolyte design.

Zwitterions also connect bulk transport with steady-state current. If matrix charges are tethered, fewer mobile

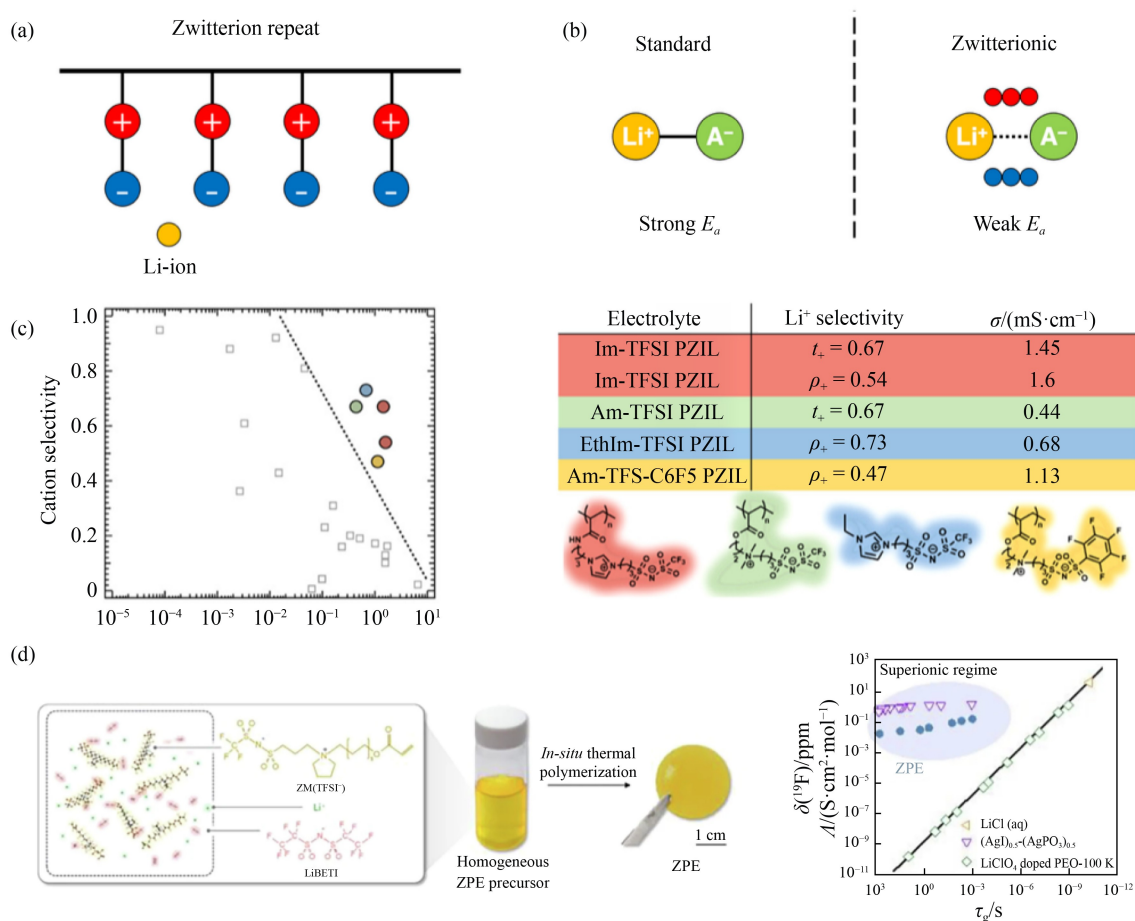


Fig. 5 Polarity control and cation selectivity in zwitterionic polymer electrolytes.

(a) Representative zwitterionic repeat motif with tethered positive and negative groups; (b) zwitterionic polarity weakens the effective Li^+ –anion association relative to a standard salt environment and lowers the apparent hopping barrier; (c) cation selectivity–conductivity comparison for polymeric zwitterionic ionic liquid electrolytes (adapted from Jones & Nguyen [57], copyright 2022, American Chemical Society); (d) dry zwitterionic polymer electrolyte design linking precursor mixing, self-standing film formation, aligned ion channels, and modified Walden analysis (adapted from Oh et al. [58], copyright 2025, Springer Nature) (Panels (a) and (b) were redrawn based on Refs. [57,58]).

anions are available to build concentration polarization. This can raise the effective Li^+ transference number and narrow the gap between AC conductivity and the current that survives under DC operation [59–62]. Zwitterionic and single-ion polymers should therefore be discussed not only as high-conductivity materials, but also as selectivity designs. One electrolyte can pair an ion-rich network with a high-polarity matrix, a rigid scaffold with soft solvating side chains, or a dynamic mechanical phase with a cation-selective transport phase [63–68]. The design question should be: which function is carried by which motif, and what measurement demonstrates that the intended coupling has been changed?

4 Translating design into steady-state cells

A decoupled bulk pathway is necessary for a working battery; however, it alone is not sufficient. The interface determines whether that pathway can be used. Three issues control this: the difference between transient and

steady-state conductivity, physical contact with a dynamically evolving electrode–electrolyte interface, and polymer stability against high-voltage cathodes.

AC impedance is useful because it is rapid and sensitive, but it counts the motion of all charged species in the system. In a cell under DC operation, species that cannot react at the electrode accumulate near the interface and build a concentration gradient. The steady-state current can then be much lower than the transient current (Figs. 6(a) and 6(b)) [59–62]. The cation transference number is therefore not a secondary detail. For lithium batteries, σ_{t_+} is often more useful than σ alone as a design quantity. Single-ion polymers address this problem by tethering the anion to the polymer backbone (Fig. 6(c)). Classic block-copolymer and multiblock examples show that a high cation transference number can improve lithium-metal cell behavior, even when absolute conductivity is not record-setting [69–72]. More recent single-ion blends have increased Li^+ conductivity and limiting current density relative to earlier single-ion polymers [73–78]. These materials still need to be compared at the same temperature, phase state, salt

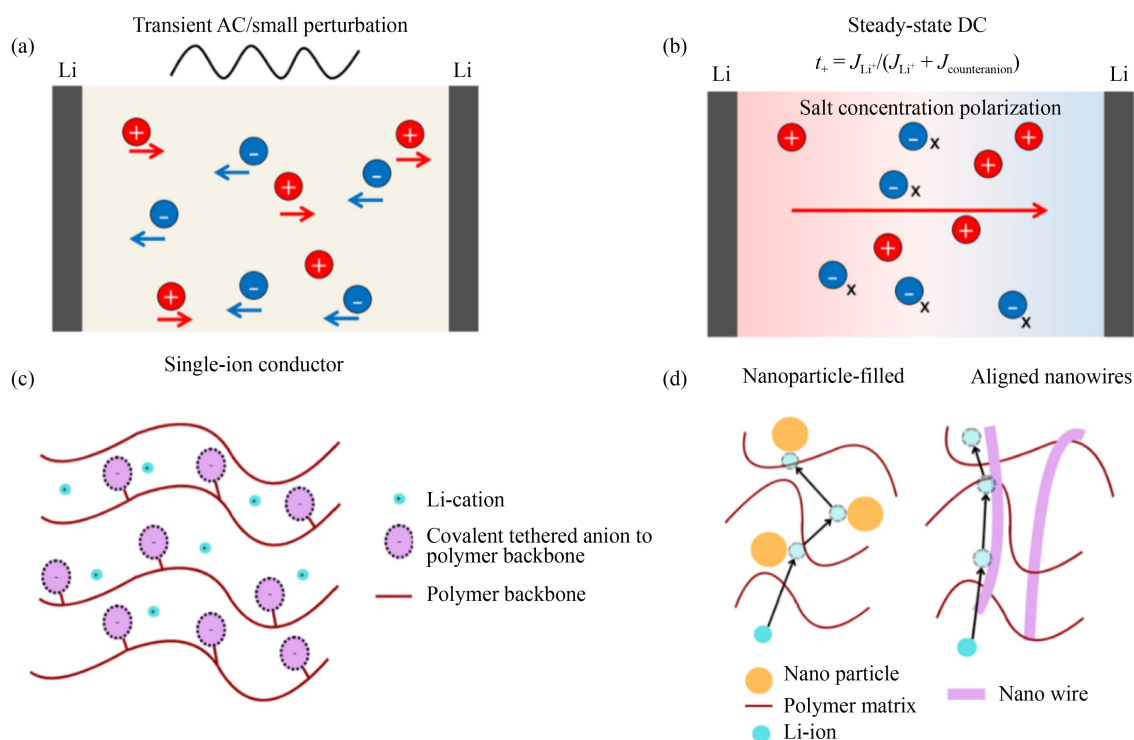


Fig. 6 Translating bulk decoupling to steady-state cell performance.

(a) Transient AC response in which all mobile charged species contribute to the measured conductivity; (b) steady-state DC response after concentration polarization, where useful current is governed mainly by cation transport; (c) high-cation-selectivity design in which anion motion is immobilized or strongly suppressed, reducing concentration polarization; (d) connected-pathway design comparing tortuous transport with a continuous, low-tortuosity pathway that maintains interfacial contact (Panels were redrawn based on (a, b) the transference-number framework in Refs. [59–62]; (c) single-ion conductor in Refs. [69–78]; (d) nanoparticles- and aligned-nanowire-based composite electrolytes in Refs. [80–85])

content, and interfacial condition. A fair comparison cannot rank them by a single metric.

Mechanical contact is the second challenge. Lithium metal undergoes substantial morphological and volume changes during plating and stripping [51,79]. A stiff or glassy electrolyte may suppress part of the deformation, but it can also lose contact or crack. Orthogonal and dynamic materials are valuable here because a soft interlayer or supramolecular phase can maintain contact while a stiffer bulk phase provides dimensional stability and mechanical integrity.

High-voltage compatibility requires both resistance to polymer oxidation and a cathode–electrolyte interphase (CEI) that sustains Li^+ transport. For polymers with decoupled ion transport, the design objective therefore extends beyond bulk conductivity to maintaining low-resistance charge transfer at the cathode. This calls for evaluating parasitic currents, interfacial resistance and surface chemistry during sustained high-voltage polarization and cycling, rather than relying on an oxidation-onset potential alone.

Composite electrolytes offer another route for interface control. Ceramic fillers can modify local polymer dynamics, salt dissociation, and boundary-layer transport. Early nanocomposite PEO work showed that inert particles can raise conductivity by changing the polymer–salt environment rather than by carrying all current themselves [80]. Aligned ceramic nanowires and garnet networks later showed how continuous inorganic pathways or high-aspect-ratio fillers can improve transport and mechanical integrity relative to particle-filled films [81–84] (Fig. 6(d)). These systems are not always examples of molecular decoupling, but they matter for device translation. Experimental claims are more convincing when one study connects chemical environment, transport pathway, and cell-level response. Fang et al. [85] used nano-X-ray tomography, Raman mapping, solid-state NMR, and cell testing to reconstruct a three-dimensional Li-ion transport network in a PEO-based conductor.

5 Conclusions and outlook

Decoupled ion transport is not another name for high conductivity. It is a change in the rate-limiting step. In the coupled regime, ions wait for polymer segments to rearrange. In the decoupled regime, ions move through a local pathway whose rate is partly independent of the main structural relaxation. Several tools are now available to test this change, including relaxation maps, Walden plots, $\sigma(T_g)$, activation barriers, tracer diffusion, and transference measurements.

The strategies discussed here are best viewed as modules within one design space. Polymer-in-salt electrolytes build ion-rich pathways. Rigid and microporous polymers preserve free volume. Supramolecular and bottlebrush networks separate mechanical support from the solvating phase. Zwitterionic and single-ion matrices screen ion pairs and improve cation selectivity. None of these modules is complete alone. A more useful target is a combination that controls pathway connectivity, hopping barriers, mechanics, and selectivity at the same time.

For the next stage, clearer evidence rather than new labels is needed. A polymer electrolyte should report not only σ , but also T_g , phase state, τ_α or an equivalent relaxation measure, cation transference number, and, where possible, NMR diffusion or a Haven-ratio estimate. If the material is intended for batteries, the same study should report steady-state current and the interfacial test conditions.

The central question is not whether polymers can ever resemble inorganic superionic conductors—some already do, at least by selected metrics. The harder question is whether a polymer can retain the advantages that brought polymers into battery research: processability, contact, toughness, and thin-film form. Decoupled transport is valuable when it preserves those advantages while giving ions a faster and more selective path than a segmental-relaxation-limited route.

Acknowledgements This work was supported by the Natural Science Foundation of Beijing (Grant No. Z220020), the National Natural Science Foundation of China (Grant Nos. 2252500158, 92372115, and 22409006), the China National Petroleum Corporation–Peking University Strategic Cooperation Project of Fundamental Research and New Cornerstone Science Foundation through the XPLOER PRIZE, and the “U35 Pei Miao Funding Program” of Changping District, Beijing (Grant No. CHPU35202502002).

Competing Interests The authors declare that they have no competing financial interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

References

1. Meyer W H. Polymer electrolytes for lithium-ion batteries.

- Advanced Materials, 1998, 10(6): 439–448
2. Stephan A M. Review on gel polymer electrolytes for lithium batteries. *European Polymer Journal*, 2006, 42(1): 21–42
 3. Quartarone E, Mustarelli P. Electrolytes for solid-state lithium rechargeable batteries: Recent advances and perspectives. *Chemical Society Reviews*, 2011, 40(5): 2525–2540
 4. Hallinan D T Jr, Balsara N P. Polymer electrolytes. *Annual Review of Materials Research*, 2013, 43: 503–525
 5. Xue Z G, He D, Xie X L. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. *Journal of Materials Chemistry A*, 2015, 3(38): 19218–19253
 6. Long L Z, Wang S J, Xiao M, et al. Polymer electrolytes for lithium polymer batteries. *Journal of Materials Chemistry A*, 2016, 4(26): 10038–10069
 7. Mindemark J, Lacey M J, Bowden T, et al. Beyond PEO-alternative host materials for Li⁺-conducting solid polymer electrolytes. *Progress in Polymer Science*, 2018, 81: 114–143
 8. Lennartz P, Paren B A, Herzog-Arbeitman A, et al. Practical considerations for enabling Li|polymer electrolyte batteries. *Joule*, 2023, 7(7): 1471–1495
 9. Song Z Y, Chen F F, Martinez-Ibañez M, et al. A reflection on polymer electrolytes for solid-state lithium metal batteries. *Nature Communications*, 2023, 14(1): 4884
 10. Fenton D E, Parker J M, Wright P V. Complexes of alkali metal ions with poly(ethylene oxide). *Polymer*, 1973, 14(11): 589
 11. Berthier C, Gorecki W, Minier M, et al. Microscopic investigation of ionic conductivity in alkali metal salts-poly(ethylene oxide) adducts. *Solid State Ionics*, 1983, 11(1): 91–95
 12. Robitaille C D, Fauteux D. Phase diagrams and conductivity characterization of some PEO-LiX electrolytes. *Journal of the Electrochemical Society*, 1986, 133(2): 315–325
 13. Ratner M A, Shriver D F. Ion transport in solvent-free polymers. *Chemical Reviews*, 1988, 88(1): 109–124
 14. Bocharova V, Sokolov A P. Perspectives for polymer electrolytes: A view from fundamentals of ionic conductivity. *Macromolecules*, 2020, 53(11): 4141–4157
 15. Borodin O, Smith G D. Mechanism of ion transport in amorphous poly(ethylene oxide)/LiTFSI from molecular dynamics simulations. *Macromolecules*, 2006, 39(4): 1620–1629
 16. Maitra A, Heuer A. Cation transport in polymer electrolytes: A microscopic approach. *Physical Review Letters*, 2007, 98(22): 227802
 17. Mongcopa K I S, Tyagi M, Mailoa J P, et al. Relationship between segmental dynamics measured by quasi-elastic neutron scattering and conductivity in polymer electrolytes. *ACS Macro Letters*, 2018, 7(4): 504–508
 18. Gadjourova Z, Andreev Y G, Tunstall D P, et al. Ionic conductivity in crystalline polymer electrolytes. *Nature*, 2001, 412(6846): 520–523
 19. Stoeva Z, Martin-Litas I, Staunton E, et al. Ionic conductivity in the crystalline polymer electrolytes PEO₆-LiXF₆, X = P, As, Sb. *Journal of the American Chemical Society*, 2003, 125(15): 4619–4626
 20. Christie A M, Lilley S J, Staunton E, et al. Increasing the conductivity of crystalline polymer electrolytes. *Nature*, 2005, 433(7021): 50–53
 21. Jones S D, Bamford J, Fredrickson G H, et al. Decoupling ion transport and matrix dynamics to make high performance solid polymer electrolytes. *ACS Polymers Au*, 2022, 2(6): 430–448
 22. Bresser D, Lyonnard S, Iojoiu C, et al. Decoupling segmental relaxation and ionic conductivity for lithium-ion polymer electrolytes. *Molecular Systems Design & Engineering*, 2019, 4(4): 779–792
 23. Yang M Y, Epps III T H. Superionic conduction in solid polymer electrolytes—Decoupling ion transport from segmental relaxation. *Polymer Chemistry*, 2026, 17(10): 971–983
 24. Wang Y Y, Agapov A L, Fan F, et al. Decoupling of ionic transport from segmental relaxation in polymer electrolytes. *Physical Review Letters*, 2012, 108(8): 088303
 25. Wang Y Y, Fan F, Agapov A L, et al. Examination of the fundamental relation between ionic transport and segmental relaxation in polymer electrolytes. *Polymer*, 2014, 55(16): 4067–4076
 26. Yoshida K, Manabe H, Takahashi Y, et al. Correlation between ionic and molecular dynamics in the liquid state of polyethylene oxide/lithium perchlorate complexes. *Electrochimica Acta*, 2011, 57: 139–146
 27. Wang Y Y, Fan F, Agapov A L, et al. Design of superionic polymers—New insights from Walden plot analysis. *Solid State Ionics*, 2014, 262: 782–784
 28. Kisiuk A, Bocharova V, Popov I, et al. Fundamental parameters governing ion conductivity in polymer electrolytes. *Electrochimica Acta*, 2019, 299: 191–196
 29. Stacy E W, Gainaru C P, Gobet M, et al. Fundamental limitations of ionic conductivity in polymerized ionic liquids. *Macromolecules*, 2018, 51(21): 8637–8645
 30. Gainaru C, Stacy E W, Bocharova V, et al. Mechanism of conductivity relaxation in liquid and polymeric electrolytes: Direct link between conductivity and diffusivity. *The Journal of Physical Chemistry B*, 2016, 120(42): 11074–11083
 31. Angell C A. Mobile ions in amorphous solids. *Annual Review of Physical Chemistry*, 1992, 43: 693–717
 32. Boyce J B, Huberman B A. Superionic conductors: Transitions, structures, dynamics. *Physics Reports*, 1979, 51(4): 189–265
 33. Fan F, Wang Y Y, Hong T, et al. Ion conduction in polymerized ionic liquids with different pendant groups. *Macromolecules*, 2015, 48(13): 4461–4470
 34. Sangoro J R, Iacob C, Agapov A L, et al. Decoupling of ionic conductivity from structural dynamics in polymerized ionic liquids. *Soft Matter*, 2014, 10(20): 3536–3540
 35. Wojnarowska Z, Feng H B, Fu Y, et al. Effect of chain rigidity on the decoupling of ion motion from segmental relaxation in polymerized ionic liquids: Ambient and elevated pressure studies. *Macromolecules*, 2017, 50(17): 6710–6721
 36. Fan F, Wang W Y, Holt A P, et al. Effect of molecular weight on the ion transport mechanism in polymerized ionic liquids. *Macromolecules*, 2016, 49(12): 4557–4570
 37. Choi U H, Ye Y S, de la Cruz D S, et al. Dielectric and

- viscoelastic responses of imidazolium-based ionomers with different counterions and side chain lengths. *Macromolecules*, 2014, 47(2): 777–790
38. Choi U H, Mittal A, Price T L, et al. Polymerized ionic liquids with enhanced static dielectric constants. *Macromolecules*, 2013, 46(3): 1175–1186
 39. Chen Q, Bao N Q, Wang J H H, et al. Linear viscoelasticity and dielectric spectroscopy of ionomer/plasticizer mixtures: A transition from ionomer to polyelectrolyte. *Macromolecules*, 2015, 48(22): 8240–8252
 40. Kashyap H K, Annapureddy H V R, Raineri F O, et al. How is charge transport different in ionic liquids and electrolyte solutions? *Journal of Physical Chemistry B*, 2011, 115(45): 13212–13221
 41. Mogurampelly S, Keith J R, Ganesan V. Mechanisms underlying ion transport in polymerized ionic liquids. *Journal of the American Chemical Society*, 2017, 139(28): 9511–9514
 42. Hayamizu K, Sugimoto K, Akiba E, et al. An NMR and ionic conductivity study of ion dynamics in liquid poly(ethylene oxide)-based electrolytes doped with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$. *The Journal of Physical Chemistry B*, 2002, 106(3): 547–554
 43. Edman L. Ion association and ion solvation effects at the crystalline-amorphous phase transition in PEO-LiTFSI. *The Journal of Physical Chemistry B*, 2000, 104(31): 7254–7258
 44. Brooks D J, Merinov B V, Goddard III W A, et al. Atomistic description of ionic diffusion in PEO-LiTFSI: Effect of temperature, molecular weight, and ionic concentration. *Macromolecules*, 2018, 51(21): 8987–8995
 45. Molinari N, Maillo J P, Kozinsky B. Effect of salt concentration on ion clustering and transport in polymer solid electrolytes: A molecular dynamics study of PEO-LiTFSI. *Chemistry of Materials*, 2018, 30(18): 6298–6306
 46. Gudla H, Hockmann A, Brandell D, et al. To hop or not to hop: Unveiling different modes of ion transport in solid polymer electrolytes through molecular dynamics simulations. *ACS Applied Polymer Materials*, 2025, 7(8): 4716–4724
 47. Diddens D, Heuer A. Lithium ion transport mechanism in ternary polymer electrolyte-ionic liquid mixtures: A molecular dynamics simulation study. *ACS Macro Letters*, 2013, 2(4): 322–326
 48. McKeown N B, Budd P M. Polymers of intrinsic microporosity (PIMs): Organic materials for membrane separations, heterogeneous catalysis and hydrogen storage. *Chemical Society Reviews*, 2006, 35(8): 675–683
 49. Adams M, Richmond V, Smith D, et al. Decoupling of ion conductivity from segmental dynamics in oligomeric ethylene oxide functionalized oxanorbornene dicarboximide homopolymers. *Polymer*, 2017, 116: 218–225
 50. Liang Q, Liu X Z, Tang J Y, et al. An ultrathin composite polymer electrolyte dual-reinforced by a polymer of intrinsic microporosity (PIM-1) and poly(tetrafluoroethylene) (PTFE) porous membrane. *Small*, 2024, 20(22): 2306994
 51. Mackanic D G, Yan X Z, Zhang Q H, et al. Decoupling of mechanical properties and ionic conductivity in supramolecular lithium ion conductors. *Nature Communications*, 2019, 10(1): 5384
 52. Huang B Q, Nian S F, Cai L H. A universal strategy for decoupling stiffness and extensibility of polymer networks. *Science Advances*, 2024, 10(48): eadq3080
 53. Wheatle B K, Keith J R, Mogurampelly S, et al. Influence of dielectric constant on ionic transport in polyether-based electrolytes. *ACS Macro Letters*, 2017, 6(12): 1362–1367
 54. Wheatle B K, Lynd N A, Ganesan V. Effect of polymer polarity on ion transport: A competition between ion aggregation and polymer segmental dynamics. *ACS Macro Letters*, 2018, 7(10): 1149–1154
 55. Savoie B M, Webb M A, Miller III T F. Enhancing cation diffusion and suppressing anion diffusion via Lewis-acidic polymer electrolytes. *The Journal of Physical Chemistry Letters*, 2017, 8(3): 641–646
 56. Ma B R, Olvera de la Cruz M. A perspective on the design of ion-containing polymers for polymer electrolyte applications. *The Journal of Physical Chemistry B*, 2021, 125(12): 3015–3022
 57. Jones S D, Nguyen H, Richardson P M, et al. Design of polymeric zwitterionic solid electrolytes with superionic lithium transport. *ACS Central Science*, 2022, 8(2): 169–175
 58. Oh K S, Lee J E, Shin J C, et al. Conflicting entropy-driven zwitterionic dry polymer electrolytes for scalable high-energy all-solid-state batteries. *Nature Communications*, 2025, 17(1): 330
 59. Doyle M, Fuller T F, Newman J. The importance of the lithium ion transference number in lithium/polymer cells. *Electrochimica Acta*, 1994, 39(13): 2073–2081
 60. Evans J, Vincent C A, Bruce P G. Electrochemical measurement of transference numbers in polymer electrolytes. *Polymer*, 1987, 28(13): 2324–2328
 61. Diederichsen K M, McShane E J, McCloskey B D. Promising routes to a high Li^+ transference number electrolyte for lithium ion batteries. *ACS Energy Letters*, 2017, 2(11): 2563–2575
 62. Shao Y Q, Gudla H, Brandell D, et al. Transference number in polymer electrolytes: Mind the reference-frame gap. *Journal of the American Chemical Society*, 2022, 144(17): 7583–7587
 63. Kishimoto K, Yoshio M, Mukai T, et al. Nanostructured anisotropic ion-conductive films. *Journal of the American Chemical Society*, 2003, 125(11): 3196–3197
 64. Kishimoto K, Suzawa T, Yokota T, et al. Nano-segregated polymeric film exhibiting high ionic conductivities. *Journal of the American Chemical Society*, 2005, 127(44): 15618–15623
 65. Kato T, Yoshio M, Ichikawa T, et al. Transport of ions and electrons in nanostructured liquid crystals. *Nature Reviews Materials*, 2017, 2(4): 17001
 66. Paren B A, Thurston B A, Neary W J, et al. Percolated ionic aggregate morphologies and decoupled ion transport in precise sulfonated polymers synthesized by ring-opening metathesis polymerization. *Macromolecules*, 2020, 53(20): 8960–8973
 67. Paren B A, Nguyen N, Ballance V, et al. Superionic Li-ion transport in a single-ion conducting polymer blend electrolyte. *Macromolecules*, 2022, 55(11): 4692–4702
 68. Zhang Z J, Liu C, Cao X, et al. Morphological evolution of ionomer/plasticizer mixtures during a transition from ionomer to

- polyelectrolyte. *Macromolecules*, 2017, 50(3): 963–971
69. Zhang H, Li C M, Piszcz M, et al. Single lithium-ion conducting solid polymer electrolytes: Advances and perspectives. *Chemical Society Reviews*, 2017, 46(3): 797–815
 70. Bouchet R, Maria S, Meziane R, et al. Single-ion BAB triblock copolymers as highly efficient electrolytes for lithium-metal batteries. *Nature Materials*, 2013, 12(5): 452–457
 71. Porcarelli L, Shaplov A S, Salsamendi M, et al. Single-ion block copoly(ionic liquid)s as electrolytes for all-solid state lithium batteries. *ACS Applied Materials & Interfaces*, 2016, 8(16): 10350–10359
 72. Nguyen H D, Kim G T, Shi J L, et al. Nanostructured multi-block copolymer single-ion conductors for safer high-performance lithium batteries. *Energy & Environmental Science*, 2018, 11(11): 3298–3309
 73. Shan C L, Wang Y L, Liang M H, et al. A comprehensive review of single ion-conducting polymer electrolytes as a key component of lithium metal batteries: From structural design to applications. *Energy Storage Materials*, 2023, 63: 102955
 74. Yang M Y, Epps III T H. Solid-state, single-ion conducting, polymer blend electrolytes with enhanced Li^+ conduction, electrochemical stability, and limiting current density. *Chemistry of Materials*, 2024, 36(4): 1855–1869
 75. Ahmed F, Choi I, Rahman M M, et al. Remarkable conductivity of a self-healing single-ion conducting polymer electrolyte, poly(ethylene-co-acrylic lithium (fluoro sulfonyl)imide), for all-solid-state Li-ion batteries. *ACS Applied Materials & Interfaces*, 2019, 11(38): 34930–34938
 76. Chen G P, Niu C Q, Chen Y B, et al. A single-ion conducting polymer electrolyte based on poly(lithium 4-styrenesulfonate) for high-performance lithium metal batteries. *Solid State Ionics*, 2019, 341: 115048
 77. Lu Y Y, Tikekar M, Mohanty R, et al. Stable cycling of lithium metal batteries using high transference number electrolytes. *Advanced Energy Materials*, 2015, 5(9): 1402073
 78. O'Reilly M V, Masser H, King D R, et al. Ionic aggregate dissolution and conduction in a plasticized single-ion polymer conductor. *Polymer*, 2015, 59: 133–143
 79. Monroe C, Newman J. Dendrite growth in lithium/polymer systems. *Journal of the Electrochemical Society*, 2003, 150(10): A1377–A1384
 80. Croce F, Appetecchi G B, Persi L, et al. Nanocomposite polymer electrolytes for lithium batteries. *Nature*, 1998, 394(6692): 456–458
 81. Chen L, Li Y T, Li S P, et al. PEO/garnet composite electrolytes for solid-state lithium batteries: From “ceramic-in-polymer” to “polymer-in-ceramic”. *Nano Energy*, 2018, 46: 176–184
 82. Liu W, Lee S W, Lin D C, et al. Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires. *Nature Energy*, 2017, 2(5): 17035
 83. Fu K, Gong Y H, Dai J Q, et al. Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries. *Proceedings of the National Academy of Sciences of the United States of America*, 2016, 113(26): 7094–7099
 84. Yang T, Zheng J, Cheng Q, et al. Composite polymer electrolytes with $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet-type nanowires as ceramic fillers: Mechanism of conductivity enhancement and role of doping and morphology. *ACS Applied Materials & Interfaces*, 2017, 9(26): 21773–21780
 85. Fang C D, Huang Y, Sun Y F, et al. Revealing and reconstructing the 3D Li-ion transportation network for superionic poly(ethylene) oxide conductor. *Nature Communications*, 2024, 15(1): 6781

Author Biography



Dr. Quanquan Pang is a tenure-track assistant professor in the School of Materials Science and Engineering at Peking University, with training in both materials science and chemistry. Dr. Quanquan Pang received a bachelor's degree in materials science and engineering from Huazhong University of Science and Technology and a Ph.D in chemistry from the University of Waterloo in 2017, followed by postdoctoral training in materials science at the Massachusetts Institute of Technology.

Dr. Quanquan Pang's research focuses on understanding and advancing electrochemical processes, which provide a fundamental connection between chemistry and energy. Of particular interest are systems that enable the interconversion of electrical and chemical energy, with an emphasis on improving their energy efficiency, energy density, and service life. The overarching goal is to enable the efficient use of renewable energy in everyday life and contribute to sustainable industry and a greener environment.