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ABSTRACT

Solid-state polymer electrolytes and high-concentration liquid electrolytes, such as water-in-salt electrolytes and ionic liquids, are emerging materials to replace the flammable organic electrolytes widely used in industrial lithium-ion batteries. Extensive efforts have been made to understand the ion transport mechanisms and optimize the ion transport properties. This perspective reviews the current understanding of the ion transport and polymer dynamics in liquid and polymer electrolytes, comparing the similarities and differences in the two types of electrolytes. Combining recent experimental and theoretical findings, we attempt to connect and explain ion transport mechanisms in different types of small-molecule and polymer electrolytes from a theoretical perspective, linking the macroscopic transport coefficients to the microscopic, molecular properties such as the solvation environment of the ions, salt concentration, solvent/polymer molecular weight, ion pairing, and correlated ion motion. We emphasize universal features in the ion transport and polymer dynamics by highlighting the relevant time and length scales. Several outstanding questions and anticipated developments for electrolyte design are discussed, including the negative transference number, control of ion transport through precision synthesis, and development of predictive multiscale modeling approaches.

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I. INTRODUCTION

Lithium ion batteries have enabled transformative technologies such as wireless electronics, electric vehicles, and renewable energies, which was recognized by the 2019 Nobel Prize in Chemistry.1 The ever-growing global energy consumption and environmental concerns with fossil fuels demand urgent development of the next-generation energy storage materials that have higher energy and power densities and withstand harsher operational conditions. The volatile and flammable carbonate based electrolytes widely used in current lithium ion batteries possess significant safety risk and are unsuitable for grid-storage applications; thus, great efforts have been made to develop alternative electrolytes with better safety and device performances. Among others, concentrated liquid electrolytes and polymer electrolytes have attracted intense research interest due to a number of promising physicochemical and electrochemical properties.

Increasing salt concentration in classical electrolytes above a threshold (typically >∼3M–5M depending on the salt–solvent combination) drastically changes the solvation environment of the ions and at sufficient concentration results in an ion-dominant solution known as “solvent-in-salt electrolytes” (SISEs).3 In these SISEs, most of the solvent molecules are bound with the ions, which confers increased electrochemical stability, allowing wider ranges of operation temperature and voltage.6,7 Room temperature ionic liquid electrolytes (ILs) can be considered as a limiting case of concentrated liquid electrolytes. These solvent-free electrolytes remain at the liquid state at ambient conditions due to the bulkiness of the ions, offering non-volatile, non-flammable, and electrochemically stable liquid electrolyte with high tunability provided by the large chemical design space for the cationic/anionic functional groups.8

Polymer electrolytes (PEs) are prepared by introducing charge carriers (salts, ILs, and/or other electrolyte solutions) into a polymeric matrix, which confer mechanical strength, flexibility,
processability, and electrochemical stability over classical liquid electrolytes. Ion conduction in PEs depends strongly on the solvation environment of the conducting ions. It is customary to classify PEs based on the solvating component(s); thus, we have salt-doped polymer electrolytes, gel polymer electrolytes (GPEs), and single-ion conductors (SICs) including polymerized ionic liquids (PILs), in which the conducting ions are solvated, respectively, by the polymer matrix, additional small-molecule solvents, and counter ions embedded in the polymer chains.

Large volumes of research have been dedicated to identifying the governing principles of ion transport and to optimizing electrolyte performances through a variety of strategies. A good number of reviews have summarized recent achievements and challenges in SISEs, ILs, salt-doped PEs, GPEs, SICs, and PILs. More focused reviews have highlighted the roles of multivalent ions, morphology and confinement, and use of theoretical and computational approaches in electrolyte design. Our understanding of ion conduction in each of these electrolytes has been greatly improved, but the wide range of composition and electrolytic properties of these materials has made it challenging to formulate a consistent and unified view of the diverse set of issues.

In this perspective, we attempt to connect and explain ion transport mechanisms for different types of classical electrolytes and PEs from a theoretical perspective. We first introduce the basic concepts needed to characterize ion transport, including both quantitative metrics (the three transport coefficients) and qualitative descriptors (microscopic ion transport mechanisms). To classify the different modes of ion motion into microscopic transport mechanisms, we focus on the changes in the ion solvation environment, which are associated with the molecular properties of the hosting solvent/polymer and the corresponding microscopic timescales. Subsequently, recent advances and current understanding of a set of microscopic, molecular properties such as ion pairing and ion correlation, salt concentration, solvent molecular weight, and the microstructure morphology. This unified view clarifies the origin of some previously reported, but not yet fully understood, universal correlations for ion transport properties found in ILs, PILs, and salt-doped PEs. For example, we propose a new theoretical explanation to the apparent universal behavior found for ion diffusion in salt-doped polymer electrolytes. We conclude with a discussion of some unresolved questions and emerging approaches that are critical for the next generation electrolyte materials.

II. CHARACTERIZING ION TRANSPORT

A. Three transport coefficients

Three important transport properties of electrolytes govern their performance in batteries—ionic conductivity $\sigma$, ion diffusion coefficient $D$, and cation transference number $t_+$. The diffusion coefficients of the ions are directly related to the extent of molecular motion, while ionic conductivity measures the collective charge transport resulting from both independent single-ion motions and correlated ion motions. The cation transference number counts the contribution of reactive ions (Li$^+$ for lithium-ion batteries) to the total conductivity in the battery system. Newman and Thomas-Alyea developed a general framework to describe transport in concentrated electrolytes based on these three coefficients, which is independent of the underlying ion transport mechanisms.

Several experimental methods are used to quantify each transport coefficient. Ionic conductivity is typically measured by AC impedance spectroscopy with small applied potentials (~10 mV). The collective salt diffusion coefficients can be obtained by the restricted diffusion method, and individual (self)-ion-diffusion coefficients can be measured with pulse-field gradient nuclear magnetic resonance (PFG-NMR). In this article, we focus on the self-diffusion coefficients; henceforth, all diffusion coefficients $D_i$ refer to the self-diffusion coefficients of the individual ions (i.e., $+$ for cation and $-$ for anion). Experimental characterization of the transference number is not as straightforward compared to the other two transport coefficients. The popular steady-state current based method relies on ideal solution behavior and thus is limited to dilute electrolytes. A more rigorous approach by Newman and co-workers requires current-interrupt experiments and open circuit potential measurements of concentration cells.

Compared to experiments, molecular simulations can unambiguously quantify all three transport properties in a single simulation setup. In addition, the estimated transport coefficients can be connected to the underlying molecular mechanisms. Ionic conductivity is calculated with the Green–Kubo relation,

$$\sigma = \lim_{t \to \infty} \frac{e^2}{6tVk_B T} \sum_{i,j} \langle (z_i\Delta R_i(t)) \cdot (z_j\Delta R_j(t)) \rangle,$$  

where $e$ is the elementary charge, $V$ is the volume of the system, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\Delta R_i(t)$ is the displacement vector of particle $i$ during time $t$, $z_i$ is the valency of ion $i$ (defined to be negative for anions), and the sum runs for all self and distinct pairs of ions in the system. The self-diffusion coefficient is calculated using the Einstein relation,

$$D_i = \lim_{t \to \infty} \frac{\langle \Delta R_i(t)^2 \rangle}{6t},$$

where $\langle \Delta R_i(t)^2 \rangle$ is the mean-square-displacement (MSD) of particle $i$ during time $t$. The cation transference number is obtained by singling out the relative contribution of the cations from Eq. (2.1),

$$t_+ = \frac{1}{\sigma} \lim_{t \to \infty} \frac{e^2}{6tVk_B T} \sum_{i,j} \langle (z_i\Delta R_i(t)) \cdot (z_j\Delta R_j(t)) \rangle,$$

where the notation in the summation means $i$ runs for all cations and $j$ runs for both cations and anions.

In ideal electrolytes, ions move independently of each other and the ionic conductivity is directly related to the ion diffusion coefficients by the Nernst–Einstein (NE) relation,

$$\sigma^{\text{NE}} = \frac{e^2}{Vk_B T} (N_+ z_+^2 D_+ + N_- z_-^2 D_-),$$
B. Ion solvation and ion transport mechanisms

The local solvation environments of the ions and their time evolution are the key microscopic features to characterize the ion transport mechanisms in the condensed phase. In classical electrolytes composed of ionizable salts dissolved in small-molecule solvents, association/dissociation events of a cation–anion pair or a solvent–ion pair can serve as the renewal event. Zhang and Maginn used molecular dynamics (MD) simulations to study transport properties of 29 different ionic liquids (ILs) and showed both $D$ and $\sigma_{\text{NE}}$ were strongly correlated to the self-diffusion coefficients. Thus, many computational studies have focused on the Nernst–Einstein conductivity and the ideal diffusion coefficient because of the slower convergence of Eq. (2.1) due to correlated ion motions, compared to the self-diffusion coefficients. Despite this, many computational studies have focused on explaining the correlation between $D$ and the host properties of the small-molecule or polymeric solvents, such as the viscosity, solvation site connectivity, polymer molecular weight ($M_w$), coordination number, and dielectric constant.

Equation (2.2) implies that $D$ can be related to a pair of characteristic length and timescales. If the long-time diffusion can be described with statistically uncorrelated renewal events, $D$ is directly proportional to the ratio of the square of average travel distance $\overline{r}_{\text{m}}$ to the associated timescale $\tau_{\text{ren}}$ for the renewal event; thus, $D \propto \overline{r}_{\text{m}}^2/\tau_{\text{ren}}$. A strong correlation between $D$ and a microscopic timescale is indicative of some underlying stochastic renewal process; therefore, identifying such a relationship can help elucidate the underlying transport mechanisms.

The difference between $\sigma$ and $\sigma_{\text{NE}}$ is thus a measure of non-ideality due to correlated ion motion, which may arise from (transient) ion pairing and ion clustering, as well as collective ion motion (as in solvent-free or concentrated ILs). As shown in many recent studies, correlated ion motion plays an important role in concentrated electrolytes, ionic liquid mixtures, and PEs. Despite this, the majority of computational studies have focused on the Nernst–Einstein conductivity and the ideal diffusion coefficient because of the slower convergence of Eq. (2.1) due to correlated ion motions, compared to the self-diffusion coefficients. Thus, many computational studies have focused on explaining the correlation between $D$ and the host properties of the small-molecule or polymeric solvents, such as the viscosity, solvation site connectivity, polymer molecular weight ($M_w$), coordination number, and dielectric constant.

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For PEs, Ratner and co-workers made early contributions by considering the local structural relaxation of the polymer as the renewal process. In their phenomenological dynamic bond percolation (DBP) model, ions were thought to hop randomly between consecutive renewal processes and form a dynamic bond with the polymer, and ion diffusion was determined by two characteristic timescales: average renewal time ($\tau_{\text{ren}}$) and hopping time ($\tau_{\text{hop}}$). In a series of MD studies for mixtures of poly(ethylene oxide) (PEO) and lithium containing salts, Borodin and Smith showed that such an ion–polymer bond is formed by multiple PEO oxygen atoms coordinating a single Li⁺ ion. Furthermore, structural relaxation of the solvating polymer is found to directly modify the ion dynamics by actively carrying the solvated cation or through changing the connectivity of the coordination sites for the cation, which was not included in the original DBP model that approximated independent renewal and hopping events. PEs with a high ion content, such as polymerized ionic liquids (polyILs), showed strong correlation between transport coefficients and microscopic timescales similar to their small-molecule counterparts.

Thus, it is useful to categorize the different ion transport mechanisms in electrolytes based on the ion solvation environment. In classical electrolytes, ions can move either independently or cooperatively with their solvating molecules. In the independent ion motion, each ion moves by constantly exchanging its adjacent (solvating) particles; thus, the timescale associated with this change in the solvation environment is a key aspect of the transport mechanism. Depending on whether this exchange is continuous in time or involves punctuated movements, the independent ion motion can be further divided into continuous (Brownian) vs hopping types of motion. In proton conducting electrolytes, protons can hop over multiple protonatable sites through a hydrogen bonding network in a concerted manner (Grotthuss hopping), resulting in an enhanced proton conduction.

Recently, a Grotthuss-like concerted hopping mechanism has been proposed also for lithium ions in highly concentrated electrolytes. In the co-diffusional motion, an ion and its coordinating particles move together without changing its solvation shell. Depending on whether solvation is made by the solvent molecules or the counter ions, co-diffusion can be further divided into solvent-mediated single-ion motion vs ion-pair (IP) correlated motion. In the co-diffusive motion, the lifetime of a solvent–ion association or an ion-pair becomes critical in determining the diffusion rate. Note that we have separated solvent exchange time and solvent–ion association time in order to distinguish between continuous independent transport and solvent-mediated co-diffusional transport mechanisms. While both describe how long an ion is in the neighborhood of a coordinating solvent, their molecular origins differ as the former is controlled by the fluidity of the solution, while the latter is controlled by the strength of the direct interaction between the solvent and the ion. In the limit of infinite lifetime of the solvent–ion association, the ion with its permanent solvation shell can be treated as a single molecular ion that would move either independently or cooperatively with the second solvation shell. As will be discussed later, the lifetime of an ion pair and the extent of ion pairing and ion clustering are strongly influenced by the dielectric constant of the solvent.

Ion transport in PEs has been traditionally described by three mechanisms according to the ion motion relative to the polymeric chain—(i) ion motion along the polymer chain (intra-chain), (ii) inter-segmental ion hopping between ion solvation sites, and (iii) ion–polymer co-diffusion. These three mechanisms can be classified under the four types of ion motion in classical electrolytes categorized by the changes in the local solvation environment (Fig. 1, colored in green). We classify the intra-chain ion motion as continuous ion diffusion, which typically involves exchanging one of the coordinating monomers to another adjacent one. The exchanging monomer can be from another polymer chain nearby, in which case we classify it as continuous chain exchange. The inter-segmental ion hopping can also occur both within a single polymer chain and between different polymer chains and usually involves simultaneously changing multiple monomer units that are coordinating the
same ion. The residence time of an ion between consecutive hopping (hopping time, $t_{hop}$) events depends on the connectivity of the ion solvation sites. The ion-polymer co-diffusion can be further split into the diffusion with the entire polymer chain (vehicular dynamics) and the segmental dynamics of the local ion-polymer coordination shell. The relative contributions of the segmental vs vehicular dynamics to the total ion diffusion are strongly related to the $M_w$ and the relaxation time of the polymer chain (Rouse time, $t_R$, for unentangled polymers), as well as the association time of the solvent–ion pair. We note that, in some literature, vehicular motion is used to describe both types of the ion-polymer co-diffusional motion. A less discussed but important mode is the bridging of multiple polymer chains by a single ion since it can affect both ion transport and polymer dynamics by forming physical cross-links that effectively increase the molecular weight of the polymer. Finally, at high salt concentration or in the cases of single-ion conductors such as polymerized ionic liquids (PILs), the correlated motion of the ion pairs plays an important role similar to the classical analog of the ion-pair mediated co-diffusion.

The schematics shown in Fig. 1 summarize the ion transport mechanisms and important timescales (colored in magenta) associated with each type discussed here, as well as the thermodynamic or structural properties of the solvent/polymer host properties (colored in blue) that influence the timescales. In many cases, multiple transport mechanisms contribute to the overall ion transport simultaneously, and their relative contributions can be modulated by changing the host properties. For example, decreasing solvent dielectric in classical electrolytes reduces the solvent-mediated ion co-diffusion while strongly increasing the correlated motion of the ion-pairs and ion-clusters. The continuous and hopping transport mechanisms would not be affected much by the solvent dielectric since the dielectric does not directly modify the fluidity of the solution or the hopping rate of the ions between adjacent solvation sites.

Another example is the effect of increasing molecular weight $M_w$ of a strongly ion-solvating polymer such as PEO. As discussed earlier, the three ion transport mechanisms of monomer exchange, ion hopping, and ion-polymer co-diffusion play important roles in ion transport in this salt-doped PE. When the $M_w$ of the host polymer is low (i.e., oligomeric electrolyte), solvent mediated co-diffusional motion, especially the vehicular mechanism, contributes dominantly to the ion transport. The global transport of the polymer is reduced as $M_w$ increases, and at very high $M_w$, the intersegmental ion hopping becomes the dominant mechanism since this motion is independent of the polymer $M_w$ (vide infra). Utilizing Fig. 1 to control the host properties affecting the microscopic timescales associated with different transport mechanisms provides a useful organizing guide for systematic design of performance electrolytes with desirable properties.

### III. Current Understanding of Ion Transport Mechanisms

In this section, we briefly review our current understanding of ion transport mechanisms in different types of electrolytes. Our discussion will be focused on two aspects: (i) comparing similarities and differences between classical electrolytes and PEs and (ii) identifying the microscopic timescales and underlying molecular mechanisms governing ion transport and their relationship to the transport coefficients. To facilitate our discussion, we use the following classification of electrolytes, which is a slightly modified version of the five types of homogeneous electrolytes identified by Hallinan and Balsara:

1. **Salt solutions**: mixtures of small-molecule solvents and salts;
2. **Room temperature ionic liquids (ILs)**: electrolytes composed of small-molecule ions only;
3. **Salt-doped dry PEs**: salts dissolved in high molecular weight polymeric solvents;
4. **Dry single-ion conductors (SICs)**: one of the ions is part of the polymeric chain that solvates the other ion; and
5. **Gel electrolytes and solvated SICs**: PE swollen with small-molecule solvents.

We have separated the classical electrolytes into salt solutions and ILs to make one-to-one comparisons with salt-doped dry PEs and dry single-ion conductors (SICs) such as polymerized ionic liquids (PILs).

#### A. Salt concentration effects in classical electrolytes

In a high-dielectric solvent and at very low concentrations, ions behave ideally; conductivity increases linearly with salt concentration, and the Nernst–Einstein relation in Eq. (2.4) holds rigorously. As the electrolyte becomes more concentrated, the ion self-diffusion...
coefficients decreases nearly exponentially as the solution viscosity increases. The combined effect of increased charge carrier concentration and slowing self-diffusion is a maximum in the conductivity at a relatively low ion concentration. Correlated and collective ion motions become important at high salt concentrations or in a low dielectric solvent, making the real conductivity ($\sigma$) usually lower than the ideal estimate from the diffusion coefficients ($\sigma_{\text{NE}}$).

In an experimental study by Li et al., the effects of salt concentration and solvent dielectric on the density, viscosity, and conductivity were examined for a set of imidazolium-based ILs dissolved in water and organic solvents. A wide range of compositions, including the neat IL, was investigated, thus covering both type I and I’ electrolytes in Table I. The viscosity of the mixtures showed a monotonic exponential increase with the mole fraction of the IL. Both types of electrolytes show the characteristic maximum conductivity at relatively low ion concentration (0.1–0.2 of ion mole fraction), as shown in Fig. 2(a), for the aqueous solution. Interestingly, however, the molar conductivities of organic electrolytes were found lower than the neat IL, while the molar conductivity of the aqueous electrolyte was considerably higher than the neat IL (not shown). Recently, McDaniel and Son studied the corresponding IL/solvent mixtures using MD simulation with explicitly polarizable force-field developed from symmetry-adapted perturbation theory (SAPT-FF); they attributed the aforementioned difference in molar conductivity between the organic and aqueous solvents to the different extent of ion correlation.

As shown in Fig. 2, the characteristic maximum and overall concentration dependence of the ionic conductivity were found in good agreement with experiments, and the estimated ion self-diffusion coefficients showed the expected exponential decrease with increasing concentration. An important solvent dependence was found in the relative magnitude of cation and anion diffusion coefficients ($D_+/D_−$). As expected from the ion size difference (BMIM$^+$ is larger than BF$_4^−$), $D_−$ is up to two times higher than $D_+$ in the high-dielectric water at low concentration, where ideal solution behavior and independent ion motion are anticipated [Fig. 2(b)]. As the solvent dielectric constant $\epsilon$ decreases from water to dichloroethane, ions showed more correlated motion. The almost identical cation and anion $D$ in 1,2-dichloroethane ($\epsilon \approx 10$, Fig. 2(d)) are a result of significant ion pairing and collective ion motion. As expected, the two ion diffusivities converge to each other. 

![FIG. 2](image-url)
other in all solvents as the concentration increases to the pure IL limit.

**B. Salt-doped dry PEs and polymer segmental dynamics**

Figure 3 shows the experimentally measured three transport coefficients of an archetypal salt-doped dry PE, PEO/Li$^{+}$TFSI$^{-}$, as a function of the number of ions per EO monomer ($r_s = r = [\text{Li}^+] / [\text{EO}]$). While the PE shares the qualitative salt concentration dependence with classical electrolytes—maximum in $\sigma$ and monotonic decrease in $D$—the solvation of ions by the polymer chain gives rise to interesting differences from classical electrolytes. In lithium salt doped PEO, x-ray crystal structures and snapshots from MD simulations both show that a single Li$^+$ ion is coordinated by typically 4–6 oxygen atoms in PEO or atoms in the anion. The strong polymer-ion solvation prevents ionic aggregation and makes the cation and anion motions less correlated. As a result, the anion diffusion coefficient in PEO/Li$^{+}$TFSI$^{-}$ is up to three times higher than the cation diffusion coefficient [Fig. 3(b)]. This implies that independent or weakly correlated ion motions are dominant in PEO/Li$^{+}$TFSI$^{-}$, despite the low dielectric constant of the host polymer ($\epsilon < 10$), in contrast to classical electrolytes with solvents of low dielectric constants, where almost equal cation and anion diffusion coefficients would be obtained at practically all concentrations [cf. Fig. 2(d)]. On the other hand, the cation transference number measured with the method by Newman and co-workers ($t_{+\text{Ne}}$) showed a negative value at high enough concentration [Fig. 3(c)]. A negative transference number implies that the cations effectively move toward the positively charged electrode in the absence of large enough concentration gradients and is postulated to occur due to significantly correlated or

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**FIG. 3.** [(a)–(c)] Effect of salt concentration on the ion transport coefficients in the PEO/Li$^{+}$TFSI$^{-}$ electrolyte. (a) $\sigma$ from AC impedance spectroscopy, (b) $D_+ \ldots$ from the PFG-NMR experiment, and (c) comparison of $t_{+}$ values measured by three different experimental methods (see text). (d) Normalized monomeric friction coefficient, $(\zeta(r_s)/\zeta(0))$, as a function of salt concentration. $\zeta$ was estimated from the polymer segmental motion measured by the QENS technique. In these figures, $r_s = r = [\text{Li}^+] / [\text{EO}]$ is the salt concentration defined as the number of Li$^+$ ions per ethylene oxide (EO) monomer. The solid line in (a) represents Eq. (3.1), which combines the linear increase in charge carrier concentration and the exponential increase in monomeric friction obtained from (d). (a) and (d) are reproduced with permission from Mongcopa et al., ACS Macro Lett. 7, 504 (2018). Copyright 2018 American Chemical Society. (b) and (c) are reproduced with permission from Pesko et al., J. Electrochem. Soc. 164, E3569 (2017). Copyright 2017 Author(s), licensed under a Creative Commons Attribution 4.0 License.
clustered ion dynamics (see Sec. V). Further studies are needed to understand these seemingly contradictory observations of independent vs correlated ion motion in PEO/Li[TFSI] from different measurements.

The nonmonotonic concentration dependence in the conductivity originates from the slowdown of local polymer segmental dynamics by salts. Recently, Mongcopa et al. suggested that the polymer segmental dynamics can be the sole factor causing the nonlinear dependence of $\sigma$ on salt concentration. They quantified the polymer segmental dynamics by estimating the monomeric friction coefficient, $\zeta$, from the quasi-elastic neutron scattering (QENS) experiment and fitting the Rouse model. As shown in Fig. 3(d), $\zeta$ is exponentially increasing with $r_s$, $\zeta(r_s)/\zeta(0) = \exp(r_s/0.085)$, where 0.085 is a temperature-dependent dimensionless constant obtained at 363 K. Combining this with the linear increase in the charge carrier concentration results in

$$\sigma(r_s) = \sigma_0 r_s \exp\left(-\frac{r_s}{0.085}\right), \quad (3.1)$$

which is in excellent agreement with the measured conductivity [shown as the solid line in Fig. 3(a)]. This result again implies independent ion motion, in apparent contradiction to the negative transference number [the black curve in Fig. 3(c)].

The strong polymer–ion solvation also influences how the ionic conductivity changes with the $M_w$ of the polymer. In general, increasing $M_w$ slows down the ion transport due to the reduced vehicular motion, but the slowdown saturates in high enough $M_w$ as ion transport occurs predominantly by local ion motion. In low molecular weight oligomer solvents based on ethylene oxide (EO), both conductivity and diffusion coefficient measurements show rapid decreases in the transport coefficients with increasing $M_w$ of the oligomer. Simulations on such oligomeric electrolytes was predominantly (over 90%) carried by vehicular motion of the ion–oligomer complex, while less than 10% of the ion diffusion occurred through inter-chain hopping or intra-chain motion. On the other hand, in the ethylene carbonate (EC) based classical electrolyte, vehicular motion and solvent exchange were found to contribute roughly equally to the overall ion diffusion, suggesting that the dominant transport mechanism of the lithium ions can be modulated with their solvation environment by changing functional groups in the solvent. In high molecular weight PEO, the ionic conductivity is independent of $M_w$ at the same salt concentration, even though the viscosity ($\eta$) of the polymer melt continues to increase following the scaling behavior, $\eta \sim M_w^{5/3}$, for sufficiently long chains. The saturation of the decreasing conductivity is observed at about the entanglement molecular weight ($M_w \approx 4$ kg/mol), but theoretical models suggested that the entanglement condition may not be necessary as long as the renewal time is much less than the Rouse time. In such high $M_w$ PE, vehicular motion is negligible due to the large $M_w$, and Li$^+$ ion transport is governed by more local ion motion—namely, intra-chain diffusion, inter-segmental hopping, and co-diffusion with the solvating polymer segments. In this case, the lifetime of the local coordination is the determining factor.

As will be illustrated in the Secs. III C and III D, attempts to improve the ion conductivity in various types of PEs have been made in two primary categories—(1) to enhance the polymer segmental dynamics by lowering the glass transition temperature, $T_g$, and/or preventing the crystallization of the polymer matrix, and (2) to decouple the ion transport from polymer segmental motion to achieve ion conduction independent from the slow segmental relaxation. These two approaches can be viewed as controlling the relative contributions in the three local ion transport mechanisms, which have complex dependence on the detailed chemical structure of the solvating polymer. Above $T_g$, the temperature dependence of ion conductivity of many PEs often follows the nonlinear Vogel–Fulcher–Tammann (VFT) equation. This implies that the ion conduction in these PEs above their $T_g$ is directly proportional to the segmental relaxation dynamics, which motivates the vast efforts to find better PEs with lower $T_g$. On the other hand, ion conduction can occur in short-chain crystalline PEO/lithium salt complexes, where the polymer segmental motion is almost frozen and ion transport is dominated by the hopping mechanism. Inspired by this, various strategies to decouple the ion transport from the structural relaxation of the polymer matrix have been proposed. However, despite decades of intensive efforts, outperforming PEO-based electrolyte systems has remained challenging until very recently. We will come back in Sec. V B to show how recent advances in polymer synthesis and mechanistic understanding of ion dynamics helped achieve this goal.

C. Ion correlations in ILs and dry single-ion conductors

Solvent-free, room temperature ionic liquids (ILs) have attracted considerable attention due to their high ionic conductivity, low vapor pressure, and wider electrochemical stability windows. As discussed in Sec. III A, correlated ion motion plays a key role for ion conduction in ILs. Historically, the extent of ion correlation was estimated using the “Walden plot,” which compares the experimentally measured conductivity to the inverse of the viscosity, $\eta$. Combining the Nernst–Einstein–Sutherland relation, $D_i = k_BT/(6\pi\eta r_i)$ yields a simple relation known as Walden’s rule:

$$\Lambda \eta = \text{constant} \times \left(\frac{1}{r_i^+} + \frac{1}{r_i^-}\right), \quad (3.2)$$

where $\Lambda$ is the molar conductivity and $r_s$ represents the hydrodynamic radius of each ions. While it is not obvious to define the hydrodynamic radius of solvent-free ILs, the value of the Walden product ($\Lambda \eta$) from the aqueous KCl solution is conventionally taken as a reference value of ideal behavior. Often, the Walden product of neat ILs falls below this ideal value (poor ILs). Earlier discussions interpreted such deviations as being caused by the formation of neutral ion pairs, but recent studies have shown that the lifetime of such ion pairs is relatively short, and correlations between not only the counter-ion pairs but also the like-charged ions are important.

Solvent-free ionic PEs can also be obtained by tethering one of the ions to the polymer backbone. The tethered ion becomes essentially immobilized, producing a single-ion conductor (SIC) that can in principle achieve a high transference number close to unity. SICs typically contain neutral segments that bridge the ionizable monomers (Fig. 4), and the ion content is often low due to
synthetic reasons. A major challenge in the development of SICs is how to obtain high mobility of the cations that are unavoidably correlated with the anions attached to the polymer. Both dielectric spectroscopy and FTIR studies on PEO-based sulfonated SICs indicate that almost all sulfonate anions are complexed with their counterions as ion-pairs or ionic aggregates, resulting in substantially lower conductivity than PEO/salt mixtures. Furthermore, SICs often have high glass transition temperatures, which reduce polymer segmental dynamics and ion conduction. To understand the role of these ionic aggregates in PEO-based SICs, Winey, Colby, and co-workers and Maranas and co-workers performed x-ray and neutron scattering as well as dielectric spectroscopy experiments. The morphology and the extent of ion aggregation of the SICs were found to depend on a number of factors—size of the cation, ion content controlled by the length of the bridging PEO segment, and temperature. Surprisingly, neither the segmental dynamics of the PEO segments nor the conductivity showed strong correlation with the morphology of ion aggregation.

Coarse-grained simulation studies by Hall et al. and Milner and co-workers suggested that ion transport in these SICs is mostly mediated by ion clusters (aggregates), and a connected network of the ion clusters is essential for high conductivity.

Polymerizing IL-based ions to form polymerized ILs (PILs) has emerged as a means of reducing the ion pair interaction in SICs. One important benefit of PILs is that they often show...
lower glass transition temperature than other SICs even at a high ion content, a result of the weaker electrostatic ion-pair interaction due to the delocalized charge on the ions. Furthermore, Sangoro et al. showed that the ionic conductivity and segmental dynamics of PILs can be strongly decoupled;\textsuperscript{97} the conductivity of PILs exceeded that of non-polymerized ILs by four orders of magnitude at their respective calorimetric glass transition temperatures \( T_g \) [Fig. 5(a)]. While many strategies to decouple the ionic conductivity from the structural dynamics have been practiced in different types of PEs,\textsuperscript{17,132} Sangoro’s work\textsuperscript{97} and other recent experiments\textsuperscript{98,118–121} showed that PILs can be advantageous to achieve a high degree of decoupling. This intriguing observation can potentially enable retaining high ionic conductivity while independently manipulating the mechanical strength of the polymer.

Despite these promises of PILs, challenges remain since the conductivity in typical PILs at ambient temperature is still too low to be practical. As shown in Fig. 5(b), the absolute ionic conductivities measured in these PILs at ambient condition are considerably lower than those in the corresponding non-polymerized ILs, suggesting that the decoupling could be merely a consequence of the quenched vehicular motion in PILs. Another problem is that the apparent transference number in the PILs seems to deviate strongly from the expected value of unity. As shown in Fig. 5(c), the inverse Haven transference number \( 1/\mathcal{H}_R = \sigma_j/\sigma = D_j/D \) measured for a set of PILs with varying cation–anion pairs is very low (often under 0.1).\textsuperscript{97} The Haven ratio should be close to unity if ions were to behave ideally. The low value of the inverse Haven ratio indicates that less than 10% of the ion diffusion contributes to the net ion conduction, presumably due to strongly correlated ion motion in these PILs. Importantly, Winne and co-workers reported a PIL based on trisaminocyclopropenium (TAC) and chloride ions that can have a higher absolute conductivity than that of its monomeric counterpart at the ambient temperature [Fig. 5(d)].\textsuperscript{98} The underlying mechanism of this truly decoupled dynamics is not yet fully understood; more theoretical and experimental efforts are needed to elucidate the design principles of PEs with decoupled segmental and ion dynamics.

D. Gel electrolytes, solvated SICs, and heterogeneous PEs

Mixing multiple components with desirable properties is a common strategy to achieve both mechanical strength and high ionic conductivity. Gel electrolytes and solvated SICs are obtained by adding “plasticizers”—such as small-molecule organic solvents, oligomers, ILs, and inorganic nanoparticles—to PEs.\textsuperscript{10,123,128} Ion transport in traditional gel electrolytes is predominantly governed by the vehicular motion of the small-molecule solvated ions.\textsuperscript{127,128} While the ionic conductivity of these electrolytes is higher than dry PEs, the presence of small-molecule solvents presents other problems including lower mechanical strength, increased inflammability, and leakage of solvent molecules. Utilizing IL-based plasticizers alleviates some of these problems.\textsuperscript{129–131} Alternatively, non-ion-solvating plasticizers can be added to interact with the polymeric component so as to interrupt the ion-polymer association, thus increasing the free ion fraction,\textsuperscript{12} and to reduce the glass transition temperature of the polymer, thus enhancing the segmental dynamics.\textsuperscript{10}

In many practical applications, it is desirable to have both ionic-rich and ionic-poor domains in the same system for separate functions [schematics in Fig. 6(a)].\textsuperscript{5} In an ideal case, conductivity in such heterogeneous electrolytes (\( \sigma_h \)) can be simply determined by the ionic conductivity (\( \sigma_j \)) and volume fraction (\( \phi_j \)) of the ion-rich conducting phase and the morphology scale factor \( f \).

\[
\sigma_h = f \phi_j \sigma_j.
\] (3.3)

In the simplest approximation, the morphology factor \( f \) depends on the spatial dimension \( d \) of the conducting phase such that \( f = 3/d \); thus, \( f = 1 \) for gyroid, \( f = 2/3 \) for lamellar, and \( f = 1/3 \) for cylindrical morphologies.\textsuperscript{13}

Many exciting advances have been made by copolymerizing ion conducting polymer segments with non-ion-solvating polymer segments.\textsuperscript{17,132} One of the most studied examples is poly(styrene)-block-poly(ethylene oxide) (PS-b-PEO; also referred to as SEO)

![FIG. 6.](image-url)
copolymers doped with lithium salts,\textsuperscript{135–138} which can form in a range of morphologies by varying the volume fraction of the conducting phase.\textsuperscript{139} Interestingly, the ionic conductivity in SEEO block copolymer (BCP) PEs was found to increase with increasing molecular weight, contrary to the homogeneous PEs.\textsuperscript{135} The synergistic improvement of both ionic conductivity and mechanical strength was attributed to the uneven ion distribution and ion dynamics at the center of the ion conducting domain and near the interface of the microphase separated domains.\textsuperscript{136} A major hurdle in these microphase separated electrolytes is the lower ionic conductivity than the theoretical prediction [Eq. (3.3)],\textsuperscript{137,140} which is due to the interfacial mixing of the PEO and PS blocks\textsuperscript{138} and grain boundaries produced by microphase separation.

A wide variety of parameters can affect the ionic conductivity and the connectivity of conducting domains. Park and Balsara observed that nearly symmetric poly(styrenesulfonate-methylbutylene) (PSS-PMB) BCPs can produce enriched nanostructures ranging from disordered to cylindrical, lamellar, and gyroid, by controlling the molecular weight and the degree of sulfonation in the PSS block.\textsuperscript{137} In lithium salt-doped BCPs, salt doping was shown to lead to dramatic increases in the order-disorder transition (ODT) temperature,\textsuperscript{137,141} and change the topology of the phase diagrams,\textsuperscript{134,135} with respect to the salt-free systems. These findings inspired a large body of theoretical\textsuperscript{142–144} and experimental\textsuperscript{145–157} investigations on the role of ion concentration in determining the phase behavior of BCPs. Many other design strategies have been practiced, such as controlling the water content,\textsuperscript{141,158} aligning conducting domains with the pressure/shear/electric field,\textsuperscript{159} end-group substitution,\textsuperscript{123,124} incorporating ILs and IL-based ionomers,\textsuperscript{160–163} precise sequencing of ionic moieties,\textsuperscript{164–166} use of multivalent ions,\textsuperscript{167} and multi-block/tapered/grafhbrush/miktoarm-star copolymerization.\textsuperscript{168–170} A consistent picture arising from these studies is that microphase-separated, aligned, and co-continuous morphology is advantageous for the improvement of ion transport properties.\textsuperscript{159,172} Notably, development of a well-defined gyroid morphology with continuous ionic channels resulted in improvement in the storage modulus, ionic conductivity, and cation transference number [Figs. 6(b) and 6(c)].\textsuperscript{124}

**IV. UNIVERSAL FEATURES IN ION TRANSPORT MECHANISMS**

**A. Scaling relations of transport coefficients and microscopic timescales**

Identifying a set of universal variables that control the macroscopic ion transport properties is key to more systematic electrolyte design. A particular focus is the prediction of ion transport coefficients based on microscopic, molecular parameters. The phenomenological DBP model\textsuperscript{41} represents early theoretical efforts, which predicts a linear correlation ($\lambda = 1$) between the ion diffusion coefficient $D$ and the inverse of the characteristic timescale for statistically uncorrelated renewal events $\tau_{ren}$ through a simple diffusion equation,

$$D \sim \frac{\tau_{ren}}{\tau_{NRT}} \sim (1/\tau_{NRT})^\lambda. \quad (4.1)$$

In general, the scaling exponent $\lambda$ on the right-hand side can differ from unity.

Theoretical studies have identified ion transport mechanisms that can result in different scaling exponents. Borodin and Smith developed a microscopic model for the PEO/Li salt electrolyte based on MD simulation results and found both intra-chain diffusion and co-diffusion with the polymer segmental motion to be equally important for the overall Li$^+$ ion diffusion.\textsuperscript{35} As shown in Fig. 7(a), the ion diffusion followed Rouse-like dynamics with a power-law scaling exponent $\lambda = 0.56$ for $\tau = 1/\tau < 10$, while excluding co-diffusional ion motion with a solvating polymer segment resulted in a linear scaling with a much reduced value of diffusivity. Another study by Maitra and Heuer derived an analytic expression for $D$ as a function of three microscopic timescales for the different ion transport mechanisms, assuming the inter-segmental ion hopping time ($\tau_{hop}$) as the renewal time in the DBP model.\textsuperscript{138} The expression sets a lower and an upper bound of the scaling exponent; a linear scaling ($\lambda = 1$) is expected when ion hopping occurs slower than the intra-chain end-to-end ion transport time ($\tau_{ete} \ll \tau_{hop}$), while sublinear scaling with $\lambda = 1/2$ is predicted for large molecular weight polymers due to chain motion at the segmental level ($\tau_{ete} \gg \tau_{hop}$). These predictions qualitatively agree with the numerical results by Borodin and Smith, although the latter found a slightly larger scaling exponent of 0.56. More recent extensions of the theory\textsuperscript{132,133} predicted a crossover from vehicular motion to local motions (such as segmental co-diffusion and hopping) with increasing molecular weight, which showed quantitative agreement with experiments over a wide range of $M_w$.

More recent atomistic MD studies suggest that the dissociation of the ion–counterion pair $\tau_{D}$ is the microscopic renewal event in a range of electrolyte systems. Figures 7(b)–7(d) show results from a set of independent studies that identified a direct correlation between $D$ and $\tau_{D}$ (also denoted as $\tau_{C}$ in some figures) in pure ILs, PILs, and PIL/IL mixtures. The first such study was by Zhang and Maginn, which simulated 29 different ILs over a range of temperatures.\textsuperscript{35} As can be seen in Fig. 7(b), a linear correlation between $D$ and $1/\tau_{D}$ was found in all the tested ILs, independent of the ion size and the system temperature. Ganesan and co-workers performed a series of atomistic MD simulation studies for imidazolium based PILs and PIL/IL mixtures.\textsuperscript{8,49,173,175,176} A dominant mechanism has been found to involve ion hopping through the formation and breakage of ion-associations between an anion and multiple polymerized cationic monomers bonded to two different polymer chains, and power law scaling between the ion transport coefficients (either $D$ or $\sigma_{NE}$) and the microscopic timescale is found for both PILs and PIL/IL mixtures when measured at various temperatures and relative compositions of IL to PIL. Interestingly, in neat PIL, the scaling exponent of this diffusivity vs ion-pair correlation time showed a subtle dependence on how the lifetime of an ion pair was calculated. When a recombination of an ion-pair was counted as still correlated [$\tau_{C}$ in Fig. 7(c)], the scaling exponent was found as $\lambda = 0.57$, remarkably similar to the PEO/Li-salt mixture studied by Borodin and Smith. On the other hand, when the ion-pair lifetime only counted up to the first dissociation of the pair [$\tau_{S}$ in the inset of Fig. 7(d); note $\tau_{S} < \tau_{C}$], linear scaling between $D$ and $1/\tau_{S}$ was observed for the same neat PIL, missing the effect of segmental motion due to the short timescale. A universal power-law correlation between $\tau_{C}$ and Nernst–Einstein conductivity $\sigma_{NE}$ was claimed...
FIG. 7. Correlations between the ion diffusion coefficients and the microscopic timescales observed in computational studies of different electrolytes: (a) result from a microscopic model for PEO\textsuperscript{1−}TFSI\textsuperscript{−} PE: [b]–[f] atomistic MD results of (b) 29 different pairs of ILs, (c) PIL (polyIL) and pure IL, (d) PIL-IL mixtures, (e) PILs with varying counter ions, and (f) aqueous and small-molecule organic electrolytes. The temperature and composition of the electrolytes are also varied in [(b)–(e)] and [(d) and (f)]. $\tau = 1/r$ in (a) represents the hopping rate of a lithium cation; $\tau_{IP}$ and $\tau_c$ represent the average ion-pair association lifetime. The wt. % in (d) represents the weight percent of the PIL in the mixture. (a)–(f) are reproduced with permission from O. Borodin and G. D. Smith, Macromolecules 39, 1620 (2006). Copyright 2006 American Chemical Society; reproduced with permission from Y. Zhang and E. J. Maginn, J. Phys. Chem. Lett. 6, 700 (2015). Copyright 2015 American Chemical Society; reproduced with permission from Mogurampelly \textit{et al.}, J. Am. Chem. Soc. 139, 9511 (2017). Copyright 2017 American Chemical Society; reproduced with permission from S. Mogurampelly and V. Ganesan, Macromolecules 51, 9471 (2018). Copyright 2018 American Chemical Society; reproduced with permission from Keith \textit{et al.}, ACS Macro Lett. 8, 387 (2019). Copyright 2019 American Chemical Society; and reproduced with permission from J. G. McDaniel and C. Y. Son, J. Phys. Chem. B 122, 7154 (2018). Copyright 2018 American Chemical Society, respectively.

for both PIL/IL mixtures based on the same ion pair\textsuperscript{29} [Fig. 7(d)] and PILs with varying counterions [Fig. 7(e)]\textsuperscript{125}, although the scaling exponent and the proportionality factor were different between the two studies; in general, larger scaling exponent closer to unity was found for PILs with shorter polymer chains.

The strong correlation between $D$ and $1/\tau_{IP}$ suggests that the homogeneous dynamics of local ion-pair association/dissociation events govern the macroscopic ion transport. The linear scaling found in neat ILs and IL/PIL mixtures confirms the predictions of earlier theoretical work, since $\tau_{IP}$ in Fig. 7(b) and $\tau_c$ in Fig. 7(d) included only the monomeric ion-pairs; thus, no polymer segmental motion is involved. That essentially the same proportionality constant was observed for the different ILs implies roughly the same average travel distance of the ions, $r_{\text{avg}}$. While varying in molecular sizes, the ions in Zhang and Maginn’s study had fairly similar ion-pair distances $r_{IP}$, which might explain the observed universal constant. Importantly, $1/\tau_{IP}$ and ionic conductivity show linear correlation even in dilute aqueous and organic electrolytes dissolving an IL BMIM\textsuperscript{+}BF\textsubscript{4}\textsuperscript{−} [Fig. 7(f)],\textsuperscript{31} where the ion hopping motion is less likely; thus, the dominance of the ion-hopping induced transport mechanism inferred from the linear scaling needs to be further validated. Interestingly, in the low-dielectric solvent 1,2-dichloroethane, $1/\tau_{IP}$ showed a good linear correlation to the true ionic conductivity $\sigma$, while the correlation to $\sigma_{\text{NE}}$ was significantly weaker ($R^2 \sim 0.94$ vs $R^2 \sim 0.86$ for $\sigma$ and $\sigma_{\text{NE}}$, respectively; not shown).\textsuperscript{31} This is surprising since significant ion aggregation was observed in this electrolyte, resulting in non-homogeneous ion environments. We suggest that since only the net ionic transport is accounted in $\sigma$, the contributions are mostly from non-clustered ions that are roughly under the same local environments. On the other hand, the idealized $\sigma_{\text{NE}}$, measuring diffusion, involves the average transport of ionic clusters of different sizes, which are not under the same environment; thus, simple linear correlation was not obtained for $\sigma_{\text{NE}}$.

B. Scaling of plateau-corrected diffusion coefficient with the chain friction coefficient

Another interesting universal scaling was suggested in an experimental study by Balsara and co-workers,\textsuperscript{177} who measured the
ion diffusion coefficients in the PEO/Li salt mixture across a range of salt concentrations and molecular weights. In all salt concentrations, the ion diffusion coefficients converge to a plateau value $D_p$ as the $M_w$ of PEO increases, but the plateau value $D_p$ was concentration dependent. Remarkably, the plateau-corrected diffusion coefficient $D - D_p$ shows a strong inverse correlation with the per-chain salt concentration $s = N \cdot r$ [Fig. 8(a)] for all the samples. The molecular origin of this correlation and the physical significance of $s$ were obscure.

We propose that the salt concentration dependent monomeric friction coefficient, $\zeta(r)$, calculated in Ref. 57 can better explain this apparently universal scaling relation. Since $D_p$ characterizes the contribution to ion diffusion purely due to local mechanisms such as ion hopping and local segment co-diffusion, $D - D_p$ can be considered as characterizing the vehicular ion motion. Thus, $D - D_p$ can be expressed as simple Rouse dynamics with the salt-concentration dependent $\zeta(r)$ such that

$$D - D_p \sim \frac{k_B T}{N \zeta(r)} \sim \frac{1}{N \zeta(r)} \approx 0.085,$$  

(4.2)

where $\zeta(r) = \zeta(0) \exp(r/0.085)$ from Ref. 57 is used for the last term. As shown in Fig. 8(b), the $D - D_p$ data in Ref. 177 show good agreement with Eq. (4.2); $D - D_p$ is inversely proportional to the chain friction $N \zeta(r)$, and the correlation is especially good for the more important fast-diffusion region (small $r$), in comparison to the originally suggested correlation to $s$. We expect the first half of Eq. (4.2) to be general in other salt-doped PEs with efficient ion solvation, while the exact concentration dependence of $\zeta(r)$ can be system specific.

Webb and co-workers recently made a theoretical attempt to understand the microscopic origin of the concentration dependence of $\zeta(r)$. Fitting MD simulation data to a modified Rouse model with increased local friction due to Li$^+$ complexation that was first suggested by Heuer and co-workers, these authors found that local increases in friction alone could not simultaneously capture the magnitude of increased polymer relaxation times and the apparent power-law exponent for Li$^+$ subdiffusion observed in the simulations. By introducing an empirical quadratic salt concentration dependence on the friction coefficient, similar to the extended Jones–Dole equation, the authors were able to reproduce the MD simulation results in all tested concentrations. The resulting expression also agrees well with the experimentally measured $\zeta(r)$ in Ref. 57. An alternative approach by Wynne proposes that the solution viscosity and $\zeta(r)$ follow the Vogel–Fulcher–Tamann (VFT) type expression consistent with the one used in Ref. 57,

$$\zeta(r) \approx \frac{m}{N_0} \exp(A + Br),$$  

(4.3)

where $r = \text{Li}^+/\text{O}$, $x = r/(3 + r)$ for Li$^+$ in PEO, $m$ is related to the fragility parameter in glass transition, and $N_0$ is the critical concentration related to a jamming transition caused by salt-induced structuring of the solvation shell. An advantage of the VFT-type expression is that it can be related to changes in the glass transition temperature of the PE due to the addition of lithium salts. While the exact functional form of $\zeta(r)$ needs to be validated by experiments at higher salt concentrations, both theories suggest that the formation of the solvation shell due to the strong ion-polymer interactions can induce nonlocal changes in the polymer dynamics.

Separating the contributions to ion dynamics into the whole molecular motion represented by $D - D_p$ and that from the local motion represented by $D_p$ can also explain the “decoupling” of ion transport from polymer segmental dynamics observed in many PILs. As shown in Fig. 5(a), the temperature dependence of the ionic conductivity and the viscosity in pure ILs follows VFT-type super-Arrhenius behavior, implying the dominant role of molecular/vehicular ion transport, i.e., continuous diffusion of small molecular ions and co-diffusion of ion pairs. On the other hand, polymerizing ILs to form PILs suppresses this molecular/vehicular motion almost completely, resulting in an Arrhenius behavior, indicating an homogeneous activated process, which depends on the local motion only ($D_p$). Thus, the reported “decoupling” in many PILs presented against the $T_g$-normalized temperature ($T_g/T$) is largely caused by suppressed vehicular motion and increased $T_g$ of the PILs without actual enhancement of the ion transport. Indeed, the absolute ionic conductivity in these PILs is much lower than that in their monomeric counterparts at the same absolute temperature [Fig. 5(b)]. An important exception is a PIL based on the TAC-CI ions, which showed a higher ambient temperature conductivity than the monomeric IL [Fig. 5(d)]. Here, the connected cation chain has to offer certain benefit to the hopping/segmental based

\[ \text{FIG. 8. Plateau-corrected diffusion coefficient } D - D_p \text{ is plotted against (a) per-chain salt concentration } s = N \cdot r \text{ and (b) chain friction coefficient } N \cdot \zeta(r) \zeta(0) \text{ on a semi-log plot. The dotted line is a fit to an inverse proportionality, } D - D_p \approx x^{-1 \cdot}, \text{ where } x \text{ is the chosen value of the abscissa. (a) is reproduced with permission from Timachova et al., Macro-} \]

molecules \text{ 48, 7882 (2015). Copyright 2015 American Chemical Society. (b) is generated using the same data as (a).}
local ion motions. We anticipate further studies aimed at understanding the microscopic mechanisms of this true decoupling in this PIL.

V. CHALLENGES AND OUTLOOKS

A. Negative transference number in strongly correlated systems

Achieving high cation transference number electrolytes (HTNCEs) is an important goal for improved energy and power density of lithium ion batteries.\(^{153}\) As demonstrated by Newman and co-workers, near unity \(t^+\) offers significantly improved performance, particularly at higher rates of discharge, even with an order of magnitude decrease in conductivity.\(^{183}\) Despite its importance, a rigorous characterization of \(t^+\) is still challenging. While approximate methods (both experimental and computational) to obtain \(t^+\) assuming ideal electrolyte behavior are widely used, they are not expected to be applicable to high-concentration electrolytes and strongly correlated systems where ion clustering and correlated ion motion are prevalent.\(^{184}\) At high enough concentrations, early studies of aqueous zinc halides showed that \(t^+\) can even become negative.\(^{185}\) A common explanation of the negative \(t^+\) in zinc electrolyte is based on the formation of complex anions (i.e., ion clusters with net negative charges),\(^{186,187}\) which has been confirmed by the Raman spectral signal of \(\text{ZnCl}_2(\text{H}_2\text{O})^+\) in the electrolyte.\(^{188}\)

Unlike the aqueous zinc electrolyte, recent discussions on the negative transference number observed in IL mixtures\(^{189}\) and PEs\(^{190}\) highlight the complication in measuring \(t^+\) in highly correlated systems using different experimental techniques. Earlier studies of most \(\text{Li}^+\) containing non-aqueous liquid electrolytes reported \(t^+\) values between 0 and 1 regardless of the method used for the measurement.\(^{190}\) Recently, Gouverneur, Schmidt, and Schönhoff found that a set of ternary mixtures of \(\text{Li}\) salt and an IL with the same anion shows negative effective \(t^+\) measured by electrophoretic NMR (eNMR), which can directly measure the ion mobility even involving correlated motion.\(^{32}\) As shown in Fig. 9, the average drift of \(\text{Li}^+\) is in the same direction as that of the anion, indicating strongly correlated ion motion or formation of complex anions. However, the proper reference frame to measure the transport coefficients has been debated by different groups.\(^{191,192}\) The existence of persistent ion pair and ion clusters in ILs and IL mixtures is also controversial\(^{193,194}\) since the apparent lifetime of an ion pair in common ILs is relatively short and complexation of multiple bulky anions such as TFSI\(^-\) with a single lithium cation needs further evidence.

A negative \(t^+\) in PE was first reported by Newman and co-workers in PEO/Na salt mixtures,\(^{32}\) followed by a series of findings in other PEs containing sodium or lithium salts.\(^{63,64,195–197}\) As shown in Fig. 3(c) from the systematic comparison of the PEO/\(\text{Li}^+\)/TFSI\(^-\) mixture by Pesko et al.,\(^{189}\) the widely used steady-state based method \((t^+,\text{SS})\) and PFG-NMR based method \((t^+,\text{NMR})\) both show fairly constant positive \(t^+\) throughout a range of salt concentrations, consistent with the near-ideal behavior of the ion transport (cf. Sec. III B), but the method by Newman and co-workers \((t^+,\text{NC})\) shows a nonmonotonic change with concentration—increasing from positive \(t^+\) and then decreasing to negative \(t^+\). It is evident that the ideal solution approximation in the former two methods cannot explain the negative \(t^+\), which would originate from correlated ion motion and ion clusters. While the method of Newman and co-workers considers correlated ion motion based on concentrated solution theory, the recent study by Rosenwinkel and Schönhoff shows only positive \(t^+\) for a similar PEO/\(\text{Li}^+\)/TFSI\(^-\) mixture.\(^{190}\) In their study, \(t^+\) was obtained with electrophoretic NMR (eNMR) measurements, which can directly measure the ion mobility including correlated motion. The origin of these contradictions remains to be understood.

Complimentary computational studies to unambiguously characterize correlated ion motion and the true \(\sigma\) and \(t^+\) are thus highly desirable, but most MD studies have focused on the idealized \(\sigma^{\text{E}}\) and \(t^{+\text{E}}\) due to the computational cost. Nevertheless, the true \(\sigma\) and \(t^+\) based on Eqs. (2.1) and (2.3) are increasingly being analyzed in pure ILs,\(^{199}\) aqueous and organic electrolytes,\(^{210}\) IL mixtures,\(^{211–213}\) dilute polyelectrolyte solutions,\(^{214}\) and PEO/Li salt mixtures.\(^{34}\) In many cases, the calculated \(t^+\) values significantly deviated from \(t^{+\text{E}}\), indicating an important role of correlated ion motion. Moreover, negative values \(t^+\) are observed in very recent MD studies of the PEO/\(\text{Li}^+\)/TFSI\(^-\) mixture\(^{216}\) and a sodium salt/IL mixture.\(^{217}\) While these studies offer valuable insights into the complex ion correlations, care must be taken since some of the models used\(^{215,216}\) are known to produce incorrect ion aggregation/phase behavior because electronic polarization is not properly accounted for.\(^{218,219}\) Validations using long-timescale simulations with more rigorous models are highly desirable. The recent development of fully first-principles based multiscale models for IL/polymer mixtures\(^{220,221}\) and a new approximation to \(\sigma\) accounting for ionic aggregates\(^{222}\) are promising progress toward computational characterization of the true \(\sigma\) and \(t^+\). We also note that all simulation studies we have discussed thus far were performed at equilibrium conditions; thus, the computed transport coefficients are only applicable in the linear response regime. It is necessary to understand how the apparently negative transference number is manifested in real devices. Thus, simulation studies under realistic device conditions are highly desirable, which must incorporate the nonequilibrium flow generated by the external electric field/concentration gradient while capturing the molecular transport mechanisms.

![FIG. 9. The electrophoretic mobility in the ternary Li/IL mixture in the dependence of the lithium salt concentration. Black squares: \(\text{H}^+\) (EMIM\(^+\)), red circles: \(\text{19F}^-\) (TFSI\(^-\)), and blue triangles: \(\text{Li}^+\). Reproduced with permission from Gouverneur et al., Phys. Chem. Chem. Phys. 20, 7470 (2018). Copyright 2018 Royal Society of Chemistry.](image-url)
B. Systematic control of transport mechanisms through precision synthesis

Precision synthesis of the chemical structure of monomer units and the sequence of the polymer chain is an emerging approach to controlling the ion transport mechanisms for systematic PE design. In a series of combined experimental and theoretical studies, Miller, Balsara, and co-workers systematically investigated a set of polyether and polyester based PEs by varying the length and functional groups in the backbone and side chains [Fig. 10(a)].114,115,197-200 Interestingly, the ionic conductivity of polyester based PEs was much lower than the polyether based PEs, and within the polyester based PEs, the conductivity did not show strong correlation to the segmental dynamics of the polymers as measured by $T_g$. Molecular dynamics simulations revealed that while the dominant transport mechanism (lithium ion hopping between adjacent solvation sites) was identical in both classes of PEs, the connectivity of these solvation sites was significantly reduced in the polyester based PEs than in PEO. A quantification of the solvation site connectivity from simulations was suggested, which showed strong correlation with the experimentally measured ionic conductivity when the differences in $T_g$ of the polymers were properly accounted for [Fig. 10(a)].201 A more recent study of polycarbonate based PEs with varying alkyl side chains also supported the dominant role of solvation site connectivity, where increased chain flexibility (lower $T_g$) actually resulted in a lower ionic conductivity due to the disruption of the conducting pathways by the non-ion solvating side chains.202 While a promising polyether was identified to show promising transport properties,203 to date, none of the newly synthesized polyester and polyether based PEs exhibited overall improved performance over the unperturbed PEO under typical battery operating conditions.

Successful improvement in ionic conductivity over PEO at room temperature can be achieved by preventing the crystallization of PEO, which occurs at 65 °C, as demonstrated by Barteau et al.212 Figure 10(b) shows the structure of the synthesized PEs and their conductivity measurement data. The key component to prevent crystallization was poly(allyl glycidyl ether) (PAGE), which has lower conductivity than PEO at high temperatures ($T > 350$ K) but more than an order of magnitude higher conductivity at room temperature. The brush-like side chain of the AGE monomer was considered responsible for disrupting the crystal packing, which motivated synthesizing a set of polymers with different spacings and lengths of the side-chain by controlled placement of AGE and EO monomers. Several electrolytes with superior properties are observed, where increasing EO content, in general, increased the overall conductivity while at least 20% of AGE was required to disrupt crystallization at room temperature. Among the tested PEs, P(EO$_3$-co-AGE) [structure shown in Fig. 10(b)] with relatively short side-chains that are separated by three EO monomers on average showed the best performance.

Precision control of the sequence of repeating units has also been utilized to manipulate the self-assembled morphology of PE, similar to the secondary and higher-order structures in biomolecules. In a series of studies, Winey and co-workers created polyethylenes containing acid groups that are placed at precisely periodic intervals.204,205-211 As schematically illustrated in Fig. 10(c), these polymers formed a highly ordered layered structure consisting of crystalline polyethylene domains folded at the acid functional groups. At very high humidity, the hydrated acid layer provided high proton conductivity exceeding that of Nafion 117 in certain sulfonate based PE [structure shown in Fig. 10(c)].212 A more recent study reported that other structures including gyroid and...
hexagonal morphologies can be formed by changing the counterions of the sulfonate acid group and the temperature, adding new pathways to designing SICs with improved ion transport.\textsuperscript{217}

C. Development of chemically specific theoretical models

Theoretical/computational studies have played a major role in understanding ion transport in both small-molecule and polymer electrolytes. Phenomenological and coarse-grained (CG) models based on key physical parameters (such as van der Waals and Coulomb interactions, solvent dielectric constant, and chain connectivity) have established some general ion transport mechanisms and provided useful insights for electrolyte design. However, these simulation results should not be interpreted as faithfully reflecting the actual behavior of the experimental systems since simulation models may not capture all the essential physics, and the quantitative predictions are sometimes based on parameters that can be quite different from the experimental conditions. For example, in CG simulations, the extent of ion aggregation in salt-doped PEs is governed by the bulk dielectric constant.\textsuperscript{203} However, it is difficult to connect the dielectric constant to the chemical structure of the polymers a priori. As the chemical diversity and complexity of electrolyte systems are rapidly expanding, limitations of these conventional simulation models are becoming more apparent, requiring further development of sophisticated models to capture the chemical specificity.

Electronic polarization is one of the key physics that is missing in many simulation studies of charged systems.\textsuperscript{219} A popular approach to implicitly treat electronic polarization is to reduce the charge of ions to account for the dielectric effect due to electronic polarization.\textsuperscript{220} While these “scaled charge models” have been successful in reproducing many of the properties of pure ILs, the reduced charge significantly alters the cohesive energy of ion pairs and clusters,\textsuperscript{204} resulting in qualitatively wrong predictions of phase behavior in high-concentration electrolytes\textsuperscript{204} and polymer electrolytes.\textsuperscript{203} Many explicitly polarizable models have been successfully applied to study small-molecule and polymer electrolytes,\textsuperscript{219,221-223} which found the important role of the many-body polarization effect on numerous systems, such as quantitative prediction of ion dynamics,\textsuperscript{223} interfacial ion distribution,\textsuperscript{224,225} phase behavior of IL/polymer mixtures,\textsuperscript{203} and nonequilibrium behavior under the external electric field,\textsuperscript{226} to name a few. The pioneering works by Borodin and co-workers\textsuperscript{24,43,227,228} illustrate how the development and use of polarizable models helped to understand the key ion transport mechanisms in dry salt-doped PEs. A growing number of explicitly polarizable models are being reported for ionic materials; thus, it is highly desirable to retest the validity of previous simulation studies with these newly developed polarizable models, especially for systems involving high-concentration salts in low dielectric environments.\textsuperscript{203} Care must be taken when analyzing quantitative dynamics from the simulations with polarizable models as conventional temperature control algorithms can be flawed in their prediction of dynamic properties of non-rigid small-molecules including most ILs.\textsuperscript{203}

Despite the increase in computational power and advanced simulation algorithms, simulating PEs with fully atomistic and polarizable force fields is still intractable because of large system sizes and slow chain conformational relaxation. Multiscale simulation approaches are thus required to address the different aspects of electrolyte properties in multiple levels of resolution.\textsuperscript{219} A critical issue is how to construct consistent models that capture important physics in different resolution. A strategy that is increasingly employed is to construct phenomenological models based on short atomistic MD simulations;\textsuperscript{219} the MD simulation provides the chemical specificity to the phenomenological model, while the latter enables access to much longer timescales that are inaccessible with atomistic MD.\textsuperscript{204} Additionally, coarse-graining resolution may require defining new effective interaction potentials to mimic physicochemical properties naturally arising collectively from the pairwise interactions in atomistic models such as ion solvation.\textsuperscript{204} Another emerging approach is proposed by Son et al., which is to construct multiscale models directly from the same quantum mechanical calculations.\textsuperscript{220,222} These SAFT-FF predicted static and dynamic properties of ILs and IL/polymer mixtures are in quantitative agreement with experimental results and showed great transferability across multiple electrolyte systems without requiring any adjustable parameters.\textsuperscript{212} Further expansion of such predictive multiscale models, especially for lithium and other small ions is desirable, but some challenges, such as incorporating strongly directional multi-body interactions, need to be overcome.\textsuperscript{217}

VI. CONCLUDING REMARKS

Recent studies of concentrated small-molecule electrolytes and polymer electrolytes for the next-generation energy storage have not only led to the discovery of new electrolyte materials with promising properties but also contributed to our understanding of ion transport in diverse environments. In this perspective, we have illustrated how the changes in the ion solvation environment and the relevant timescales can be used to systematically describe different ion transport mechanisms, to link macroscopic transport coefficients to microscopic timescales, and to understand many non-ideal solution behaviors observed in these electrolytes. Due to the strong solvent–ion interactions, increasing salt concentration induces a rapid increase in solvent viscosity and local friction in the small-molecule electrolytes and dry salt-doped PEs, respectively, resulting in a non-monotonic change in ionic conductivity. Ion-pairing and correlated ion motion play important roles in ILs and SICs, where direct correlation is found between the lifetime of the microscopic ion-pair and the macroscopic transport coefficient. The competition between independent transport (intra-chain motion or intersegmental hopping) vs co-diffusional (vehicular or polymer segmental) ion motion with the solvating polymer produces interesting molecular weight dependence of the ionic conductivity in PEs. Constructing BCPs with heterogeneous solvation ability forms diverse morphologies with nanoconfined conducting PE domains, which provides a promising route to designing new electrolytes with superior properties.

In addition to reviewing recent progress in ion transport in a diversity of electrolytes, we have attempted to provide a new theoretical perspective that unifies previous experimental/theoretical findings in terms of simple scaling relations. The strong similarity in the scaling relation between the ion transport coefficients and the ion association timescales found in organic electrolytes, ILs,
salt-doped PEs, PILs, and IL/PIL mixtures suggests that homogeneous and local ion dynamics dominate the transport in all these electrolytes. Similarly, the salt concentration effect on ion diffusion in PEs is shown to be primarily due to the concentration-dependent monomeric friction coefficient, \( \zeta \), and the good inverse scaling between the plateau-corrected diffusion coefficient \( D_p \) and the chain friction \( N(r) \) affords a more natural and consistent interpretation of \( D - D_p \) as reflecting the vehicular contribution to ion transport. These new insights can help better explain and understand the empirically observed universal-like scaling in ion transport and polymer dynamics in previously reported experiments and computer simulation studies.

Looking ahead, there are many challenges and opportunities for better understanding and optimization of ion transport in small-molecule and polymer electrolytes. The controversy over the negative transference number observed in IL mixtures and salt-doped PEs calls for better understanding of the existing characterization techniques or developing new ones. Predictive computational models can provide the definitive molecular picture to help resolve the disagreement in the literature. However, this requires improved computational models that can faithfully capture all the essential physics in the system; the recent developments in polarizable force fields are important steps toward constructing such models. Sophisticated synthetic methods have led to the creation of PEs with highly tunable ion transport properties, approaching industrially viable room temperature ionic conduction. The ability to rapidly screen the diverse chemical space with efficient multiscale models can significantly accelerate the design of new electrolytes. Synergistic collaboration between experimental and computational studies, as well as parallel and comparative studies in both small and polymer electrolytes, is expected to yield new insights into the ion transport mechanisms and expedite the next revolution in energy storage.

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DATA AVAILABILITY

All data except those in Fig. 8(b) were from published literature, with the references given in the figure captions. Figure 8(b) was generated from the data in Fig. 8(a) (taken from Ref. 177) using Eq. (4.2). These data are available from the authors upon request.

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