Importance of the Ion-Pair Lifetime in Polymer Electrolytes

Harish Gudla, Yunqi Shao, Supho Phunnarungsi, Daniel Brandell, and Chao Zhang*

ABSTRACT: Ion pairing is commonly considered as a culprit for the reduced ionic conductivity in polymer electrolyte systems. However, this simple thermodynamic picture should not be taken literally, as ion pairing is a dynamical phenomenon. Here we construct model poly(ethylene oxide)--bis(trifluoromethane)sulfonimide lithium salt systems with different degrees of ion pairing by tuning the solvent polarity and examine the relation between the cation--anion distinct conductivity $\sigma_{\Delta}^{+}$ and the lifetime of ion pairs $\tau_{\Delta}$ using molecular dynamics simulations. It is found that there exist two distinct regimes where $\sigma_{\Delta}^{+}$ scales with $1/\tau_{\Delta}$ and $\tau_{\Delta}$, respectively, and the latter is a signature of longer-lived ion pairs that contribute negatively to the total ionic conductivity. This suggests that ion pairs are kinetically different depending on the solvent polarity, which renders the ion-pair lifetime highly important when discussing its effect on ion transport in polymer electrolyte systems.

On pairing in electrolyte solutions results from a delicate balance between ion-solvent and ion-ion interactions. One common approach to define an ion pair is to use Bjerrum's criterion, in which the distance $r_{\Delta}$ is smaller than the effective range of $-q_{\Delta} q_{\Delta}/2e \kappa_{0} T$ (half of the Bjerrum length) with $\varepsilon$ as the dielectric constant of the solution, $q_{\Delta}$ and $q_{\Delta}$ being the ionic charges, the Boltzmann constant $k_{B}$, and the temperature $T$. Bjerrum's criterion suggests that the solvent polarity plays a critical role in the formation of ion pairs, rendering a distinction between contact ion pairs (CIIPs) and solvent-separated ion pairs (SSIPs). In addition, it implies that the formation of pairs of equal ionic species is unlikely to occur due to the electrostatic repulsion but that the possibility of forming triplets or larger aggregates, for example, an anion--cation--anion cluster, cannot be excluded.

The idea that ion pairing affects the ionic conductivity was introduced early on by Arrhenius, who ascribed the decrease of the equivalent conductivity at a higher concentration to the formation of charge-neutral ion pairs. This idea has been put forward using the molar conductivity ratio $\Lambda_{EIS}/\Lambda_{NMR}$ measured by electrochemical impedance spectroscopy (EIS) and pulse-field gradient NMR to quantify the ionicity (the degree of dissociativity), particularly for ionic liquids and polymer electrolytes. Nevertheless, it has been realized that deviations of the ionic conductivity from the Nernst–Einstein relation cannot solely be attributed to the formation of ion pairs, where other factors such as the hydrodynamic interactions manifested via viscosity can play an important role.

To describe the effect of ion pairing on the ionic conductivity, one needs an observable that can be accessed both theoretically and experimentally. The key quantity used here is the cation--anion distinct conductivity $\sigma_{\Delta}^{+}$ from liquid-state theory. 

$$\sigma_{\Delta}^{+} = \lim_{t \to \infty} \frac{1}{3 k_{B} T \Omega} \left| \sum_{i,+} \sum_{j,-} \langle q_{i,+} q_{j,-} \Delta r_{i,+}(t) \cdot \Delta r_{j,-}(t) \rangle \right|$$

where $\Omega$ is the volume of the system, and $\Delta r(t)$ is the displacement vector of each ion at time $t$. Note that $\sigma_{\Delta}^{+}$ is experimentally measurable and directly related to the Onsager transport coefficient $\Omega_{\Delta}$. Somewhat unexpectedly, $\sigma_{\Delta}^{+}$ is often found positive (instead of negative as in Arrhenius’ picture) in different types of electrolyte systems, spanning categories from aqueous electrolyte solutions to polymer ionic liquids. This suggests that the existence of ion pairs, as evinced by a number of spectroscopic experiments, does not necessarily imply a negative contribution to the measured ionic conductivity but can instead contribute to an increase in the transport of ions. Therefore, understanding the ion pairing effect on polymer electrolytes is crucial, as their application in energy storage systems is largely limited by a low ionic conductivity.

The crucial point to this conundrum lies in the fact that Bjerrum’s convention is a thermodynamic criterion, while the ionic conductivity is a dynamical property. Therefore, the lifetime of charge-neutral ion pairs needs to be considered.

Received: July 29, 2021
Accepted: August 25, 2021
Published: August 27, 2021
explicitly when discussing the contribution of ion pairing to the ionic conductivity, in addition to the distance criterion due to the thermodynamic stability. In other words, an ion pair should be "long-lived enough to be a recognizable kinetic entity." Theoretically, the lifetime of ion pairs $\tau_{+−}$ can be extracted from the normalized time correlation function of the cation−anion pairs in molecular dynamics (MD) simulations:

$$f_{\text{SSP}}(r_{ij}; s) = \prod_{i<j} \theta(r_{c,\text{prod}} - r_{ij}(t))$$

(4)

where $r_{c,\text{prod}}$ is the product SSP boundary, which corresponds to the cation−anion distance at the half height of the second peak in the radial distribution function (RDF). Then, $r_c$ in eq 2 should be replaced by the reactant SSP boundary $r_{c,\text{react}}$ which is at the first maximum of the cation−anion RDF.

To investigate the relation between $\sigma_{+−}$ and $r_{c,\text{react}}$ in polymer electrolyte systems, we constructed simulation boxes consisting of 200 poly(ethylene oxide) (PEO) polymer chains each with 25 ethylene oxide (EO) repeating units and 400 bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) ([Li$^+$]/[EO] concentration = 0.08). As indicated by Bjerrum’s criterion, the solvent polarity strongly modulates the ion pairing. This motivated us to apply the charge scaling method to PEO molecules to change the degree of ion pairing. General AMBER force field (GAFF) parameters were used for describing bonding and nonbonding interactions in PEO and LiTFSI, and all MD simulations were performed using GROMACS 2018.1. All systems were properly equilibrated to make sure that the simulation length is larger than the Rouse time of the polymer. Details for the system setup and MD simulations can be found in the Supporting Information Section A.1.

Before discussing our main result, it is necessary to check how structural and transport properties change when we tweak...
the handle of the solvent polarity. Here, the solvent polarity is described by the dielectric constant of the system \( \varepsilon_P \) which was computed for each polymer electrolyte system (see Section A.2 in the Supporting Information for details).

The RDFs of Li–N(TFSI) are plotted in Figure 1a, where peaks in the Li–N(TFSI) RDF increase significantly when \( \varepsilon_P \) becomes smaller. This is a sign of formation of ion pairs, which is also evinced in Figure 2. Accordingly, there is an optimal value in the total Green–Kubo conductivity \( \sigma_{G-K} \) when the solvent polarity is modulated as seen in Figure 1b. Both of these results support our previous observations of the effect of solvent polarity on the Li\(^+\) transportation in PEO-LiTFSI systems\(^{42,43,44} \) and agree with other recent studies of polymer electrolyte systems.\(^{23,26,45,47} \)

Figure 1c,d, however, demonstrates novel phenomena. The lifetime of ion pairs increases when \( \varepsilon_P \) is either high or low, and it reaches a minimum at the intermediate value of \( \varepsilon_P \) (see Section A.3 in the Supporting Information for further details of calculations of the lifetime of ion pairs and a comparison of outcomes from eq 3 and eq 4). Inspecting Figure 1b,c, one may attempt to relate the opposite trend shown in the total ionic conductivity \( \sigma_{G-K} \) to that of \( \tau_{+-} \). However, the lifetime increases much more rapidly at a lower dielectric constant regime \( \varepsilon_P < 2.3 \) in comparison to that at a higher dielectric constant regime \( \varepsilon_P > 3 \). This suggests that there are different types of ion pairs in polymer electrolyte systems under investigation here. Looking at the cation–anion distinct conductivity \( \sigma_{+-}^{d} \), one can clearly see that it goes from positive to negative when \( \varepsilon_P \) becomes smaller. (Note that \( \sigma_{+-}^{d} > 0 \) corresponds to anticorrelated cation–anion movements for the sign convention used in this work.) In particular, the rapid decrement in \( \sigma_{+-}^{d} \) at lower \( \varepsilon_P \) seems in accord with the rapid increment in \( \tau_{+-} \). These observations also point to the direction that these two key properties of ion pairs, namely, \( \sigma_{+-}^{d} \) and \( \tau_{+-} \), must be closely related.

This leads to our main result shown in Figure 3. What we find is that there exist two distinct regimes: \( \sigma_{+-}^{d} \) scales with \( 1/\tau_{+-} \) (for higher values of \( \varepsilon_P \)), and \( \sigma_{+-}^{d} \) scales with \( \tau_{+-} \) (for lower values of \( \varepsilon_P \)). Moreover, the transition between these two regimes shows a combined feature. Therefore, the general scaling relation we propose for polymer electrolyte systems is

\[
\sigma_{+-}^{d} = \frac{A}{\tau_{+-}} + B \tau_{+-}
\]

(5)

where both \( A \) and \( B \) are system-dependent coefficients. Therefore, what matters to discussions of the ion-pairing effect on transport properties in polymer electrolytes is not whether ion pairs are present or not in the system but how long they live. By establishing the scaling relation for ion pairs from MD simulations, one could predict the lifetime of ion pairs using the measured value of \( \sigma_{+-}^{d} \) in experiments.\(^{27} \)

Then, the immediate question that appears is, Why do shorter-lived ion pairs scale with \( 1/\tau_{+-} \) while longer-lived counterparts scale with \( \tau_{+-} \)? The first scaling relation seems rather general, as already observed in ionic liquids, organic electrolytes, polymer ionic liquids, and salt-doped homopolymers.\(^{23,26,45,47} \) This is reminiscent of the Walden rule or the Stokes–Einstein relation. The second scaling relation we find in this work is a consequence of that \( \tau_{+-} \) computed from the SSP method is equal to the inverse of the reactive flux rate constant \( 1/k_{RF} \) for the ion-pair dissociation, and \( 1/k_{RF} \) is proportional to the concentration of ion pairs from the law of mass action. Since \( \sigma_{+-}^{d} \) is also proportional to the number of ion pairs, this leads to the observation that \( \sigma_{+-}^{d} \) scales linearly with \( \tau_{+-} \).

It is worth mentioning that \( \sigma_{+-}^{d} \) includes both contributions from the longer-lived ion pairs and the remainder. This suggests that one could further separate these two contributions for longer-lived pairs

\[
\sigma_{+-}^{d,\text{pairing}} = \lim_{\tau_{+-} \to 0} \frac{1}{3d_{i}k_{B}TQ} \sum_{j,+} \sum_{j,-} \langle q_{j,+} q_{j,-} \Delta r_{j,+}(t) \Delta r_{j,-}(t) \rangle_{\tau_{+-}}, \Delta r_{j,+}(t) \rangle
\]

f_{SSP}(\tau_{+-}, s) \]

(6)

where \( f_{SSP} \) is the same function given by eq 4. Then, the contribution from the remainder is simply \( \sigma_{+-}^{d,\text{nonpairing}} = \sigma_{+-}^{d} - \sigma_{+-}^{d,\text{pairing}} \). Here, the parameter \( s \) is chosen to be 2 ns, as decided by the convergence of the conductivity calculation (see Section A.4 in the Supporting Information).

The result of this decomposition is shown in Figure 1d. The \( \sigma_{+-}^{d,\text{pairing}} \) remains zero until a lower value of \( \varepsilon_P \). This agrees with the appearance of longer-lived ion pairs as seen in Figure 1c. More interestingly, in the presence of longer-lived ion pairs, the \( \sigma_{+-}^{d,\text{pairing}} \) is negative, but the \( \sigma_{+-}^{d,\text{nonpairing}} \) is positive instead. To understand why, we made a toy model of a NaCl solution where all Na–Cl ions are paired up with holonomic constraints. Details for the system setup and MD simulations can be found in Section B of the Supporting Information.

Mean square charge displacements (MSCD, i.e., quantities inside the square bracket in eq 1 and eq 6) of this toy model are shown in Figure 4, for the total ionic conductivity \( \sigma_{G-K} \) self-conductivities \( \langle \sigma_{++} + \sigma_{--} \rangle \), and the sum of cation–cation and anion–anion distinct conductivities \( \langle \sigma_{++}^{d} + \sigma_{--}^{d} \rangle \) as well as \( \sigma_{+-}^{d,\text{pairing}} \) and \( \sigma_{+-}^{d,\text{nonpairing}} \). Since all Na–Cl ion pairs are permanent by construction, the total ionic conductivity as the sum of all these individual contributions mentioned above must be zero (i.e., the slope of the MSCD “total” is zero), as evinced in Figure 4. Moreover, self-conductivities \( \langle \sigma_{++} + \sigma_{--} \rangle \)
should be exactly the negative of the direct part of the cation–anion distinct conductivity $\sigma_{+,-}^{d}$, as seen also in Figure 4. On the basis of these considerations, we know that the sum of $\sigma_{+,+}^{d}$, $\sigma_{+,-}^{d}$, and $\sigma_{-,-}^{d}$nonpairing is zero as well. As shown in Figure 4, $\sigma_{+,-}^{d}$ and $\sigma_{-,-}^{d}$ are negative, while $\sigma_{+,-}^{d}$nonpairing is positive in the toy model with permanent ion pairs. This provides a rationale to the opposite signs of $\sigma_{+,-}^{d}$pairing and $\sigma_{+,-}^{d}$nonpairing as seen in Figure 1d of PEO-LiTFSI systems. Nevertheless, one should be aware that the situation with ion aggregates will be different, as $\sigma_{+,-}^{d}$ and $\sigma_{+,-}^{d}$ could be positive instead.

To sum up, following Bjerrum’s criterion, we have constructed PEO-LiTFSI systems in our MD simulations with different degrees of ion pairing by modulating the solvent polarity. What we found is that there exist two distinct regimes where the cation–anion distinct conductivity $\sigma_{+,-}^{d}$ scales with $1/\tau_{+,-}$ and with $\tau_{+,-}$ respectively. The linear scaling of $\sigma_{+,-}^{d}$ with respect to the lifetime of the ion pairs $\tau_{+,-}$ is a signature of longer-lived ion pairs that reduce the total ionic conductivity. By establishing this scaling relation, one could infer the lifetime of ion pairs from the experimentally measured cation–anion distinct conductivity. This further suggests that what matters to discussions of the ion-pairing effect on transport properties in polymer electrolytes is not the presence of ion pairs but the corresponding lifetime.

In the scaling relation we found in our MD simulations (eq 5), the coefficient $A$ is positive, which suggests anticorrelated movements of cation–anions and shorter-lived ion pairs. This hints that ion aggregates analyzed in previous MD studies of the PEO-LiTFSI system would not populate in this scenario, in line with conclusions drawn from other experimental works for polymer electrolytes. Nevertheless, it is worth noting that early experiments on aqueous ionic solutions show that $\sigma_{+,-}^{d}$ can flip the sign from negative (correlated) to positive (anticorrelated) when the salt concentration is increased, which is intriguing. This clearly indicates that the cation–anion distinct conductivity $\sigma_{+,-}^{d}$ is a sensitive probe to the convoluted ion–ion correlations, which calls for further investigations from both experiments and simulations to understand its nature and its relationship with other static and dynamical properties in electrolyte systems.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.1c02474.

Descriptions of the setup and MD simulations of PEO-LiTFSI systems and NaCl solution with permanent ion pairs (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Chao Zhang — Department of Chemistry-Ångström Laboratory, Uppsala University, 75121 Uppsala, Sweden; orcid.org/0000-0002-7167-0840; Email: chao.zhang@kemi.uu.se

**Authors**

Harish Gudla — Department of Chemistry-Ångström Laboratory, Uppsala University, 75121 Uppsala, Sweden

Yunqi Shao — Department of Chemistry-Ångström Laboratory, Uppsala University, 75121 Uppsala, Sweden

Supho Phunnarungsri — Department of Chemistry-Ångström Laboratory, Uppsala University, 75121 Uppsala, Sweden

Daniel Brandell — Department of Chemistry-Ångström Laboratory, Uppsala University, 75121 Uppsala, Sweden; orcid.org/0000-0002-8019-2801

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work has been supported by the European Research Council (ERC), Grant No. 771777 “FUN POLYSTORE”, and the Swedish Research Council (VR), Grant No. 2019-05012. The authors are thankful for the funding from the Swedish National Strategic e-Science program eSSENCE and STAndUP for Energy. The simulations were performed on the resources provided by the Swedish National Infrastructure for Computing (SNIC) at NSC, PDC, and UPPMAX.

**REFERENCES**

(1) Marcus, Y.; Hefter, G. Ion pairing. Chem. Rev. 2006, 106, 4585–4621.

(2) Macchioni, A. Ion pairing in transition-metal organometallic chemistry. Chem. Rev. 2005, 105, 2039–2074.

(3) Rehm, T. H.; Schmuck, C. Ion-pair induced self-assembly in aqueous solvents. Chem. Soc. Rev. 2010, 39, 3597–3611.

(4) Brak, K.; Jacobsen, E. N. Asymmetric ion-pairing catalysis. Angew. Chem., Int. Ed. 2013, 52, 534–561.

(5) Rajput, N. N.; Qu, X.; Sa, N.; Burrell, A. K.; Persson, K. A. The coupling between stability and ion pair formation in magnesium electrolytes from first-principles quantum mechanics and classical molecular dynamics. J. Am. Chem. Soc. 2015, 137, 1–10.

(6) Huang, Y.; Liang, Z.; Wang, H. A dual-ion battery has two sides: the effect of ion-pairs. Chem. Commun. 2020, 56, 10070–10073.

(7) Bjerrum, N. Untersuchungen über Ionenaussaatat. I. Kgl. Danske Vid. Selskab. Math.-Fys. Medd. 1926, 7, 1–48.

(8) Evans, J.; Vincent, C. A.; Bruce, P. G. Electrochemical measurement of transference numbers in polymer electrolytes. Polymer 1987, 28, 2324–2328.
The Journal of Physical Chemistry Letters

10 Fawcett, W. R. Liquids, solutions, and interfaces: From classical macroscopic descriptions to modern microscopic details. Oxford University Press: Oxford, UK, 2004.

11 MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. On the concept of ionicity in ionic liquids. J. Phys. Chem. B 2009, 11, 4962–4967.

12 Ueno, K.; Tokuda, H.; Watanabe, M. Ionicity in ionic liquids: correlation with ionic structure and physicochemical properties. Phys. Chem. Chem. Phys. 2010, 12, 1649–1658.

13 Stolwijk, N. A.; Kösters, J.; Wiencierz, M.; Schönhoff, M. On the extraction of ion association data and transference numbers from ionic diffusivity and conductivity data in polymer electrolytes. Electrochim. Acta 2013, 102, 451–458.

14 Harris, K. R. Relations between the fractional Stokes-Einstein and Nernst-Einstein Equations and velocity correlation coefficients in ionic liquids and molten salts. J. Phys. Chem. B 2010, 114, 9572–9577.

15 Kashyap, H. K.; Annapureddy, H. V. R.; Raineri, F. O.; Margulis, C. J. How is charge transport different in ionic liquids and electrolyte solutions? J. Phys. Chem. B 2011, 115, 13212–13221.

16 Kirchner, B.; Malberg, F.; Firaha, D. S.; Hollóczki, O. Ion pairing in ionic liquids. J. Phys.: Condens. Matter 2015, 27, 463002.

17 Shao, Y.; Shigenobu, K.; Watanabe, M.; Zhang, C. Role of viscosity in deviations from the Nernst–Einstein relation. J. Phys. Chem. B 2020, 124, 4774–4780.

18 Hansen, J. P.; McDonald, I. R. Theory of simple liquids. Academic Press: Amsterdam, Netherlands, 2006.

19 Zhong, E. C.; Friedman, H. L. Self-diffusion and distinct diffusion of ions in solution. J. Phys. Chem. 1988, 92, 1685–1692.

20 Woolf, L. A.; Harris, K. R. Velocity correlation coefficients as an expression of particle-particle interactions in (electrolyte) solutions. J. Chem. Soc., Faraday Trans. I 1978, 74, 933–947.

21 Vargas Barbosa, N. M.; Roling, B. Dynamic ion correlations in solid and liquid electrolytes: How do they affect charge and mass transport? ChemElectroChem 2020, 7, 367–385.

22 Fong, K. D.; Self, J.; McCloskey, B. D.; Persson, K. A. Ion correlations and their impact on transport in polymer-based electrolytes. Macromolecules 2021, 54, 2575–2591.

23 McDaniel, J. G.; Son, C. Y. Ion correlation and collective dynamics in BMIM/BF4-based organic electrolytes: from dilute solutions to the ionic liquid limit. J. Phys. Chem. B 2018, 122, 7154–7169.

24 Li, Z.; Bouchal, R.; Mendez-Morales, T.; Rollet, A.-L.; Rizzi, C.; Le Vot, S.; Favier, F.; Rotenberg, B.; Borodin, O.; Fontaine, O.; et al. Transport properties of Li-TFSI water-in-salt Electrolytes. J. Phys. Chem. B 2019, 123, 10514–10521.

25 Shao, Y.; Hellström, M.; Yllö, A.; Mindemark, J.; Hermansson, K.; Behler, J.; Zhang, C. Temperature effects on the ionic conductivity in concentrated alkaline electrolyte solutions. Phys. Chem. Chem. Phys. 2020, 22, 10426–10430.

26 Fong, K. D.; Self, J.; McCloskey, B. D.; Persson, K. A. Onsager transport coefficients and transference numbers in polyethylene solutions and polymerized ionic liquids. Macromolecules 2020, 53, 9503–9512.

27 Pfeifer, S.; Ackermann, F.; Sälzer, F.; Schönhoff, M.; Roling, B. Quantification of cation-cation, anion-anion and cation-anion correlations in Li salt/glyme mixtures by combining very-low-frequency impedance spectroscopy with diffusion and electrophoretic NMR. Phys. Chem. Chem. Phys. 2021, 23, 628–640.

28 Park, K.-H.; Choe, S. R.; Choi, J.-H.; Park, S. a.; Cho, M. Real-time probing of ion pairing dynamics with 2DIR spectroscopy. ChemPhysChem 2010, 11, 3632–3637.

29 Stange, P.; Fumino, K.; Ludwig, R. Ion speciation of protic ionic liquids in water: Transition from contact to solvent-separated ion pairs. Angew. Chem., Int. Ed. 2013, 52, 2990–2994.

30 Chaurasia, S. K.; Singh, R. K.; Chandra, S. Ion-polymer complexation and ion-pair formation in a polymer electrolyte PEO-LiTFSI containing an ionic liquid having same anion: A Raman study. Vib. Spectrosc. 2013, 68, 190–195.

31 Mindemark, J.; Lacey, M. J.; Bowden, T.; Brandell, D. Beyond PEO—Alternative host materials for Li+ conducting solid polymer electrolytes. Prog. Polym. Sci. 2018, 81, 114–143.

32 Choo, Y.; Halat, D. M.; Villaluenga, I.; Timachova, K.; Balsara, N. P. Diffusion and migration in polymer electrolytes. Prog. Polym. Sci. 2020, 103, 101220.

33 Popovic, J.; Brandell, D.; Ohno, S.; Hatzell, K. B.; Zheng, J.; Hu, Y.-Y. Polymer-based hybrid battery electrolytes: theoretical insights, recent advances and challenges. J. Mater. Chem. A 2021, 9, 6050–6069.

34 Robinson, R. A.; Stokes, R. H. Electrolyte solutions the measurement and interpretation of conductance, chemical potential, and diffusion in solutions of simple electrolytes; Butterworths: London, UK, 1965.

35 Luzar, A. Resolving the hydrogen bond dynamics conundrum. J. Chem. Phys. 2000, 113, 10663–10675.

36 Rapaport, D. Hydrogen bonds in water: Network organization and lifetimes. Mol. Phys. 1983, 50, 1151–1162.

37 Luzar, A.; Chandler, D. Hydrogen-bond kinetics in liquid water. Nature 1996, 379, 55–57.

38 Laage, D.; Hynes, J. T. On the residence time for water in a solute hydration shell: Application to aqueous halide solutions. J. Phys. Chem. B 2008, 112, 7697–7701.

39 Kirby, B. J.; Jungwirth, P. Charge scaling manifesto: A way of reconciling the inherently macroscopic and microscopic natures of molecular simulations. J. Phys. Chem. Lett. 2019, 10, 7531–7536.

40 Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and testing of a general amber force field. J. Comput. Chem. 2004, 25, 1157–1174.

41 Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. SoftwareX 2015, 1–2, 19–25.

42 Gudla, H.; Zhang, C.; Brandell, D. Effects of solvent polarity on Li-ion diffusion in polymer electrolytes: An all-atom molecular dynamics study with charge scaling. J. Phys. Chem. B 2020, 124, 8124–8131.

43 Wheelte, 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 Lett. 2018, 7, 1149–1154.

44 Shen, K.-H.; Hall, L. M. Effects of ion size and dielectric constant on ion transport and transference number in polymer electrolytes. Macromolecules 2020, 53, 10086–10096.

45 Zhang, Y.; Maginn, E. J. Direct correlation between ionic liquid transport properties and ion pair lifetimes: A molecular dynamics study. J. Phys. Chem. Lett. 2015, 6, 700–705.

46 Mogurampelly, S.; Keith, J. R.; Ganesan, V. Mechanisms underlying ion transport in polymerized ionic liquids. J. Am. Chem. Soc. 2017, 139, 9511–9514.

47 Shen, K.-H.; Hall, L. M. Ion conductivity and correlations in model salt-doped polymers: Effects of interaction strength and concentration. Macromolecules 2020, 53, 3655–3668.

48 Molinari, N.; Mailoa, J. P.; Kozinsky, B. Effect of salt concentration on ion clustering and transport in polymer solid electrolytes: A molecular dynamics study of PEO-LiTFSI. Chem. Mater. 2018, 30, 6298–6306.

49 Rey, I.; Lassegue, J.; Grondin, J.; Servant, L. Infrared and Raman study of the PEO-LiTFSI polymer electrolyte. Electrochim. Acta 1998, 43, 1505–1510.

50 Popovic, J.; Pfaffenhuber, C.; Melchior, J. P.; Maier, A. Determination of individual contributions to the ionic conduction in liquid electrolytes: Case study of LiTf/LiPF6 polymer electrolyte. Electrochim. Commun. 2015, 60, 195–198.