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Polymer Architecture-Induced Trade-off between Conductivities and Transference Numbers in Salt-Doped Polymeric Ionic Liquids

Zidan Zhang, Nico Marioni, Harnoor S. Sachar, and Venkat Ganesan*

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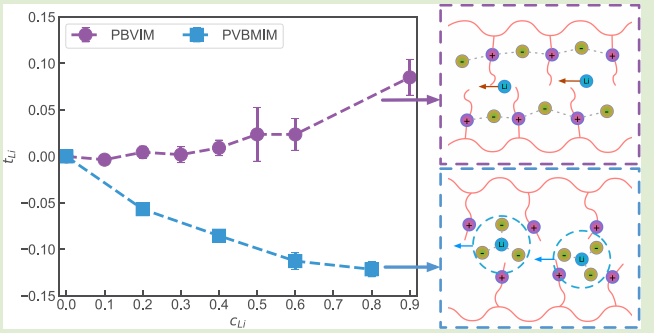
ABSTRACT: Recent experiments have demonstrated that polymeric ionic liquids that share the same cation and anion but possess different architectures can exhibit markedly different conductivity and transference number characteristics when doped with lithium salt. In this study, we used atomistic molecular simulations on polymer chemistries inspired by the experiments to probe the mechanistic origins underlying the competition between conductivity and transference numbers. Our results indicate that the architecture of the polycationic ionic liquid plays a subtle but crucial role in modulating the anion−cation interactions, especially their dynamical coordination characteristics. Chemistries leading to longer-lived anion−cation coordinations relative to lithium−anion coordinations lead to lower conductivities and higher transference numbers. Our results suggest that higher conductivities are accompanied by lower transference numbers and vice versa, revealing that alternative approaches may need to be considered to break this trade-off in salt-doped polyILs.



Polymeric ionic liquids (polyILs) are charged macromolecules consisting of monomeric ionic liquids (ILs) as repeating units.[1−3] Such materials not only inherit the unique physicochemical characteristics from their corresponding ILs, but also exhibit desirable mechanical properties representative of polymers.[4,5] As a result, polyILs have garnered significant interest in the pursuit of safe and conductive electrolytes for energy storage applications.[6−8]

In an effort to transition polyILs toward lithium ion batteries, attention has turned toward the properties of lithium salt-doped polyILs.[6,9−11] In salt-doped *monomeric* ILs, it has been generally observed that the diffusivity of all ions (lithium, IL anions, and IL cations) and the overall conductivity decrease with an increase in lithium salt concentration, c_{Li}.[12−15] This has been revealed to be a consequence of the increased viscosity arising from the formation of lithium−anion clusters.[16−20] In contrast, in salt-doped polyILs, recent work by Forsyth and co-workers on (poly-(diallyldimethylammonium) bis(fluorosulfonyl)imide (PDADMA-FSI)) showed that the diffusivity of mobile ions and the overall conductivity increase with increasing c_{Li} up to mole ratio 2:1 (number of cations to lithium ions).[10] Other studies have also demonstrated similar conductivity characteristics for salt-doped polyIL systems, leading to increasing interest in such materials.[21−25]

While conductivity and mechanical characteristics have been a significant focus of research on electrolytes, *transference numbers*, especially that of lithium ions, is now recognized as being an equally important property for applications.[26−31] The latter, defined as the fraction of current carried by lithium relative to the total current, has been suggested to play an important role in influencing the charging rate of the battery,[32] concentration polarization effects,[33,34] and dendrite formation on electrodes.[35] Experimental and computational studies have demonstrated that salt-doped *monomeric* ILs generally exhibit negative transference numbers over a range of salt concentrations.[36−39] This undesirable feature has been rationalized to be a result of the formation of anion-rich lithium clusters which migrate as an aggregate under an external field, leading to the observed "negative" lithium current.[40,41] Based on such a picture, a number of recent studies have demonstrated that use of Li-coordinating additives which reduce the Li-anion coordinations can be used as a strategy to invert the sign of the transference numbers in such systems.[42−45]

Salt-doped poly *cationic* ILs represent systems in which the anions are expected to coordinate to the less mobile polymer backbone and hence represent an alternative approach to release (partially) the lithium−anion coordinations and thereby influence the lithium transference numbers. However, in contrast to salt-doped monomeric ILs, there is still a lack of

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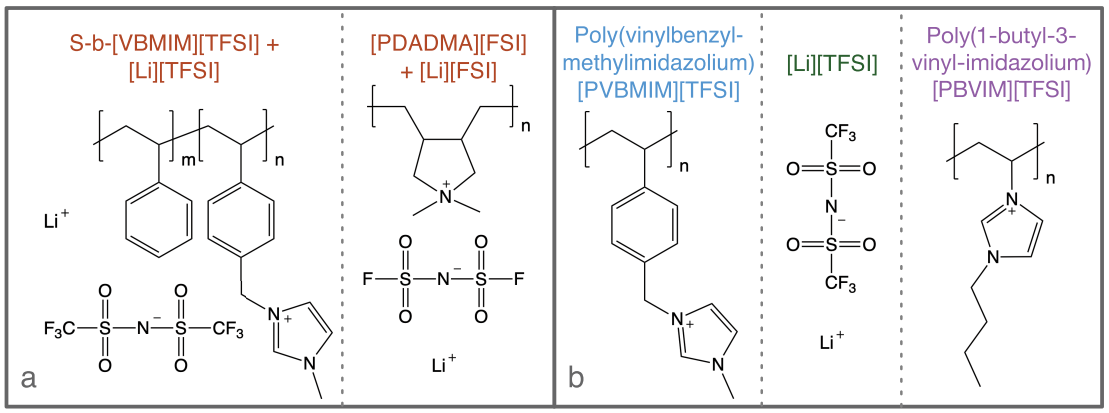

Figure 1. (a) The experimentally probed systems that show *negative* t_{Li} (salt-doped S-*b*-[VBMIM][TFSI] from Elabd's work[47]) and *positive* t_{Li} (salt-doped [PDADMA][FSI] from Forsyth's work[10]). (b) An illustration of chemical details of the polyILs PVBMIM and PBVIM systems with anion $TFSI^-$ and lithium ion probed in our simulations.

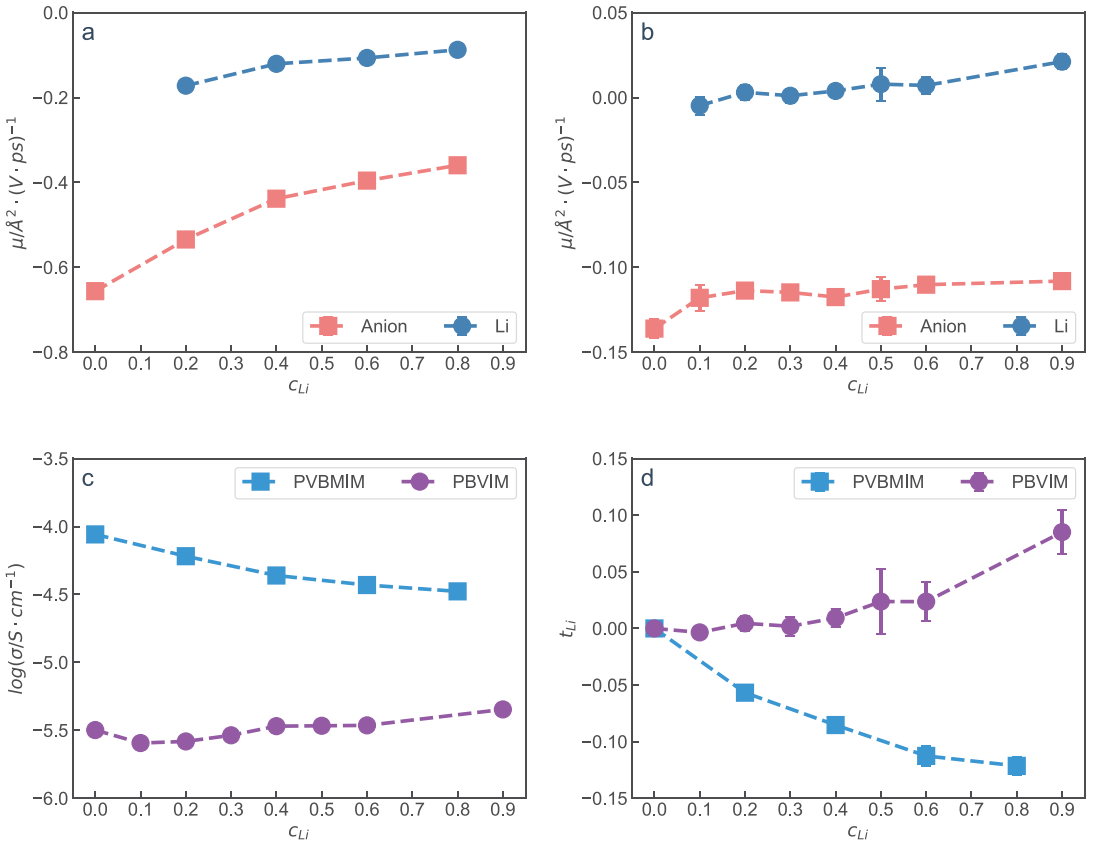

Figure 2. Anion and lithium ion mobilities for (a) PVBMIM and (b) PBVIM systems (under the polymer-centric reference frame). (c) True conductivity, σ, and (d) lithium ion transference numbers, t_{Li}, for PVBMIM and PBVIM systems.

clarity on the influence of the physicochemical characteristics of the polyILs on the conductivities and transference numbers in salt-doped polyILs. For example, the study by Forsyth and co-workers reported transference numbers to be positive (around 0.5, based on the Bruce–Vincent and Watanabe method[46]) and increased with salt concentrations (at lower salt concentrations).[10] In contrast, a recent work by Elabd and co-workers in the context of the salt-doped styrene-based poly(vinylbenzylmethylimidazolium) bis(trifluoromethanesulfonyl)imide (S-*b*-[VBMIM][TFSI]) copolymer[47] observed negative transference numbers (based on the Newman–Balsara method[48]) which decreased with increasing salt concentrations. Interestingly, significant differences in conductivity values were also noted between the two experimentally probed systems. For instance, at T = 80 °C and c_{Li} = 0.5, the log σ ($S \cdot cm^{-1}$) was −6.46 in Forsyth's work,[10] whereas it was −3.27 in Elabd's work.[47]

This study is inspired by the above-discussed experiments and seeks to understand the origins of the differences in the conductivities and the signs of transference numbers reported. Interestingly, the two experimentally probed polyILs are very similar in chemical nature (cf. Figure 1a) and share the same cation and anion of the IL. Hence, we hypothesize that the property differences likely arise from the location of the

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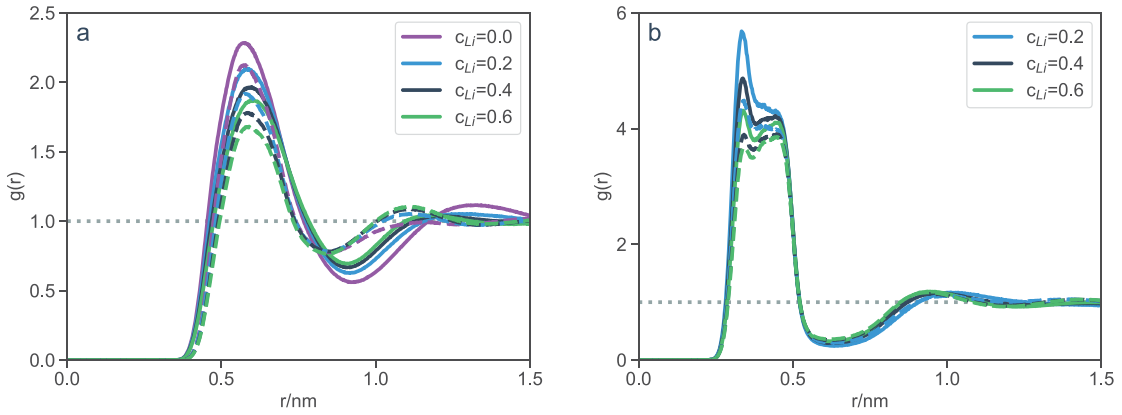

Figure 3. Radial distribution functions $g(r)$ for (a) anion−cation ($TFSI^-$−imidazolium$^+$) and (b) lithium−anion (Li^+−$TFSI^-$). The solid and dashed lines are for PVBMIM and PBVIM systems, respectively. The center of mass of each functional group is adopted for the analysis.

cationic group relative to the polymer backbone. While some studies have probed the influence of polymer architecture on the morphology and transport in single-ion conductors,[49−52] there is less clarity on the role of the added salt and the influence upon lithium transference numbers. Through our investigation, we hope to shed light on the role of polymer architecture on ion transport properties and address whether simultaneously high conductivities and positive transference numbers can be achieved in salt-doped polyILs.

Toward the above objectives, we used atomistic molecular dynamics simulations in conjunction with a combination of equilibrium and nonequilibrium methodologies to study the conductivities, transference numbers, and structural, dynamical origins in two systems depicted in Figure 1b, whose chemical structures are inspired by the experimentally probed systems (cf. Figure 1a). We use the terminology PVBMIM and PBVIM to refer to the two simulated systems.

All simulations are conducted at 600 K to have faster dynamics and better statistics. This temperature is expected to be above the glass transition temperature, T_g, of the probed systems. We note that the experimental measurements of conductivity and transference number were also conducted at temperatures above T_g.[10,47] More detailed information on the force field parameters (nonpolarizable force field with scaled partial charges[53]) and the methodology of atomistic simulations is presented in SI Section S1.[54,55] We used the framework of nonequilibrium simulations under an external electric field (detailed in our earlier studies[54,55]) to probe the ionic mobilities μ_i ($i \in (TFSI^-, Li^+)$). The fitting of the ionic mobility μ is shown in SI Section S2. As discussed earlier, experiments have used different methods for quantifying the transference number, and recent work has raised questions about the appropriate reference frame of simulations to compare with experiments.[27,56,57] In this context, we note that recent experiments have shown that the diffusivity of polyILs scales as N^{-2},[58] where N represents the number of units in the polymer. In the limit of large N (representative of experiments), the mobility of the polycation is expected to be small relative to the other units, and hence we adopt a polymer-centric frame of reference for analysis of our simulation results.[30] In such a framework, only the mobilities of the anion $TFSI^-$ and lithium contribute to the conductivity (the results for the center of mass reference frame are discussed in SI Section S3). The overall true conductivity σ is given as

$$\sigma = \sum_i F z_i c_i \mu_i \tag{1}$$

where F is the Faraday constant, z_i is the effective charge, c_i is the concentration, and μ_i is the ionic mobility of ion i. The lithium ion transference number, t_{Li}, can be calculated from the ionic mobilities:

$$t_{Li} = \frac{c_{Li}\mu_{Li}}{c_{Li}\mu_{Li} - c_{TFSI}\mu_{TFSI}} \tag{2}$$

We begin the discussion with the results of ionic mobilities for the anion and lithium in Figures 2a. It can be seen that in PVBMIM systems, the ionic mobilities for both anion and lithium ions are negative. It is to be expected that the ionic mobility for anions is negative under an external electric field. However, the negative mobility values for lithium ions indicate that they are moving toward the *wrong* direction, suggesting correlated motion between lithium and anions. In contrast, for PBVIM systems (Figure 2b), it is seen that the ionic mobility for lithium ion is positive but much smaller in magnitude compared to PVBMIM systems. Further, it can be seen that the magnitude of ionic mobilities for PVBMIM systems decreases with an increase in salt concentration. In contrast, anionic mobility in PBVIM systems is seen to have a weak dependence on salt concentration, while the lithium ion mobility exhibits a slight increase at higher salt concentrations.

In Figures 2c and d, we compare the salt concentration dependence of the total conductivity, σ, and lithium transference number, t_{Li}, of the PVBMIM and PBVIM systems. Similar to the results observed for the anion and lithium mobilities, we observe that the conductivity decreases with salt concentration in the PVBMIM system but increases with salt loading in the PBVIM system. Further, in qualitative accord with the experimental findings,[10,47] we also observe that the conductivity of PVBMIM systems are an order of magnitude higher than those in PBVIM systems. In comparing the transference numbers of lithium, we observe that (in agreement with experiments) t_{Li} for PVBMIM systems are negative and decrease with c_{Li}.[10,47] In contrast, t_{Li} of PBVIM systems are positive and increase with c_{Li}. We do note that the absolute magnitudes of the transference numbers observed in our simulations are lower than those seen in experiments. We speculate that such differences arise from the much higher temperatures (600 K) employed in our studies relative to the

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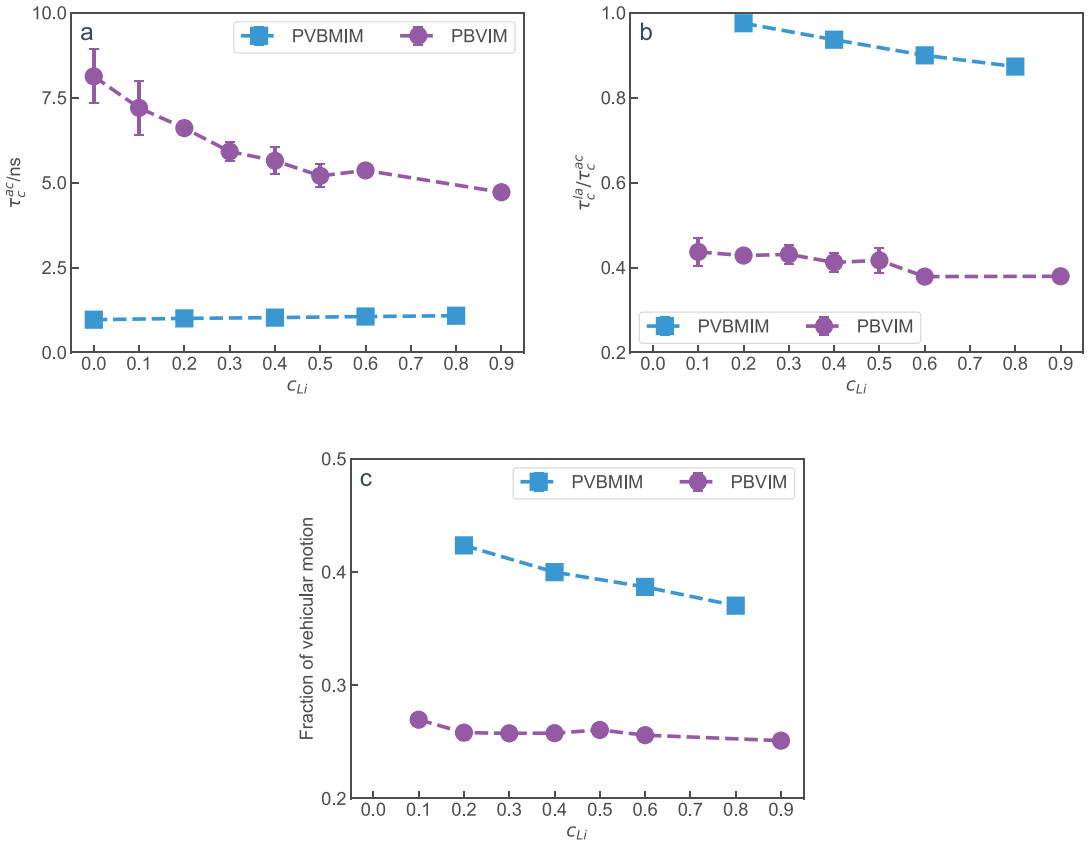

Figure 4. (a) The anion−cation *intermittent* association lifetimes, τ_c^{ac}. (b) The ratio of the ion pair relaxation time scales of lithium−anion (τ_c^{la}) to anion−cation (τ_c^{ac}). (c) The fraction of lithium ions executing vehicular motion.

experiments or the different methodologies underlying the transference number measurements in experiments.

Having established qualitative agreement between our simulation results and the experimental observations, we now turn to probe the mechanisms underlying the differences between the PVBMIM and PBVIM systems. Our earlier studies have examined the structural features of salt-doped PBVIM systems[59,60] and demonstrated the formation of cation−anion−lithium−anion−cation cocoordinations, which replace the cation−anion−cation coordinations in pure polyILs. Such cocoordinations were shown to speed up the polymer segmental dynamics, and as a result, the dynamics of cocoordinated anions and lithium ions. Such results were shown to explain the salt concentration dependencies of anion and lithium mobilities in PBVIM systems.[59,60] In SI Section S4, we demonstrate that for the salt concentrations probed here, the lithium ions in both PVBMIM and PBVIM systems exist almost entirely (more than 96%) in such cocoordinated structures. Hence, we focus on the movement of such cocoordinated ions to understand the origin of the results in Figure 2.

From the t_{Li} results displayed above in Figure 2d, one may hypothesize that the transference number, t_{Li}, is a result of the competition of the anion−cation and lithium−anion interactions underlying the above-discussed cocoordinations. Specifically, if the anions can easily dissociate from the cations, then the lithium ions can move cooperatively with multiple anions in a manner similar to the *vehicular motion* noted in monomeric ionic liquids (ILs). In such a case, a negative t_{Li} value can be expected. In contrast, if the anions cannot easily dissociate from cations or, alternatively, if lithium can dissociate more easily from the anions, a positive t_{Li} manifests.

To unravel the above competition between anion−cation and anion−lithium interactions, the radial distribution functions $g(r)$ were calculated, and are shown in Figures 3a and 3b (the complete results of $g(r)$ are shown in SI Section S5). It can be seen from Figure 3a that at a specified c_{Li}, the anion−cation interactions in PVBMIM system are comparable, but slightly larger than in the PBVIM system. Similarly, the lithium−anion interactions at certain c_{Li} in the PVBMIM system (cf. Figure 3b) are also stronger than those in the PBVIM system.

The above results indicate that while $g(r)$ by itself displays differences between the two systems, the hypothesized competition between anion−cation and lithium−anion interactions is not borne out in our results, and instead we observe that the PVBMIM system exhibits stronger interactions on both fronts. Moreover, the differences in $g(r)$ are also seen to be not substantial enough to explain the significant differences noted in the conductivities and transference numbers.

The $g(r)$ results discussed above can be understood by noting that a unique feature of the systems considered in our study is that the cation and the anion are identical among the two systems and only differ in the architecture of the polyILs. However, despite the similarity in interaction characteristics, since the cations are located closer to the polymer backbone in PBVIM systems, the cations are expected to be less mobile, and the anions which are coordinated with the cations are expected to exhibit longer association lifetimes.[61] In contrast, since the cations are farther from the polymer backbone in the PVBMIM system, the anions are expected to exhibit shorter

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association lifetimes and be more mobile. So, we turn to an analysis of the differences in the dynamical aspects of coordination of anion−cation and anion−lithium ion pairs.

The results for the anion−cation association lifetimes τ_c^{ac} (the detailed information for the analysis and fitting of τ_c can be found in SI Section S6) displayed in Figure 4a confirm our hypothesis and indeed display longer association times in PBVIM systems compared to PVBMIM systems. Such stronger (dynamical) anion−cation coordinations in PBVIM systems will facilitate the lithium ions to more easily get rid of the anion solvation shell. In contrast, since the anions are coordinated more weakly (dynamically) to the cations in the PVBMIM system, the lithium ions are expected to more likely move with their surrounding anions in the solvation shell. To prove this hypothesis, in Figure 4b we present results for the ratio of lithium−anion (τ_c^{la}) to that of the anion−cation association time scale (τ_c^{ac}). From the results displayed, it can be seen that τ_c^{la}/τ_c^{ac} is about 0.87−0.98 in the PVBMIM system, which is much higher than that in the PBVIM system (0.38−0.44).

The above results explain the differences in the transference numbers noted between the PVBMIM and PBVIM systems. Indeed, based on a comparison of the lithium−anion and anion−cation association time scales, we expect the lithium ions in PVBMIM systems more likely to exhibit a vehicular motion with the anions present in its solvation shell. Such vehicular motion leads to a lower and negative transference number due to the effective charge of such "clusters." In contrast, the anions in PBVIM systems prefer to stay much longer with the cation rather than move with the lithium ions and lead to positive and higher lithium ion transference numbers. We provide a direct validation of this proposal by quantifying the lithium's vehicular motion in PVBMIM and PBVIM systems. Toward this objective, we define lithium ions as effecting vehicular motion if they travel continuously with at least two anions (to present a *negative* t_{Li}) for a distance of the size of TFSI anion (5 Å). In Figure 4c, we present results for the average fraction of lithium ions exhibiting such vehicular motion, wherein we see that the fraction of such lithium in the PVBMIM system is around 0.4, whereas, in PBVIM, the fraction is closer to 0.25.

We note that the above results also serve to rationalize the other differences noted between the PBVIM and PVBMIM systems. More explicitly, the longer cation−anion association times observed in PBVIM systems are expected to lead to a lower mobility of the anions, and as a consequence, of the cocoordinated lithium ions. Hence, the conductivities of the PBVIM systems are observed to be lower than that of the PVBMIM systems. Further, as discussed in the study by Forsyth and co-workers[10] and our earlier work,[59] the increase in anion and lithium mobilities with salt concentrations in PBVIM systems arise from the influence of cation−anion−lithium cocoordinations in breaking the direct cation−anion−cation coordinations. We demonstrated that such physics leads to lithium ions displaying a larger increase (compared to anions) as a function of c_{Li} as observed in Figure 2b. Such results explain the increase in the lithium ion transference numbers as a function of salt loading observed in Figure 2d. In contrast, since the anions are only weakly (dynamically) coordinated with the cations in the PVBMIM system, the cocoordinations induced by lithium ions exert only a weak influence on the polymer segmental dynamics (cf. SI Section S7). As a result, the anion mobilities are slowed significantly with the addition of salt as seen in Figure 2a (see SI Section S8 for a more elaborate explanation in terms of the different types of anions and their dynamics as classified in our previous work[59]). Hence, the lithium ion transference numbers increase in magnitude (but decrease in absolute value) with an increase in c_{Li}.

To summarize, our above results clarify the subtle influence of polymer architecture in explaining the origin of the differences in the conductivities and transference numbers noted between the PBVIM and PVBMIM systems. Explicitly, PVBMIM systems are characterized by the cation being farther from the backbone. Hence, the anion−cation coordinations exhibit shorter lifetimes, leading to faster anion (and lithium) mobilities and higher conductivities. Correspondingly, the lithium−anion coordinations exhibit *relatively* longer lifetimes and result in a greater fraction of lithium exhibiting vehicular motion with its anion solvation shell. Moreover, the influence of cation−anion−lithium−anion−cation cocoordinations is much more mitigated, and the addition of salt reduces the mobility of the anions. Such effects lead to negative transference numbers, which decrease with addition of salt. In contrast, in PBVIM systems, the cations are closer to the backbone. Hence, such systems are characterized by anion−cation coordinations with longer lifetimes, which lead to slower anion (and lithium) mobilities, lower conductivities, and a smaller fraction of lithium exhibiting vehicular motion with its anion solvation shell. Moreover, addition of salt leads to cation−anion−lithium−anion−cation cocoordinations, which speed up the polymer dynamics and the mobilities of the anions and lithiums. The latter leads to the positive transference numbers which increase with addition of salt but lower conductivities.

In conclusion, our results serve to highlight that the competition between the anion−cation and anion−lithium association lifetimes is influenced by the architecture of the polyIL. Facilitating higher conductivities requires weakening the anion−cation coordinations but leads to a negative impact on the transference numbers. Overall, our results suggest the existence of a trade-off between conductivities and transference numbers in salt-doped polyILs, which may either require strategies similar to those explored in the context of monomeric ILs and/or an exploration of other chemistries.[42−44]

■ ASSOCIATED CONTENT

Supporting Information

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Additional simulation details and results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Venkat Ganesan − *McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States;* orcid.org/0000-0003-3899-5843; Email: venkat@che.utexas.edu

Authors

Zidan Zhang − *McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States;* orcid.org/0000-0002-6909-8742

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Nico Marioni − *McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States*

Harnoor S. Sachar − *McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmacrolett.3c00376

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ohno, H. Molten salt type polymer electrolytes. *Electrochim. Acta* **2001**, *46*, 1407−1411.

(2) Matsumi, N.; Sugai, K.; Miyake, M.; Ohno, H. Polymerized Ionic Liquids via Hydroboration Polymerization as Single Ion Conductive Polymer Electrolytes. *Macromolecules* **2006**, *39*, 6924−6927.

(3) Nishimura, N.; Ohno, H. 15th anniversary of polymerised ionic liquids. *Polymer* **2014**, *55*, 3289−3297.

(4) Ganesan, V. Ion transport in polymeric ionic liquids: recent developments and open questions. *Molecular Systems Design & Engineering* **2019**, *4*, 280−293.

(5) Park, M. J. Confinement-entitled morphology and ion transport in ion-containing polymers. *Molecular Systems Design & Engineering* **2019**, *4*, 239−251.

(6) Wang, X.; Kerr, R.; Chen, F.; Goujon, N.; Pringle, J. M.; Mecerreyes, D.; Forsyth, M.; Howlett, P. C. Toward High-Energy-Density Lithium Metal Batteries: Opportunities and Challenges for Solid Organic Electrolytes. *Adv. Mater.* **2020**, *32*, 1905219.

(7) Shen, X.; Zhang, X.-Q.; Ding, F.; Huang, J.-Q.; Xu, R.; Chen, X.; Yan, C.; Su, F.-Y.; Chen, C.-M.; Liu, X.; Zhang, Q. Advanced Electrode Materials in Lithium Batteries: Retrospect and Prospect. *Energy Material Advances* **2021**, *2021*, 1205324.

(8) Wang, J.; Li, S.; Zhao, Q.; Song, C.; Xue, Z. Structure Code for Advanced Polymer Electrolyte in Lithium-Ion Batteries. *Adv. Funct. Mater.* **2021**, *31*, 2008208.

(9) Eshetu, G. G.; Mecerreyes, D.; Forsyth, M.; Zhang, H.; Armand, M. Polymeric ionic liquids for lithium-based rechargeable batteries. *Molecular Systems Design & Engineering* **2019**, *4*, 294−309.

(10) Wang, X.; Chen, F.; Girard, G. M. A.; Zhu, H.; MacFarlane, D. R.; Mecerreyes, D.; Armand, M.; Howlett, P. C.; Forsyth, M. Poly(Ionic Liquid)s-in-Salt Electrolytes with Co-coordination-Assisted Lithium-Ion Transport for Safe Batteries. *Joule* **2019**, *3*, 2687−2702.

(11) Chen, F.; Wang, X.; Armand, M.; Forsyth, M. Cationic polymer-in-salt electrolytes for fast metal ion conduction and solid-state battery applications. *Nat. Mater.* **2022**, *21*, 1175−1182.

(12) Li, Z.; Smith, G. D.; Bedrov, D. Li+ Solvation and Transport Properties in Ionic Liquid/Lithium Salt Mixtures: A Molecular Dynamics Simulation Study. *J. Phys. Chem. B* **2012**, *116*, 12801−12809.

(13) Yoon, H.; Best, A. S.; Forsyth, M.; MacFarlane, D. R.; Howlett, P. C. Physical properties of high Li-ion content N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide based ionic liquid electrolytes. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4656−4663.

(14) Sun, Y.; Yang, T.; Ji, H.; Zhou, J.; Wang, Z.; Qian, T.; Yan, C. Boosting the Optimization of Lithium Metal Batteries by Molecular Dynamics Simulations: A Perspective. *Adv. Energy Mater.* **2020**, *10*, 2002373.

(15) Judeinstein, P.; Zeghal, M.; Constantin, D.; Iojoiu, C.; Coasne, B. Interplay of Structure and Dynamics in Lithium/Ionic Liquid Electrolytes: Experiment and Molecular Simulation. *J. Phys. Chem. B* **2021**, *125*, 1618−1631.

(16) Haskins, J. B.; Bennett, W. R.; Wu, J. J.; Hernández, D. M.; Borodin, O.; Monk, J. D.; Bauschlicher, C. W.; Lawson, J. W. Computational and Experimental Investigation of Li-Doped Ionic Liquid Electrolytes: [pyr14][TFSI], [pyr13][FSI], and [EMIM][BF4]. *J. Phys. Chem. B* **2014**, *118*, 11295−11309.

(17) Giffin, G. A.; Moretti, A.; Jeong, S.; Pilar, K.; Brinkkötter, M.; Greenbaum, S. G.; Schönhoff, M.; Passerini, S. Connection between Lithium Coordination and Lithium Diffusion in [Pyr12O1][FTFSI] Ionic Liquid Electrolytes. *ChemSusChem* **2018**, *11*, 1981−1989.

(18) Lourenço, T. C.; Zhang, Y.; Costa, L. T.; Maginn, E. J. A molecular dynamics study of lithium-containing aprotic heterocyclic ionic liquid electrolytes. *J. Chem. Phys.* **2018**, *148*, 193834.

(19) Ray, P.; Balducci, A.; Kirchner, B. Molecular Dynamics Simulations of Lithium-Doped Ionic-Liquid Electrolytes. *J. Phys. Chem. B* **2018**, *122*, 10535−10547.

(20) Tong, J.; Wu, S.; von Solms, N.; Liang, X.; Huo, F.; Zhou, Q.; He, H.; Zhang, S. The Effect of Concentration of Lithium Salt on the Structural and Transport Properties of Ionic Liquid-Based Electrolytes. *Frontiers in Chemistry* **2020**, *7*, 945.

(21) Wang, A.; Xu, H.; Liu, X.; Gao, R.; Wang, S.; Zhou, Q.; Chen, J.; Liu, X.; Zhang, L. The synthesis of a hyperbranched star polymeric ionic liquid and its application in a polymer electrolyte. *Polym. Chem.* **2017**, *8*, 3177−3185.

(22) Wang, A.; Liu, X.; Wang, S.; Chen, J.; Xu, H.; Xing, Q.; Zhang, L. Polymeric ionic liquid enhanced all-solid-state electrolyte membrane for high-performance lithium-ion batteries. *Electrochim. Acta* **2018**, *276*, 184−193.

(23) Pablos, J. L.; García, N.; Garrido, L.; Catalina, F.; Corrales, T.; Tiemblo, P. Polycationic scaffolds for Li-ion anion exchange transport in ion gel polyelectrolytes. *J. Mater. Chem. A* **2018**, *6*, 11215−11225.

(24) Pablos, J. L.; García, N.; Garrido, L.; Guzmán, J.; Catalina, F.; Corrales, T.; Tiemblo, P. Highly efficient mixed Li+ transport in ion gel polycationic electrolytes. *J. Membr. Sci.* **2018**, *545*, 133−139.

(25) Chen, T.-L.; Sun, R.; Willis, C.; Krutzer, B.; Morgan, B. F.; Beyer, F. L.; Han, K. S.; Murugesan, V.; Elabd, Y. A. Impact of ionic liquid on lithium ion battery with a solid poly(ionic liquid) pentablock terpolymer as electrolyte and separator. *Polymer* **2020**, *209*, 122975.

(26) Bocharova, V.; Sokolov, A. P. Perspectives for Polymer Electrolytes: A View from Fundamentals of Ionic Conductivity. *Macromolecules* **2020**, *53*, 4141−4157.

(27) Shao, Y.; Gudla, H.; Brandell, D.; Zhang, C. Transference Number in Polymer Electrolytes: Mind the Reference-Frame Gap. *J. Am. Chem. Soc.* **2022**, *144*, 7583−7587.

(28) Fang, C.; Mistry, A.; Srinivasan, V.; Balsara, N. P.; Wang, R. Elucidating the Molecular Origins of the Transference Number in Battery Electrolytes Using Computer Simulations. *JACS Au* **2023**, *3*, 306−315.

(29) Fang, C.; Halat, D. M.; Balsara, N. P.; Wang, R. Dynamic Heterogeneity of Solvent Motion and Ion Transport in Concentrated Electrolytes. *J. Phys. Chem. B* **2023**, *127*, 1803−1810.

(30) Fang, C.; Yu, X.; Chakraborty, S.; Balsara, N. P.; Wang, R. Molecular Origin of High Cation Transference in Mixtures of Poly(pentyl malonate) and Lithium Salt. *ACS Macro Lett.* **2023**, *12*, 612−618.

(31) Shao, Y.; Zhang, C. Bruce−Vincent transference numbers from molecular dynamics simulations. *J. Chem. Phys.* **2023**, *158*, 161104.
(32) Patel, S. N. 100th Anniversary of Macromolecular Science Viewpoint: Solid Polymer Electrolytes in Cathode Electrodes for Lithium Batteries. Current Challenges and Future Opportunities. *ACS Macro Lett.* **2021**, *10*, 141−153.
(33) Doyle, M.; Fuller, T. F.; Newman, J. The importance of the lithium ion transference number in lithium/polymer cells. *Electrochim. Acta* **1994**, *39*, 2073−2081.
(34) Dwelle, K. A.; Willard, A. P. The limited influence of transference number on the performance of nanoscale batteries. *J. Chem. Phys.* **2020**, *152*, 074702.
(35) Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. *Energy Environ. Sci.* **2011**, *4*, 3243−3262.
(36) Gouverneur, M.; Schmidt, F.; Schönhoff, M. Negative effective Li transference numbers in Li salt/ionic liquid mixtures: does Li drift in the "Wrong" direction? *Phys. Chem. Chem. Phys.* **2018**, *20*, 7470−7478.
(37) Harris, K. R. Comment on "Negative effective Li transference numbers in Li salt/ionic liquid mixtures: does Li drift in the "Wrong" direction?" by M. Gouverneur, F. Schmidt and M. Schönhoff, Phys. Chem. Chem. Phys. *Physical Chemistry Chemical Physics* **2018**, *20* (47), 30041−30045.
(38) Schönhoff, M.; Cramer, C.; Schmidt, F. Reply to the 'Comment on "Negative effective Li transference numbers in Li salt/ionic liquid mixtures: does Li drift in the "Wrong" direction?"' by K. R. Harris. *Phys. Chem. Chem. Phys.* **2018**, *20*, 30046−30052.
(39) Kubisiak, P.; Wróbel, P.; Eilmes, A. Molecular Dynamics Investigation of Correlations in Ion Transport in MeTFSI/EMIM−TFSI (Me = Li, Na) Electrolytes. *J. Phys. Chem. B* **2020**, *124*, 413−421.
(40) Brinkkötter, M.; Giffin, G. A.; Moretti, A.; Jeong, S.; Passerini, S.; Schönhoff, M. Relevance of ion clusters for Li transport at elevated salt concentrations in [Pyr12O1][FTFSI] ionic liquid-based electrolytes. *Chem. Commun.* **2018**, *54*, 4278−4281.
(41) France-Lanord, A.; Grossman, J. C. Correlations from Ion Pairing and the Nernst-Einstein Equation. *Phys. Rev. Lett.* **2019**, *122*, 136001.
(42) Molinari, N.; Kozinsky, B. Chelation-Induced Reversal of Negative Cation Transference Number in Ionic Liquid Electrolytes. *J. Phys. Chem. B* **2020**, *124*, 2676−2684.
(43) 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.
(44) Sudoh, T.; Shigenobu, K.; Dokko, K.; Watanabe, M.; Ueno, K. Li+ transference number and dynamic ion correlations in glyme-Li salt solvate ionic liquids diluted with molecular solvents. *Phys. Chem. Chem. Phys.* **2022**, *24*, 14269−14276.
(45) Nürnberg, P.; Atik, J.; Borodin, O.; Winter, M.; Paillard, E.; Schönhoff, M. Superionicity in Ionic-Liquid-Based Electrolytes Induced by Positive Ion−Ion Correlations. *J. Am. Chem. Soc.* **2022**, *144*, 4657−4666.
(46) Dong, D.; Sälzer, F.; Roling, B.; Bedrov, D. How efficient is Li+ ion transport in solvate ionic liquids under anion-blocking conditions in a battery? *Phys. Chem. Chem. Phys.* **2018**, *20*, 29174−29183.
(47) Chen, T.-L.; Lathrop, P. M.; Sun, R.; Elabd, Y. A. Lithium-Ion Transport in Poly(ionic liquid) Diblock Copolymer Electrolytes: Impact of Salt Concentration and Cation and Anion Chemistry. *Macromolecules* **2021**, *54*, 8780−8797.
(48) Pesko, D. M.; Timachova, K.; Bhattacharya, R.; Smith, M. C.; Villaluenga, I.; Newman, J.; Balsara, N. P. Negative Transference Numbers in Poly(ethylene oxide)-Based Electrolytes. *J. Electrochem. Soc.* **2017**, *164*, No. E3569.
(49) Hall, L. M.; Stevens, M. J.; Frischknecht, A. L. Effect of Polymer Architecture and Ionic Aggregation on the Scattering Peak in Model Ionomers. *Phys. Rev. Lett.* **2011**, *106*, 127801.
(50) Hall, L. M.; Seitz, M. E.; Winey, K. I.; Opper, K. L.; Wagener, K. B.; Stevens, M. J.; Frischknecht, A. L. Ionic Aggregate Structure in Ionomer Melts: Effect of Molecular Architecture on Aggregates and the Ionomer Peak. *J. Am. Chem. Soc.* **2012**, *134*, 574−587.
(51) Abbott, L. J.; Lawson, J. W. Effects of Side Chain Length on Ionic Aggregation and Dynamics in Polymer Single-Ion Conductors. *Macromolecules* **2019**, *52*, 7456−7467.
(52) Kadulkar, S.; Brotherton, Z. W.; Lynch, A. L.; Pohlman, G.; Zhang, Z.; Torres, R.; Manthiram, A.; Lynd, N. A.; Truskett, T. M.; Ganesan, V. The Importance of Morphology on Ion Transport in Single-Ion, Comb-Branched Copolymer Electrolytes: Experiments and Simulations. *Macromolecules* **2023**, *56*, 2790−2800.
(53) Zhang, Z.; Zofchak, E.; Krajniak, J.; Ganesan, V. Influence of Polarizability on the Structure, Dynamic Characteristics, and Ion-Transport Mechanisms in Polymeric Ionic Liquids. *J. Phys. Chem. B* **2022**, *126*, 2583−2592.
(54) Zhang, Z.; Wheatle, B. K.; Krajniak, J.; Keith, J. R.; Ganesan, V. Ion Mobilities, Transference Numbers, and Inverse Haven Ratios of Polymeric Ionic Liquids. *ACS Macro Lett.* **2020**, *9*, 84−89.
(55) Zhang, Z.; Sass, J.; Krajniak, J.; Ganesan, V. Ion Correlations and Partial Ionicities in the Lamellar Phases of Block Copolymeric Ionic Liquids. *ACS Macro Lett.* **2022**, *11*, 1265−1271.
(56) Gao, K. W.; Fang, C.; Halat, D. M.; Mistry, A.; Newman, J.; Balsara, N. P. The Transference Number. *Energy & Environmental Materials* **2022**, *5*, 366−369.
(57) Lorenz, M.; Kilchert, F.; Nürnberg, P.; Schammer, M.; Latz, A.; Horstmann, B.; Schönhoff, M. Local Volume Conservation in Concentrated Electrolytes Is Governing Charge Transport in Electric Fields. *J. Phys. Chem. Lett.* **2022**, *13*, 8761−8767.
(58) Lan, P.; Zhao, Q.; Lv, G.; Sheridan, G. S.; Cahill, D. G.; Evans, C. M. Molecular-Weight Dependence of Center-of-Mass Chain Diffusion in Polymerized Ionic Liquid Melts. *Macromolecules* **2023**, *56*, 3383−3392.
(59) Zhang, Z.; Nasrabadi, A. T.; Aryal, D.; Ganesan, V. Mechanisms of Ion Transport in Lithium Salt-Doped Polymeric Ionic Liquid Electrolytes. *Macromolecules* **2020**, *53*, 6995−7008.
(60) Zhang, Z.; Lin, D.; Ganesan, V. Mechanisms of ion transport in lithium salt-doped polymeric ionic liquid electrolytes at higher salt concentrations. *J. Polym. Sci.* **2022**, *60*, 199−213.
(61) Keith, J. R.; Mogurampelly, S.; Wheatle, B. K.; Ganesan, V. Influence of side chain linker length on ion-transport properties of polymeric ionic liquids. *J. Polym. Sci., Part B: Polym. Phys.* **2017**, *55*, 1718−1723.

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