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Enhancing Cation Diffusion and Suppressing Anion Diffusion via Lewis-Acidic Polymer Electrolytes

Brett M. Savoie, Michael A. Webb, and Thomas F. Miller III*

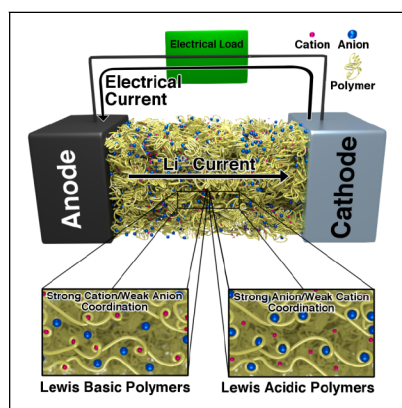
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Abstract

Solid polymer electrolytes (SPE) have the potential to increase both the energy density and stability of lithium-based batteries, but low Li^+ conductivity remains a barrier to technological viability. SPEs are designed to maximize Li^+ diffusivity relative to the anion, while maintaining sufficient salt solubility. It is thus remarkable that polyethylene oxide (PEO), the most widely used SPE, exhibits Li^+ diffusivity that is an order of magnitude smaller than that of typical counter-ions at moderate salt concentrations. We show that Lewis-basic polymers like PEO favor slow cation and rapid anion diffusion while this relationship can be reversed in Lewis-acidic polymers. Using molecular dynamics, polyboranes are identified that achieve up to ten-fold increases in Li^+ diffusivities and significant decreases in anion diffusivities, relative to PEO in the dilute-ion regime. These results illustrate a general principle for increasing Li^+ diffusivity and transference number with chemistries that exhibit weaker cation and stronger anion coordination.

Graphical TOC Entry



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PEO-based materials are among the most successful SPEs, with net conductivities on the order of $10^{-4} - 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at ambient temperature.¹⁻⁴ However, net conductivity actually overstates electrolyte performance, since only Li^+ typically participates in the electrode chemistries in lithium-based batteries (Fig. 1A). Measurements of the Li^+ transference number, T_{Li} (the ratio of Li^+ conductivity to the total conductivity), show that anions are responsible for most of the conductivity in PEO,⁵⁻⁷ and ion diffusivity measurements reveal that anion diffusivity is an order of magnitude larger than Li^+ diffusivity for common salts at typical concentrations.^{8,9} Most strategies for increasing T_{Li} have focused on immobilizing the anion,¹⁰⁻¹³ while the primary strategy for increasing overall diffusion rates has been to decrease the glass-transition temperature, T_g , of the polymer.^{3,4} However, neither approach addresses the fundamental ion-polymer interactions that are responsible for asymmetric cation and anion conduction.

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The major finding of this work is that the low Li^+ diffusivity and high anion diffusivity that characterize PEO-based SPEs can be reversed to favor Li^+ conduction in Lewis-acidic polymers. In conventional SPEs based on polyethers and other Lewis-basic units, salt solubility is driven by strong cation-polymer interactions.^{11,14,15} However, this preferential coordination of cations leads to both the high relative diffusivity of weakly coordinated anions and the low diffusivity of Li^+ (Fig. 1B). The trade-off between strong cation coordination and diffusivity suggests that the strategy of driving salt solubility with relatively stronger anion-polymer interactions and weaker cation-polymer interactions may enhance SPE performance. To investigate this trade-off, we present over 100 microseconds of MD simulations to characterize the ion diffusivities, coordination structures, and solvation free energies in PEO and four Lewis-acidic polyboranes (Fig. 1C). The employed force-fields are parameterized from *ab initio* electronic structure calculations without experimental fitting; this approach provides a consistent level of theory for all studied polymers and enables the description of the Lewis-acidic polymers for which experimental data does not exist (See Supporting Information for a discussion of force-field validation and full description of the computational

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3 methods).

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5 Throughout this study, we primarily focus on the dilute-ion regime, with additional
6 finite-concentration results presented in the supporting information. Consideration of the
7 dilute-ion regime enables isolation of the ion-polymer interactions that are responsible for the
8 solvation and transport of each ion,^{16,17} while avoiding ion-pairing effects^{18,19} and increases
9 in polymer viscosity^{2,15} that arise at higher ion concentrations. For many polymer-salt
10 combinations, the relative ion-diffusivity in the dilute-ion regime correlates strongly with
11 results obtained at higher concentrations.^{17,20–22}

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13 To illustrate the relative Li⁺ and anion diffusivities in a Lewis-basic environment, Fig.
14 1B presents MD simulations of ion diffusion in PEO in the dilute-ion regime. Results are
15 presented for several anions, including Cl⁻, triflate, and TFSI; these anions vary in both size
16 and charge delocalization, with larger anions possessing increased charge delocalization and
17 reduced Li-salt lattice energies.^{18,23} Comparison of the cation and anion diffusivities in PEO
18 reveals that the anion diffusivities dramatically exceed that of Li⁺ by eight- to thirty-fold,
19 depending on the anion. For PEO:LiTFSI, the simulated dilute ion concentration diffusivities
20 presented in Fig. 1B and Table 1 ($7.9 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ for Li⁺ and $5.9 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ for TFSI)
21 show good agreement with NMR-based diffusivity measurements at similar temperatures and
22 at dilute concentrations ($7-9 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ for Li⁺ and $4-5 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ for TFSI).⁸
23 Direct comparison between theory and experiment for PEO:LiCl and PEO:LiTriflate in Fig.
24 1B is not possible, as ion-pairing occurs even at the lowest concentrations that have been
25 experimentally studied.^{19,24,25}

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27 Fig. 2 examines the molecular basis for the preferential anion diffusion in PEO. Fig. 2a
28 (top row) presents representative coordination structures of all ions in PEO, and Fig. 2b (top
29 panel) shows histograms of the number of polymer atoms that coordinate each ion. Strong
30 coordination of Li⁺ in PEO is reflected in the helical distortion of the polymer structure
31 about the ion and the strongly peaked distribution of coordination structures (Fig. 2a). In
32 contrast, each anion is weakly associated with a large number of methylene units from several
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3 PEO segments, and a broad distribution of coordination structures is observed (Fig. 2b).
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5 These results demonstrate the intrinsic disadvantage that the coordination characteristics of
6
7 PEO-based polymers represent to increasing Li^+ diffusivity and T_{Li} .
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10 Additionally, Fig. 2 reveals that the asymmetric coordination of cations and anions in
11
12 PEO is reversed in the Lewis-acidic polyboranes. Fig. 2a (left column) shows that the charge
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14 distributions of Lewis-acidic polymers is essentially inverted with respect to PEO; whereas
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16 PEO exhibits large negative charges that are localized on the oxygen and delocalized positive
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18 charges on the carbon backbone, the Lewis-acidic polymers exhibit large positive charges
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20 that are localized on the boron and delocalized negative charges on the remaining polymer
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22 atoms. This inversion of the charge distribution between PEO and the Lewis-acidic polymers
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24 is reflected in the weaker coordination of Li^+ and stronger coordination of the anions in the
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26 ion-coordination structures (Fig. 2a) and coordination-structure distributions (Fig. 2b).
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28 Weak coordination of Li^+ in the Lewis-acidic polymers is indicated by the larger number
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30 of polymer atoms coordinated with Li^+ (Fig. 2a) and broader distribution of coordination
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32 structures (Fig. 2b), relative to PEO. In contrast, the anion coordination structures in the
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34 Lewis-acidic polymers include fewer polymer atoms and narrower distributions. Analysis of
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36 the ion-polymer radial-distribution functions (Fig. S1) also demonstrates the same trend.
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38 These results indicate stronger anion coordination and weaker cation coordination in the
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40 Lewis-acidic polymers.
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42
43 Fig. 3 demonstrates that weaker coordination of Li^+ in the Lewis-acidic polymers sub-
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45 stantially improves the Li^+ diffusivity, relative to PEO. In two of the Lewis-acidic polymers,
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47 CBC and HBCC, Li^+ diffusivity is increased four- to ten-fold, respectively. A third polymer,
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49 HBC, shows comparable Li^+ diffusivity to PEO, while CBCC shows suppressed Li^+ diffusiv-
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51 ity. To confirm that the increased Li^+ diffusivity is primarily cause by increased lability of the
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53 coordination structures and not increased polymer segmental motion, polymer-ion contact
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55 autocorrelation functions $\langle h(0)h(t) \rangle$ (see Methods, Fig. 3b) and monomer-unit mean-squared
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57 displacement (MSD) (Fig. 3c) were calculated for each system. The data presented in Fig.
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3b confirm that the shorter duration of the polymer-ion contacts correlates strongly with the observed Li^+ diffusion. The monomer-unit MSDs shown in Fig. 3c are less correlated with the Li^+ transport, although we note that local polymer fluctuations are important for facilitating transitions of Li^+ among coordination structures.^{18,26} Notably, in both CBC and HBCC the Li^+ MSD significantly exceeds the monomer-unit MSD, which indicates that the primary mechanism of Li^+ transport is due to changes in coordination and not due to coupled diffusion with individual polymer segments.

Similarly, Fig. 4 demonstrates that stronger coordination of Cl^- in the Lewis-acidic polymers substantially reduces the Cl^- diffusivity, relative to PEO. Fig. 4a shows that the rapid Cl^- diffusion observed in PEO is suppressed in all of the Lewis-acidic polymers. Figs. 4b and 4c show the calculated polymer- Cl^- contact autocorrelation functions and polymer monomer unit MSDs, respectively. As in the case of Li^+ , rapid diffusion coincides with short-lived polymer- Cl^- contacts, with the Lewis-acidic polymers all showing longer-lived polymer- Cl^- contacts relative to PEO. Fig. S2 contains the corresponding results for triflate and TFSI^- ; in all cases longer-lived anion-polymer contacts correlate with decreased anion diffusivity, with most of the Lewis-acidic polymers showing longer-lived anion-polymer contacts in comparison with PEO. The mechanism that emerges from these ion-diffusion simulations is that the Lewis-acidic polymers generally increase the strength of anion-polymer interactions and decrease the strength of Li^+ -polymer interactions, leading to an increase in Li^+ diffusion and relatively suppressed anion diffusion.

Fig. 5a shows that in all cases, the Lewis-acidic polymers exhibit improved T_{Li} in comparison to PEO. The two Lewis-acidic polymers with the highest Li^+ diffusivity, HBCC and CBC, also exhibit the largest improvements in T_{Li} , reflecting that these polymers achieve both increased Li^+ diffusivity and decreased anion diffusivity. The magnitude of the improvement in T_{Li} also varies depending on the anion, with Cl^- showing the largest improvements in all Lewis-acidic polymers.

The increased anion coordination in the Lewis-acidic polymers is also reflected in the

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3 relative contribution of the anion solvation to the total salt solvation. Fig. 5b presents the
4 ion-resolved solvation free energies associated with transferring each ion from vacuum into
5 each polymer, revealing that all combinations of Li-salt and Lewis-acidic polymer exhibit
6 total solvation free energies that exceed the lattice energies of the salts. This suggests the
7 capacity of the Lewis-acidic polymers to dissolve the studied salts, although the extent of ion-
8 pairing cannot be established solely from dilute-ion simulations and is explored separately
9 in Fig. S3. The capacity of the Lewis-acidic polymers to dissolve Li-salts is also supported
10 by liquid-electrolyte studies; for instance, LiTriflate is soluble in borane-based Lewis-acidic
11 solvents²⁷ and both LiF and LiCl exhibit solubility increases of several orders of magnitude
12 in liquid electrolytes when boranes are used as cosolvents.^{13,28} Fig. 5c presents the fractional
13 contribution of each anion to the total salt solvation free energy, demonstrating that the
14 increases in T_{Li} are mirrored by increases in the relative contribution of the anion solvation
15 free energy to the total salt solvation free energy. Taken together, the results in Fig. 5
16 suggest that high T_{Li} and high salt solubility can be simultaneously achieved by driving
17 solubility with strong anion solvation while leaving Li^+ only weakly complexed.

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34 Additional simulations performed at finite ion concentration with the LiTFSI salt indicate
35 that, in some cases, the Lewis-acidic polymers exhibit comparable ion-pairing to PEO and
36 increased conductivity (Fig. S3). Following previous work,²⁹⁻³² the finite ion concentration
37 simulations are performed with scaled partial charges on the ions to account for the effects of
38 electronic polarizability, which reduces the viscosity and ion-pairing. This approach makes
39 the finite ion concentration simulations more approximate than the dilute-ion simulations
40 discussed earlier, while still enabling qualitative comparisons of ion-pairing and conductivity
41 among polymers. Fig. S3 shows that, in comparison to PEO, the Lewis-acidic polymers dis-
42 play increased T_{Li} in some, but not all, cases. In particular, CBC:LiTFSI exhibits increased
43 conductivity and reduced levels of ion-pairing compared to PEO:LiTFSI.

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The current work represents a systematic computational study of ion transport in Lewis-
acidic polymers and suggests a strategy for developing alternative polymer chemistries for

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3 lithium-based electrolytes. Dilute-ion simulations of PEO demonstrate that strong Li^+ co-
4 ordination and weak anion coordination manifest in dramatically suppressed Li^+ transport
5 relative to several common anions (Fig. 1b). In contrast, in Lewis-acidic polymers, relatively
6 weaker Li^+ coordination and stronger anion coordination (Fig. 2) result in up to a ten-fold
7 increase in Li^+ diffusivity (Fig. 3) and twenty-fold increase in T_{Li} (Fig. 4a). The mechanism
8 for the improved performance of the Lewis-acidic polymers is shorter-lived Li^+ -polymer con-
9 tacts (Fig. 3b) and longer-lived anion polymer contacts (Fig. 4b) that liberate Li^+ diffusion
10 relative to the anion in the Lewis-acidic polymers. Comparisons of the ion-resolved solvation
11 free energies in each polymer demonstrate that the Lewis-acidic polymers also exhibit lower
12 Li^+ solvation free energies (Fig. 4b) while generally increasing the relative contribution of
13 the anion to the total salt solvation free energy (Fig. 4c). These results present a consistent
14 picture of increasing SPE figures-of-merit via weakening Li^+ coordination and strengthening
15 anion coordination using Lewis-acidic polymer chemistries. Given the extremely slow pace
16 of developing viable SPEs that are based on alternatives to polyether chemistry, the identi-
17 fication of a class of polymers that potentially overcomes the intrinsic limitations of PEO is
18 encouraging.

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36 PEO was the first polymer electrolyte discovered¹⁴ and is still the majority component
37 of the highest-performing SPEs,^{3,33} but new polymer chemistries are required to make SPEs
38 a viable alternative to liquid electrolytes.¹ Recent increases in Li^+ diffusivity and conduc-
39 tivity have primarily been achieved through extrinsic innovations—the addition of nanopar-
40 ticles and plasticizers,^{1,34} the use of low-lattice energy salts,^{35,36} and the synthesis of amor-
41 phous, branched polymers^{3,4}—while leaving the underlying ether-based polymer chemistry
42 unchanged. Likewise, the main strategies for increasing T_{Li} include slowing anion diffusion
43 via covalent immobilization,^{10,12} Lewis-acidic additives,^{11,13} or dilute Lewis-acidic polymer
44 moieties,^{37,38} while leaving strong Li^+ coordination in place.

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The current study demonstrates that the fundamental ion-polymer interactions respon-
sible for both low D_{Li} and T_{Li} in PEO-based polymers can be favorably reversed in a Lewis-

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3 acidic environment. Although the detailed study of the electrochemical decomposition of
4 these materials is outside the scope of the current study,³⁹ prior uses of Lewis-acidic molec-
5 ular additives^{11,13} suggest that the proposed polymer chemistries may be sufficiently stable
6 for battery applications. We also note that electrode interfacial impedance and dendrite
7 growth pose significant materials challenges for the improvement of battery technologies,¹
8 although the high Li^+ diffusivity and T_{Li} for the Lewis-acidic polymers could potentially
9 reduce these effects.² The results presented here indicate that removing Lewis-basic units
10 entirely or developing polymer chemistries with complementary weak Lewis-basic and strong
11 Lewis-acidic moieties is a potentially more promising approach than optimizing D_{Li} and T_{Li}
12 in the context of polyether chemistry. Likewise, developing anions with strong polymer-
13 specific interactions is an opportunity for further improvement. The optimal balance will
14 ultimately be determined by the solvating capacity and stability of the resulting polymer.
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Table 1: Apparent ion diffusivities and monomer-unit diffusivities^a calculated for each of the polymer electrolytes in the dilute-ion regime.^b

Polymer	$D_{\text{Li}}^{\text{app}}$	$D_{\text{Cl}}^{\text{app}}$	$D_{\text{triflate}}^{\text{app}}$	$D_{\text{TFSI}}^{\text{app}}$	$D_{\text{seg}}^{\text{app}}$
PEO	0.79(6)	22(2)	11(1)	5.9(6)	1.05(2)
CBC	2.7(3)	2.4(3)	7.1(7)	17(1)	1.63(2)
CBCC	0.16(1)	0.66(6)	1(2)	0.8(1)	0.79(1)
HBC	0.56(9)	1.3(3)	1.3(2)	1.3(1)	2.07(6)
HBCC	6(1)	4.0(7)	16(3)	16(3)	1.37(2)

^aCalculated based on the average MSD of oxygen or boron in each polymer

^bFor all cases, apparent diffusivity is based on the MSD at $t = 150$ ns, as described in the methods section. Units of $10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ are reported. Numbers in parentheses indicate the statistical uncertainty in the last reported digit.

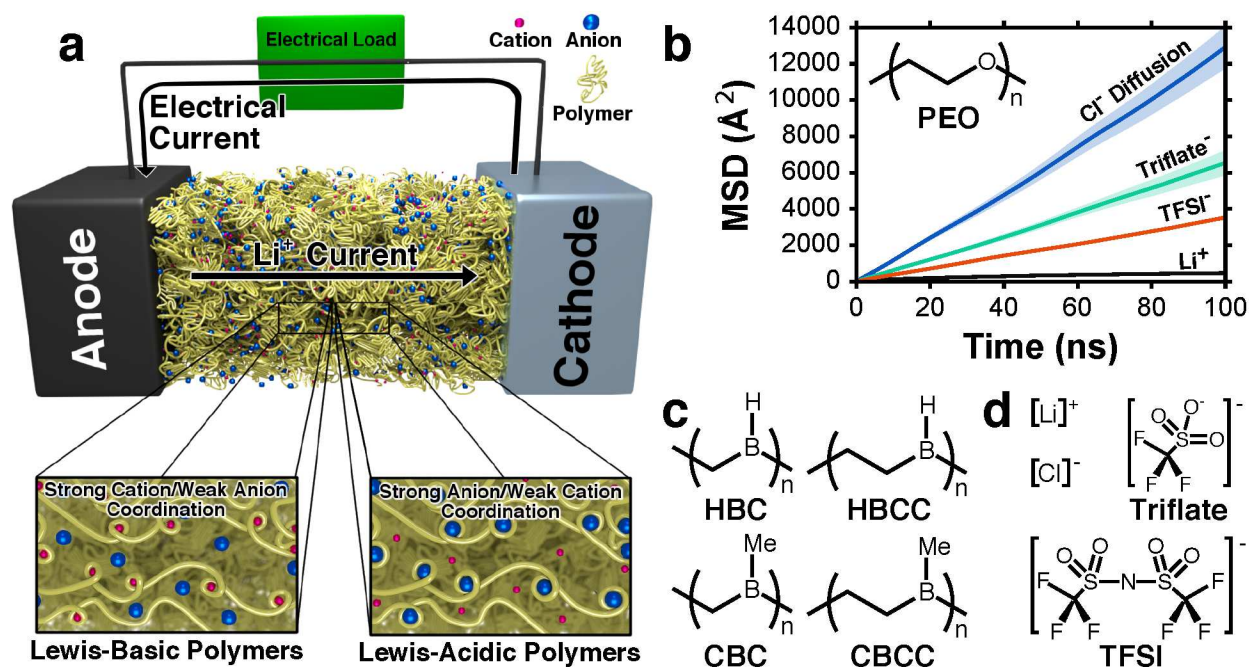


Figure 1: Overview of the new polymer electrolyte concept, motivating problem, and materials. (a) Schematic depiction of solid polymer electrolyte operation in Lewis-basic polymers and Lewis-acidic polymers. Cations are preferentially complexed in the conventional Lewis-basic environment, whereas anion complexation is promoted in Lewis-acidic environments. (b) Mean-squared displacement of Li^+ and several anions in PEO in the dilute-ion regime, based on MD trajectories at 400 K. The asymmetric transport of anions and cations in PEO is reflected in the higher diffusivities of all anions relative to Li^+ . Average values are plotted as solid lines and standard errors are plotted as shaded regions. (c) Chemical structures of the Lewis-acidic polymers simulated in this study. (d) Chemical structures of the ions simulated in this study.

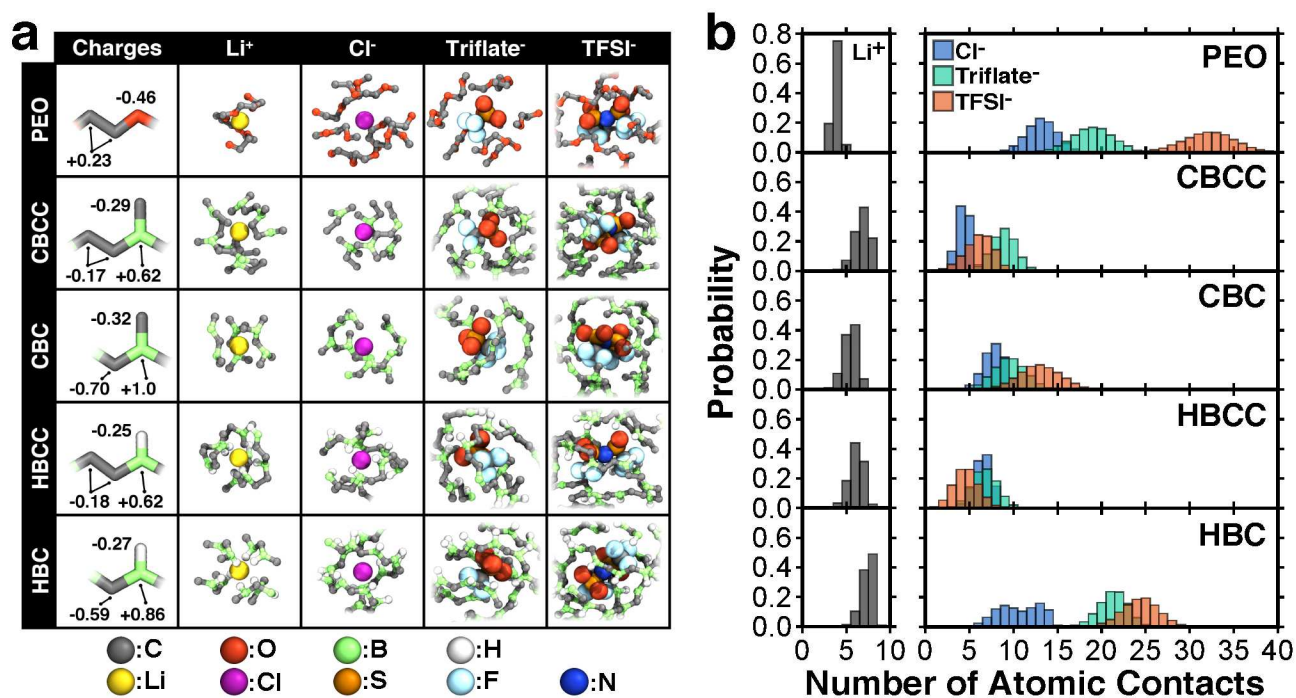


Figure 2: Contrasting ion coordination behavior in Lewis-basic and Lewis-acidic polymers. (a) Representative coordination structures of each ion in each polymer. The CHELPG derived partial charges used in the MD simulations are shown in the left column. (b) Histograms of the number of polymer-ion contacts averaged across the simulations. All data is derived from MD trajectories at 400 K in the dilute-ion regime.

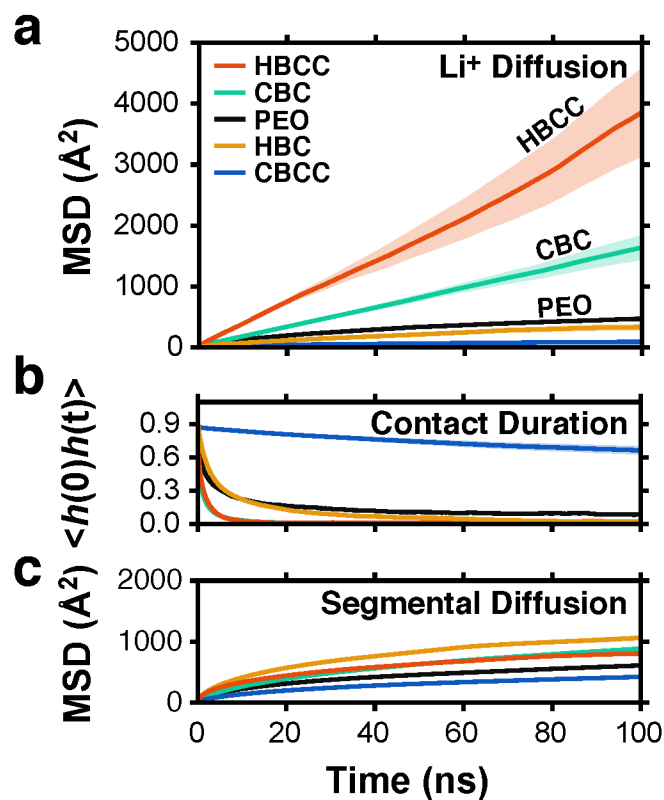


Figure 3: Contrasting Li^+ transport behavior in Lewis-basic and Lewis-acidic polymers. (a) Comparison of the mean-squared displacement (MSD) of Li^+ in all polymers. (b) Contact durations for Li^+ and the predominant binding atoms in each polymer (see Figure 2a, O for PEO; CH_3 for CBC; CH_2 for CBCC; and H for HBC and HBCC). (c) MSD of the polymer monomer units. All data is derived from MD trajectories at 400 K in the dilute-ion regime. Average values are plotted as solid lines and standard errors are plotted as shaded regions.

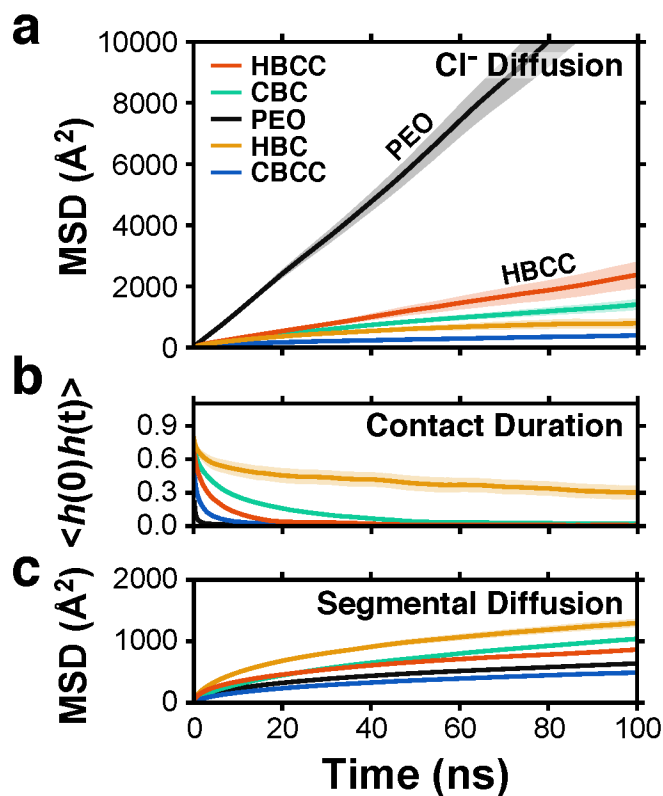


Figure 4: Contrasting Cl^- transport behavior in Lewis-basic and Lewis-acidic polymers. (a) Comparison of the mean-squared displacement (MSD) of Cl^- in all polymers. (b) Contact durations for Cl^- and its predominant binding atom in each polymer (see Figure 2a, C for PEO and B for all Lewis-acidic polymers). (c) MSD of the polymer monomer units. All data is derived from MD trajectories at 400 K in the dilute-ion regime. Average values are plotted as solid lines and standard errors are plotted as shaded regions.

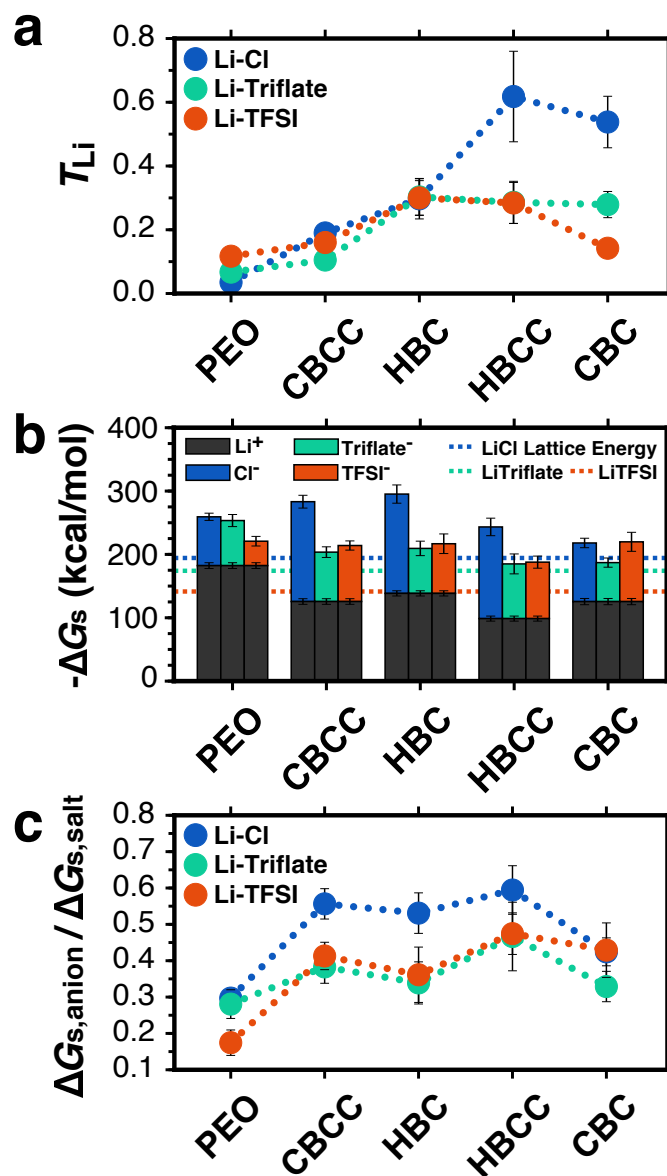


Figure 5: Comparison of T_{Li} and ion solvation free energies in Lewis-basic and Lewis-acidic polymers. (a) Transference numbers for all salts in the dilute-ion regime. Dotted lines are a guide to the eye. (b) Solvation free energies for each ion in each polymer and the lattice energies of the corresponding Li-salts (dotted lines). (c) Fractional contribution of each anion to the total salt solvation free energy for each polymer. All free energies are calculated via thermodynamic integration at 400 K in the dilute-ion regime. The anion solvation free energies have an additional contribution from the quantum chemical relaxation of the solvation structures calculated via free-energy perturbation.