

# Effect of High Salt Concentration on Ion Clustering and Transport in Polymer Solid Electrolytes: a Molecular Dynamics Study of PEO-LiTFSI

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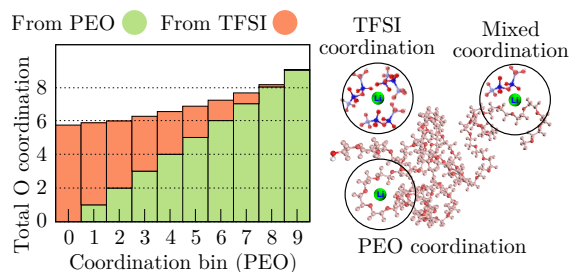
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## Abstract

Currently available solid polymer electrolytes for Li-ion cells require deeper understanding and significant improvement in ionic transport properties in order to enable their use in high-power batteries. We use molecular dynamics simulations to model the solid amorphous polymer electrolyte system comprising poly(ethylene) oxide (PEO), lithium and bis(trifluoromethane)sulfonimide anion (TFSI), exploring effects of high salt concentrations relevant for battery applications. Using statistical analysis of ion distribution and transport, we investigate the significant effect that salt concentration

has on ion mobility. At practical salt concentrations a previously undetected ensemble of Li-TFSI clusters emerges where Li ions have significantly lower coordination by the polymer, and this results in their significantly lower mobility compared to Li ions coordinated by the polymer. We also find the tendency for cation-anion clusters to be asymmetrical, with the anions in greater number than Li cations, which may further affect transport properties of this material. Our methodology enables us to suggest strategies for improvement of transport properties and can be generalized to other polymer-Li-salt combinations.

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## Introduction

Wide-spread adoption of environmentally friendly electric vehicles demands battery systems that are safe and have high energy density and high power capabilities.<sup>1,2</sup> Efficiency, power and safety of cells are controlled largely by the properties of the electrolyte. Solid amorphous polymer materials are seen as attractive candidates to replace today’s liquid electrolytes, due to their tunable mechanical properties, low density, scalable processing and less flammable nature.<sup>3-8</sup> On the other hand, the overall low room-temperature ionic conductivity and low transference number in commonly used polymer electrolytes present major challenges for high power rechargeable battery applications.<sup>9-13</sup> The best performing electrolytes, based on poly(ethylene) oxide (PEO), have been intensively investigated but showed only limited

improvement since their first implementation in the 1970s.<sup>14-16</sup> The combination of PEO and Li bis(trifluoromethane) sulfonimide (TFSI) salt is the most commonly used polymer electrolyte for lithium-ion batteries, mainly due to its good solvating properties.<sup>11,17,18</sup> Unfortunately, there is limited capability to experimentally characterize ionic interactions in these materials, due to the difficulty in decoupling individual movements and correlations of cations, anions and polymers, and the existence of multiple time scales governing overall dynamics and transport. As a result, detailed understanding of ionic transport mechanisms and conductivity limitations are presently insufficient. At the same time, this information is critical for rational optimization of these classes of materials and design of new materials with significantly improved conductivity.

In this work we study the important PEO-Li-TFSI system using molecular dynamics simulations and address the impact of cation coordination, cooperative motion and clustering on ionic transport. In addition to clarifying the microscopic transport mechanisms governing this particular electrolyte, our qualitative understanding of these phenomena form a valuable platform for studying and designing a wide range of polymeric systems. Our simulations and analysis result in three unexpected findings: 1. The anion plays a crucial role in lithium coordination, and families with different coordination are found in the system (Figure 1), 2. Prominent clusters of LiTFSI appear at higher salt concentration 3. The composition of the salt clusters exhibits asymmetry, preferring larger numbers of TFSI anions than Li cations and resulting in a lower contribution to the cooperative motion of Li ions. Previous molecular dynamics simulations on highly concentrated electrolytes have been successful in clarifying the combination of mechanisms of lithium transport, namely intra-chain motion, inter-chain hopping, and segmental motion with a chain.<sup>19,20</sup> However, there is a lack of specific understanding on the relationship between coordination, cooperative ion motion and clustering, especially at salt concentrations relevant to practical operation regimes. The majority of computational works in the literature focus on the dilute limit, explaining the comparatively high lithium conductivity in PEO,<sup>21</sup> but ignoring the correlation between mobile species and

structural effects found in highly concentrated electrolytes. There are a couple of important findings common to most studies present in the literature: 1. the evidence of 4-7 oxygen atoms coordinating lithium, and 2. the intrinsic coupling between the polymer motion and the cation.<sup>19,22-26</sup> Both these results highlight the importance of the coupling between the PEO chains, which contains oxygen atoms in its backbone, and the lithium atoms. Motivated by experimental speculations,<sup>27</sup> recent works from Diddens *et al.* used molecular dynamics techniques to investigate whether the addition of ionic-liquid molecules could enhance lithium mobility. The higher lithium diffusivity in such a ternary system compared to the PEO-LiTFSI binary system can be attributed to the plasticizing effect of the ionic-liquid molecules.<sup>5</sup> The findings showed that essentially all lithium ions are still coordinated by the PEO chains. This, in conjunction with the number of recent publications on PEO-LiTFSI systems<sup>28-32</sup> further testifies to the renewed interest in and to the importance of fundamental understanding of the PEO-LiTFSI coordination environment at technologically-relevant salt concentration. However, the link between cation coordination and mobility as well as cation-anion clustering, especially at salt concentrations relevant to practical applications, are left largely unanswered. Our approach combines fully-atomistic molecular models with statistical correlation analysis and allows us to gain insights into the structural and dynamical aspects of polymer electrolytes at realistic salt concentrations and polymer molecular weights.

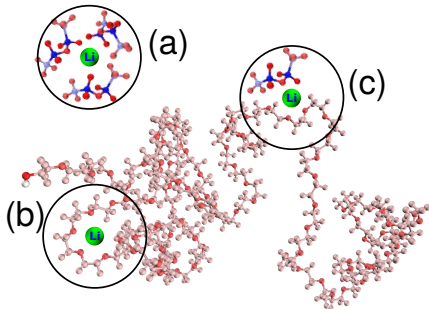


Figure 1: Schematic representation of different coordination environments of Li ion. (a) refers to a anion-only coordination, (b) shows a PEO-only one-chain coordination and (c) sketches a PEO-TFSI mixed coordination environment.

# Simulation methods and force-field validation

The simulated systems contain 40 PEO chains, each 100 monomers long and terminated with hydrogen, with 480 LiTFSI for 4 M case (35 760 total atoms) and 120 LiTFSI for 1 M case (30 000 total atoms). The interactions at the molecular level are described using the all atoms PCFF+ force-field, except for the point charges assigned to Li and TFSI atoms where we use a reduced total cation/anion charge of 0.75  $|e|$ . Charge rescaling in classical force fields is commonly found to be necessary to reproduce structural and transport properties of alkaline salts in organic electrolyte systems.<sup>33,34</sup> Alternatively some works advocate the use of more complex polarizable force-fields,<sup>35</sup> but that approach is significantly more computationally expensive. We find that charge rescaling is able to capture both structure and dynamics sufficiently well for our mechanistic studies. To validate the force field and charge parameters we present below the comparisons with experimental values for density and conductivity (and radial distribution function in the electronic supplementary information).

Table 1 summarizes the partial charges assigned to the atoms composing the anion in all the different scenarios investigated in this study. Polymer builder and force-field parameters

Table 1: Summary of the partial charges assigned to the atoms composing the anion in three different scenarios: 1. normal dynamics, 2. and 3. we artificially chose the charges to obtain more and less polar configurations respectively. A charge of 0.75  $|e|$  is used for Li.

Atom type	Charges [ $e$ ]		
	Normal	Polar	Spread
N	-0.482	-2.25	-0.05
S	+1.308	0.00	-0.05
O	-0.624	0.00	-0.05
C	+0.748	+0.75	-0.05
F	-0.314	0.00	-0.05
Total	-0.750	-0.750	-0.750

are provided by the Medea package from Materials Design, Inc. All molecular dynamics simulations have periodic boundary conditions and are performed using the LAMMPS simulation package.<sup>36</sup> A velocity-Verlet integrator with a time step of  $\delta t = 1.0$  fs has been used

to evolve the equations of motion. Pressure and temperature were enforced on the systems with a Nosé-Hoover barostat ( $1000 \delta t = 1$  ps coupling) and thermostat ( $100 \delta t = 0.1$  ps coupling),<sup>37-39</sup> respectively. The structures used in this investigation are generated by packing the systems into a periodic simulation cell at a target mass density 40% smaller than the pure PEO mass density (25 °C,  $M_W \sim 5000$ <sup>40</sup>) to reduce stagnation in the generation routine. The equilibration routine relies on a series of energy minimization, compression/decompression and annealing stages broadly based on previous works<sup>41,42</sup> (details in the electronic supplementary information). In order to validate our simulation method and force-field, we computed the mass density and conductivity (and radial distribution function, see electronic supplementary information) as a function of salt concentration at 80 °C. The density is calculated after the equilibration procedure over a 0.5 ns simulation where the density is recorded every  $100 \delta t = 0.1$  ps to ensure sufficiently uncorrelated values. The reported mass density and standard deviation are computed from the 5000 recorded values. For 1 M and 4 M the computed mass density is  $(1.129 \pm 0.003) \text{ gcm}^{-3}$  and  $(1.335 \pm 0.003) \text{ gcm}^{-3}$ , respectively. The experimental mass density for pure PEO (25 °C,  $M_W \sim 5000$ ) was found to be  $1.12 \text{ gcm}^{-3}$ ,<sup>40</sup> and  $2.023 \text{ gcm}^{-3}$  for LiTFSI.<sup>43</sup> Therefore, we expect the density to increase for larger salt concentrations, as observed in our simulations.  $1.2 \text{ gcm}^{-3}$  and  $1.3 \text{ gcm}^{-3}$  are the mass density values for 1.0 M and 4.1 M, respectively, computed from the experimental molal density<sup>44</sup>(details in the electronic supplementary information). These mass density results are in reasonable agreement with the experimental trends and absolute values, although temperature and uncertainties of the experimental values are unknown. In order to further test the force-field, we quantitatively investigate ionic conductivity of the polymer-salt system. The conductivity values are calculated from a 140 ns simulation using the Wheeler-Newman approach for concentrated solutions.<sup>45</sup> This simulation time was identified as sufficient to reach the diffusive regime of Li and TFSI (see supplementary information). Figure 2 shows the comparison between the computed Li ionic conductivity values and the experimental ones from ref.<sup>44</sup> The experimental values are within a factor of two from the computed ones

and, more importantly, the correct trend for cationic conductivity as a function of Li-salt concentration is reproduced. The radial distribution function (RDF) between lithium atoms and all the oxygen atoms in the system is also computed to verify the structural properties of the model. Albeit slightly shifted as compared to results from polarizable force-field<sup>46</sup> and experiments,<sup>47</sup> the RDF shows the commonly-observed strong Li-oxygen peak. Similarly to the literature, the peak includes coordination from all oxygen atoms in the system, meaning the observed shift is equal for all oxygen atoms regardless of whether they belong to the TFSI anion or the PEO backbone. This observation is important in the context of the clustering results presented later, as no bias towards PEO or TFSI oxygen atoms is introduced by the charge rescaling. It is worth highlighting that while a smaller charge rescaling than the one adopted here is expected to shift the peak closer to the value obtained with polarizable force-fields, it is also expected to further underestimate the conductivity and, therefore, worsen the comparison between the computed and experimental conductivity. A charge rescaling of 75 %, as adopted in this work, is deemed a reasonable compromise. These results give us the confidence in the transferability of the force-field necessary to perform molecular dynamics simulation on this systems. The PEO-LiTFSI structures then undergo the dynamics simu-

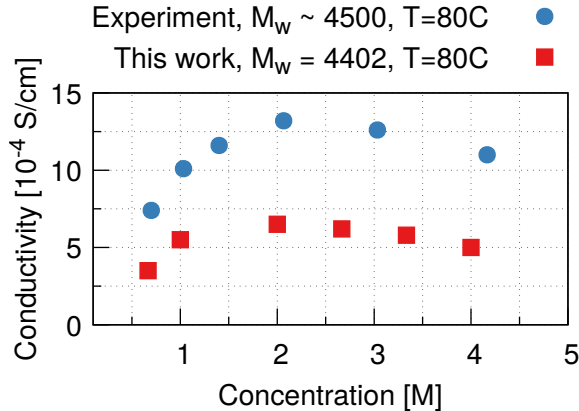


Figure 2: Li ionic conductivity values as a function of Li-TFSI salt concentration. The experimental values are from.<sup>44</sup>

lation needed for the mobility analysis: 20 ns dynamics with a constant number of particles, constant pressure (1 bar) and constant temperature (80 °C). Snapshots of the structures for

post-processing are saved every 100 ps.

## Results and Discussion

To investigate the importance of concentration and clustering on the cation mobility in the PEO-Li-TFSI system we examine the statistics of Li motion as a function of its coordination by the negative atomic species of the polymer and the salt anion. First, we study in detail the role of high salt concentration and its effect on the coordination of Li by the polymer chains. We then identify the influence of different coordination environments on the short-time ionic dynamics and highlight asymmetries in the composition of Li-TFSI clusters. Lastly, we use molecular dynamics for a variety of scenarios with structural constraints and modifications in order to provide design ideas for improving cation mobility.

### Effect of concentration on cation coordination

Figure 3 provides the relative statistics of Li coordination by PEO and by TFSI in the Li-TFSI-PEO system. We consider oxygens from either the anion or the polymer backbone or both as “coordinating” if found within a sphere of radius 4.00 Å centered on every cation present in the system. The 4.00 Å radius ensures that we minimize the noise due to temperature in the determination of the coordination cage. A more detailed discussion on the choice of the cutoff radius can be found in the electronic supplementary information. Figure 3a-b shows the summary of the findings for the 4 M case while Figure 3c-d for the lower salt concentration of 1 M. Looking at Figure 3b-left, we observe that there is a large fraction of Li ions with a small coordination number (less than four) if we only take into account oxygens from PEO. It is clear that the anion plays a substantial role in the coordination of Li, especially for the fraction of cations which are under-coordinated by the PEO oxygen. In particular, for the 4 M case we found approximately 15% of the cations that have no coordination by PEO at all. Figure 3a presents the oxygen contribution from the TFSI anion to



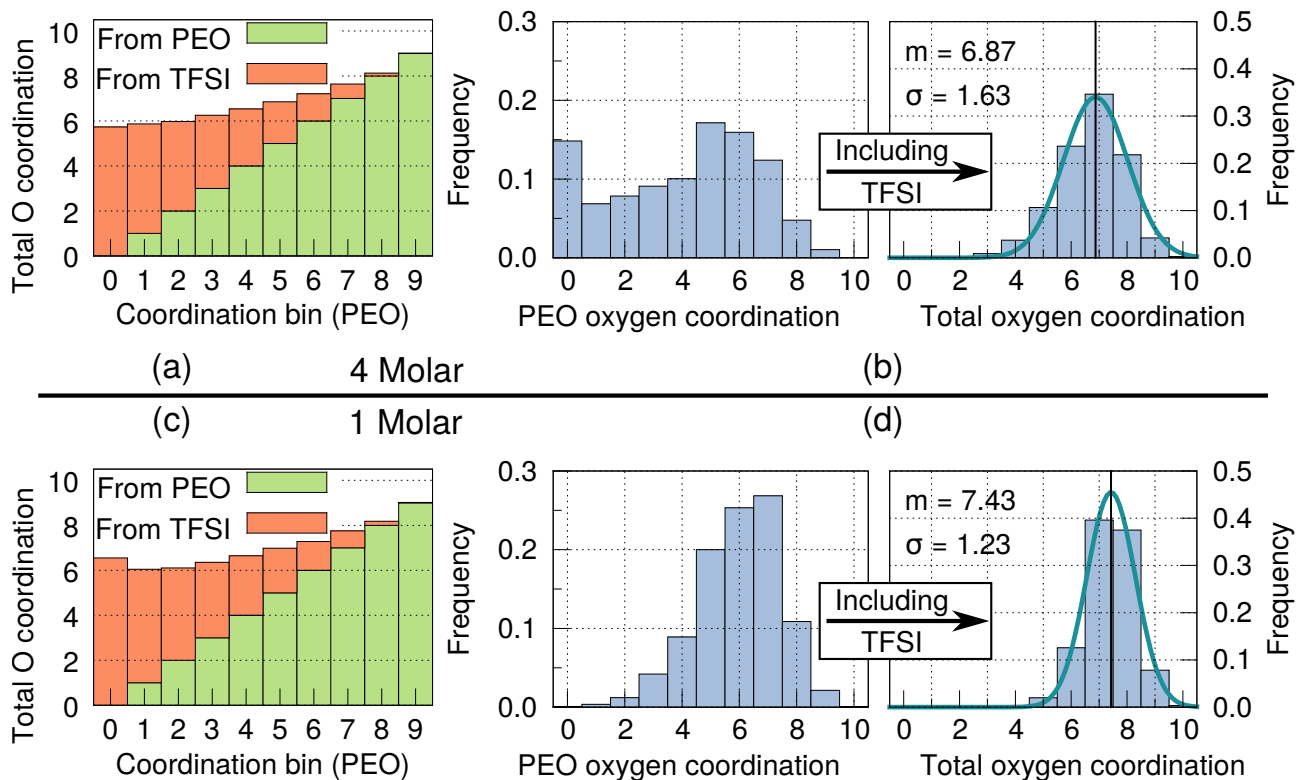


Figure 3: From left to right: (a) Relative contribution to the cation total coordination of Li by oxygens from the TFSI anion and the PEO backbone, (b)-left coordination distribution when only the oxygens from the polymer are taken into account and (b)-right total coordination distribution where both anion and polymer oxygens are counted. From top to bottom: 4.00 M and 1.00 M salt concentration.

the Li coordination for different PEO coordination environments. Combining the anion contribution (Figure 3a) with the PEO contribution of coordination (Figure 3b-left) we obtain the total distribution of oxygen surrounding the cations in the system, Figure 3b-right. We also notice that the majority of Li ions are coordinated by a single PEO chain, confirming previous suggestions.<sup>24,26</sup> More specifically, for the 1 M case  $\sim 80\%$  of Li is coordinated by one chain and almost all the rest by two chains. For the 4 M case  $\sim 75\%$  of Li is coordinated by one chain and  $\sim 10\%$  by two chains, and  $\sim 15\%$  of Li is not coordinated by the polymer at all (details in electronic supplementary information). On the one hand the overall oxygen coordination distribution is barely modified going from the 1 M to the 4 M salt concentration and the total 6-7 oxygen coordination is consistent with previous studies on dilute salt concentrations.<sup>21,23,48</sup> However, in contrast with earlier work, by looking more closely at the

origin of the coordinating oxygen, we find that the oxygens from TFSI account for 39 % and 19 % of the total count for respectively the 4 M and 1 M salt concentrations. The unexpected finding is that an ensemble of Li ions exists that is not coordinated by any oxygen from the polymer backbone (see Figure 3b-left), instead associating only with TFSI anions, especially at high salt concentrations. The landscape in which cations move is significantly altered by the presence of the anion and this has a strong effect on its mobility, as we describe in the next section.

### **Effect of concentration on ion motion**

In this section we analyze the dynamics of the different cation coordination environments by studying the mobility of the cations contained in such configurations. In order to decouple the effect of structure and composition of the polymer on Li dynamics, we perform controlled computational experiments and study how Li atoms move under different local constraints. We note that the short-time mechanistic information would be lost by calculating the overall diffusion constant as an average over the entire system trajectory. As it is widely conjectured that for polymers with high molecular weight Li conductivity is determined mainly by segmental dynamics,<sup>49,50</sup> we investigate the motion of Li in different coordination environments over short time intervals, primarily focusing on the effects of high salt concentration and of coupling among different mobile species. To this end we compute the average distance traveled by all the cations in a given coordination bin over a time period of 100 ps. The 100 ps time window is used to investigate the dynamics and flexibility of the qualitatively different coordination cages in which the lithium is trapped, and not to infer long-scale diffusion properties. Figure 4 summarizes the findings for the two salt concentrations under investigation. We notice that for lower salt concentration we obtain a higher cation mobility than for the more concentrated case, consistent with experimental observations.<sup>51,52</sup> Moreover different coordination environments do not lead to significant differences in the mobility for the 1 M case. On the other hand, the 4 M case produces a different behavior: the more

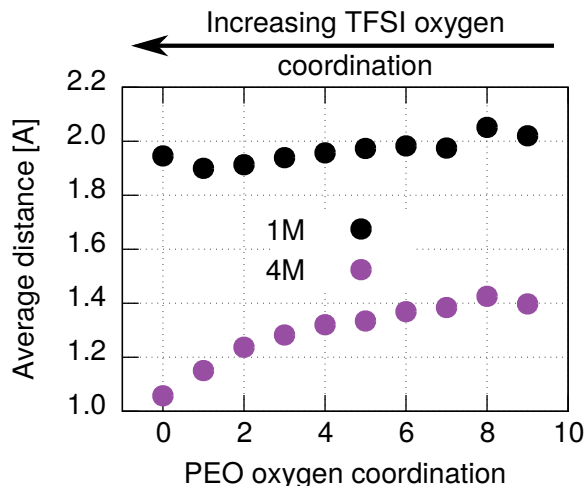


Figure 4: Average distance in Angstrom traveled by the cations in a specific oxygen (from the polymer) coordination bin over 100 ps for both the 1 M (black dots) and 4 M (purple dots) salt concentration.

the Li cation is coordinated by the anion, the lower its mobility is, by up to 40% at full TFSI-coordination. In the next section we show that these observations are the consequence of clusters of salt nucleating in the system.

## Clustering of anions and cations

An important observation from Figure 3a, c and Figure 4 is that the anion-cation coordination has a noticeable effect on the cation mobility, hence we analyze the spatial correlation between the two components by looking at clusters they form during the simulation, i.e. configuration where anions and cations are located nearby. We identify clusters by following a variant of the single-linkage clustering algorithm, iteratively grouping Li cations with TFSI anions based on a threshold distance of  $3.25 \text{ \AA}$  between any (negatively charged) TFSI atom and Li. Starting from a lithium in the system we look for all the negatively charged atomic species in the anion within the cutoff, i.e., nitrogen, oxygen and fluorine atoms. If any are found, we proceed by looking for lithium atoms, other than the initial one, within the same cutoff but now centered on all negative species of the anions found at the previous step. The

operation is repeated until no new species are found. The cluster composition is determined by counting the cations and anions. We then repeat the operation from a different starting lithium atom. Figure 5a-b present the distribution of cluster compositions at 4 M salt concentration on the left, (a), and the biggest cluster during the entire simulation on the right, (b). Figure 5c-d show the same information for the 1 M case. The black diagonal line

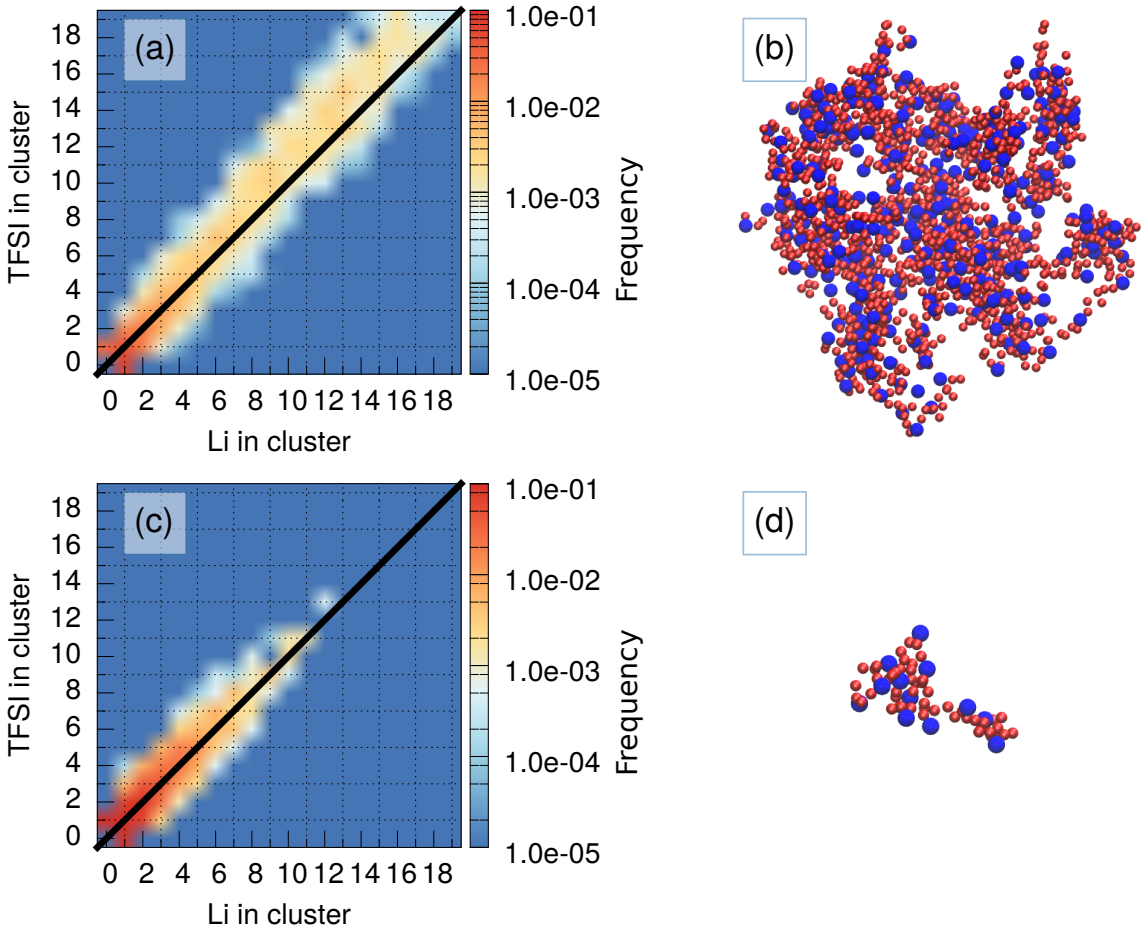


Figure 5: Cluster analysis. (a)-(b) refer to the 4 M case while (c)-(d) to the 1 M one. The plots on the left, (a)-(c), summarize the cluster compositions during the simulation. The plots on the right, (b)-(d), show the biggest cluster formations found during the dynamics.

on Figure 5a and c corresponds to clusters with symmetric compositions, i.e. equal count of anions and cations. We denote with  $(C_iA_j)^{i-j}$  the cluster with the number of Li atoms  $i$ , TFSI molecules  $j$ , and charge  $i - j$ . At both salt concentration the most common clusters are small, containing only a few atoms/molecules. The most frequent species are always the  $(C_1A_0)^{1+}$  and  $(C_0A_1)^{1-}$  representing Li and TFSI isolated from each other, see Table 2, and

$(C_1A_1)^0$  corresponding to a dimer. As expected from electrostatic considerations, extreme cases where there is a high composition asymmetry (high total charge) are not present. This observation also explains the lower amount of small clusters with even size ( $i + j = 2n$ ) compared to the nearest odd sizes ( $i + j = 2n \pm 1$ ) in Table 2. Ignoring the contribution from neutral clusters, the major contribution to even clusters is from  $i - j = \pm 2$ , which carries a double positive/negative charge. One notable observation is the tendency for big clusters to have an anion predominance in their composition. This can be noticed from the asymmetry of the distribution of frequencies with respect to the black diagonal line in Figure 5a and c as well as from Table 2. Since the total number of Li and TFSI are equal in the simulation, looking at the difference between  $(C_1A_0)^{1+}$  and  $(C_0A_1)^{1-}$ , the isolated species, we can determine the overall asymmetry in the cluster compositions. In the 4 M case there are almost three times as many isolated Li ions than isolated TFSI molecules (6.5% versus 2.3%). This implies that over the entire population of non-trivial clusters ( $i + j > 1$ ) there is an overall asymmetry, with the majority of clusters containing an excess of TFSI and thus negatively charged. At lower concentration we see a higher percentage of isolated  $(C_1A_0)^{1+}$  cation

Table 2: (cation + anion) / (total number of cation and anion) percentage for all asymmetric clusters with size: (cation + anion)  $\leq 8$ . The first column reports a given cluster size followed by all the positive cluster combinations possible at that size. The negative clusters with the same total size have switched cation/anion indices and opposite cluster charge. For every cluster size and concentration we report the summation over all the positive (cation > anion) and negative (anion > cation) clusters, separately.

Cation + Anion: Positive combinations (reverse indices and charge for negative)	1 M		4 M	
	Positive	Negative	Positive	Negative
1: $(C_1A_0)^+$ — Free species	13 %	> 12 %	6.5 %	> 2.9 %
3: $(C_2A_1)^{1+}$ , $(C_3A_0)^{3+}$	6.4 %	< 6.8 %	1.7 %	> 1.5 %
4: $(C_3A_1)^{2+}$ , $(C_4A_0)^{4+}$	0.2 %	< 0.5 %	0.1 %	= 0.1 %
5: $(C_3A_2)^{1+}$ , $(C_4A_1)^{3+}$ , $(C_5A_0)^{5+}$	2.4 %	< 4.1 %	0.7 %	< 0.8 %
6: $(C_4A_2)^{2+}$ , $(C_5A_1)^{4+}$ , $(C_6A_0)^{6+}$	0.1 %	< 0.7 %	0.1 %	< 0.2 %
7: $(C_4A_3)^{1+}$ , $(C_5A_2)^{3+}$ , $(C_6A_1)^{5+}$ , $(C_7A_0)^{7+}$	0.9 %	< 2.1 %	0.4 %	< 0.5 %
8: $(C_5A_3)^{2+}$ , $(C_6A_2)^{4+}$ , $(C_7A_1)^{6+}$ , $(C_8A_0)^{8+}$	0.2 %	< 0.5 %	0.1 %	< 0.2 %

and  $(C_0A_1)^{1-}$  anion species, and clusters are overall smaller. This is consistent with 1 M

Li-TFSI concentration being lower than the solubility limit at these conditions and model parameters. At the same time cluster composition is more symmetric than at 4 M salt concentration: negatively charged clusters still account for the majority, however with a small margin. While the existence of clusters is expected based on similar observations on other salts,<sup>26,53-55</sup> the asymmetry in the clusters has not been discussed before. We explain this observation using the Li-O coordination statistics. As shown earlier, due to a combination of steric and electrostatic interactions, Li prefers to be coordinated by about 6-7 oxygens, regardless of their chemical origin. There is thus competition for Li ions from both the PEO chain and the TFSI and a sizable population of Li is coordinated by both PEO and TFSI. Since PEO oxygens provide some of the negative charge environment to stabilize the coordination of Li, there will be Li-TFSI clusters that are overall negative, hence Li-deficient. It has been previously shown that clusters are undesired since they lower the ability of the system to transport ionic charge.<sup>55</sup> The impact of different Li-salt concentration on transport properties such as transference number is uncertain since different conflicting effects on increasing salt concentrations have been observed experimentally,<sup>28,56-61</sup> and are likely system-dependent. We anticipate that the asymmetry in the cluster composition may have a significant effect on the overall transport properties of the system. On one hand, small negatively charged clusters such as  $(C_1A_2)^{1-}$  or  $(C_2A_3)^{1-}$  would transport Li in the direction opposite to where positive Li ions move during battery operation, thereby reducing the Li transference number. On the other hand, the higher concentration and higher mobility of free Li and than that of clusters could counterbalance this effect. Further in-depth investigations of the effect of correlation and asymmetry on macroscopic transport properties, in the context of concentrated solution theory, would help in assessing their interplay and relative importance. It is worth highlighting the robustness of the observation on asymmetrical clustering. Similar results are observed when focusing on only oxygen atoms within a cutoff of 4.00 Å, consistent with the analysis presented earlier on Li coordination (see electronic supplementary informations).

## Effect of constraints on ion motion

Here we present efforts to gain microscopic understanding of the role of cations and anions and their correlation in transport properties. For this study we focus on the 4 M salt concentration. Our approach is to perform computational experiments by introducing controlled modifications and constraints in the electrolyte system. Similar modifications are normally hard to reproduce experimentally, and, therefore, our conclusions drawn from the following results should be interpreted as an effort to gain mechanistic understanding, decouple competing influences on ionic transport and develop strategies for polymer design with higher conductivity.

The first investigation consists of fixing in space a given number of atoms in the simulation and observing the implications on the mobility of the cations; the total number of fixed atoms is 480. In Figure 6a we show the result of freezing all the nitrogen belonging to TFSI, which immobilizes the anions. This allows us to study the impact of anion mobility on the cation mobility. First we notice that fixing the nitrogen positions has the obvious effect of decreasing the mobility of the cations that are predominantly coordinated by TFSI. Furthermore, freezing the nitrogens has an effect on the mobility of Li cations that are mainly surrounded by oxygens coming from the polymer backbone as well. This is explained by observing that, even if not directly limited in their movements, PEO chains experience numerous constraints when all the anion present in the system are frozen, hence the polymer segmentation motion is hindered.

In Figure 6b we freeze directly every PEO chain in 12 points, i.e., roughly every 8 monomers. In this case, we observe that the major change in mobility is found in cations that are mainly PEO-coordinated. The effect on cations that are mainly coordinated by the anion is weaker than the effect on cations coordinated by the polymer when we immobilize the nitrogens of TFSI. This suggests that the mobility of Li-TFSI clusters is not severely altered by reducing the freedom of movement of the chains. Given that Li mobility noticeably changes when the movement of PEO chains is restricted, we conclude that polymer chain

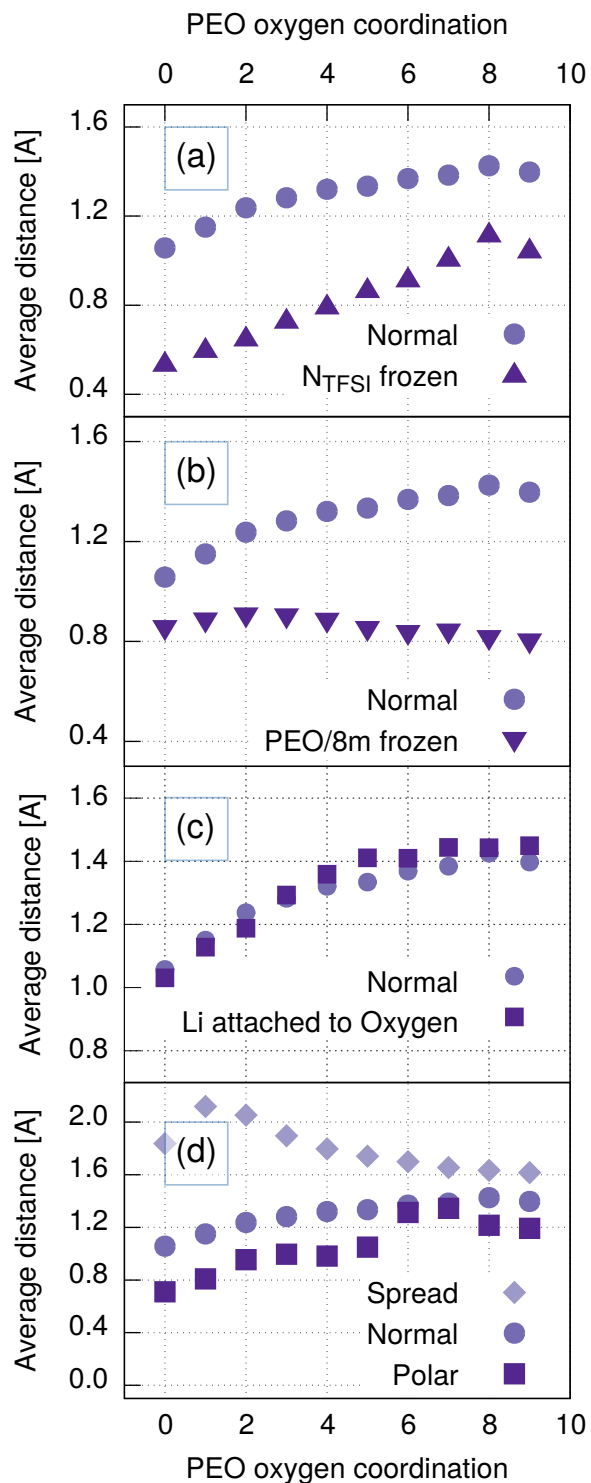


Figure 6: Molecular dynamics modifications to better understand the potential implications of four effects: 1. immobilized anion (corresponding to (a) where we freeze all the nitrogen from TFSI). 2. less mobile chains (corresponding to (b) where we freeze every PEO chain in 12 points). 3. Li atoms bonded to the closest PEO oxygen, if any is coordinated (corresponding to (c)). 4. different charge repartition on the anion (corresponding to (d) where we reorganize the charges on TFSI atoms according to Table 1).



motion plays a central role in cation diffusion, and any restrictions would result in lower Li mobility; this observation is supported by the literature.<sup>23,62</sup> Specifically, these results can be used to predict that any modification involving sufficiently aggressive cross-linking of PEO chains will negatively affect the cation mobility.

In the second investigation we isolate the effect of PEO chain segmental motion on Li motion. The procedure is as follows: 1. create a permanent bond between every Li and the closest PEO oxygen (if any is coordinating Li), 2. re-equilibrate the system with the procedure outlined in the Simulation set-up and force-field validation section and 3. perform the motion analysis. Figure 6c shows the results of this study. We do not find any significant differences in the short-time motion of Li between the normal dynamics and the simulation where we attach every Li to the closest PEO oxygen. This clearly shows that in the unmodified real system Li atoms are tightly bound to their host polymer chains. As mentioned above, we find that in the vast majority of Li is associated with a single PEO chain, and it is apparent that Li diffusion, on this time scale, is driven by the segmental motion of the polymer. Our constrained simulation thus proves that inter-chain hops are very rare events, and any motion along the host chain is much slower than the overall Li diffusion brought about by the motion of the chain itself. To verify that this behavior is not an artifact of the limited timescale of our simulations, we performed longer dynamics simulations of over 200 ns. During those runs we observed on average only one inter-chain hop event per Li, which confirms that Li stays attached to a particular PEO chain for a long time, and segmental motion determines the overall Li transport. An additional interesting observation is that motion of Li along the chain is not significant on this time scale either, contrary to the often-discussed picture of transport in PEO electrolytes.

Lastly, we alter the partial charges of the atoms composing the TFSI anion in order to obtain either a highly polar or more even charge distributions across all atoms, while keeping the total charge constant (see Table 1). The results on the cation mobility are illustrated in Figure 6d. Increasing the polarity of the anion negatively effects transport properties

of the polymer electrolyte system in two ways: first the mobility of the Li ions is reduced across all coordination bins, and second the anion-cation clustering is increased; the opposite is observed for the even charge distribution case (details in electronic supplementary information). On the one hand these results depend on the charge distribution chosen for our system and highlight the importance of having a reliable method to determine the total and partial charges of the species involved in the simulation. On the other hand, they show the importance of having an anion where the net charge is spread out as much as possible across all the atoms. This not only increases the cation mobility (see Figure 6d) but also decreases the agglomeration effect and the TFSI-Li coordinated movement (details in electronic supplementary information).

## Conclusion

With the use of a fully atomistic molecular dynamics model, we addressed aspects of Li coordination, ion-salt clustering and cooperative motion in the widely-used PEO-Li-TFSI electrolyte. There are three important points we learned from our investigation.

First, we highlighted the key role that the anion has in coordinating the Li cation in the system. While this is true at both salt concentrations studied, this effect is weaker for the lower salt concentration case. On the other hand, it becomes increasingly important at practically relevant high salt concentration, resulting in the appearance of a new ensemble of cations under-coordinated by the oxygens from the polymer chains. We also showed that the salt-coordinated Li ions have weaker correlation with the motion of the PEO chains and are up to 40% less mobile.

Detailed analysis further shows that the appearance of the aforementioned new ensemble of under-coordinated Li ions implies the formation of large cation-anion clusters. Such clusters show the tendency to have a larger number of anions compared to cations in their composition. This unexpected asymmetry in the clusters' composition could have a signif-

icant impact on overall transport properties of the electrolytes than the mere presence of evenly-populated clusters. The conduction of Li ions as part of negatively-charged clusters may counteract the motion of the more abundant positively charged isolated Li ions. Experimental characterization of the cluster population and detailed measurements of transference number as a function of salt concentration would be beneficial in understanding these effects.

Finally, we show that by restricting the movement of either the PEO chains or the anions have negative effects on the Li mobility. Both these modifications produce a negative impact regardless of the specific coordinating environment of Li and therefore should be avoided or minimized in any design of a PEO-based polymer electrolyte. It is also apparent that the dominant mechanism of transport even at high concentration is the segmental motion of PEO chains to which Li ions are attached for a long time, hopping only rarely and thus relying on the polymer reptation for its diffusion. Finally, we showed that having less polar anions has a two-fold positive effect. The first is that the mobility of Li ions increases significantly, especially for those that are TFSI-coordinated, and the second is that the clustering effect is reduced, indicating higher solubility.

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## Supporting Information Available

Supporting Information: equilibration procedure, Li-O, Li-Li and  $N_{TFSI}$ - $N_{TFSI}$  radial distribution function, example MSD plot, oxygen coordination cage, coordinating chains, clustering procedure, clustering with different cutoff and only considering oxygen atoms, clustering with modified charges. This material is available free of charge via the Internet at

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