

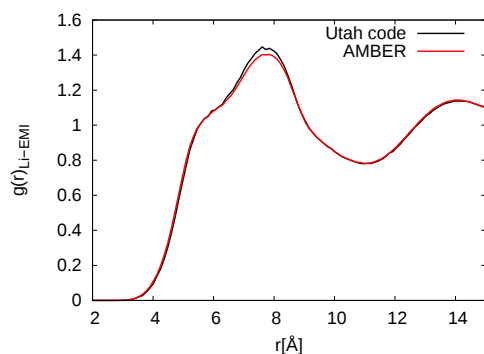
Supporting information to Influence of cation on lithium ion coordination and transport in ionic liquid electrolytes: A molecular dynamics simulation study

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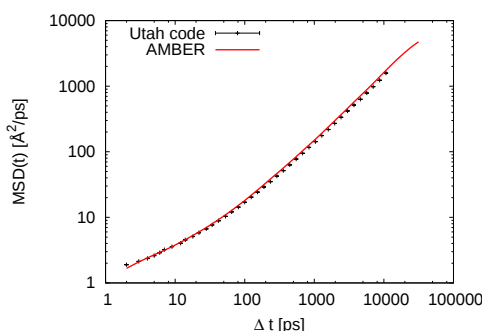
1 Comparison AMBER and Utah group code

Table 1: Comparison of densities for both simulation packages for the system $Li_{0.096,e}$

	Exp.	AMBER	Utah code
ρ [g cm ⁻³]	1.42	1.42	1.42



(a) RDF



(b) MSD

Fig. 1: Comparison of dynamical and structural properties for AMBER and the Utah code

In Fig. 1b the MSD of Li^+ for both packages is shown. The simulation utilizing the modified AMBER10 package is more than a factor 2 longer. Therefore, the MSD is represented by a line while the other one which is obtained via the Utah group code by points including the error bar. The agreement between both packages is excellent.

Radial distribution functions contain information about the accumulation of particles around a center. The investigated systems contain three species. As mentioned in the main article, Lithium ions are coordinated by TFSI oxygens. The second coordination shell is formed by the IL cation, emim. Therefore, in Fig. 1a the radial distribution function of emim around Li^+ is presented. The second coordination shell is strongly influenced by the first one due to electrostatic interactions between emim and TFSI. Thus, we only focus on this RDF. The RDF shows as well as the MSD a good agreement. The small difference in the first coordination shell can be explained by the bond constraining algorithm since AMBER10 constrains only

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the bonds containing hydrogen while the Utah code constrains all bonds. However, the agreement is good bearing in mind the differences of the packages as the tapering function for dipole-dipole interaction or the treatment of electrostatics.

In summary, the agreement between both packages is very good having in mind the different MD algorithms.

2 0.9[emim][TFSI]/0.1[Li][TFSI] ILE

2.1 Densities

Table 2: Comparison of densities for both polarization states with experimental values for $Li_{0.096,e}$ at $T=423$ K

	Exp.	$\alpha_0=0.00$	$\alpha_0=1.00$	$\alpha_0=1.36$
ρ [g cm ⁻³]	1.42	1.41	1.42	1.42

The density can influence the dynamics of the systems. In Tab. 2 the densities of the simulations are compared with the experimental determined one. The reduction of the O_{TFSI} polarization with respect to the ref.¹ has no influence on the densities. Thus, the agreement with both experiment and original version of APPLE&P is excellent. The simulation with $\alpha(O_{TFSI})$ shows a slightly lower density but the deviation is less than 1 %.

2.2 Clustering

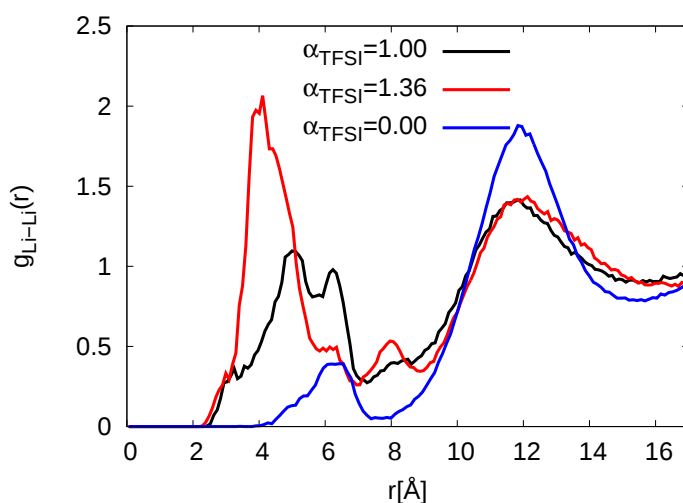


Fig. 2: Comparison of RDF for Li-Li for different TFSI oxygen polarization and ionic liquid cations

Previous works with the increased TFSI oxygen polarization found lithium ion dimers^{2,3}. In Fig. 2 the RDF's of lithium ions with themselves is shown. It can be clearly seen that, regardless which IL cation is used, the lithium ion clustering vanishes once the TFSI oxygen polarization is decreased to $1.00 \text{ \AA}^{-3}$. It seems that TFSI is not longer able to form a stable bridge between two lithium ions.

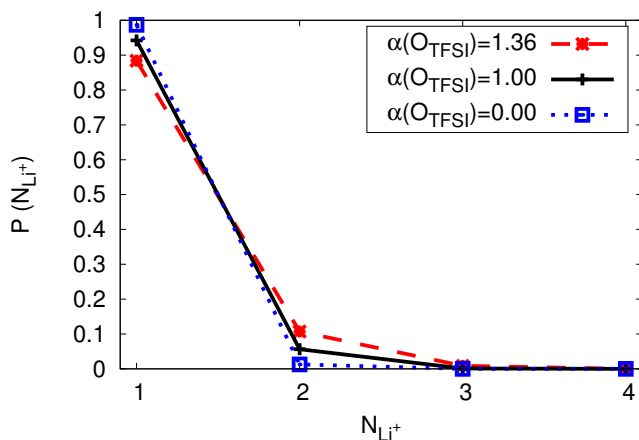


Fig. 3: Probability to find a specific number of lithium ions (N_{Li^+}) around N_{TFSI} within a cutoff of 5 Å

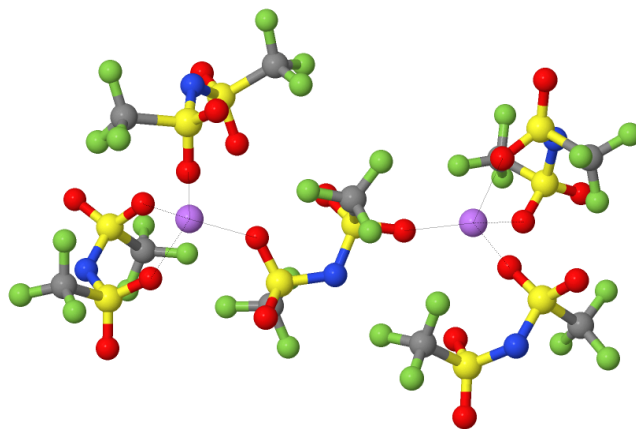


Fig. 4: TFSI as a bridge between two lithium ions

In order to study ion clustering in more detail, we have determined the probability to find a specific number of lithium ions (N_{Li^+}) in the first coordination shell of N_{TFSI} . The cutoff (5 Å) is chosen according to the radial distribution function (shown in the main text).

Fig. 3 clearly shows that reducing O_{TFSI} polarizability increase the probability to find only one lithium ion in the first coordination shell of N_{TFSI} . It becomes also obvious that the probability to find more than two lithium ions in the first coordination shell is nearly zero. While the probability for one lithium increases by reducing O_{TFSI} polarizability, the probability for two lithium decreases. Using $\alpha(O_{TFSI}) = 1.36 \text{ Å}^3$ leads to $P(N_{Li^+} \approx 10 \%)$. Reducing O_{TFSI} polarizability results in $P(N_{Li^+}) \approx 5 \%$. Thus, weaken the Li-TFSI interaction decrease to probability for TFSI to act as a bridge between two lithium ions. Switching off the polarizability of O_{TFSI} results in a probability $P(N_{Li^+} \approx 1 \%)$. Thus, reducing O_{TFSI} decreases the probability for ion clustering. An exemplary ion cluster i shown in 4.

3 Influence of LiTFSI concentration

3.1 Clustering

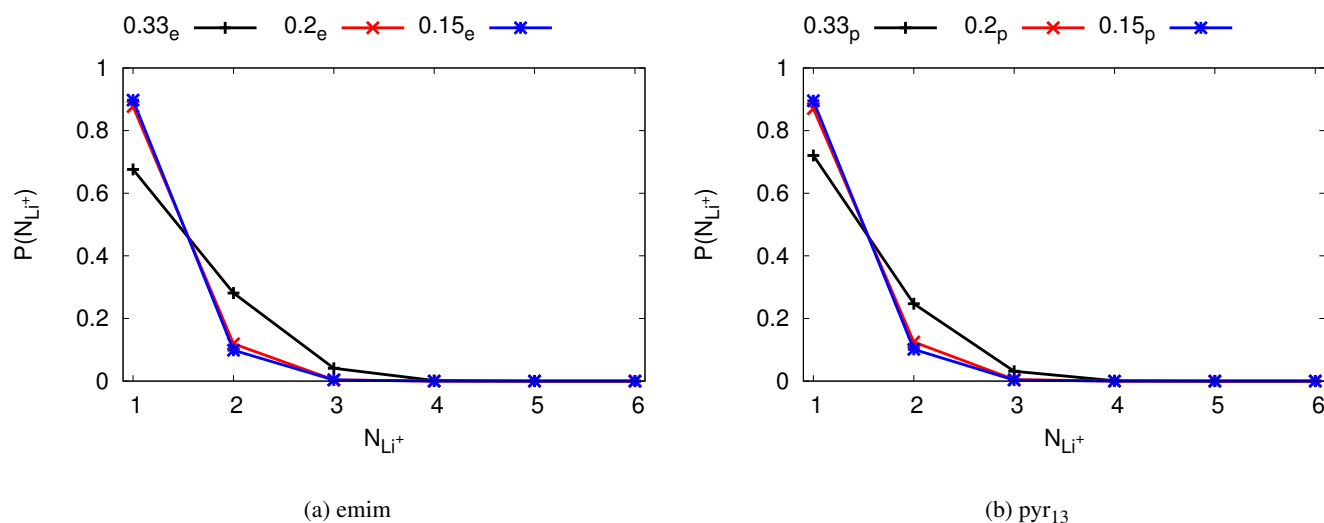


Fig. 5: Comparison of probabilities to find a specific number of lithium ions in the first coordination shell of N_{TFSI} as a function of LiTFSI concentration depending on IL cation

In order to study ion clustering also as a function of LiTFSI concentration depending on the IL cation, we determine the probability to find a specific number of lithium ions in the first coordination shell of Li^+ . The concentrations 0.2 and 0.15 are quite similar. Further addition of LiTFSI leads to lower probability to find only one lithium ion in the first coordination shell of N_{TFSI} but the probability to find two or three lithium ions increases. Thus, increasing LiTFSI concentration changes the clustering in the system.

The comparison of the two IL cationic species indicates that the clustering of lithium ions around TFSI is nearly independent from the IL cationic species. This is in accordance with the investigation of the local environment of lithium ions in the main article.

References

- 1 McOwen, D. W.; Seo, D. M.; Borodin, O.; Vatamanu, J.; Boyle, P. D.; Henderson, W. A. *Energy Environ. Sci.* **2014**, 7, 416426.
- 2 Borodin, O.; Smith, G. D.; Henderson, W. *The Journal of Physical Chemistry B* **2006**, 110, 1687916886.
- 3 Lesch, V.; Jeremias, S.; Moretti, A.; Passerini, S.; Heuer, A.; Borodin, O. *The Journal of Physical Chemistry B* **2014**, 118, 73677375.