

## Insights into solvation and dynamics behaviors of lithium salt in organic- and ionic liquids-based electrolytes

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## 1. Introduction

Tables (S1 and S2) list the results of distinct types of conductivity at 298K, Meanwhile, the values of density, viscosity and conductivity for the electrolyte systems containing 200 pairs of LiTFSI at 298K were given in Table S3. Figure S1 presents the radial distribution function of the lithium salt LiTFSI at 313K in the organic (DMC and DEC) and the ILs ([C<sub>2</sub>mim][BF<sub>4</sub>], [C<sub>2</sub>mim][TFSI], [C<sub>4</sub>mim][BF<sub>4</sub>] and [C<sub>4</sub>mim][TFSI]) solvents. Finally, the radial distribution function of the cation Li<sup>+</sup> in the simulations of 200 pairs of LiTFSI is shown in Figure S2.

## 2. Conductivity

According to the difference of ionic species and correlations, we can divide the total conductivity ( $\sigma_{tot}$ ) into five distinct sub-terms, viz. cation-self ( $\sigma_{cat}^s$ ), anion-self ( $\sigma_{an}^s$ ), cation-distinct ( $\sigma_{cat}^d$ ), anion-distinct ( $\sigma_{an}^d$ ), and cation/anion-distinct ( $\sigma_{cat,an}^d$ ),

$$\sigma_{tot} = \sigma_{cat}^s + \sigma_{an}^s + \sigma_{cat}^d + \sigma_{an}^d + \sigma_{cat,an}^d \quad (S-1),$$

where  $\sigma_{cat}^s$  and  $\sigma_{an}^s$  are conductivity types for self (uncorrelated) ions, as well as  $\sigma_{cat}^d$ ,  $\sigma_{an}^d$  and  $\sigma_{cat,an}^d$  are conductivity types for distinct (correlated) ions. The  $\sigma_{cat}^d$  and  $\sigma_{an}^d$  describe the correlations between two distinct cations and between two distinct anions, respectively; while the  $\sigma_{cat,an}^d$  describes the correlations between one cation and one anion.

The five conductivity types, viz.  $\sigma_{cat}^s$ ,  $\sigma_{an}^s$ ,  $\sigma_{cat}^d$ ,  $\sigma_{an}^d$ , and  $\sigma_{cat,an}^d$ , can be calculated using the equations below:

$$\sigma_{cat}^s = \lim_{t \rightarrow \infty} \frac{1}{6tVK_bT} \sum_i^{cation} \langle (q_i[R_i(t) - R_i(0)]) \cdot (q_i[R_i(t) - R_i(0)]) \rangle \quad (S-2)$$

$$\sigma_{an}^s = \lim_{t \rightarrow \infty} \frac{1}{6tVK_bT} \sum_i^{anion} \langle (q_i[R_i(t) - R_i(0)]) \cdot (q_i[R_i(t) - R_i(0)]) \rangle \quad (S-3)$$

$$\sigma_{cat}^d = \lim_{t \rightarrow \infty} \frac{1}{6tVK_bT} \sum_i^{cation} \sum_{j \neq i}^{cation} \langle (q_i[R_i(t) - R_i(0)]) \cdot (q_j[R_j(t) - R_j(0)]) \rangle \quad (S-4)$$

$$\sigma_{an}^d = \lim_{t \rightarrow \infty} \frac{1}{6tVK_bT} \sum_i^{anion} \sum_{j \neq i}^{anion} \langle (q_i[R_i(t) - R_i(0)]) \cdot (q_j[R_j(t) - R_j(0)]) \rangle \quad (S-5)$$

$$\sigma_{cat,an}^d = \lim_{t \rightarrow \infty} \frac{2}{6tVK_bT} \sum_i^{cation} \sum_j^{anion} \langle (q_i[R_i(t) - R_i(0)]) \cdot (q_j[R_j(t) - R_j(0)]) \rangle \quad (S-6)$$

The results of the five conductivity types for the organic and ILs solvent systems are given in Table S1 and Table S2, respectively.

**Table S1.** Results of the conductivity (S/m) types for the organic solvent systems

conductivity	DEC		DMC	
	298K	313K	298K	313K
$\sigma_{cat}^s$	2.835	2.396	0.228	1.066
$\sigma_{an}^s$	1.408	1.176	0.992	0.551
$\sigma_{cat}^d$	-1.233	-0.385	0.996	1.283
$\sigma_{an}^d$	-0.819	-0.605	-0.644	-0.119
$\sigma_{cat,an}^d(\times 10^{-9})$	-4.090	-0.199	0.168	1.249
$\sigma_{tot}$	2.191	2.582	1.572	2.781

**Table S2.** Results of the conductivity (S/m) types for the ILs solvent systems

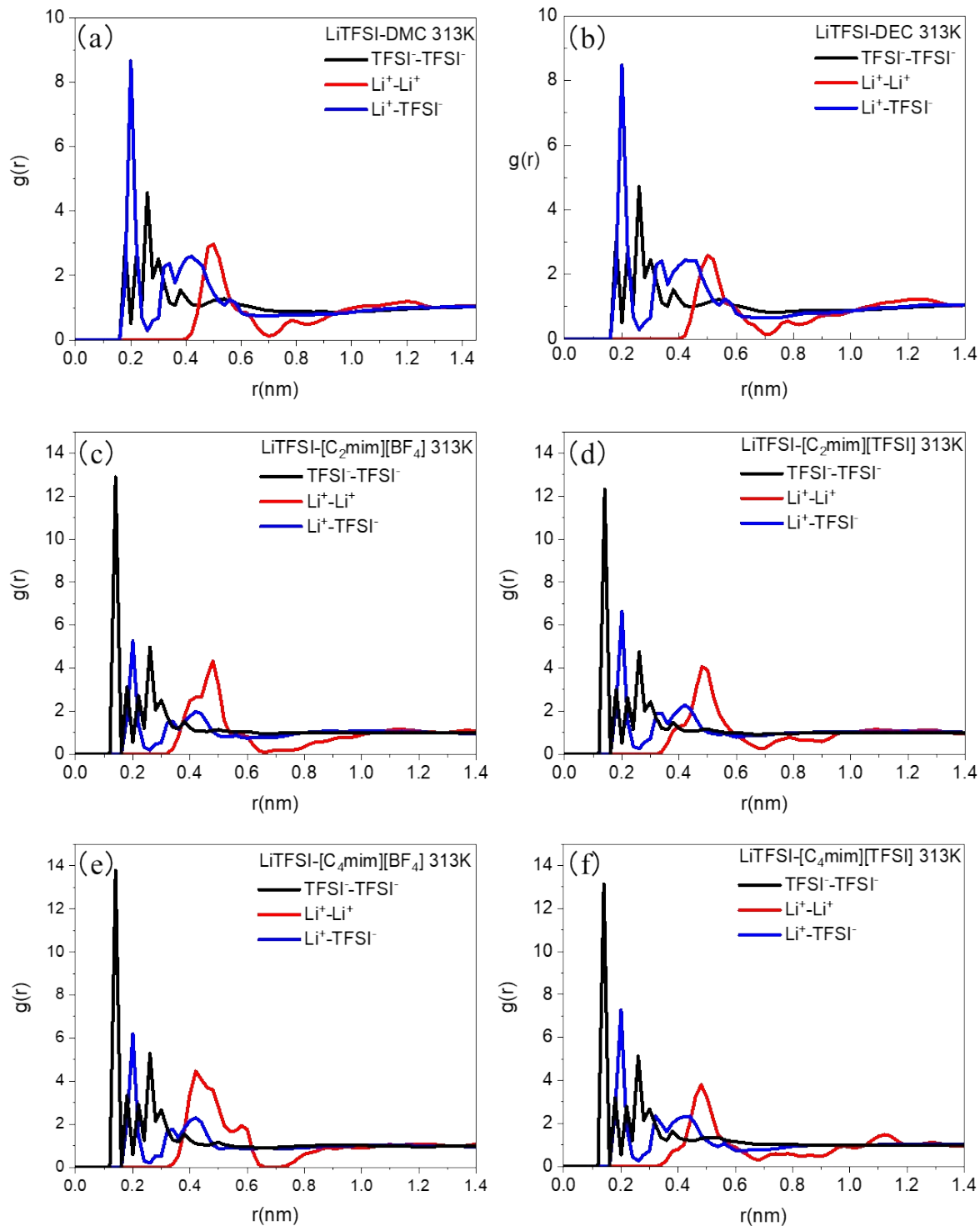
conductivity	[C <sub>2</sub> mim][BF <sub>4</sub> ]		[C <sub>2</sub> mim][TFSI]		[C <sub>4</sub> mim][BF <sub>4</sub> ]		[C <sub>4</sub> mim][TFSI]	
	298K	313K	298K	313K	298K	313K	298K	313K
$\sigma_{cat}^s$	4.262	0.959	2.724	0.874	10.166	2.558	7.627	2.478
$\sigma_{an}^s$	1.246	0.459	0.513	0.399	3.913	0.841	1.826	0.611
$\sigma_{cat}^d$	-0.374	0.070	-0.36	-0.479	-5.144	-0.435	-2.854	0.135
$\sigma_{an}^d$	-0.869	-0.148	-0.129	-0.031	-3.342	-0.574	-1.524	-0.140
$\sigma_{cat,an}^d(\times 10^{-9})$	-0.426	2.942	1.07	-14.262	-1.553	0.561	-1.162	3.018
$\sigma_{tot}$	4.265	1.34	2.748	0.763	5.593	2.39	5.075	3.084

### 3. Physicochemical Properties of 200 pairs of LiTFSI-based electrolyte

**Table S3.** The calculated densities, viscosities and conductivities of the MD simulations for the organic- and IL-based electrolytes with 200 pairs of LiTFSI.

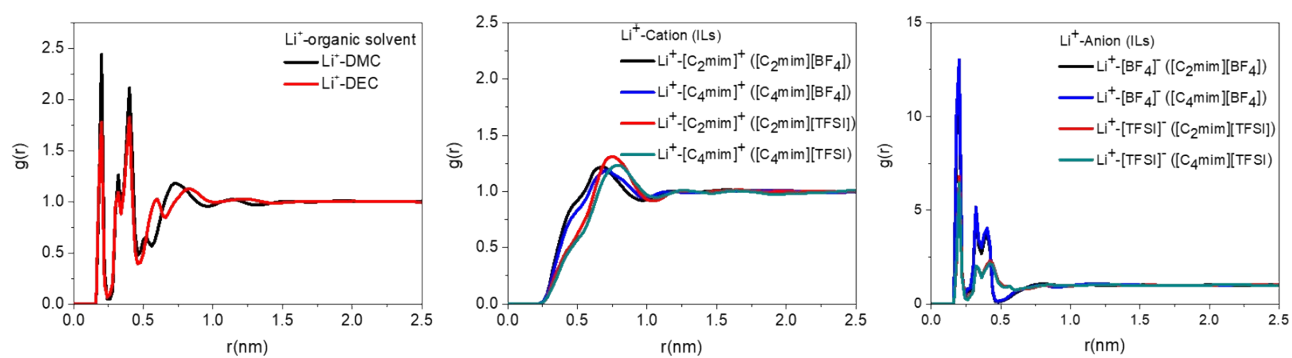
<b>Solvents</b>	<b>Density</b>	<b>Viscosity</b>	<b>Conductivity</b>
<b>DMC</b>	1.475	0.203	1.425
<b>DEC</b>	1.375	0.752	1.007
<b>[C<sub>2</sub>mim][BF<sub>4</sub>]</b>	1.545	1.309	3.682
<b>[C<sub>2</sub>mim][TFSI]</b>	1.735	1.612	2.128
<b>[C<sub>4</sub>mim][BF<sub>4</sub>]</b>	1.505	1.291	3.389
<b>[C<sub>4</sub>mim][TFSI]</b>	1.732	0.818	4.041

## 4. RDF plots for the electrolyte systems containing 40 pairs of LiTFSI at 313K



**Figure S1.** Radial distribution function of the lithium salt LiTFSI at 313K in the organic solvents (a) DMC and (b) DEC, and the ILs solvents (c) [C<sub>2</sub>mim][BF<sub>4</sub>], (d) [C<sub>2</sub>mim][TFSI], (e) [C<sub>4</sub>mim][BF<sub>4</sub>] and (f) [C<sub>4</sub>mim][TFSI].

## 5. RDF plots for the electrolyte systems containing 200 pairs of LiTFSI at 298K



**Figure S2.** Composite graph of the radial distribution functions representing the spatial correlations of the cation  $\text{Li}^+$  with (a) the two organic solvent molecules, and with the (b) cations and (c) anions of the four ILs solvents at 298K.