Insights into the solvation and dynamic behaviors of a lithium salt in organic- and ionic liquid-based electrolytes

Tong, Jiahuan; Xiao, Xingqing; Liang, Xiaodong; von Solms, Nicolas; Huo, Feng; He, Hongyan; Zhang, Suojiao

Published in:
Physical Chemistry Chemical Physics

Link to article, DOI:
[10.1039/c9cp01848d](https://doi.org/10.1039/c9cp01848d)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Tong, J., Xiao, X., Liang, X., von Solms, N., Huo, F., He, H., & Zhang, S. (2019). Insights into the solvation and dynamic behaviors of a lithium salt in organic- and ionic liquid-based electrolytes. *Physical Chemistry Chemical Physics*, 21, 19216-19225 . <https://doi.org/10.1039/c9cp01848d>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

Jiahuan Tong^{a,b}, Xingqing Xiao^{c†}, Xiaodong Liang^a, Nicolas von Solms^{a*}, Feng Huo^{b*}, Hongyan He^b, Suojiang

Zhang^{b*}

^a Department of Chemical & Biochemical Engineering, Technical University of Denmark, DK 2800 Kgs. Lyngby, Denmark

^b Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P.R. China

^c Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, United States

ABSTRACT:

The new-generation lithium-ion batteries use ionic liquids (ILs) as electrolyte solution, greatly enhancing the safety and energy storage capacity of battery. Fundamental molecular insights are useful for understanding the advantages of high conductivity of ILs solvent electrolytes over organic solvent ones. In this work, we computationally studied two organic solvents (DMC and DEC) and four ILs solvents ([C_nmim][BF₄] and [C_nmim][TFSI] (n=2, 4)) to examine the physicochemical properties of the high concentration electrolytes. As expected, the ILs solvent electrolytes exhibit higher density and viscosity, larger self-diffusion coefficient and conductivity than the organics solvent electrolytes. Further, the microstructures of the lithium salt LiTFSI in various solvent electrolytes were investigated to explore the effect of the organic and ILs solvents on the ionic associations of the ions Li⁺ and TFSI⁻. The structural analysis of LiTFSI revealed that the organic solvents restrict the free motion of the ions, reducing the conductivity of the electrolytes. The [BF₄]-type ILs electrolytes have higher conductivity than the [TFSI]-type ILs electrolytes, especially the [C₄mim][BF₄] with the highest conductivity among the ILs-based electrolytes. More importantly, the dissolution of LiTFSI in the ILs solvents is an anion-driven process was proved.

KEYWORDS: Electrolyte Solvation, Imidazole-based Ionic liquids, Dissolution Behavior, Physicochemical Properties

[†] J. Tong and X. Xiao contribute equally to this work.

* Corresponding authors: E-mails: nvs@kt.dtu.dk (N.vonSolms); huofeng@ipe.ac.cn (F.Huo); sjzhang@ipe.ac.cn (S.Zhang).

1. Introduction

Lithium-based battery, as opposed to traditional alkaline battery, has emerged as a novel rechargeable energy storage device due to its high charge density and low self-discharge.^{1,2} Technically, lithium-ion battery utilizes the transportations of lithium ions from the negative electrode to the positive electrode in organic solvent electrolytes to achieve the charging/discharge process.^{3,4} Lithium bis(trifluoromethylsulfonyl) imide (LiTFSI), a most commonly-used lithium salt, takes advantage of its two unique sulfonyl groups to effectively disperse the negative charges on the anions so as to yield more free Li^+ cations for charge transport, thus exhibiting higher ionic conductivities than other lithium salts, such as LiClO_4 , LiPF_6 , in both liquid and solid polymer electrolytes.

Thus far, most of studies on the development of high-performance lithium-ion battery still involve the use of organic solvent electrolytes, such as propylene carbonate, diethyl carbonate, and dimethyl carbonate. Peng *et al.* utilized multinuclear magnetic resonance to study the solvation behaviors of two lithium salts, viz. lithium hexafluorophosphate (LiPF_6) and lithium tetrafluoroborate (LiBF_4), in the mixed electrolytes of ethylene carbonate /dimethyl carbonate, and they found that low solvent polarity favors ion aggregations in both LiPF_6 and LiBF_4 electrolytes.⁵ Fulfer *et al.* investigated the structure and dynamics of electrolytes composed of LiPF_6 in various linear organic carbonates using a combination of linear and two dimensional infrared spectroscopies. Their experimental results indicated that all the linear carbonates can form tetrahedral solvation shells around the ion Li^+ , thereby strengthening the interactions between Li^+ and the carbonate group ($-\text{CO}$).^{6,7} Heckmann *et al.* added LiPF_6 and LiTFSI into dimethyl carbonate, diethyl carbonate or ethyl methyl carbonate to produce high-concentration electrolytes for dual-ion batteries and dual-graphite batteries. They demonstrated that the use of the newly-formulated electrolytes enables a highly reversible cycling stability for the lithium-ion batteries, thus providing high specific discharge capacities.⁸ However, the uses of organic solvent electrolyte in the lithium-ion battery exist two flaws: (i) the inevitable chemical reactions within the electrolyte decrease battery lifetime and (ii) the high inflammability of organic substances increases the risk of fire or explosion. Therefore, developing safe and sustainable novel electrolytes for the lithium-ion battery is a crucial challenge in current energy storage industry.

Ionic liquids (ILs), an environmentally-friendly green solvent, is an alternative to traditional organic solvent in battery manufacturing industry, because of its unique physicochemical properties, such as high thermal stability, negligible vapor pressure (i.e., neither flammable nor volatile), and high ionic conductivity.^{9,10} The IL is a molten salt in the liquid state at room temperature, which exists a large number of free cations/anions and short-lived ion pairs. Generally, when using the ILs as solvent to dissolve lithium salt, the free IL ions are easy to associate with the Li^+ through ionic coupling interactions. The formation of ion association increases ionic strength, thereby improving the electrical conductivity of solutions. Hu *et al.* developed a novel polymeric ionic liquid-based gel electrolyte and then characterized several important property parameters, such as thermal stability, ionic conductivity, and electrochemical stability. They found that this polymeric electrolyte film exhibits high polymer

segmental mobility, a large number of charge carriers as well as high mobility.¹¹ To develop novel high-safety lithium-ion battery, Yang *et al.* improved the electrolyte by mixing pyrrolidinium-based ionic liquid with organic additive and LiTFSI. Their work indicated when the content of ionic liquid in the mixed electrolyte is 65 vol%, the LiFePO₄/Li cells produced by the mixed electrolyte showed a good cycle performance at room temperature, delivering high reversible capacities in the range of 152-157 mAhg⁻¹ at 0.1 C.¹² Borodin *et al.* conducted computational studies on the transportations of the ions Li⁺ in the ILs-based electrolytes.¹³ They simulated the self-diffusion of Li⁺ in ionic liquids, N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide ([mppy][TFSI]) and N,N-dimethyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ([mmpy][TFSI]), and found that the ion self-diffusion coefficients follow the order Li⁺ < TFSI⁻ < mmpy⁺ or mppy⁺.¹⁴

To enhance the electrochemical performance of lithium-ion battery, it is necessary to examine the solvation behaviors of lithium salt in varied electrolyte solutions. Fundamental molecular insights are useful for understanding the advantages of novel ILs solvent electrolytes over traditional organic solvent electrolytes. However, few studies were conducted to provide a systematic comparison of the organic- and IL-based electrolytes, especially in high concentration of lithium salt solution. Further, a detailed discussion regarding “how the cation/anion moieties in ILs affect the physicochemical properties of the ILs-based electrolytes” is lacked in other studies. Understanding the effect of IL cation/anion moieties on the dissolution of Li salt in the electrolytes is useful in improving the ionic conductivities of ILs-based electrolytes. In this work, we conducted atomistic molecular dynamics (MD) simulations to examine the solvation behaviors of LiTFSI in two organic solvent electrolytes (viz. dimethyl carbonate (DMC) and diethyl carbonate (DEC)) and four 1- alkyl -3- methyl imidazole ILs solvent electrolytes (viz. [C_nmim][BF₄] and [C_nmim][TFSI] (n=2,4)). The physicochemical properties of the electrolyte solutions, such as density, viscosity, self-diffusion coefficient, and conductivity, were calculated to compare the organic and ILs solvent electrolytes. The microstructures of LiTFSI were analyzed further in various solvent electrolytes by evaluating the radial distribution function (*g(r)*) and ionic coordination number (*N*) to explore the correlations between structural and physical properties at a micro-scale level.

2. Simulation Method and Model

All the atomistic MD simulations in this work were conducted for the lithium salt LiTFSI with a concentration of 2 mol/L when got solvated in the organic solvents of dimethyl carbonate (DMC) and diethyl carbonate (DEC), and the ionic liquids of [C_nmim][BF₄] and [C_nmim][TFSI] (n=2,4), at 298K and 313K, respectively. The general Amber force field (GAFF)¹⁵ was used to describe the atom types for DMC, DEC. The validity of the GAFF to describe pure organic electrolyte solvents, for instance DMC, DEC and ethylene carbonate (EC), was studied by Zhang *et al.*¹⁶; an average deviation between the computed and experimentally-measured liquid density is within 3%. An optimized all atom force field improved by Liu *et al.*¹⁷ based on the AMBER force field was used to

describe $[\text{C}_n\text{mim}]^+$, $[\text{BF}_4]^-$, $[\text{TFSI}]^-$, which accurately characterized the density, diffusion coefficient, and conductivity of ILs in their simulation study, The partial charges of these organic solvents and ILs were obtained by following the restrained electrostatic potential (RESP) procedure.¹⁸ To accurately capture the thermodynamic and transport properties of ILs in this work, scaled down the atomic partial charges by a charge scaling factor of 0.8 to alleviate the problem associated with overestimating the electrostatic interactions between ions due to polarization effects.^{19,20} Using the reduced partial charges and the polarizable force field, Schmollngruber *et al.*²¹ simulated and compared the diffusion coefficient and the electrical conductivity of ILs, and found that their results are comparable in the two approaches.

To keep a consistent salt concentration in our simulations, 40 ion pairs $\text{Li}^+\text{-TFSI}^-$ were placed in a periodic boundary box containing 135 DMC or 94 DEC for organic solvents, and 75 $[\text{C}_2\text{mim}][\text{BF}_4]$ or 61 $[\text{C}_4\text{mim}][\text{BF}_4]$ or 45 $[\text{C}_2\text{mim}][\text{TFSI}]$ or 39 $[\text{C}_4\text{mim}][\text{TFSI}]$ for ILs, respectively (Figure 1). The initial configurations of the simulated models were constructed by using Packmol package.²² All the MD simulations were carried out in the Gromacs software.²³ Details of the simulation procedure are given as follows. Each simulation system is relaxed in the canonical (NVT) ensemble for the first 5ns and then in the isothermal-isobaric (NPT) ensemble for the next 5ns. Production simulation is carried out for 30ns in the NPT ensemble and for 10 ns in the microcanonical (NVE) ensemble to achieve the configurational equilibria. The Verlet algorithm with a time step of 1.0 fs is employed to integrate Newton's equations of motion. The van der Waals interaction is treated with the Lennard-Jones potential and the electrostatic interaction is evaluated using the Particle Mesh Ewald (PME) technique. During the simulation, the trajectories are recorded at every 0.1ps for further post-analysis.

Figure 1. Structures of the ions and solvent molecules involved in our MD simulations: (a) lithium (Li^+); (b) [bis(trifluoromethanesulfonyl)imide] (TFSI^-); (c) dimethyl carbonate (DMC); (d) diethyl carbonate (DEC); (e) 1-ethyl-3-methylimidazolium ($[\text{C}_2\text{mim}]^+$); (f) 1-butyl-3-methylimidazolium ($[\text{C}_4\text{mim}]^+$); (g) tetrafluoroborate ($[\text{BF}_4]^-$).

3. Results and Discussions

3.1 Physicochemical properties

3.1.1 Density

Aqueous electrolyte solutions with high density offer battery a more powerful energy. In this work, the average bulk density (ρ) of the electrolyte solutions was calculated in 30ns NPT ensemble equilibration simulations using the equation (1)²⁴

$$\langle \rho \rangle = \frac{\sum n_i M_i}{\langle V \rangle} \quad (1)$$

Where n_i is the amount of substance of component i, $\langle V \rangle$ is the volume, M_i is the molar mass of component i.

The densities of both the LiTFSI-organic solvent and LiTFSI-ILs solvent electrolytes at 298K and 313K (Table 1) were firstly calculated. Meanwhile, the experimentally-measured densities of these pure solvents are given in Table 1. Obviously, the addition of the lithium salt LiTFSI to the electrolytes causes the increase of density due to their strong mutual interactions between Li^+ and TFSI^- (The ion-ion interactions will be discussed in detail at a molecular level later). This observation has been reported in other studies of ILs/ Li^+ mixtures.²⁵ By comparing the organic solvents DMC and DEC with the ILs solvents $[\text{C}_n\text{mim}][\text{TFSI}]$ and $[\text{C}_n\text{mim}][\text{BF}_4]$ in Table 1, it is seen that the computed density of the LiTFSI-ILs solvent electrolytes is higher than that of the LiTFSI-organic solvent electrolytes at each temperature. Additionally, it is found that for a common anion ($[\text{BF}_4]^-$ or $[\text{TFSI}]^-$), $[\text{C}_2\text{mim}]$ -type ILs solvent electrolytes have higher density than $[\text{C}_4\text{mim}]$ -type electrolytes, while for a common cation ($[\text{C}_2\text{mim}]^+$ or $[\text{C}_4\text{mim}]^+$), $[\text{TFSI}]$ -type ILs solvent electrolytes have higher density than $[\text{BF}_4]$ -type ILs solvent electrolytes. As the temperature increases from 298K to 313K, the densities of both the LiTFSI-organic solvent and LiTFSI-ILs solvent electrolytes experience a notable decrease, which is in accordance with Yang's experimental observation.²⁶

Table 1. Density (unit: g/cm^3) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes*.

Temperature(K)	DMC	DEC	$[\text{C}_2\text{mim}][\text{TFSI}]$	$[\text{C}_2\text{mim}][\text{BF}_4]$	$[\text{C}_4\text{mim}][\text{TFSI}]$	$[\text{C}_4\text{mim}][\text{BF}_4]$
298	1.471(1.07 ^a)	1.373(0.98 ^b)	1.743(1.52 ^c)	1.538(1.28 ^c)	1.672(1.42 ^c)	1.429(1.19 ^c)
313	1.448	1.361	1.708	1.534	1.599	1.383

*Densities of these pure solvents at 298K are provided in parentheses.

(a) Tojo et al. experiment (ref.²⁷). (b) Shukla et al. experiment (ref.²⁸). (c) Zhang et al. experiment (ref.²⁹).

3.1.2 Viscosity

The electrolyte with moderate viscosity can effectively prevent the solvents from evaporation, thereby reducing environmental pollution and increasing energy storage capacity of battery. In this work, the zero-shear viscosity was calculated in 30ns NPT ensemble equilibration simulations using the Green-Kubo (GK) formula³⁰

$$\eta = \frac{V}{10K_bT} \int_0^\infty \langle \sum_{xy} P_{xy}(0) P_{xy}(t) \rangle dt \quad (2),$$

where V is the volume of the system, T is the temperature, K_b is the Boltzmann constant, and P_{xy} refers to an independent component of stress in the x - y direction.

The calculated viscosity of the six electrolyte systems was given in Table 2. It is seen that the four LiTFSI-ILs solvent electrolytes, viz. [C₂mim][TFSI], [C₂mim][BF₄], [C₄mim][TFSI] and [C₄mim][BF₄], have higher viscosity than the two LiTFSI-organic solvent electrolytes, viz. DMC and DEC, at 298K and 313K. Additionally, for the ILs solvent electrolytes with the common anion ([BF₄]⁻ or [TFSI]⁻), we observed that the viscosity of [C₂mim]-type electrolytes is a little higher than [C₄mim]-type electrolytes, indicating that the viscosity of the [C_nmim]-type ILs solvent electrolytes is affected by the chain length n of cyclic carbonate. As the temperature increases, both the organic and ILs solvent electrolytes encounter a decrease in viscosity.

Table 2. Viscosity (unit: kg/m·s) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

Temperature(K)	DMC	DEC	[C ₂ mim][TFSI]	[C ₂ mim][BF ₄]	[C ₄ mim][TFSI]	[C ₄ mim][BF ₄]
298	0.396	0.949	1.924	1.554	1.035	1.537
313	0.116	0.663	1.491	1.154	0.836	0.802

3.1.3 Self-diffusion coefficient

A high rate of self-diffusion of ions can enhance the conductivity of electrolyte for lithium-ion battery. Therefore, according to the Einstein equation, we calculated the self-diffusion coefficient (D) of the Li⁺ and TFSI⁻ ions in the organic and ILs solvent electrolytes, which is a function of the mean square displacement (MSD) of ions in solution, as given in equation (3):

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle \sum_{i=1}^N [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle \quad (3)$$

where $\vec{r}_i(t)$ indicates the positional vector of the center of mass of the i th ion at a given time t . In this work, we calculated the MSDs of Li⁺ and TFSI⁻ in solution over the time interval (t) from 2ns to 6ns, as an example of the LiTFSI-DMC and LiTFSI-[C₂mim][BF₄] electrolytes at 298K (Figure 2). Through linearly fitting the slope of the MSD- t plots, we can obtain the self-diffusivity coefficients of Li⁺ and TFSI⁻ in the electrolytes, as listed in Table 3.

As compared to the organic solvents DMC and DEC, the ILs solvents allow the Li^+ and TFSI^- ions move more freely in the electrolytes, as evidenced by the self-diffusion coefficients in Table 3. As a matter of fact, it occurs on many ILs, including, but not limited to, $[\text{C}_n\text{mim}][\text{TFSI}]$ and $[\text{C}_n\text{mim}][\text{BF}_4]$.^{31,32} Ray et al. point out that the mobility of Li^+ in solution is proportional to the strength of the interionic interactions within the electrolytes.³³ In our work, stronger cation-anion coupling interactions were observed in the ionic-type solvents rather than in the molecular-type solvents, increasing the ionic strength of the ILs electrolytes. Therefore, ionic association facilitates the mobility of cation/anion in the ILs electrolytes. (Detailed discussions can be seen later in the text). No matter what the solvents are, the arising temperature increases the kinetic energy of systems, eventually resulting in the increase of self-diffusion of ions. Further, our simulation results revealed that Li^+ and TFSI^- have higher diffusion rates in the $[\text{C}_4\text{mim}]$ -type electrolyte than in the $[\text{C}_2\text{mim}]$ -type electrolyte, which differs from the results of density and viscosity studies. Among all the organic and ILs solvents, the $[\text{C}_4\text{mim}][\text{BF}_4]$ was found to be the best solvent, facilitating the transport of Li^+ and TFSI^- in solution. Since stronger coordination with the surrounding solvent molecules, the cation Li^+ exhibits lower rate of diffusion in the electrolytes than the anion TFSI^- (The solvation behaviors of Li^+ and TFSI^- will be discussed in detail later in the text).

Figure 2. The plots of mean square displacement (MSD) of Li^+ and TFSI^- vs. simulation time (t) in the solvents DMC and $[\text{C}_2\text{mim}][\text{BF}_4]$ at 298K.

Table 3. Self-diffusion coefficients (unit: $10^{-12} \text{ m}^2/\text{s}$) of the lithium salt LiTFSI in the organic and ILs solvent electrolytes.

T(K)	LiTFSI-DMC		LiTFSI-DEC		LiTFSI- [C ₂ mim][BF ₄]		LiTFSI- [C ₂ mim][TFSI]		LiTFSI- [C ₄ mim][BF ₄]		LiTFSI- [C ₄ mim][TFSI]	
	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻

298	0.24	0.44	0.17	0.25	1.43	3.01	1.75	3.84	5.83	6.57	5.62	6.24
313	0.55	0.81	0.19	0.28	2.17	4.94	2.08	4.18	6.24	6.65	6.74	6.83

1

2 3.1.4 Conductivity

3 High-performance electrochemical device requires its electrolyte having a high ionic conductivity. To
4 compare the organic and ILs solvents, we examined the total conductivity of the cation Li^+ and the anion TFSI^- in
5 the six electrolytes using the equation (4):

$$6 \quad \sigma = \lim_{t \rightarrow \infty} \frac{1}{6tVK_bT} \sum_{i,j}^N \langle ([R_i(t) - R_i(0)]q_i) \cdot ([R_j(t) - R_j(0)]q_j) \rangle \quad (4),$$

7 where N is the number of ions in the electrolyte, V is the volume, k_b is the Boltzmann's constant, T is the
8 temperature, q_x ($x = i, j$) indicates the charge of the x^{th} ion, and $R_x(t)$ ($x = i, j$) is the position of the x^{th} ion at
9 a given time t . The angle bracket $\langle \dots \rangle$ denotes an ensemble average and the sum Σ runs over all the ions in the
10 electrolyte. According to the difference of ionic species and correlations, we could divide the total conductivity
11 (σ_{tot}) into five distinct sub-terms^{34,35}, viz. cation-self (σ_{cat}^s), anion-self (σ_{an}^s), cation-distinct (σ_{cat}^d), anion-
12 distinct (σ_{an}^d), and cation/anion-distinct ($\sigma_{\text{cat,an}}^d$), which σ_{cat}^s and σ_{an}^s are conductivity types for self
13 (uncorrelated) ions, while σ_{cat}^d , σ_{an}^d and $\sigma_{\text{cat,an}}^d$ are conductivity types for distinct (correlated) ions. The σ_{cat}^d
14 and σ_{an}^d describe the correlations between two distinct cations and between two distinct anions, respectively; while
15 the $\sigma_{\text{cat,an}}^d$ describes the correlations between one cation and one anion. These five conductivity types, which are
16 general expressions derived from linear response and conservation laws, can be applied for any binary ILs of
17 symmetric and asymmetric charge. Details on the calculations of the five sub-terms are given in Supporting
18 Information, and the results of the five conductivity types for the organic and ILs solvent systems are shown in
19 [Table S1](#) and [Table S2](#), respectively.

20 We calculated the total conductivity (σ_{tot}) of the six electrolytes at 298K, as listed in [Figure 3\(a\)](#). Simulation
21 results revealed that the four ILs solvents exhibit a notable higher ionic conductivity than the two organic solvents,
22 implying that ionic-type solvents have higher conductivity than molecular-type solvents. It is also seen that the
23 conductivity of the two $[\text{C}_4\text{mim}]^+$ -type electrolytes is 5.593 S/m and 5.075 S/m, which is a little higher than the
24 two $[\text{C}_2\text{mim}]$ -type electrolytes of 4.265 S/m and 2.748 S/m. The $[\text{C}_4\text{mim}][\text{BF}_4]$ with the highest conductivity
25 among the electrolytes is considered to be the best solvent to dissolve LiTFSI. A number of high-conductivity ILs-
26 based electrolytes have been reported in other experimental work. Rosol *et al.*³⁶ experimentally measured the
27 conductivity of LiTFSI in the 1-butyl-3-methylimidazolium thiocyanate ($[\text{C}_4\text{mim}][\text{SCN}]$) electrolyte, showing a
28 high conductivity 3 S/m at the salt concentration $[\text{LiTFSI}] = 0.4$ mol/L. Zygadlo-Monikowska *et al.*³⁷ examined a
29 class of imidazolium ILs with short polyoxyethylene chain ($[\text{Im } n\text{EO}]^+[\text{X}]^-$; where $n=0, 3, 7, 20$ and $\text{X}=\text{Cl}, \text{BF}_4,$
30 $\text{N}(\text{CF}_3\text{SO}_2)_2$), and found that the electrolytes produced by these imidazolium ILs are good solvents for lithium

1 salts, such as LiBF_4 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. Especially for the $[\text{BuMeIm } 3\text{EO}][\text{BF}_4]$ electrolyte, a low viscosity and
2 high conductivity can be achieved even at high salt concentration of LiBF_4 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in solution. Kalaga
3 *et al.*³⁸ studied the solvation of LiTFSI in the electrolyte of 1-methyl 1-propylpiperidinium
4 bis(trifluoromethylsulfonyl)imide. They revealed that as the salt concentration $[\text{LiTFSI}]$ increases from 0.2 M to
5 1.0 M, this kind of ionic liquid electrolyte has a notable increase in conductivity. Chagnes *et al.*³⁹ used the mixture
6 of γ -Butyrolactone and 1-butyl 3-methyl-imidazolium tetrafluoroborate (BmimBF_4) (ratio: 3/2, v/v) as electrolyte
7 to solvate LiBF_4 . Their experiment indicates that as the temperature arises, this mixture exhibits a higher
8 conductivity in solution, even up to 9.5 S/m at 25 °C. The aforementioned experimental observations reflect a
9 common fact that ionic conductivity depends on the unique molecular structure of the ILs, and on the temperature
10 and salt concentration applied, which qualitatively agree to our simulation results. Figure 3(b,c) shows each
11 individual contribution of the five sub-terms to the total conductivity of the LiTFSI -organic and LiTFSI -ILs
12 solvent electrolytes, respectively. The uncorrelated conductivity types σ_{cat}^s and σ_{an}^s of the cations Li^+ and the
13 anions TFSI^- that are positive values for both organic and ILs solvents, contribute positively to the total
14 conductivity of the electrolyte. The correlated conductivity types σ_{cat}^d and σ_{an}^d of the same ionic species are close
15 to zero for the $[\text{C}_2\text{mim}]$ -type electrolytes, making little contribution to the total conductivity; while the σ_{cat}^d and
16 σ_{an}^d for the $[\text{C}_4\text{mim}]$ -type electrolytes are unfavorable to the total conductivity due to the negative values. Since
17 the correlated conductivity type $\sigma_{cat,an}^d$ of the distinct ionic species is almost zero for all the six electrolytes, we,
18 therefore, neglect the contribution between the cations and anions.

19
20 **Figure 3.** (a) Results of the total conductivity σ_{tot} (S/m) of the six electrolytes at 298K. (b) Results of the five conductivity
21 types, viz. σ_{cat}^s , σ_{an}^s , σ_{cat}^d , σ_{an}^d and $\sigma_{cat,an}^d$, for (b) the two organic solvent systems and (c) the four ionic liquids solvent
22 systems at 298K.

1

2 **3.2 Microstructural analysis**

3 Radial Distribution Function (RDF)⁴⁰ provides a molecular insight into exploring the correlations between
 4 structural and physical properties at a micro-scale level. We investigated the RDF, $g(r)$, for center of mass of the
 5 ions in the six electrolytes:

$$6 \quad g(r) = \frac{\langle \sum_{i,j} \delta(r-r_{ij}) \rangle}{N\rho} \quad (5),$$

7 where N is the number of particles, ρ is the number density, r_{ij} is the spatial distance of the particles i and j , and
 8 $\langle \dots \rangle$ indicates an ensemble average.

9 The coordination number (N)²⁵ is identified by integrating the site-site RDF along the radial direction. The
 10 coordination number $N_{(i-j)}$ of the particle i , herein, is defined to be the number of the molecule j surrounding the
 11 particle i in its first solvation shell, as calculated in equation (6):

$$12 \quad N_{(i-j)} = 4\pi\rho_j \int_0^{r'} g_{ij}(r)r^2 dr \quad (6),$$

13 where r' is the first minimum in the $g(r)$ plot, r is the distance and ρ_j is the density of particle j .

14 In this section, the effect of solvents on the density distributions of cations and anions was examined firstly
 15 to explore the ionic association tendency of Li^+ and TFSI $^-$ in various solvent electrolytes. Later, the electrolyte
 16 solvation of the cation Li^+ was discussed in the organic and ILs solvents to reveal the solution interactions between
 17 solute and solvent.

18
 19 3.2.1 The effect of solvents on the density distributions of cations and anions

20 The RDF of the lithium salt LiTFSI in various solvent electrolytes at 298K were shown in Figure 4 to study
 21 the effect of solvents on the density distributions of the cation Li^+ and the anion TFSI $^-$. It is clear to see that
 22 regardless of the solvents (Figure 4) and temperatures (Figure S1), the primary peak in the $g(r)$ plots of the Li^+ -
 23 TFSI $^-$ always appear at the position of around 0.2 nm, indicating that the Li^+ and TFSI $^-$ have a strong coordination
 24 in the electrolytes and the structural stability is affected less by the temperature. Seo *et al.*⁴¹ systematically studied
 25 the ionic association of lithium salts in electrolyte, and reported that the changes of temperature slightly affect the
 26 coordination structure of Li^+ and TFSI $^-$, which is in accordance with our simulation results. Followed by the
 27 primary peak, there are another two secondary peaks in the $g(r)$ plots of the Li^+ -TFSI $^-$, which exist at 0.32nm and
 28 0.42nm, respectively. Seo *et al.*⁴¹ considered that the cis-trans isomerism of TFSI $^-$ is the main cause for the two
 29 secondary peaks. However, in their study, they did not clarify a question how the cis-trans isomerism of TFSI

affects the presence of the two secondary peaks in the $g(r)$ plots of the Li^+ -TFSI $^-$. By analyzing our MD simulations, we found that more cis-TFSI appear at the peak position of 0.32nm, while more trans-TFSI at 0.42nm (Figure 4a). Further, we investigated the interactions of the cation Li^+ with the oxygen (O) and nitrogen (N) atoms within the anion TFSI $^-$ to shed light on the coordination mechanism of the ions Li^+ and TFSI $^-$ in the electrolytes. Take the LiTFSI-DMC electrolyte system as an example (Figure 5), where the density distributions of the Li^+ -O(TFSI) and Li^+ -N(TFSI) were demonstrated. The computed coordination numbers (N) of Li^+ -O(TFSI) and Li^+ -N(TFSI) are $N_{(\text{Li-O})}=2.5$ and $N_{(\text{Li-N})}=0.7$, implying that each cation Li^+ preferentially coordinates with the O(TFSI) atoms, not the more electronegative N(TFSI $^-$) atom in the electrolytes. The same conclusions were drawn by Li *et al.*⁴² in their simulation study of the LiTFSI-acetamide electrolyte.

The interactions of the cations Li^+ in various solvent electrolytes can be examined by plotting the Li^+ - Li^+ RDF (Figure 4). Strong interaction between Li^+ promotes the fast ion transport in electrolytes, thereby improving the performance of Li-ion battery. As observed in Figure 4, the $g(r)$ plots of the Li^+ - Li^+ of the four ILs-type electrolytes exhibit a larger peak value and a closer peak location than those of the two organic solvent electrolytes, implying that the cations Li^+ have stronger mutual interactions in the ILs solvents than in the organic solvents. We computed the coordination numbers ($N_{(\text{Li-Li})}$) of the Li^+ - Li^+ in the two organic solvents and the four ILs solvents: $N_{(\text{Li-Li})}=1.4$ for DMC, $N_{(\text{Li-Li})}=1.5$ for DEC, $N_{(\text{Li-Li})}=2.1$ for $[\text{C}_2\text{mim}][\text{BF}_4]$, $N_{(\text{Li-Li})}=1.9$ for $[\text{C}_2\text{mim}][\text{TFSI}]$, $N_{(\text{Li-Li})}=2.7$ for $[\text{C}_4\text{mim}][\text{BF}_4]$, and $N_{(\text{Li-Li})}=1.7$ for $[\text{C}_4\text{mim}][\text{TFSI}]$. Obviously, the strengths of the Li^+ - Li^+ interactions in the six electrolytes follow the order: $[\text{C}_4\text{mim}][\text{BF}_4] > [\text{C}_2\text{mim}][\text{BF}_4] > [\text{C}_2\text{mim}][\text{TFSI}] > [\text{C}_4\text{mim}][\text{TFSI}] > \text{DEC} > \text{DMC}$. Additionally, we calculated the average positions of the primary peak in the $g(r)$ plots of the Li^+ - Li^+ : 0.46nm for the ILs solvents and 0.51nm for the organic solvents, which is in consistency with the observations in the LiTFSI crystal by Nowinski *et al.*⁴³

The $g(r)$ plots of the TFSI $^-$ -TFSI $^-$ in Figure 4 indicated a variety of association behaviors of the anions TFSI $^-$ when dissolved in the organic and ILs solvents. Obviously, the ILs solvents (Figure 4(c-f)) rather than the organic solvents (Figure 4(a,b)) can facilitate the ionic association of TFSI $^-$, resulting in a notable peak at around 0.13nm in the $g(r)$ plot of the TFSI $^-$ -TFSI $^-$, especially for $[\text{C}_2\text{mim}][\text{BF}_4]$ (Figure 4c) and $[\text{C}_4\text{mim}][\text{BF}_4]$ (Figure 4e). Due to the presence of the anion $[\text{BF}_4]^-$ in the $[\text{C}_n\text{mim}][\text{BF}_4]$ solvents, the anion TFSI $^-$ of the lithium salt (LiTFSI) is repelled to self-aggregate into a cluster, causing a highly-protruding peak at the position of 0.13nm (Figure 4(c,e)). However, in the $[\text{C}_n\text{mim}][\text{TFSI}]$ solvents, the anion TFSI $^-$ of the lithium salt (LiTFSI) is distributed uniformly in the electrolytes and simultaneously interacts with other ions TFSI $^-$ and Li^+ , resulting in two sizeable peaks at around 0.13nm and 0.20nm (Figure 4(d,f)). Additionally, we can observe that the position of the primary peak in the $g(r)$ plot of the TFSI $^-$ -TFSI $^-$ shifts forward from 0.18nm in the organic solvents (Figure 4(a,b)) to 0.13nm in the ILs solvents (Figure 4(c-f)). The mobility of ions in solution depends on ionic strength. In the organic- and IL-based electrolytes, the ionic strength is a function of the coordination number (N) of ion-ion. A small value of $N_{(\text{TFSI-TFSI})}$ indicates a low mobility of the anion TFSI $^-$ in the solvents. We computed the $N_{(\text{TFSI-TFSI})}$ in the organic

1 and ILs solvents: $N_{(\text{TFSI-TFSI})}=1.31$ for DMC, $N_{(\text{TFSI-TFSI})}=1.38$ for DEC, $N_{(\text{TFSI-TFSI})}=1.83$ for $[\text{C}_2\text{mim}][\text{BF}_4]$, $N_{(\text{TFSI-TFSI})}=1.55$ for $[\text{C}_2\text{mim}][\text{TFSI}]$, $N_{(\text{TFSI-TFSI})}=1.87$ for $[\text{C}_4\text{mim}][\text{BF}_4]$, and $N_{(\text{TFSI-TFSI})}=1.57$ for $[\text{C}_4\text{mim}][\text{TFSI}]$. By
2 comparing the values of $N_{(\text{TFSI-TFSI})}$, we found that the ionic strength of the anions TFSI⁻ in the organic solvents is
3 weaker than that in the ILs solvents, indicating that the free motion of the anions TFSI⁻ is restricted in the organic
4 solvents. This observation about the structural distribution of TFSI⁻ proves our previous calculations in Table 3:
5 lower the self-diffusion coefficients of TFSI⁻ in the organic solvents as compared to in the ILs solvents.
6

Figure 4. Radial distribution function of the lithium salt LiTFSI at 298K in the organic solvents (a) DMC and (b) DEC, and the ILs solvents (c) [C₂mim][BF₄], (d) [C₂mim][TFSI], (e) [C₄mim][BF₄] and (f) [C₄mim][TFSI].

Figure 5. (a) Simulation snapshot of the cation Li^+ (purple sphere) surrounded by the anion TFSI^- in the first solvation shell for the LiTFSI -DMC electrolyte at 298K. (b) Site-site radial distribution function ($g(r)$) and coordination number (N) of Li^+ - $\text{O}(\text{TFSI}^-)$ (red trace) and Li^+ - $\text{N}(\text{TFSI}^-)$ (blue trace) in the LiTFSI -DMC electrolyte.

3.2.2 The electrolyte solvation of lithium salt in the organic and ILs solvents

Figure 6(a) presents the spatial correlations of the cation Li^+ with the two organic solvent molecules DMC and DEC at 298K. It is clear to see that there are two peaks existing in the $g(r)$ plots of both the Li^+ -organic solvents: one is at 0.2nm and the other is at 0.4nm, which signifies that the organic solvents DMC and DEC form a two-layer solvation shell to wrap the cation Li^+ . A small value of $N_{(\text{Li-Li})}$ indicates a low mobility of the cation Li^+ in the electrolytes. As stated above, the values of $N_{(\text{Li-Li})}$ in the DMC and DEC solvents are 1.4 and 1.5, respectively. Also, we computed the coordination numbers (N) of the Li^+ -DMC and Li^+ -DEC: $N_{(\text{Li-DMC})}=2.4$ and $N_{(\text{Li-DEC})}= 2.5$. It is found that the $N_{(\text{Li-Li})}$ is smaller than the $N_{(\text{Li-organic solvent})}$ in both the DMC or DEC solvents, indicating that the organic molecules hinder the free motions of Li^+ in the electrolytes. It is the main reason why the diffusion rates of the lithium salt (LiTFSI) are slow in the organic solvent (Table 3).

Figures 6(b,c) present the spatial correlations of the cation Li^+ in LiTFSI with the cations ($[\text{C}_2\text{mim}]^+$ and $[\text{C}_4\text{mim}]^+$) and anions ($[\text{BF}_4]^-$ and $[\text{TFSI}]^-$) of the four ILs solvents at 298K. For both the $[\text{BF}_4]^-$ -type and $[\text{TFSI}]^-$ -type ILs solvents, only a small peak takes place at a relatively-far position of about 0.7nm in the $g(r)$ plots of the Li^+ -cation(ILs) (Figure 6b), indicating a weak interaction between Li^+ and the ILs cations $[\text{C}_2\text{mim}]^+$ and $[\text{C}_4\text{mim}]^+$.

In contrast, a strong interaction between Li^+ and the ILs anions $[\text{BF}_4]^-$ and $[\text{TFSI}]^-$ is observed in both the $[\text{C}_2\text{mim}]$ -type and $[\text{C}_4\text{mim}]$ -type ILs solvents, as evidenced by a protruding peak occurring at 0.2nm (Figure 6c). Also, we found that the peak values in the $g(r)$ plots of the Li^+ - $[\text{BF}_4]^-$ reach up to 10 or more, which are higher than that of around 6.5 in the $g(r)$ plots of the Li^+ - $[\text{TFSI}]^-$ (Figure 6c). It reflects a fact that it is easier to disperse the ions $\text{Li}^+(\text{LiTFSI})$ into the $[\text{BF}_4]$ -type ILs solvents, rather than into the $[\text{TFSI}]$ -type ILs solvents. Our hypothesis about the reason is that the anion $[\text{BF}_4]^-$ exhibits a higher polarity than the $[\text{TFSI}]^-$, leading to a stronger coordination with the ions $\text{Li}^+(\text{LiTFSI})$. Thus, it is reasonable to believe that the dissolution of LiTFSI in ILs solvents is an anion-driven process.

Figure 6. Composite graph of the radial distribution functions representing the spatial correlations of the cation Li^+ with (a) the two organic solvent molecules, and with the (b) cations and (c) anions of the four ILs solvents at 298K.

To avoid simulation errors resulting from a small electrolyte system with 40 ion pairs of $\text{Li}^+\text{-TFSI}$, we examined a large electrolyte system including 200 LiTFSI and organic/ILs solvent molecules. The 674 DMC, 469 DEC, 371 $[\text{C}_2\text{mim}][\text{BF}_4]$, 221 $[\text{C}_4\text{mim}][\text{BF}_4]$, 304 $[\text{C}_2\text{mim}][\text{TFSI}]$, and 194 $[\text{C}_4\text{mim}][\text{TFSI}]$ were added separately to solvate the 200 LiTFSI to maintain a same concentration of 2 mol/L. Following the above computational procedure, we calculated the density, viscosity, and conductivity of both the LiTFSI -organics and LiTFSI -ILs solvent electrolytes, as listed in Table S3. The spatial correlations of the cation Li^+ with the DMC and DEC, the cations ($[\text{C}_2\text{mim}]^+$ and $[\text{C}_4\text{mim}]^+$), and the anions ($[\text{BF}_4]^-$ and $[\text{TFSI}]^-$) were shown in Figure S2. In observation of Tables (1, 2 and S1) and Figures (6 and S2), we found that the two systems of 40 and 200 LiTFSI exhibit the same physicochemical properties and microstructures of the electrolytes, proving the reliability of our simulation results.

4. Conclusions

Ionic liquids that are used as electrolytes in battery manufacturing industry enhance the safety, energy storage capacity, cycling life of lithium-ion battery. Fundamental molecular insights are useful for understanding the advantages of novel ILs solvent electrolytes over traditional organic solvent electrolytes. In this work, atomistic

MD simulations were employed to investigate the solvation behaviors of the lithium salt LiTFSI in two organic solvent (DMC and DEC) and four ILs solvent ($[\text{C}_n\text{mim}][\text{BF}_4]$ and $[\text{C}_n\text{mim}][\text{TFSI}]$, $n=2,4$) electrolytes.

We firstly calculated the physicochemical properties of both the organic and ILs solvent electrolytes. Simulation results revealed that the LiTFSI-ILs solvent electrolytes have higher density and viscosity, larger self-diffusion coefficient and conductivity than the LiTFSI-organics solvent electrolytes, indicating that the ILs-based electrolytes exhibit stronger energy power, lower solvent evaporation, and faster ion transport than the organics-based electrolytes. Later, we examined the effect of the organic and ILs solvents on the ionic associations of the ions Li^+ and TFSI^- by evaluating the radial distribution function ($g(r)$) and ionic coordination number (N_i). For both the organic and ILs solvent electrolytes, the cation Li^+ has strong interactions with the anion TFSI^- through coordinating with the O(TFSI) atom, not the more electronegative N(TFSI) atom. The cis-trans isomerism of TFSI^- was observed to appear near Li^+ at the positions of 0.32nm and 0.42nm, respectively. By calculating the coordination number $N_{(\text{Li}^+)}$ of the Li^+-Li^+ , we found that the $[\text{BF}_4]^-$ -type ILs have a fastest ion transport, followed by the $[\text{TFSI}]^-$ -type ILs, DEC, and DMC. The organic solvents restrict the free motion of the anion TFSI^- , resulting in a low conductivity for the organics-based electrolytes, while the ILs solvents facilitate the ionic association of the TFSI^- , causing a high conductivity for the ILs-based electrolytes. Additionally, we realized that the dissolution of LiTFSI in ILs solvents is an anion-driven process. The presence of high-polarity anion like $[\text{BF}_4]^-$ in the solution promotes the coordination with the ion $\text{Li}^+(\text{LiTFSI})$, improving the electrolyte solvation of the lithium salt.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgment

This work was supported by Department of Chemical & Biochemical Engineering, Technical University of Denmark; General Program Youth of National Natural Science Foundation of China (21606232); General Program of National Natural Science Foundation of China (21878295); Major Program of National Natural Science Foundation of China (21890762); Beijing Natural Science Foundation (2192052); Key Research Program of Frontier Sciences, CAS (QYZDB-SSW-SLH022).

References

- 1 (1) L. Zhou, K. Zhang, Z. Hu, Z. Tao, L. Mai, Y.M. Kang, S. L. Chou, J. Chen, Recent Developments on and
2 Prospects for Electrode Materials with Hierarchical Structures for Lithium-Ion Batteries, *Adv. Energy. Mater.*,
3 2018, **8**, 1-23.
- 4 (2) H. Zhang, H. Zhao, M. A. Khan, W. Zou, J. Xu, L. Zhang, J. Zhang, Recent Progress in Advanced Electrode
5 Materials, Separators and Electrolytes for Lithium Batteries, *J. Mater. Chem. A*, 2018, **6**, 20564-20620.
- 6 (3) K. M. Diederichsen, K. D. Fong, R. C. Terrell, K. A. Persson, B. D. McCloskey, Investigation of Solvent Type
7 and Salt Addition in High Transference Number Nonaqueous Polyelectrolyte Solutions for Lithium Ion Batteries,
8 *Macromolecules*, 2018, **51**, 8761–8771.
- 9 (4) S. Chen, K. Wen, J. Fan, Y. Bando, D. Golberg, Progress and Future Prospects of High-Voltage and High-
10 Safety Electrolytes in Advanced Lithium Batteries: From Liquid to Solid Electrolytes, *J. Mater. Chem. A*, 2018,
11 **6**, 11631–11663.
- 12 (5) J. Peng, M. Gobet, M. Devany, K. Xu, A. W. Cresce, O. Borodin, S. Greenbaum, Multinuclear Magnetic
13 Resonance Investigation of Cation-Anion and Anion-Solvent Interactions in Carbonate Electrolytes, *J. Power.*
14 *Sources*, 2018, **399**, 215–222.
- 15 (6) K. D. Fulfer, D. G. Kuroda, Ion Speciation of Lithium Hexafluorophosphate in Dimethyl Carbonate Solutions:
16 An Infrared Spectroscopy Study, *Phys. Chem. Chem. Phys.*, 2018, **20**, 22710–22718.
- 17 (7) K. D. Fulfer,; D. G. Kuroda, A Comparison of the Solvation Structure and Dynamics of the Lithium Ion in
18 Linear Organic Carbonates with Different Alkyl Chain Lengths, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25140–
19 25150.
- 20 (8) A. Heckmann, J. Thienenkamp, K. Beltrop, M. Winter, G. Brunklaus, T. Placke, Towards High-Performance
21 Dual-Graphite Batteries Using Highly Concentrated Organic Electrolytes, *Electrochim. Acta.*, 2018, **260**, 514–
22 525.
- 23 (9) P. Bose, D. Deb, S. Bhattacharya, Ionic Liquid Based Nanofluid Electrolytes with Higher Lithium Salt
24 Concentration for High-Efficiency, Safer, Lithium Metal Batteries, *J. Power Sources*, 2018, **406**, 176–184.
- 25 (10) T. Chen, W. H. Kong, Z. W. Zhang, L. Wang, Y. Hu, G. Y. Zhu, R. P. Chen, L. B. Ma, W. Yan, Y. R. Wang,
26 J. Liu, Z. Jin, Ionic Liquid-Immobilized Polymer Gel Electrolyte with Self-Healing Capability, High Ionic
27 Conductivity and Heat Resistance for Dendrite-Free Lithium Metal Batteries, *Nano Energy*, 2018, **54**, 17–25.
- 28 (11) X. Hu, R. Muchakayala, S. Song, J. Wang, J. Chen, M. Tan, Synthesis and Optimization of New Polymeric
29 Ionic Liquid Poly(diallyldimethylammonium) Bis(trifluoromethane Sulfonyl)imide Based Gel Electrolyte Films,
30 *Int. J. Hydrogen. Energy*, 2018, **43**, 3741–3749.
- 31 (12) B. Yang, C. Li, J. Zhou, J. Liu, Q. Zhang, Pyrrolidinium-Based Ionic Liquid Electrolyte with Organic

- 1 Additive and LiTFSI for High-Safety Lithium-Ion Batteries, *Electrochim. Acta.*, 2014, **148**, 39–45.
- 2 (13) O. Borodin, G. D. Smith, Development of Many-Body Polarizable Force Fields for Li-Battery
3 Applications: 2. LiTFSI-Doped Oligoether, Polyether, and Carbonate-Based Electrolytes, *J. Phys. Chem. B*, 2006,
4 **110**, 6293–6299.
- 5 (14) O. Borodin, G. D. Smith, W. Henderson, Li⁺ Cation Environment, Transport, and Mechanical Properties of
6 the LiTFSI Doped N-Methyl-N-alkylpyrrolidinium+TFSI- Ionic Liquids, *J. Phys. Chem. B*, 2006, **110**, 16879–
7 16886.
- 8 (15) J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, Development and Testing of a General
9 Amber Force Field, *J. Comput. Chem.*, 2004, **25**, 1157–1174.
- 10 (16) Y. Zhang, Y. Zhang, M. J. McCready, E. J. Maginn, Evaluation and Refinement of the General AMBER
11 Force Field for Nineteen Pure Organic Electrolyte Solvents, *J. Chem. Eng. Data*, 2018, **63**, 3488-3502.
- 12 (17) Z. Liu, S. Huang, W. Wang, A Refined Force Field for Molecular Simulation of Imidazolium-Based Ionic
13 Liquids, *J. Phys. Chem. B*, 2004, **108**, 12978-12989.
- 14 (18) C. I. Bayly, P. Cieplak, W. D. Cornell, P. A. Kollman, A Well-Behaved Electrostatic Potential Based Method
15 Using Charge Restraints for Deriving Atomic Charges: The RESP Model, *J. Phys. Chem.*, 1993, **97**, 10269–10280.
- 16 (19) E. J. Maginn, Molecular Simulation of Ionic Liquids: Current Status and Future Opportunities. *J. Phys.*
17 *Condens. Matter.*, 2009, **21**, 373101-373118.
- 18 (20) M. Salanne, Simulations of Room Temperature Ionic Liquids: From Polarizable to Coarse-Grained Force
19 Fields. *Phys. Chem. Chem. Phys.* 2015, **17**, 14270–14279.
- 20 (21) M. Schmollngruber, V. Lesch, C. Schröder, A. Heuer, O. Steinhauser, Comparing Induced Point-Dipoles and
21 Drude Oscillators. *Phys. Chem. Chem. Phys.* 2015, **17**, 14297–14306.
- 22 (22) L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, PACKMOL : A Package for Building Initial
23 Configurations, *Softw. News. Updat.*, 2009, **30**, 2157–2164.
- 24 (23) D. V. D. Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, H. J. C. Berendsen, GROMACS: Fast, Flexible,
25 and Free, *J. Comput. Chem.*, 2005, **26**, 1701–1718.
- 26 (24) J. Wang, T. J. Hou, Application of Molecular Dynamics Simulations in Molecular Property Prediction. 1.
27 Density and Heat of Vaporization. *J. Chem. Theory Comput.* 2011, **7**, 2151–2165.
- 28 (25) T. C. Lourenco, Y. Zhang, L. T. Costa, E. J. Maginn, A Molecular Dynamics Study of Lithium-Containing
29 Aprotic Heterocyclic Ionic Liquid Electrolytes, *J. Chem. Phys.*, 2018, **148**, 193834-193843.

- 1 (26) C. C. Yang, H. Y. Hsu, C. R. Hsu, Transport Properties of LiTFSI-Acetamide Room Temperature Molten
2 Salt Electrolytes Applied in an Li-Ion Battery, *Z. Naturforsch. A*, 2007, **62**, 639–646.
- 3 (27) J. Tojo, J. Canosa, A. Rodríguez, J. Ortega, R. Dieppa, Densities and Excess Molar Properties of Dimethyl
4 Carbonate with Alkanes (C-6 to C-10) and VLE of Dimethyl Carbonate with Alkanes (C-9 to C-10) at 101.3 KPa.
5 *J. Chem. Eng. Data*, 2004, **49**, 86–93.
- 6 (28) K. Shukla, V.C. Srivastava, Diethyl Carbonate: Critical Review of Synthesis Routes, Catalysts Used and
7 Engineering Aspects. *RSC Advances*, 2016, **6**, 32624–32645.
- 8 (29) S. Zhang, Q. Zhou, X. Lu, Y. Song, X. Wang, Physicochemical Properties of Ionic Liquid Mixtures, 2017,
9 <https://doi.org/10.1007/978-94-017-7573-1>.
- 10 (30) F. M. Gene, Nonequilibrium Statistical Mechanics, 2008, <https://doi.org/10.1002/9783527618958>
- 11 (31) Hayamizu. K, Aihara. Y, Nakagawa. H, Nukuda. T, Price. W. S, Ionic Conduction and Ion Diffusion in Binary
12 Room-Temperature Ionic Liquids Composed of [Emim][BF₄] and LiBF₄. *J. Phys. Chem. B*, 2004, **108**, 19527–
13 19532.
- 14 (32) Noda. A, Hayamizu. K, Watanabe. M, Pulsed-Gradient Spin-Echo ¹H and ¹⁹F NMR Ionic Diffusion
15 Coefficient, Viscosity, and Ionic Conductivity of Non-Chloroaluminate Room-Temperature Ionic Liquids. *J. Phys.*
16 *Chem. B*, 2001, **105**, 4603–4610.
- 17 (33) Ray. P, Balducci. A, Kirchner. B, Molecular Dynamics Simulations of Lithium-Doped Ionic-Liquid
18 Electrolytes. *J. Phys. Chem. B*, 2018, **122**, 10535–10547.
- 19 (34) J. G. McDaniel, C. Y. Son, Ion Correlation and Collective Dynamics in BMIM/BF₄-Based Organic
20 Electrolytes: From Dilute Solutions to the Ionic Liquid Limit, *J. Phys. Chem. B*, 2018, **122**, 7154–7169.
- 21 (35) H. K. Kashyap, H. V. R. Annapureddy, F. O. Raineri, C. J. Margulis, How Is Charge Transport Different in
22 Ionic Liquids and Electrolyte Solutions?, *J. Phys. Chem. B*, 2011, **115**, 13212–13221.
- 23 (36) Z. P. Rosol, N. J. German, S. M. Gross, Solubility, Ionic Conductivity and Viscosity of Lithium Salts in Room
24 Temperature Ionic Liquids. *Green Chem.*, 2009, **11**, 1453–1457.
- 25 (37) Zygadło-Monikowska. E, Florjańczyk. Z, Kubisa. P, Biedroń. T, Sadurski. W, Puczyłowska. A, Langwald.
26 N, Ostrowska. J, Lithium Electrolytes Based on Modified Imidazolium Ionic Liquids. *Int. J. Hydrog. Energy*, 2014,
27 **39**, 2943-2952.
- 28 (38) Kalaga. K, Rodrigues. M. T. F, Gullapalli. H, Babu. G, Arava. L. M. R, Ajayan. P. M, Quasi-Solid Electrolytes
29 for High Temperature Lithium Ion Batteries. *ACS Appl. Mater. Interfaces*, 2015, **7**, 25777–25783.

- 1 (39) Chagnes. A, Diaw. M, Carré. B, Willmann. P, Lemordant. D, Imidazolium-Organic Solvent Mixtures as
2 Electrolytes for Lithium Batteries, *J. Power Sources*, 2005, **145**, 82–88.
- 3 (40) T. Méndez-Morales, J. Carrete, S. Bouzón-Capelo, M. Pérez-Rodríguez, Ó. Cabeza, L. J. Gallego, L. M.
4 Varela, MD Simulations of the Formation of Stable Clusters in Mixtures of Alkaline Salts and Imidazolium-Based
5 Ionic Liquids. *J. Phys. Chem. B*, 2013, **117**, 3207–3220.
- 6 (41) D. M. Seo, O. Borodin, S. D. Han, P. D. Boyle, W. A. Henderson, Electrolyte Solvation and Ionic Association
7 II. Acetonitrile-Lithium Salt Mixtures: Highly Dissociated Salts, *J. Electrochem. Soc.*, 2012, **159**, 1489-1500.
- 8 (42) S. Li, Z. Cao, Y. Peng, L. Liu, V. Wang, S. Wang, J. Q. Wang, T. Yan, X. P. Gao, D. Y. Song, P. W. Shen,
9 Molecular Dynamics Simulation of LiTFSI-Acetamide Electrolytes: Structural Properties, *J. Phys. Chem. B*, 2008,
10 **112**, 6398–6410.
- 11 (43) J. L. Nowinski, P. Lightfoot, P. G. Bruce, Structure of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, a Novel Salt for Electrochemistry, *J.*
12 *Mater. Chem.*, 1994, **4**, 1579-1580.

13

14

15

Table Captions

Table 1. Density (unit: g/cm³) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

Table 2. Viscosity (unit: kg/m·s) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

Table 3. Self-diffusion coefficients (unit: 10⁻¹² m²/s) of the lithium salt LiTFSI in the organic and ILs solvent electrolytes.

Table 1. Density (unit: g/cm³) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes*.

Temperature(K)	DMC	DEC	[C ₂ mim][TFSI]	[C ₂ mim][BF ₄]	[C ₄ mim][TFSI]	[C ₄ mim][BF ₄]
298	1.471(1.07 ^a)	1.373(0.98 ^b)	1.743(1.52 ^c)	1.538(1.28 ^c)	1.672(1.42 ^c)	1.429(1.19 ^c)
313	1.448	1.361	1.708	1.534	1.599	1.383

*Densities of these pure solvents at 298K are provided in parentheses.

(a) Tojo et al. experiment (ref. ²⁷). (b) Shukla et al. experiment (ref. ²⁸). (c) Zhang et al. experiment (ref. ²⁹).

Table 2. Viscosity (unit: kg/m·s) for the LiTFSI-organic and LiTFSI-ILs solvent electrolytes.

Temperature(K)	DMC	DEC	[C ₂ mim][TFSI]	[C ₂ mim][BF ₄]	[C ₄ mim][TFSI]	[C ₄ mim][BF ₄]
298	0.396	0.949	1.924	1.554	1.035	1.537
313	0.116	0.663	1.491	1.154	0.836	0.802

Table 3. Self-diffusion coefficients (unit: 10⁻¹² m²/s) of the lithium salt LiTFSI in the organic and ILs solvent electrolytes.

T(K)	LiTFSI-DMC		LiTFSI-DEC		LiTFSI-[C ₂ mim][BF ₄]		LiTFSI-[C ₂ mim][TFSI]		LiTFSI-[C ₄ mim][BF ₄]		LiTFSI-[C ₄ mim][TFSI]	
	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻	Li ⁺	TFSI ⁻
298	0.24	0.44	0.17	0.25	1.43	3.01	1.75	3.84	5.83	6.57	5.62	6.24
313	0.55	0.81	0.19	0.28	2.17	4.94	2.08	4.18	6.24	6.65	6.74	6.83

Figure Captions

Figure 1. Structures of the ions and solvent molecules involved in our MD simulations: (a) lithium (Li^+); (b) [bis(trifluoromethanesulfonyl)imide] (TFSI^-); (c) dimethyl carbonate (DMC); (d) diethyl carbonate (DEC); (e) 1-ethyl-3-methylimidazolium ($[\text{C}_2\text{mim}]^+$); (f) 1-butyl-3-methylimidazolium ($[\text{C}_4\text{mim}]^+$); (g) tetrafluoroborate ($[\text{BF}_4]^-$).

Figure 2. The plots of mean square displacement (MSD) of Li^+ and TFSI^- vs. simulation time (t) in the solvents DMC and $[\text{C}_2\text{mim}][\text{BF}_4]$ at 298K.

Figure 3. (a) Results of the total conductivity σ_{tot} (S/m) of the six electrolytes at 298K. (b) Results of the five conductivity types, viz. σ_{cat}^s , σ_{an}^s , σ_{cat}^d , σ_{an}^d and $\sigma_{\text{cat,an}}^d$, for (b) the two organic solvent systems and (c) the four ionic liquids solvent systems at 298K.

Figure 4. Radial distribution function of the lithium salt LiTFSI at 298K in the organic solvents (a) DMC and (b) DEC, and the ILs solvents (c) $[\text{C}_2\text{mim}][\text{BF}_4]$, (d) $[\text{C}_2\text{mim}][\text{TFSI}]$, (e) $[\text{C}_4\text{mim}][\text{BF}_4]$ and (f) $[\text{C}_4\text{mim}][\text{TFSI}]$.

Figure 5. (a) Simulation snapshot of the cation Li^+ (purple sphere) surrounded by the anion TFSI^- in the first solvation shell for the LiTFSI -DMC electrolyte at 298K. (b) Site-site radial distribution function ($g(r)$) and coordination number (N) of Li^+ -O(TFSI^-) (red trace) and Li^+ -N(TFSI^-) (blue trace) in the LiTFSI -DMC electrolyte.

Figure 6. Composite graph of the radial distribution functions representing the spatial correlations of the cation Li^+ with (a) the two organic solvent molecules, and with the (b) cations and (c) anions of the four ILs solvents at 298K.

Figure 1. Structures of the ions and solvent molecules involved in our MD simulations: (a) lithium (Li^+); (b) [bis(trifluoromethanesulfonyl)imide] (TFSI^-); (c) dimethyl carbonate (DMC); (d) diethyl carbonate (DEC); (e) 1-ethyl-3-methylimidazolium ($[\text{C}_2\text{mim}]^+$); (f) 1-butyl-3-methylimidazolium ($[\text{C}_4\text{mim}]^+$); (g) tetrafluoroborate ($[\text{BF}_4]^-$).

Figure 2. The plots of mean square displacement (MSD) of Li^+ and TFSI^- vs. simulation time (t) in the solvents DMC and $[\text{C}_2\text{mim}][\text{BF}_4]$ at 298K.

(a)

Solvent	DMC	DEC	[C ₂ mim][BF ₄]	[C ₂ mim][TFSI]	[C ₄ mim][BF ₄]	[C ₄ mim][TFSI]
σ_{tot} (S/m)	2.191	1.572	4.265	2.748	5.593	5.075

Figure 3. (a) Results of the total conductivity σ_{tot} (S/m) of the six electrolytes at 298K. (b) Results of the five conductivity types, viz. σ_{cat}^s , σ_{an}^s , σ_{cat}^d , σ_{an}^d and $\sigma_{\text{cat,an}}^d$, for (b) the two organic solvent systems and (c) the four ionic liquids solvent systems at 298K.

Figure 4. Radial distribution function of the lithium salt LiTFSI at 298K in the organic solvents (a) DMC and (b) DEC, and the ILs solvents (c) [C₂mim][BF₄], (d) [C₂mim][TFSI], (e) [C₄mim][BF₄] and (f) [C₄mim][TFSI].

Figure 5. (a) Simulation snapshot of the cation Li^+ (purple sphere) surrounded by the anion TFSI^- in the first solvation shell for the LiTFSI -DMC electrolyte at 298K. (b) Site-site radial distribution function ($g(r)$) and coordination number (N) of $\text{Li}^+-\text{O}(\text{TFSI}^-)$ (red trace) and $\text{Li}^+-\text{N}(\text{TFSI}^-)$ (blue trace) in the LiTFSI -DMC electrolyte.

Figure 6. Composite graph of the radial distribution functions representing the spatial correlations of the cation Li^+ with (a) the two organic solvent molecules, and with the (b) cations and (c) anions of the four ILs solvents at 298K.

1

2