Electronic Supplementary Material (ESI) for Materials Advances.

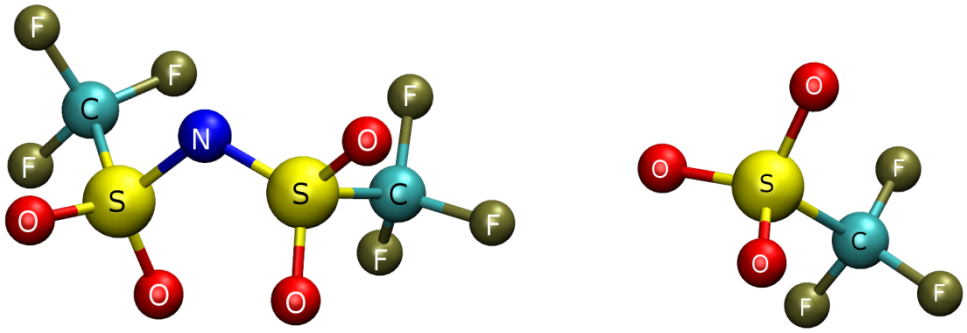
SUPPORTING INFORMATION

Insights into the structure and ionic transport in 'water-in-bisalt' electrolytes for lithium-ion batteries

Thejus R. Kartha, Dhileep N. Reddy and Bhabani S. Mallik*

Department of Chemistry, Indian Institute of Technology Hyderabad, Sangareddy 502285, Telangana, India

Non-Bonded Force field parameters



Atom	σ [nm]	ε [kJ mol^{-1}]	Charge (unscaled)
Li	0.233700	0.670000	+1.000000
N	0.325000	0.711280	- 0.846520
S$_{TFSI}$	0.356359	1.046000	+ 1.327211
O$_{TFSI}$	0.295992	0.878640	- 0.623515
C$_{TFSI}$	0.339967	0.457730	+ 0.204906
F$_{TFSI}$	0.311815	0.255224	- 0.120609
S$_{OTF}$	0.356359	1.046000	+1.150636
O$_{OTF}$	0.295992	0.878640	-0.655529
C$_{OTF}$	0.339967	0.457730	+0.302293
F$_{OTF}$	0.311815	0.255224	-0.162114

Bonded Force Field Parameters (GROMACS .itp file, charges are not scaled)

TFSI$^-$

```
[ atoms ]
;   nr  type  resi  res  atom  cgnr     charge      mass
     1    f     1   TFS    F1    1    -0.120609     19.00000
     2   c3     1   TFS    C1    2     0.204906     12.01000
     3    f     1   TFS    F2    3    -0.120609     19.00000
     4    f     1   TFS    F3    4    -0.120609     19.00000
     5   sy     1   TFS    S1    5     1.327211     32.06000
     6    o     1   TFS    O3    6    -0.623515     16.00000
     7    o     1   TFS    O4    7    -0.623515     16.00000
     8   ne     1   TFS    N1    8    -0.846520     14.01000
     9   s6     1   TFS    S2    9     1.327211     32.06000
    10    o     1   TFS    O1   10    -0.623515     16.00000
    11    o     1   TFS    O2   11    -0.623515     16.00000
    12   c3     1   TFS    C2   12     0.204906     12.01000
    13    f     1   TFS    F5   13    -0.120609     19.00000
    14    f     1   TFS    F6   14    -0.120609     19.00000
    15    f     1   TFS    F4   15    -0.120609     19.00000

[ bonds ]
;   ai     aj funct   r             k
     1      2   1    1.3497e-01    2.9865e+05 ;     F1 - C1
     2      3   1    1.3497e-01    2.9865e+05 ;     C1 - F2
     2      4   1    1.3497e-01    2.9865e+05 ;     C1 - F3
     2      5   1    1.8087e-01    1.9481e+05 ;     C1 - S1
     5      6   1    1.4660e-01    4.1254e+05 ;     S1 - O3
     5      7   1    1.4660e-01    4.1254e+05 ;     S1 - O4
     5      8   1    1.6723e-01    2.6535e+05 ;     S1 - N1
     8      9   1    1.5540e-01    3.6928e+05 ;     N1 - S2
     9     10   1    1.4533e-01    4.2903e+05 ;     S2 - O1
     9     11   1    1.4533e-01    4.2903e+05 ;     S2 - O2
     9     12   1    1.8075e-01    1.9539e+05 ;     S2 - C2
    12     13   1    1.3497e-01    2.9865e+05 ;     C2 - F5
    12     14   1    1.3497e-01    2.9865e+05 ;     C2 - F6
    12     15   1    1.3497e-01    2.9865e+05 ;     C2 - F4

[ pairs ]
;   ai     aj    funct
     1      6      1 ;     F1 - O3
     1      7      1 ;     F1 - O4
     1      8      1 ;     F1 - N1
     2      9      1 ;     C1 - S2
     3      6      1 ;     F2 - O3
     3      7      1 ;     F2 - O4
     3      8      1 ;     F2 - N1
     4      6      1 ;     F3 - O3
     4      7      1 ;     F3 - O4
     4      8      1 ;     F3 - N1
     5     10      1 ;     S1 - O1
     5     11      1 ;     S1 - O2
     5     12      1 ;     S1 - C2
     6      9      1 ;     O3 - S2
     7      9      1 ;     O4 - S2
     8     13      1 ;     N1 - F5
     8     14      1 ;     N1 - F6
     8     15      1 ;     N1 - F4
    10     13      1 ;     O1 - F5
    10     14      1 ;     O1 - F6
    10     15      1 ;     O1 - F4
    11     13      1 ;     O2 - F5
    11     14      1 ;     O2 - F6
    11     15      1 ;     O2 - F4

[ angles ]
;   ai     aj     ak    funct   theta         cth
     1      2      3      1    1.0736e+02    5.9321e+02 ;     F1 - C1     - F2
     1      2      4      1    1.0736e+02    5.9321e+02 ;     F1 - C1     - F3
     1      2      5      1    1.0968e+02    5.2819e+02 ;     F1 - C1     - S1
     2      5      6      1    1.0785e+02    5.4752e+02 ;     C1 - S1     - O3
     2      5      7      1    1.0785e+02    5.4752e+02 ;     C1 - S1     - O4
     2      5      8      1    1.0219e+02    5.3614e+02 ;     C1 - S1     - N1
     3      2      4      1    1.0736e+02    5.9321e+02 ;     F2 - C1     - F3
     3      2      5      1    1.0968e+02    5.2819e+02 ;     F2 - C1     - S1
     4      2      5      1    1.0968e+02    5.2819e+02 ;     F3 - C1     - S1
     5      8      9      1    1.1918e+02    5.7220e+02 ;     S1 - N1     - S2
     6      5      7      1    1.2141e+02    6.0701e+02 ;     O3 - S1     - O4
     6      5      8      1    1.0965e+02    5.8827e+02 ;     O3 - S1     - N1
     7      5      8      1    1.0965e+02    5.8827e+02 ;     O4 - S1     - N1
     8      9     10      1    1.1910e+02    5.9287e+02 ;     N1 - S2     - O1
     8      9     11      1    1.1910e+02    5.9287e+02 ;     N1 - S2     - O2
     8      9     12      1    1.0819e+02    1.3623e+02 ;     N1 - S2     - C2
     9     12     13      1    1.0968e+02    5.2819e+02 ;     S2 - C2     - F5
     9     12     14      1    1.0968e+02    5.2819e+02 ;     S2 - C2     - F6
     9     12     15      1    1.0968e+02    5.2819e+02 ;     S2 - C2     - F4
    10      9     11      1    1.2005e+02    6.1580e+02 ;     O1 - S2     - O2
    10      9     12      1    1.0861e+02    5.4702e+02 ;     O1 - S2     - C2
    11      9     12      1    1.0861e+02    5.4702e+02 ;     O2 - S2     - C2
    13     12     14      1    1.0736e+02    5.9321e+02 ;     F5 - C2     - F6
    13     12     15      1    1.0736e+02    5.9321e+02 ;     F5 - C2     - F4
    14     12     15      1    1.0736e+02    5.9321e+02 ;     F6 - C2     - F4
```

```
[ dihedrals ] ; propers
;    i      j      k      l   func    C0         C1         C2         C3         C4         C5
     1      2      5      6      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F1-    C1-    S1-    O3
     1      2      5      7      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F1-    C1-    S1-    O4
     1      2      5      8      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F1-    C1-    S1-    N1
     2      5      8      9      3   30.54320   22.17520    0.00000    8.36800    0.00000    0.00000 ;     C1-    S1-    N1-    S2
     3      2      5      6      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F2-    C1-    S1-    O3
     3      2      5      7      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F2-    C1-    S1-    O4
     3      2      5      8      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F2-    C1-    S1-    N1
     4      2      5      6      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F3-    C1-    S1-    O3
     4      2      5      7      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F3-    C1-    S1-    O4
     4      2      5      8      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F3-    C1-    S1-    N1
     5      8      9     10      3   55.78946    0.00000  -55.78946    0.00000    0.00000    0.00000 ;     S1-    N1-    S2-    O1
     5      8      9     11      3   55.78946    0.00000  -55.78946    0.00000    0.00000    0.00000 ;     S1-    N1-    S2-    O2
     5      8      9     12      3   55.78946    0.00000  -55.78946    0.00000    0.00000    0.00000 ;     S1-    N1-    S2-    C2
     6      5      8      9      3   30.54320   22.17520    0.00000    8.36800    0.00000    0.00000 ;     O3-    S1-    N1-    S2
     7      5      8      9      3   30.54320   22.17520    0.00000    8.36800    0.00000    0.00000 ;     O4-    S1-    N1-    S2
     8      9     12     13      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     N1-    S2-    C2-    F5
     8      9     12     14      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     N1-    S2-    C2-    F6
     8      9     12     15      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     N1-    S2-    C2-    F4
    10      9     12     13      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     O1-    S2-    C2-    F5
    10      9     12     14      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     O1-    S2-    C2-    F6
    10      9     12     15      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     O1-    S2-    C2-    F4
    11      9     12     13      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     O2-    S2-    C2-    F5
    11      9     12     14      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     O2-    S2-    C2-    F6
    11      9     12     15      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     O2-    S2-    C2-    F4
```

OTF⁻

```
[ atoms ]
;   nr  type  resi  res  atom  cgnr     charge      mass       ; qtot   bond_type
     1    f     1   OTF    F1    1    -0.162114     19.00000 ; qtot -0.162
     2   c3     1   OTF    C1    2     0.302293     12.01000 ; qtot 0.140
     3    f     1   OTF    F2    3    -0.162114     19.00000 ; qtot -0.022
     4    f     1   OTF    F3    4    -0.162114     19.00000 ; qtot -0.184
     5   sy     1   OTF    S1    5     1.150636     32.06000 ; qtot 0.967
     6    o     1   OTF    O2    6    -0.655529     16.00000 ; qtot 0.311
     7    o     1   OTF    O3    7    -0.655529     16.00000 ; qtot -0.344
     8    o     1   OTF    O1    8    -0.655529     16.00000 ; qtot -1.000

[ bonds ]
;   ai     aj funct   r             k
     1      2   1    1.3497e-01    2.9865e+05 ;     F1 - C1
     2      3   1    1.3497e-01    2.9865e+05 ;     C1 - F2
     2      4   1    1.3497e-01    2.9865e+05 ;     C1 - F3
     2      5   1    1.8075e-01    1.9539e+05 ;     C1 - S1
     5      6   1    1.4533e-01    4.2903e+05 ;     S1 - O2
     5      7   1    1.4533e-01    4.2903e+05 ;     S1 - O3
     5      8   1    1.4533e-01    4.2903e+05 ;     S1 - O1

[ pairs ]
;   ai     aj    funct
     1      6      1 ;     F1 - O2
     1      7      1 ;     F1 - O3
     1      8      1 ;     F1 - O1
     3      6      1 ;     F2 - O2
     3      7      1 ;     F2 - O3
     3      8      1 ;     F2 - O1
     4      6      1 ;     F3 - O2
     4      7      1 ;     F3 - O3
     4      8      1 ;     F3 - O1

[ angles ]
;   ai     aj     ak    funct   theta         cth
     1      2      3      1    1.0736e+02    5.9321e+02 ;     F1 - C1     - F2
     1      2      4      1    1.0736e+02    5.9321e+02 ;     F1 - C1     - F3
     1      2      5      1    1.0968e+02    5.2819e+02 ;     F1 - C1     - S1
     2      5      6      1    1.0861e+02    5.4702e+02 ;     C1 - S1     - O2
     2      5      7      1    1.0861e+02    5.4702e+02 ;     C1 - S1     - O3
     2      5      8      1    1.0861e+02    5.4702e+02 ;     C1 - S1     - O1
     3      2      4      1    1.0736e+02    5.9321e+02 ;     F2 - C1     - F3
     3      2      5      1    1.0968e+02    5.2819e+02 ;     F2 - C1     - S1
     4      2      5      1    1.0968e+02    5.2819e+02 ;     F3 - C1     - S1
     6      5      7      1    1.2005e+02    6.1580e+02 ;     O2 - S1     - O3
     6      5      8      1    1.2005e+02    6.1580e+02 ;     O2 - S1     - O1
     7      5      8      1    1.2005e+02    6.1580e+02 ;     O3 - S1     - O1

[ dihedrals ] ; propers
; treated as RBs in GROMACS to use combine multiple AMBER torsions per quartet
;    i      j      k      l   func    C0         C1         C2         C3         C4         C5
     1      2      5      6      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F1-    C1-    S1-    O2
     1      2      5      7      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F1-    C1-    S1-    O3
     1      2      5      8      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F1-    C1-    S1-    O1
     3      2      5      6      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F2-    C1-    S1-    O2
     3      2      5      7      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F2-    C1-    S1-    O3
     3      2      5      8      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F2-    C1-    S1-    O1
     4      2      5      6      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F3-    C1-    S1-    O2
     4      2      5      7      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F3-    C1-    S1-    O3
     4      2      5      8      3    0.60436    1.81307    0.00000   -2.41742    0.00000    0.00000 ;     F3-    C1-    S1-    O1
```

Table S1: Constituents of the systems of different concentrations.

Total number of molecules	No. of Li^+	No. of $TFSI^-$	No. of OTF^-	No. of water	Corresponding concentration
1000	57	42	15	943	5.1 m LiTFSI, 1.7 m LiOTF
1000	96	70	26	904	9 m LiTFSI, 3 m LiOTF
1000	148	106	42	852	15 m LiTFSI, 5 m LiOTF
1000	193	137	56	807	21 m LiTFSI, 7 m LiOTF

Table S2: Ionic conductivities from the current autocorrelation function.

Concentration of Electrolyte	*Temperature [K]*	*CACF integral cutoff [ps]*	*log Ionic Conductivity [mS cm^{-1}]*
5.1 m LiTFSI, 1.7 m LiOTf	*298.15*	*1 – 3*	*1.425*
9 m LiTFSI, 3 m LiOTf	*287.95*	*1 – 3*	*1.345*
9 m LiTFSI, 3 m LiOTf	*298.15*	*1 – 3*	*1.472*
9 m LiTFSI, 3 m LiOTf	*327.85*	*1 – 3*	*1.677*
9 m LiTFSI, 3 m LiOTf	*347.45*	*1 – 3*	*1.854*
15 m LiTFSI, 5 m LiOTf	*298.15*	*10 – 25*	*0.882*
21 m LiTFSI, 7 m LiOTf	*298.15*	*10 – 25*	*0.902*

Table S3: Fitting parameters of the ion cage correlation function for Li–O_{anion} interactions.

Temperature **[K]**	*LiTFSI [m]*	*LiOTF* **[m]**	a_0	τ_1 *[ps]*	τ_2 *[ps]*	*Correlation coefficient*
298.15	*5.1*	*1.7*	1.02033	48.1471	0.515144	0.999618
			1.03305	40.0989	0.523274	0.999654
			1.01411	42.8584	0.540225	0.999632
287.95	*9*	*3*	0.949172	115.1	0.548081	0.99791
			0.881211	176.585	0.602537	0.996521
			0.911435	131.229	0.591116	0.997702
298.15	*9*	*3*	0.934887	103.887	0.568765	0.998824
			0.920482	117.761	0.551427	0.997345
			0.926534	118.64	0.56465	0.998055
327.85	*9*	*3*	1.04032	27.7114	0.490971	0.999679
			1.02523	29.442	0.512611	0.999858
			1.0342	27.3171	0.502573	0.999733
347.45	*9*	*3*	1.03322	17.5079	0.507619	0.999707
			1.05056	16.8972	0.481333	0.999312
			1.02474	17.0258	0.522158	0.999806
298.15	*15*	*5*	0.904277	147.463	0.597415	0.998113
			0.873953	177.267	0.601865	0.996003
			0.91374	141.979	0.583978	0.998317
298.15	*21*	*7*	0.868283	224.473	0.603767	0.996791
			0.840487	281.271	0.631235	0.995501
			0.848863	271.326	0.62679	0.995585

Table S4: Fitting parameters of the ion cage correlation function for Li–O_{water} interactions.

Temperature **[K]**	*LiTFSI [m]*	*LiOTF* **[m]**	a_0	τ_1 *[ps]*	τ_2 *[ps]*	*Correlation coefficient*
298.15	*5.1*	*1.7*	1.03798	17.9347	0.596552	0.999277
			1.03157	17.6376	0.609246	0.999455
			1.03047	17.8831	0.612194	0.999429
287.95	*9*	*3*	1.05988	30.6168	0.544962	0.999231
			1.07015	30.6512	0.529005	0.999056
			1.06243	31.3487	0.54077	0.999219
298.15	*9*	*3*	1.06634	24.4001	0.531665	0.999008
			1.0624	24.2774	0.535641	0.999143
			1.06571	25.1879	0.52561	0.999151
327.85	*9*	*3*	1.03479	13.7313	0.583756	0.99938
			1.0365	13.9514	0.577705	0.999356
			1.03585	14.1791	0.580553	0.999395
347.45	*9*	*3*	1.02544	10.5111	0.600852	0.999502
			1.02639	10.3584	0.598574	0.999471
			1.02632	10.4184	0.601204	0.999469
298.15	*15*	*5*	1.05624	39.4172	0.524616	0.999532
			1.08091	36.8368	0.488154	0.999042
			1.06937	38.76	0.505223	0.999351
298.15	*21*	*7*	0.869959	89.9256	0.520717	0.997487
			0.913859	68.8989	0.476866	0.998377
			0.902849	78.1586	0.504852	0.998416

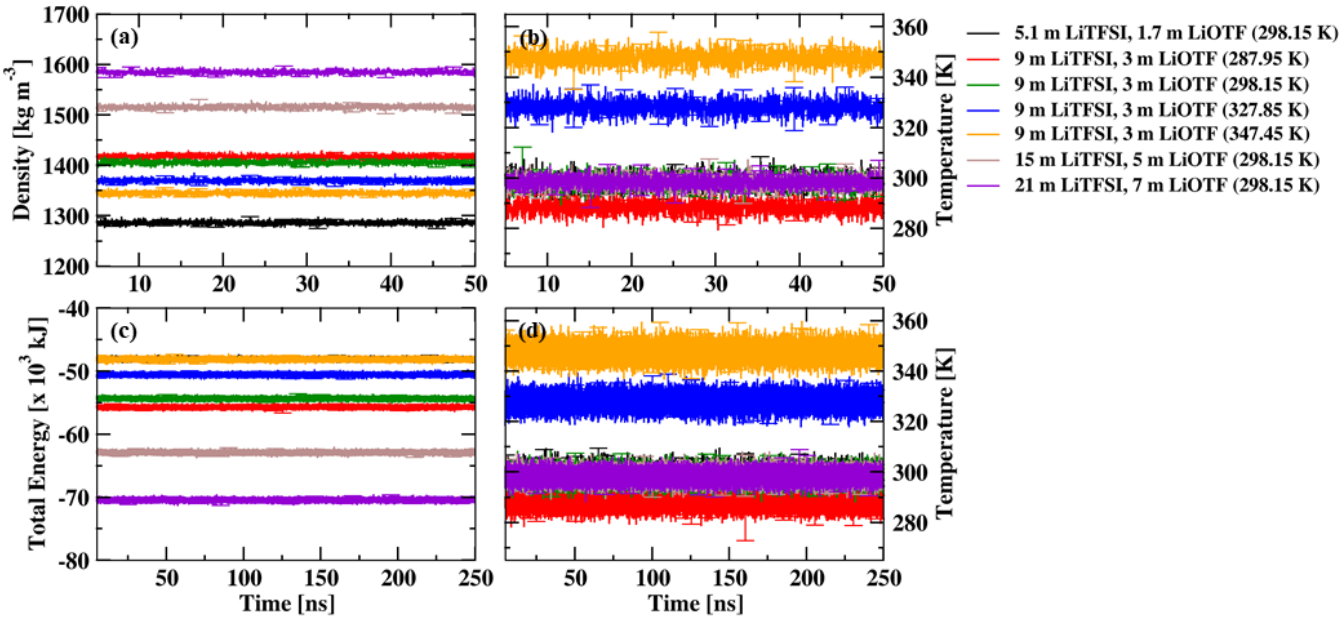


Figure S1. Physical properties converging during the molecular dynamics simulations of different concentrations of the WiBS electrolyte at different temperatures: (a) Density during 50 ns of NPT (b) Temperature during 50 ns of NVT (c) Total energy during 250 ns of NVE (d) Temperature during 250 ns of NVE.

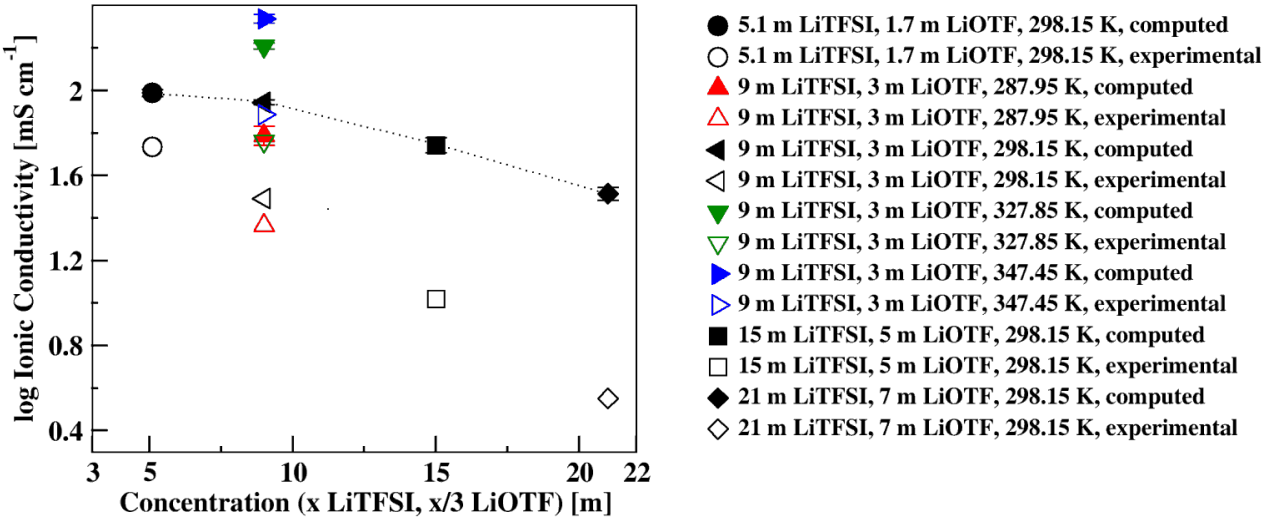


Figure S2. Ionic conductivities calculated by the Nernst-Einstein method for WiBS electrolyte mixtures at different concentrations and temperatures. The experimental values[1] for each calculated value are also provided for reference.

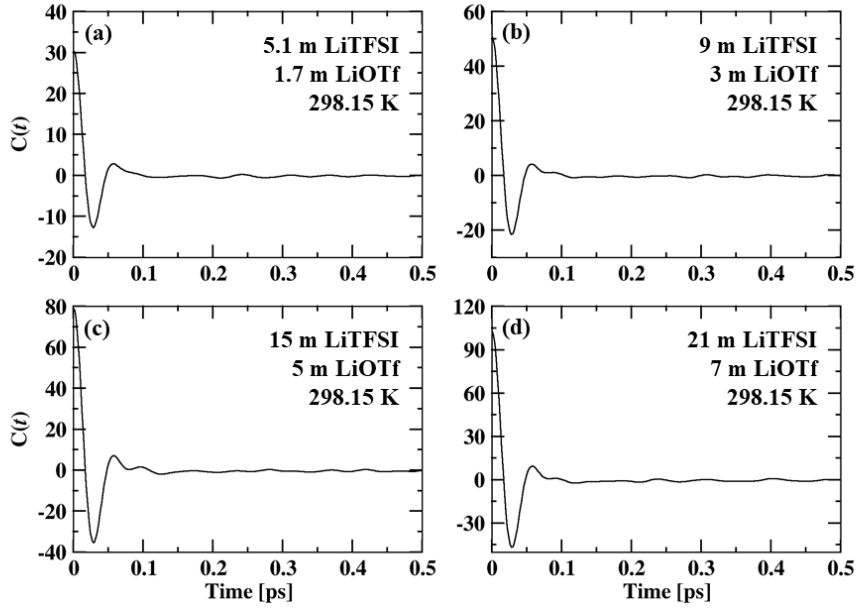


Figure S3. Current autocorrelation functions of the electrolytes of different concentrations at 298.15 K.

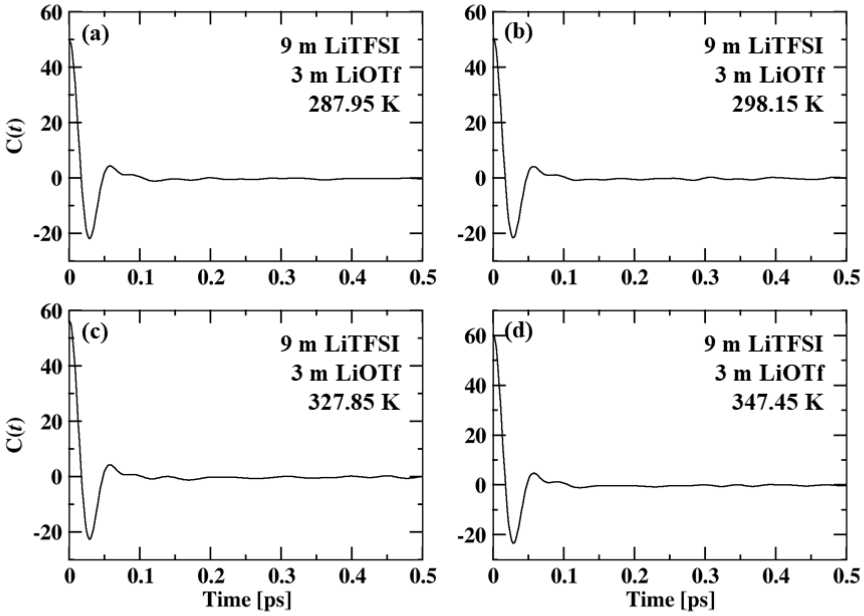


Figure S4. Current autocorrelation functions of the 9 m LiTFSI – 3 m LiOTf electrolyte at different temperatures.

REFERENCES

[1] M.S. Ding, A. von Cresce, K. Xu, Conductivity, Viscosity, and Their Correlation of a Super-Concentrated Aqueous Electrolyte, J. Phys. Chem. C. 121 (2017) 2149–2153. https://doi.org/10.1021/acs.jpcc.6b12636.