

**Electronic Supplementary Information (ESI)**

**Linear ether-based highly concentrated electrolytes  
for Li-sulfur batteries**

*Toru Ishikawa*<sup>1</sup>, *Shohei Haga*<sup>1</sup>, *Keisuke Shigenobu*<sup>3</sup>, *Taku Sudoh*<sup>1</sup>, *Seiji Tsuzuki*<sup>2</sup>, *Wataru Shinoda*<sup>3</sup>, *Kaoru Dokko*<sup>1,2</sup>, *Masayoshi Watanabe*<sup>2</sup>, *Kazuhide Ueno*<sup>1,2</sup>

1 Department of Chemistry and Life Science, Yokohama National University, 79-5 Tokiwadai,  
Hodogaya-ku, Yokohama, Kanagawa, 240-8501, Japan

2 Institute of Advanced Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku,  
Yokohama, Kanagawa, 240-8501, Japan

3 Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku,  
Okayama, Okayama, 700-8530, Japan

## Numerical data

**Table S1.** Calculated and experimental densities of the electrolytes at 323 K.

| Sample                        | Density / g cm <sup>-3</sup> |                   | Error / % |
|-------------------------------|------------------------------|-------------------|-----------|
|                               | MD <sup>a</sup>              | Exp. <sup>b</sup> |           |
| [Li(BME) <sub>3</sub> ][TFSA] | 1.098                        | 1.105             | 0.6       |
| [Li(EPE) <sub>3</sub> ][TFSA] | 1.090                        | 1.078             | 1.1       |

<sup>a</sup> Density values obtained from the MD simulations.

<sup>b</sup> Experimental density values.

## MD simulation

In-house software, the MPDynPFF program <sup>1</sup> was utilized for the all-atom MD simulations, and the *NPT* ensemble condition was applied to the simulations. The system temperature and pressure were kept at 403 K (or 323 K for the calculation of densities) and 0.1 MPa by a Nosé–Hoover chain thermostat <sup>2-4</sup> and an Andersen barostat <sup>5</sup>, respectively. The time constants for the thermostat and the barostat were set at 0.5 and 2 ps, respectively. All C–H bonds were held rigid using the SHAKE/RATTLE algorithm,<sup>6</sup> and reversible RESPA was employed for the multiple-time step integration of the equations representing the motion of atoms.<sup>7-8</sup> The Lennard-Jones interaction was truncated at 12 Å, whilst long-range electrostatic and induced polarization interactions were estimated using the Ewald method.<sup>9</sup> The time-step size for updating the electrostatic interactions in the Ewald reciprocal space was 8 fs, whereas that for the other interactions was 2 fs. Periodic boundary conditions were employed for all three dimensions.

To reduce any biases arising from the initial arrangement of molecules, the following procedures were carried out for the preparation of the initial structures. The system was initially allowed to evolve at 453 K and 10 MPa from the low-density condition of the initial box size for 50 ps, and was subsequently equilibrated at 453 K and 0.1 MPa for 1 ns. Additionally, at least 1 ns equilibration MD runs were then performed at 403 K (or 323 K) without changing the pressure, and a 20 ns production run was carried out to collect the trajectory data at 0.2 ps intervals for analysis. The number of molecules in a cubic cell ( $\sim 27 \text{ nm}^3$ ) was listed as follows for consistency purposes: Li[TFSA]/BME = 50/150 and Li[TFSA]/EPE = 50/150. Only for the illustration of liquid structures of the electrolytes, the number of molecules was changed as following: Li[TFSA]/BME = 400/1200 and Li[TFSA]/EPE = 400/1200, and the cell size was  $\sim 340 \text{ nm}^3$ .

For the purpose of these simulations, the OPLS-AA-based polarizable force field was employed, as described in our previous report.<sup>10-11</sup> For structural analysis, visualization of the structures was carried out using VMD software.<sup>12</sup>

## Force field parameters.

The force field parameters were modified to reproduce the molecular structures and the stabilization energy of  $\text{Li}^+$ -solvent and  $\text{Li}^+$ -[TFSA] $^-$  pair optimized at MP2(full)/6-311++G\*\* level of theory based on the OPLS-based parameters obtained from literatures.<sup>10-11, 13-15</sup> Atomic charges were determined based on the atomic charges obtained by electrostatic potential fitting<sup>16-17</sup> based on the MP2/6-311++G\*\* wave function.

The total potential was defined by the following equation as described in our previous literature:<sup>10-11</sup>

$$U(r^N) = \sum_{i=1}^{N_{bond}} \frac{1}{2} k_b (r - r_0)^2 + \sum_{i=1}^{N_{angle}} \frac{1}{2} k_\theta (\theta - \theta_0)^2 + \sum_{i=1}^{N_{torsion}} \frac{1}{2} k_t (1 + \cos(n\varphi + \delta)) + \sum_{i=1}^N \sum_{j>i}^N 4\epsilon \left\{ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right\} + \sum_{i=1}^N \sum_{j>i}^N \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + U_{ind}(r^N) \#(Eq. S1)$$

The first three and last three terms describe intramolecular interactions and non-bonding interactions, respectively. Here,  $k_b$ ,  $k_\theta$ , and  $k_t$  are the force constants in each term,  $r_0$  and  $\theta_0$  are the bond length and angle at the energy minimum,  $n$  is the number of waves,  $\delta$  is the phase,  $\epsilon$  is the potential depth at the minimum,  $\sigma$  is the distance at the potential is zero,  $\epsilon_0$  is the vacuum permittivity and  $q_i$  is the partial charge on  $i$ -th atom, respectively. The final term is the induction term, which is based on the isotropic atomic-induced dipole model and is described by the following equation:

$$U_{ind}(r^N) = - \sum_{i=1}^N \mu_i \cdot E_i^0 - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \mu_i \cdot T_{ij} \cdot \mu_j + \sum_{i=1}^N \frac{\mu_i \cdot \mu_i}{2\alpha_i} \#(Eq. S2)$$

$\mu_i (= \alpha_i E_{Total})$  is the induced dipole moment,  $\alpha_i$  is the isotropic atomic dipole polarizability of the  $i$ -th atom.  $E_{Total}$  is the total electric field.  $E_i^0$  is the electric field created by partial atomic charges, and  $T_{ij}$  is the second order dipole tensor. <sup>10-11, 18</sup>

**Table S2.** Bond stretching parameters.

| Bond   | $k_b / \text{kcal mol}^{-1} \text{ \AA}^{-2}$ | $r_0 / \text{\AA}$ |
|--------|---|--------------------|
| CS–CS  | 268.0   | 1.529              |
| CS–CT  | 268.0   | 1.529              |
| CS–HC  | 340.0   | 1.090              |
| CT–HT  | 331.0   | 1.090              |
| OES–CS | 570.0   | 1.408              |
| OES–CT | 570.0   | 1.408              |
| CF–FC  | 884.0   | 1.340              |
| SO–CF  | 471.0   | 1.835              |
| SO–OS  | 1274.0  | 1.450              |
| NI–SO  | 744.0   | 1.600              |

**Table S3.** Angle bending parameters.

| Angle    | $k_\theta / \text{kcal mol}^{-1} \text{ rad}^{-2}$ | $\theta_0 / \text{deg.}$ |
|----------|--|--------------------------|
| CS–CS–CS | 58.35  | 112.7                    |
| CS–CS–CT | 58.35  | 112.7                    |
| CS–CS–HC | 37.50  | 110.7                    |
| CS–CT–HT | 37.43  | 110.7                    |
| CT–CS–HC | 37.43  | 110.7                    |
| HC–CS–HC | 33.00  | 107.8                    |
| HT–CT–HT | 33.00  | 107.8                    |

|           |        |       |
|-----------|--------|-------|
| CS-OES-CS | 55.00  | 106.8 |
| CS-OES-CT | 55.00  | 106.8 |
| OES-CS-CS | 80.00  | 109.0 |
| OES-CS-HC | 35.00  | 109.0 |
| OES-CS-CT | 80.00  | 109.0 |
| OES-CT-HT | 35.00  | 109.0 |
| FC-CF-FC  | 187.00 | 108.6 |
| FC-CF-SO  | 166.00 | 110.4 |
| OS-SO-OS  | 232.00 | 120.2 |
| OS-SO-NI  | 189.00 | 111.4 |
| CF-SO-OS  | 208.00 | 102.6 |
| CF-SO-NI  | 195.00 | 100.2 |
| SO-NI-SO  | 80.00  | 121.0 |

**Table S4.** Torsional parameters.

| Dihedral    | $k_t / \text{kcal mol}^{-1}$ |         |         | $\delta / \text{degree}$ |
|-------------|------------------------------|---------|---------|--------------------------|
|             | $n = 1$                      | $n = 2$ | $n = 3$ |                          |
| CS-CS-CS-CT | 1.743                        | 0.157   | 0.279   | 0.0                      |
| CS-CS-CS-HC | 0.0                          | 0.0     | 0.366   | 0.0                      |
| CS-CS-CT-HT | 0.0                          | 0.0     | 0.366   | 0.0                      |
| HC-CS-CS-CT | 0.0                          | 0.0     | 0.366   | 0.0                      |
| HC-CS-CS-HC | 0.0                          | 0.0     | 0.318   | 0.0                      |
| HC-CS-CT-HT | 0.0                          | 0.0     | 0.318   | 0.0                      |

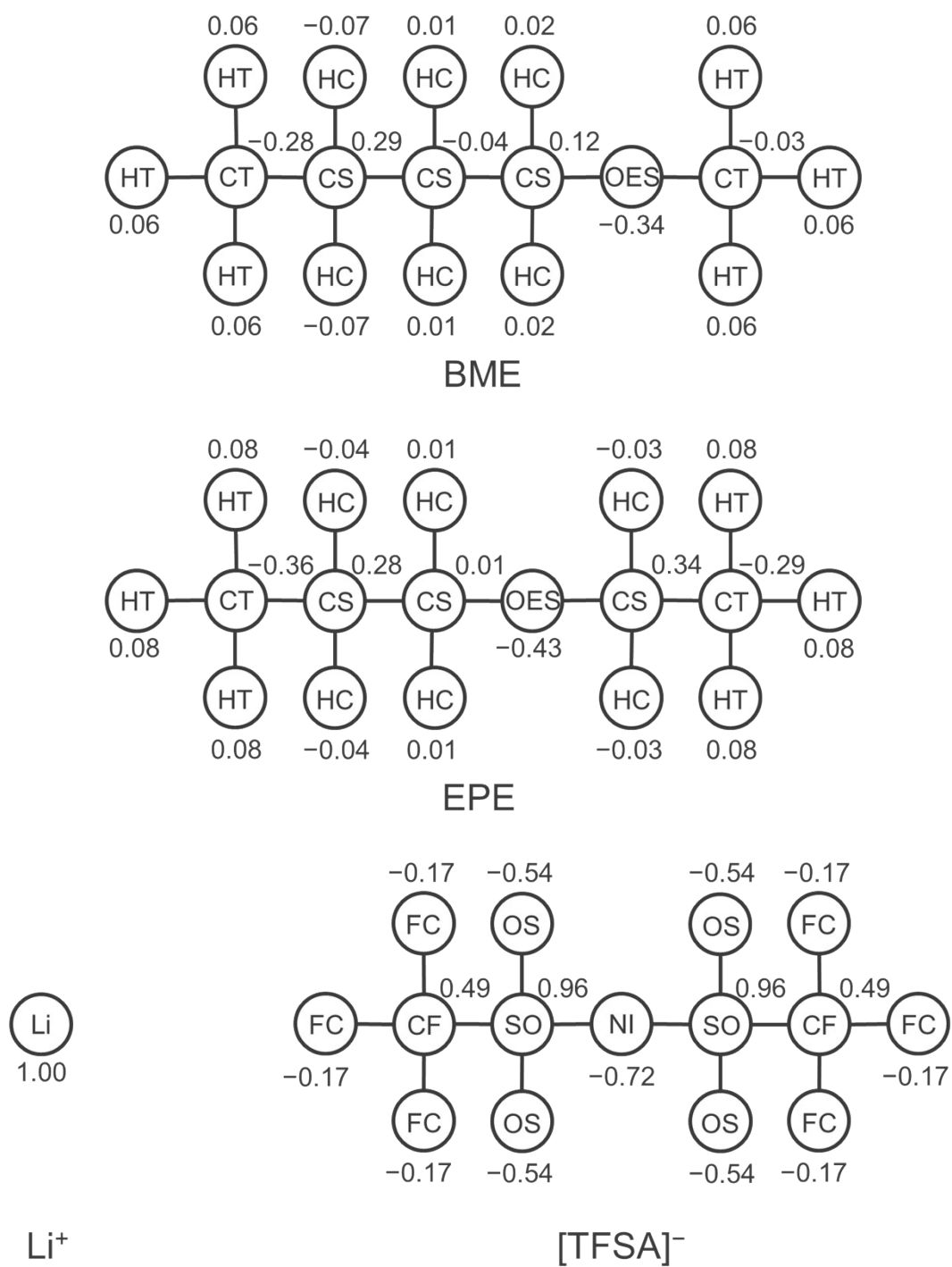
|              |       |       |        |         |
|--------------|-------|-------|--------|---------|
| CS-CS-CS-OES | 3.204 | 2.111 | -0.598 | 0.0     |
|              | 3.844 |       |        | -0.249  |
| CS-CS-OES-CS |       | 1.867 |        | 57.41   |
|              |       |       | 1.720  | -124.67 |
|              | 3.844 |       |        | -0.249  |
| CS-CS-OES-CT |       | 1.867 |        | 57.41   |
|              |       |       | 1.720  | -124.67 |
|              | 3.844 |       |        | -0.249  |
| CS-OES-CS-CT |       | 1.867 |        | 57.41   |
|              |       |       | 1.720  | -124.67 |
| CS-OES-CS-HC | 0.0   | 0.0   | 0.67   | 0.0     |
| CS-OES-CT-HT | 0.0   | 0.0   | 0.67   | 0.0     |
| CT-OES-CS-HC | 0.0   | 0.0   | 0.67   | 0.0     |
| OES-CS-CS-CT | 3.204 | 2.111 | -0.598 | 0.0     |
| OES-CS-CS-HC | 0.0   | 0.0   | 0.366  | 0.0     |
| OES-CS-CT-HT | 0.0   | 0.0   | 0.366  | 0.0     |
| FC-CF-SO-NI  | 0.0   | 0.0   | 0.0    | 0.0     |
| FC-CF-SO-OS  | 0.0   | 0.0   | 0.171  | 0.0     |
| SO-NI-SO-CF  | 7.833 | 0.500 | -0.764 | 0.0     |
| SO-NI-SO-OS  | 0.0   | 0.0   | -0.004 | 0.0     |

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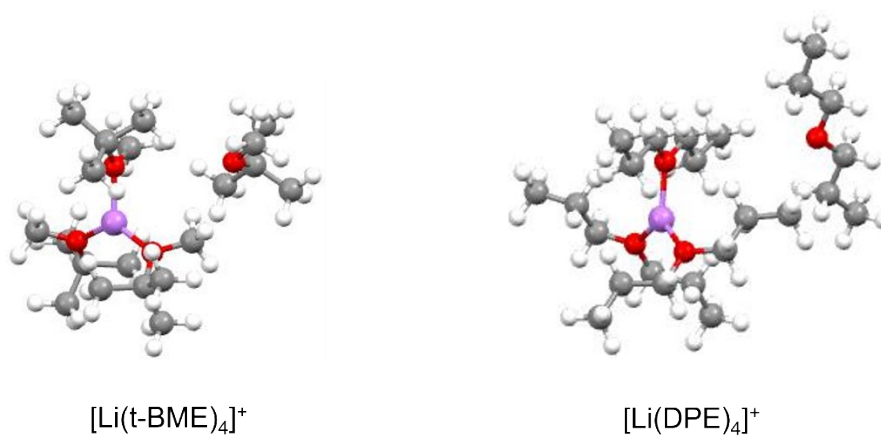


**Table S5.** Nonbonding parameters.

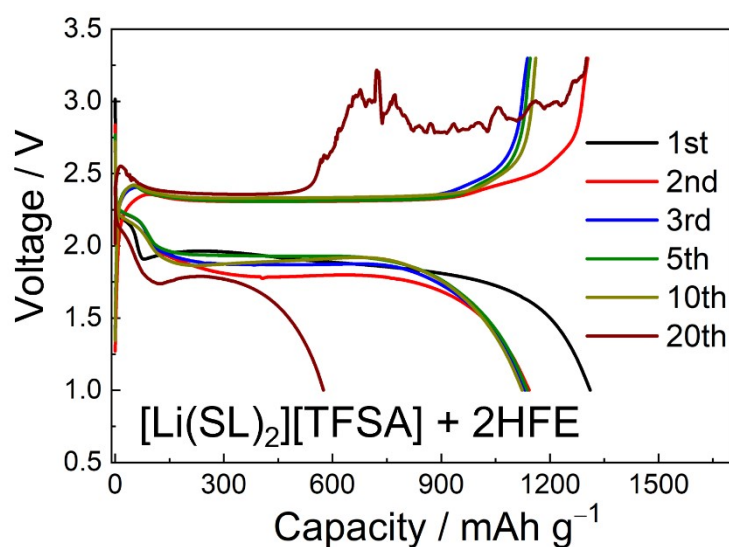
| Atom | $\sigma / \text{\AA}$ | $\varepsilon / \text{kcal mol}^{-1}$ | $\alpha / \text{a.u.}$ |
|------|-----------------------|--------------------------------------|------------------------|
| OES  | 3.03                  | 0.210                                | 7.000                  |
| CS   | 3.50                  | 0.066                                | 9.000                  |
| CT   | 3.50                  | 0.066                                | 9.000                  |
| HC   | 2.50                  | 0.030                                | 2.000                  |
| HT   | 2.50                  | 0.030                                | 2.000                  |
| LI   | 2.58                  | 0.003                                | 0.000                  |
| CF   | 3.50                  | 0.066                                | 9.000                  |
| FC   | 2.95                  | 0.054                                | 2.500                  |
| OS   | 3.08                  | 0.130                                | 5.000                  |
| SO   | 3.55                  | 0.250                                | 16.000                 |
| NI   | 3.45                  | 0.170                                | 8.000                  |



**Figure S1.** Atom types and atomic charges,  $q$ , of solvents and Li[TFSA] used for the MD simulation.



**Figure S2** The optimized geometries for  $[\text{Li}(\text{t-BME})_4]^+$  and  $[\text{Li}(\text{DPE})_4]^+$  complex cations. Purple:  $\text{Li}^+$ , red: O, grey: C, and light grey: H. O–Li lengths are 1.93 Å (coordinated) and 4.73 Å (uncoordinated) for  $[\text{Li}(\text{t-BME})_4]^+$ , 1.97 Å (coordinated) and 6.10 Å (uncoordinated) for  $[\text{Li}(\text{DPE})_4]^+$ .



**Figure S3** Charge-discharge curves of Li-S pouch cells using  $[\text{Li}(\text{SL})_2][\text{TFSA}]$ -2HFE at charge-discharge rate of 1/20 C ( $1\text{C} = 8.4 \text{ mA cm}^{-2}$ ) with the cutoff voltage of 1.0 and 3.3 V at 30 °C. Sulfur loading;  $5.05 \text{ mg cm}^{-2}$ , E/S;  $4.0 \text{ } \mu\text{L mg}^{-1}$ .

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