Atomistic Insights Into Deep Eutectic Electrolytes: The Influence of Urea On The Electrolyte Salt LiTFSI in View of Electrochemical Applications

SUPPLEMENTARY MATERIAL

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Coordination numbers for urea and TFSI around lithium ions

Figure 1: Coordination number of TFSI (a) and urea (b) molecules around lithium ions.
Occurrence probabilities for neighboring TFSI and urea molecules around lithium ions

Figure 2: Probability for a coordination of lithium ions by a specific number of TFSI and urea molecules in the first coordination shell.
Residence times of TFSI ions around lithium

Figure 3: Autocorrelation function to determine the residence time $\tau$ of TFSI in the first coordination shell of lithium ions with a distance criterion of $r = 0.27$ nm. The colors denote different urea concentrations according to $U_{1:1}$ (red line), $U_{1:3}$ (blue line) and $U_{1:6}$ (black line).
Radial distribution functions

Figure 4: Center-of-mass radial distribution functions $g(r)$ for urea around lithium (top), urea around TFSI (middle) and lithium around lithium (bottom) for different urea concentrations as denoted in the legend.
Local/bulk partition coefficient

The coordination numbers of species $\beta$ and $\gamma$ around lithium ions were used to calculate the local/bulk partition coefficient

$$K_p(r) = \frac{\langle N_\beta(r) \rangle}{\langle N_\gamma(r) \rangle} \frac{N_0^\beta}{N_0^\gamma}$$

(1)

which expresses the affinity to lithium ions. The brackets $\langle .. \rangle$ denote the mean coordination number at distance $r$ and the superscript '0' indicates the total number of molecules in the simulation box$^{1,2}$.

Figure 5: Local/bulk partition coefficient $K_p(r)$ for urea ($\beta$) and TFSI ions ($\gamma$) around lithium ions.
Diffusion coefficients

Table 1: Diffusion coefficients $D_i$ in $1 \times 10^{-5}$ cm$^2$ s$^{-1}$ for all three species depending on the urea concentration. The late onset of diffusive motion inhibits the calculation of $D_i$ for the U$_{1:1}$ mixture.

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_i$ (U$_{1:3}$)</th>
<th>$D_i$ (U$_{1:6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>urea</td>
<td>0.026</td>
<td>0.152</td>
</tr>
<tr>
<td>TFSI</td>
<td>0.007</td>
<td>0.067</td>
</tr>
<tr>
<td>lithium</td>
<td>0.010</td>
<td>0.072</td>
</tr>
</tbody>
</table>
Potential energies

![Potential energies graph]

Figure 6: Coulomb (Coul) and Lennard-Jones (LJ) potential energies between the different compounds for the different mixtures.

References
