Supplementary Information

Oxygen-Enriched Electrolytes Based on Perfluorochemicals for a High-Capacity Lithium-Oxygen Battery

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Contents:
1. Miscibilization of PFCs with aprotic solvents in the presence of LiPFOS (Fig. S1–S3)
2. Comparison of oxygen solubility among the different electrolytes (Table S1)
3. Electrochemical stability analysis of PFC-based electrolytes (Fig. S4–S5)
4. DC polarization and AC impedance measurements of PFC-based electrolytes (Fig. S6)
5. Compatibility analysis of PFC-based electrolyte with Li metal (Fig. S7)
6. Charging/discharging characteristics of the Li-O₂ cells fabricated with PFC-based electrolytes (Fig. S8–S9)
1. Miscibilization of PFC with aprotic solvents in the presence of LiPFOS

![Fig. S1](image1.png)

**Fig. S1** Images of TEGDME solutions containing BrC₆F₁₃ in the presence of (a) 1.0 M LiTFSI and (b) 2.0 M LiPFOS.

![Fig. S2](image2.png)

**Fig. S2** Miscibility of BrC₆F₁₃ (○) and BrC₆F₁₃ (●) with TEGDME depending on the LiPFOS concentration.

![Fig. S3](image3.png)

**Fig. S3** Miscibility of BrC₆F₁₃ with DMSO (○) and TEGDME (●) depending on the LiPFOS concentration.
2. Comparison of oxygen solubility among the different electrolytes

Table S1 Oxygen solubility of the electrolytes

<table>
<thead>
<tr>
<th>supporting electrolyte</th>
<th>solvent</th>
<th>oxygen solubility (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M LiTFSI</td>
<td>PC-EC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.7&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.0 M LiTFSI</td>
<td>DMSO</td>
<td>6.2&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.0 M LiTFSI</td>
<td>Triglyme</td>
<td>7.3&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.0 M LiTFSI</td>
<td>TEGDME</td>
<td>8.4</td>
</tr>
<tr>
<td>2.0 M LiPFOS</td>
<td>TEGDME</td>
<td>8.9</td>
</tr>
<tr>
<td>2.0 M LiPFOS</td>
<td>TEGDME-BrC&lt;sub&gt;6&lt;/sub&gt;F&lt;sub&gt;13&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13</td>
</tr>
</tbody>
</table>

<sup>a</sup>) 1:1 wt.  <sup>b</sup>) 60 wt% BrC<sub>6</sub>F<sub>13</sub>.  <sup>c</sup>) Zhang et al. <sup>1</sup>

3. Electrochemical stability analysis of PFC-based electrolytes

![Cyclic voltammograms](image)

**Fig. S4** Cyclic voltammograms recorded for TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS with 60 wt% BrC<sub>6</sub>F<sub>13</sub> under an argon (black) and an oxygen (red) atmosphere at a scan rate of 50 mV/s.
**Fig. S5** Cyclic voltammograms recorded for TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS with 60 wt% BrC₆F₁₃ in the absence (black) and presence (red) of Li₂O₂ under an argon atmosphere at a scan rate of 50 mV/s. The solutions were stored with Li₂O₂ for one month prior to the measurements.

4. **DC polarization and AC impedance measurements of PFC-based electrolytes**

![Graph](image)

**Fig. S6** (a) A chronoamperogram for the DC polarization and (b) AC impedance spectra before (○) and after (●) polarization obtained for the symmetric Li coin cell fabricated with a TEGDME solution containing 2.0 M LiPFOS with 60 wt% BrC₆F₁₃. I₀ and Iₚ represent the initial and steady-state current, respectively.

5. **Compatibility analysis of PFC-based electrolyte with Li metal**

![Graph](image)

**Fig. S7** AC impedance spectra obtained for the symmetric Li coin cells fabricated with TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS with 60 wt% BrC₆F₁₃ recorded with storage time of 1 (black), 10 (green), 20 (blue) and 30 (red) days.
6. Charging/discharging characteristics of the Li-O₂ cells fabricated with PFC-based electrolytes

![Figure S8](image)

**Fig. S8** Examples of charging/discharging curves of the Li-O₂ cells composed of TEGDME solutions containing (a) 1.0 M LiTFSI, and (b) 2.0 M LiPFOS and 60 wt% BrC₆F₁₃ at a current density of 0.2 mA/cm² in the 2.0–4.2 V voltage range when the charging/discharging capacity was limited to ca. 800 mAh/g. Black, red and blue curves represent 1ˢᵗ, 5ᵗʰ and 10ᵗʰ cycle, respectively. Inset: Discharging capacity dependence on the cycle number.

![Figure S9](image)

**Fig. S9** Examples of charging/discharging curves of the Li-O₂ cells composed of TEGDME solutions containing 2.0 M LiPFOS with 25 wt% BrC₆F₁₉ (black), 31 wt% BrC₆F₁₇ (blue), and 60 wt% BrC₆F₁₃ (red) at a current density of 0.2 mA/cm² in the 2.0–4.2 V voltage range.
Reference