Electronic Supplementary Information

The Importance of Solvent Selection in Li-O₂ Cells

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Experimental

Materials

LiTFSI (99.95% ; Sigma Aldrich), LiNO₃ (99.999 %; Alfa Aesar) are commercially available. The various salts were dried under high vacuum (<1 mTorr). Ethylene glycol dimethyl ether (glyme, abbreviated G1) (99.9 %), diethylene glycol dimethyl ether (diglyme, G2) (99.5 %), triethylene glycol dimethyl ether (traglyme, G3) (99 %) and tetraethylene glycol dimethyl (tetraglyme, G4) (99 %) were purchased from Sigma Aldrich and dried over molecular sieves (4 Å) for one week before use. H₂O content of the solvents was checked by Karl Fischer titration prior to the experiments and was found to be less than 15 ppm of H₂O for all glymes.

For the air cathodes, we used carbon paper matrices from MARKETECH International Inc. These porous carbon matrices have a specific surface area of 400 m²/g. Glassy separators were obtained from Whatman, while polyethylene separators were acquired from Cellguard. Before use, the cathodes and glassy separators were dried overnight at 120 °C under high vacuum.

Li-O₂ cells assembly

Li-O₂ cells were prepared from monolithic carbon paper in 180 µL electrolyte solution and a lithium metal anode. The cell contained a body made of Kel-F (polychlorotrifluoroethene) squeezed between two stainless steel plates and two valves for insertion of oxygen. For the experiments that involve using used cell component, cells after operation were flushed with argon gas and introduced into glove-box. Then each component (anode, cathode, and separator) was reused without any washing treatments.

Electrochemical measurements

Before the test, cells were flushed with pure oxygen (99.999%), with a pressure slightly higher than 1 atm at room temperature, and stabilized for 1 h. The electrochemical measurements were carried out using computerized potentiostat-galvanostat VMP3 systems from Bio-Logic (Seyssinet-Pariset, France).
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<thead>
<tr>
<th>n</th>
<th>Name</th>
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<tr>
<td>1</td>
<td>Monoglyme</td>
<td>G1</td>
</tr>
<tr>
<td>2</td>
<td>Diglyme</td>
<td>G2</td>
</tr>
<tr>
<td>3</td>
<td>Triglyme</td>
<td>G3</td>
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<tr>
<td>4</td>
<td>Tetraglyme</td>
<td>G4</td>
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Table S1. The structure and names of the glymes used in the current study

![Figure S1](Fig. S1) Cycling behavior of Li-O₂ cells with G2 containing 1 M LiNO₃ [black filled squares] vs the behavior of cells with various new components introduced after cell capacity fading at current density of 65 µA/cm²