Supplementary Information

“Coupling of Nitroxyl Radical as Electrochemical Charging Catalyst and Ionic Liquid for Calcium Plating/Stripping toward a Rechargeable Calcium-Oxygen Battery”

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1. Materials

![Chemical structure](image1)

**Figure S1.** Chemical structure

**Table S1.** Materials composition of cathode

<table>
<thead>
<tr>
<th>Sample</th>
<th>PTMA</th>
<th>Ketjen black</th>
<th>Calcium oxide</th>
<th>Teflon binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>23.5</td>
<td>32.1</td>
<td>35.4</td>
<td>9.1</td>
</tr>
<tr>
<td>No.2</td>
<td>0</td>
<td>35.6</td>
<td>55.1</td>
<td>9.3</td>
</tr>
<tr>
<td>No.3</td>
<td>24.5</td>
<td>64.6</td>
<td>0</td>
<td>10.9</td>
</tr>
</tbody>
</table>

(\% by weight)

2. Experimental

![Schematic illustration](image2)

**Figure S2.** Schematic illustration of Air-cell
3. Results

3.1 Gas analysis

GC/MS spectra of the samples after electrochemical CaO decomposition test are shown in Figure S3. The gas cylinders involved nitrogen which was caused by the air involved at injection of sample gas into GC/MS spectrometer. Therefore, the amount of oxygen due to CaO decomposition was corrected by subtracting the contribution of air from the amount of oxygen measured by GC/MS.

![GC/MS spectra after electrochemical CaO decomposition test](image)

**Figure S3.** GC/MS spectra after electrochemical CaO decomposition test
3.2 CV curves of Ca(TFSA)$_2$-DEMETFSA electrolyte at 60 °C

Figure S4. CV curves of Ca(TFSA)$_2$-DEMETFSA electrolyte at 60 °C
3.3 Photographs of Ca chips and quartz cell

(a)                                   (b)

Figure S5. Photographs of Ca chips before (left) and after (right) immersing into the DEMETFSA electrolyte (a), and the quartz cell (b)

3.4 Raman spectral line assignment

Figure S6. Raman spectra of (a) the SEI on Ca chips in DEMETFSA, (b) the SEI in MPN, (c) DEMETFSA, and (d) Ca(TFSA)$_2$. 
3.5 TOF-SIMS spectra for negative ions

Surface analysis of Ca on Pt plate in Ca(TFSA)$_2$-DEMETFSA electrolyte was made by TOF-SIMS technique. The TOF-SIMS spectrometer was directly conducted through transfer chamber to an argon glove box in order to avoid moisture exposure of the sample. Three signals derived from DEME were detected at $m/z = 116$, 132, and 146.

![Figure S7. TOF-SIMS spectrum of Ca-deposited Pt plate in DEMETFSA electrolyte](image)

3.6 Cell performance of Ca-O$_2$ cell using Ca(TFSA)$_2$-DEMETFSA electrolyte at 60 °C

![Figure S8. Cycle performance of Ca-O$_2$ cell using Ca(TFSA)$_2$-DEMETFSA electrolyte at 60 °C.](image)
Discharge-charge curves at the 1st cycle under various discharge/charge currents were displayed in Figure S9. The upper limit of operation for the Ca-O₂ cell was 0.25mA/cm². This is because oxygen molecules diffuse slowly in high viscous electrolyte. Therefore, the supply of oxygen cannot keep up at air electrode.

![Figure S9. Rate performance of Ca-O₂ cell](image)

3.7 Cycle performance of PTMA/Li and PTMA/Ca cells at 60 °C

We fabricated two types of radical battery, i.e., PTMA/LiTFSA-DEMETFSA/Li cell and PTMA/Ca(TFSA)₂-DEMETFSA/Ca cell. Charging was started under argon at 60 °C.

![Figure S10. Cycle performance of the PTMA/Li and PTMA/Ca cells at 60 °C.](image)

The electrolytes used were (a) LiTFSA-DEMETFSA, and (b) Ca(TFSA)₂-DEMETFSA.
3.8 Estimation of the contribution rate of the Ca anode to capacity fading at 60 °C

After the 3rd discharge/charge cycle under 0.154 mA/cm² was finished, the anode in Ca-O₂ battery was replaced with fresh Ca chips. We restarted the discharge/charge cycle test at 60 °C. The discharge capacity recovered to 67 % of the 1st cycle (red line).

Figure S11. Effect of renewing Ca anode
3.9 Photographs of the cathodes after charge/discharge cycle test

Figure S12. Photographs of the cathodes after charge/discharge cycle test
3.10 Characterization of the white precipitates on the cathode after discharge

White precipitates were observed at cathode of Ca-O$_2$ battery using Ca(TFSA)$_2$-DEMETFSA electrolyte after discharge. They were characterized by Raman and XPS techniques. As shown in Figure S12a, calcium peroxide was not detected. Calcium oxide was not activated by Raman spectroscopy. The XPS profiles are described in Figure S13. The XPS signals for Ca-2p and O-1s photoelectrons were detected after discharge.

**Figure S13.** Raman spectra of (a) the white precipitates, and (b) Reagents of CaO and CaO$_2$

**Figure S14.** XPS profiles of the white precipitates on the cathode after discharging.
3.11 Gas analysis after charging

We exchanged from oxygen to argon in the gas cylinder after discharging Ca-O₂ battery using Ca(TFSA)₂-DEMETFSA electrolyte (discharge: 1945 mAh/g), and started charging (charge: 1380 mAh/g). We conducted a GC/MS test on the gas after charging.

![GC/MS profiles after charging the cell with gas cylinder by filling argon](image1)

**Figure S15.** GC/MS profiles after charging the cell with gas cylinder by filling argon

3.12 Discharge/charge cycles of Ca-O₂ battery using Ca(ClO₄)₂-DEMETFSA electrolyte

We fabricated a Ca-O₂ battery using Ca(ClO₄)₂-DEMETFSA electrolyte to investigate the effect of anion of cell performance. The Ca-O₂ battery worked as a primary cell.

![Discharge/charge cycles of Ca-O₂ battery using Ca(ClO₄)₂-DEMETFSA electrolyte](image2)

**Figure S16.** Discharge/charge cycles of Ca-O₂ battery using Ca(ClO₄)₂-DEMETFSA electrolyte.

The concentration of Ca(ClO₄)₂ was 0.1 mol/L.