Electronic Supplementary Information

A novel lithium-oxygen cell based on oxygen-peroxide redox couple
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Three-electrode cell assemble and battery test.

Carbon material (ketjen black, Lion, 90 wt%) and polytetrafluoroethylene powder (PTFE, DAIKIN, 10 wt%) were carefully mixed in a mortar and pestle with small amount of ethanol to form an electrode sheet. The obtained electrode sheet was layered with a carbon paper (TGP-H-030, Toray) to use as the gas-diffusion electrode. The fabricated gas-diffusion electrodes were dried at 80 ºC under vacuum to remove the residual ethanol. The carbon loading level of the gas-diffusion electrode was 10.5 ± 0.2 mgcm$^{-2}$. An electrolyte solution was prepared by dissolving 10 M of LiCl and saturated with LiOH·H$_2$O with nitrogen bubbling. A conventional three-electrode cell (Fig. S1) equipped with a Pt/Pt-black counter electrode, a Ag/AgCl reference electrode and the gas-diffusion electrode as the working electrode, were built in a nitrogen filled glove bag to avoid the absorption of carbon dioxide into the electrolyte solution. The fabricated cell was tested in a chamber filled with pure oxygen. Constant-current charging-discharging tests were carried out using a standard battery charger (BTS-2004, Nagano). The current density of all the charging-discharging tests was 1.0 mAcm$^{-2}$ in capacity-limited mode except the rate capability test in Fig. 4 (b). The cyclic voltammograms in Fig. 3 were taken using a potentiostat/galvanostat (Solartron Model 1287A).
After the electrochemical tests, all the cells were immediately disassembled in the nitrogen-filled glove bag. The gas-diffusion electrodes were carefully rinsed with dry ethanol (Kishida) and dried at 80 °C under vacuum. The dried electrodes were transferred into an argon-filled glove box for storage.

Supplementary Fig. S1 Schematic representative of the three-electrode cell in the present work. The whole set up of the three-electrode cell was placed in a oxygen filled chamber. Since the Ag/AgCl reference electrode is not stable in alkaline solution, the cell was separated with a salt bridge filled with a gel of a KCl aqueous solution.
Characterization of the electrodes after the electrochemical tests.

The discharging products were characterized using X-ray diffractometer (RINT-2500, Rigaku) with Cu-Kα₁,₂ radiations. The electrode was placed in an air-free XRD sample holder in the argon-filled glove box. Reitveld refinement was carried out using RIETAN-FP and the refinement results are shown in Fig. S2 and Table S1.

The surface morphologies of the electrodes were observed using a scanning electron microscope (Hitachi, S-4800).
Supplementary Fig. S2 A refined XRD pattern of discharged electrode. Fitting result of the measured diffraction pattern (brown) and the simulated pattern (green) was good. The diffraction peak at 25 ° is assigned to graphite. And the peaks at 38 ° and 44 ° were corresponding to the air-free aluminum sample holder.

Supplementary Table S1 Reitveld refinement results of the discharged electrode.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>g</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B / Å²</th>
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<td>2c</td>
<td>1.0</td>
<td>1/3</td>
<td>2/3</td>
<td>1/4</td>
<td>1.0</td>
</tr>
<tr>
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<td>2a</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>O1</td>
<td>4f</td>
<td>1.0</td>
<td>1/3</td>
<td>2/3</td>
<td>0.8509(2)</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Space group: P63/mmc, a = 3.1684(3) Å, c = 7.715(12) Å, $R_{wp} = 13.03$, $R_p = 9.63$, $R_e = 5.30$, $R_B = 9.12$, $R_F = 5.10$, $S = 2.46$. 