A rechargeable lithium-oxygen battery with dual mediators stabilizing the carbon cathode

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Supplementary Figure 1 | Comparisons of specific energy (Wh/kg) and energy density (Wh/L) of a Li-air cell discharged via surface route (left) and solution route (right). The models were optimised respectively for each different route independently. Overall, the solution route results in a higher specific energy and energy density than the surface route. We assume the rest porous volume after discharge is filled with electrolyte.

<table>
<thead>
<tr>
<th>Pore diam. (nm)</th>
<th>100</th>
<th>200</th>
<th>500</th>
<th>Pore filling ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wh/kg_{(cathode)}</td>
<td>1065</td>
<td>623</td>
<td>277</td>
<td>60%</td>
</tr>
<tr>
<td>Wh/L_{(cathode)}</td>
<td>1475</td>
<td>776</td>
<td>320</td>
<td>70%</td>
</tr>
</tbody>
</table>

* The specific energy refers to the total weight of cathode at end of discharge, including carbon, Li2O2 and electrolyte in the pore structure. Assuming $\rho(Li_2O_2) = 2.3 \text{ g cm}^{-3}$ and $\rho(\text{electrolyte}) = 1 \text{ g cm}^{-3}$.

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Supplementary Figure 2 | Schematic of a cell with a GDL based porous carbon electrode, which is flooded with electrolyte and lacks gas diffusion channels for O₂.

Supplementary Figure 3 | (a) Discharge and charge curves of GDL based porous carbon electrodes, cycled in 25 mM DBBQ- 25mM TEMPO in 0.3 M LiClO₄ in DME under 1 atm O₂ at an areal current density of 1 mA cm⁻². At ~ 2 mAh cm⁻² areal, the discharge curve bends downwards (dash line). SEM images beyond 2 mAh cm⁻² areal discharge (marked with arrow) showing (b) little evidence of a passivating Li₂O₂ film on the carbon surface; (c) the clogged pores at the electrode/gas interface of the porous carbon GDL and (d) the unclogged pores at the electrode/electrolyte interface of the GDL.
Supplementary Figure 4 | Discharge and charge curves of GDL based porous carbon electrodes (a) cycled in 25 mM DBBQ-25mM TEMPO in 0.3 M LiClO₄ in DME under 1 atm O₂ at a range of areal current densities and (b) cycled with different concentrations of DBBQ-TEMPO in 0.3 M LiClO₄ in DME under 1 atm O₂ at an areal current density of 1 mA cm⁻².

Supplementary Figure 5 | (a) Cycling profiles and (b) corresponding operando pressure response in head space above the Li-O₂ cell with GDLs cycling in 25 mM DBBQ-25 mM TEMPO-0.3 M LiClO₄ in DME under 1 atm O₂ at 20 °C.
Supplementary Figure 6 | Amount of O$_2$ consumption on discharge (blue) and evolution on charge (red) in DEMS experiment with 25 mM DBBQ- 25mM TEMPO in 0.3 M LiClO$_4$ in DME.

Supplementary Figure 7 | Amounts of Li$_2$CO$_3$ from electrolyte decomposition in the $^{13}$C-carbon cathodes at the end of discharge on each cycle. Determined by subjecting the electrodes to acid to liberate $^{12}$CO$_2$ from the Li$_2^{13}$CO$_3$. The electrolyte solution was 0.3 M LiClO$_4$ in DME without (black) and with (red) 25 mM DBBQ- 25 mM TEMPO mediators under 1 atm O$_2$. 
**Supplementary Figure 8** | Schematics of an airtight Swagelok cell for volatile solvents.