

Supporting information

**Exploration of potential-limited protocols to prevent inefficiencies in Li-O₂
batteries during charge**

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Experimental details

Materials and Reagents

Lithium metal, lithium bis-trifluoromethane sulfonimide (LiTFSI, Sigma Aldrich, $\geq 99.0\%$ pure) powder, 1,2-dimethoxyethane (DME, Honeywell, inhibitor-free, $\geq 99\%$ pure), lithium iodide (LiI, Acros Organics, $\geq 99\%$ pure, anhydrous), borosilicate glass fibre separators (Whatman) and Super P GDL carbon electrodes (Sigracet 39BB) were purchased from commercial suppliers. All materials were stored in a glovebox (<1 ppm H_2O , <0.1 ppm O_2) under an inert Ar atmosphere when not in use.

Preparation of electrolyte

1,2-dimethoxyethane (DME) was purified in contact with metallic sodium overnight, distilled immediately afterwards and stored in contact with 3 Å molecular sieves in the same glovebox as the electrodes. Prior to use, lithium bis-trifluoromethane sulfonimide (LiTFSI) powder was dried at $150\text{ }^\circ\text{C}$ under vacuum for 24 hours, and lithium iodide (LiI) was dried at $200\text{ }^\circ\text{C}$ under vacuum for 24 hours. The baseline electrolyte was prepared with 1 M LiTFSI in DME, then 0.1 M LiI was added to prepare the redox mediator-containing electrolyte.

Cell Assembly

The Li- O_2 cells were assembled with a Swagelok setup sealed in a glass chamber, which is then filled with O_2 gas, and the electrodes were connected to the potentiostat via external cables. Prior to use, glass fibre separators were rinsed three times in ethanol and acetone to remove calcium carbonate and other impurities. Super P GDL carbon electrodes and glass fibre separators were dried under vacuum at $120\text{ }^\circ\text{C}$ prior to use. Inside the Swagelok cell, a 5.5 mm diameter Li metal disc was placed, followed by a glass fibre separator onto which 150 μL of the electrolyte was then pipetted, followed by a 9.525 mm diameter Super P GDL carbon electrode. To facilitate the diffusion of O_2 , a stainless steel mesh was placed on top of the cathode to act as the current collector. Then another positive plunger with a through-hole inside was pressed from the other side of the Swagelok cell. This top plunger was connected to a Swagelok Quick-Connect valve. For testing, the cell was connected to a

chamber of volume $\sim 100 \text{ cm}^3$ filled with O_2 at 1.5 bar. The cell was rested for 8 hours prior to cycling to ensure complete electrode wetting and saturation of the electrolyte with O_2 .

X-ray diffraction (XRD)

XRD was performed on a Panalytical X'pert Pro diffractometer, operated at 40 kV and 40 mA with a Cu source. Reference XRD data was reconstructed from .cif files found on the Crystallography Open Database (COD). Li_2O_2 COD ID: 2100227, ref [1]. $\text{LiOH}\cdot\text{H}_2\text{O}$ COD ID: 2106174, ref [2]. LiOH COD ID: 9008958, ref [3].

Scanning electron microscopy (SEM)

SEM was performed at 5 kV under secondary electron mode with Tescan Mira 3, which is equipped with a FEG Schottky emitter.

Additional Characterisation

SEM

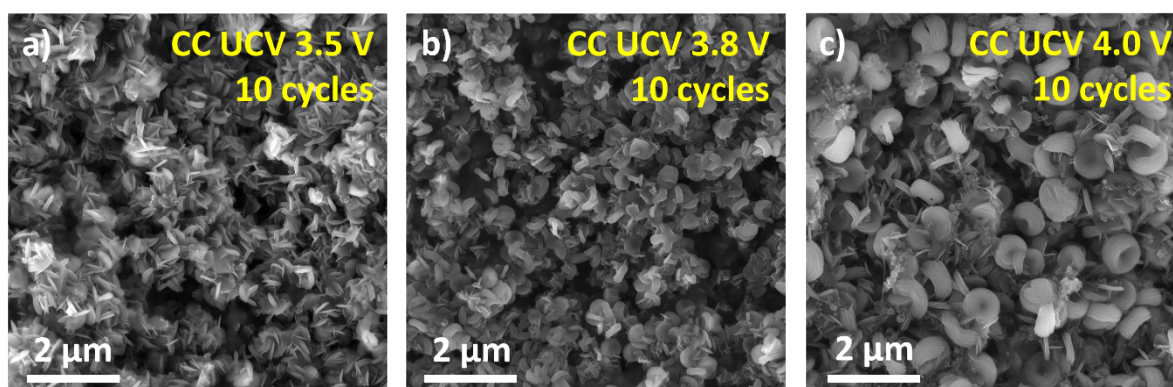


Figure S1 SEM images of electrodes from Li-O_2 cells after 10 cycles cycled with a CC protocol at varying upper-cut-off voltages (UCVs); **a)** 3.5 V, **b)** 3.8 V and **c)** 4.0 V.

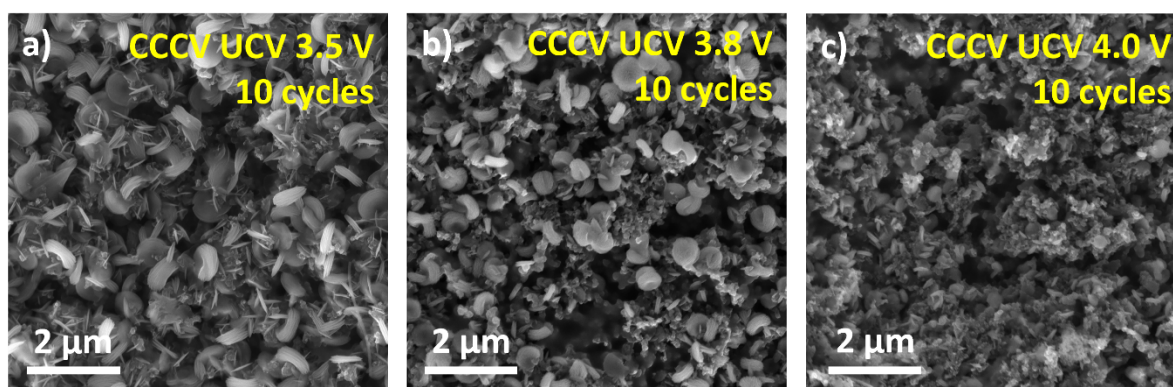


Figure S2 SEM images of electrodes from Li-O_2 cells after 10 cycles cycled with a CCCV protocol at varying upper-cut-off voltages (UCVs); **a)** 3.5 V, **b)** 3.8 V and **c)** 4.0 V.

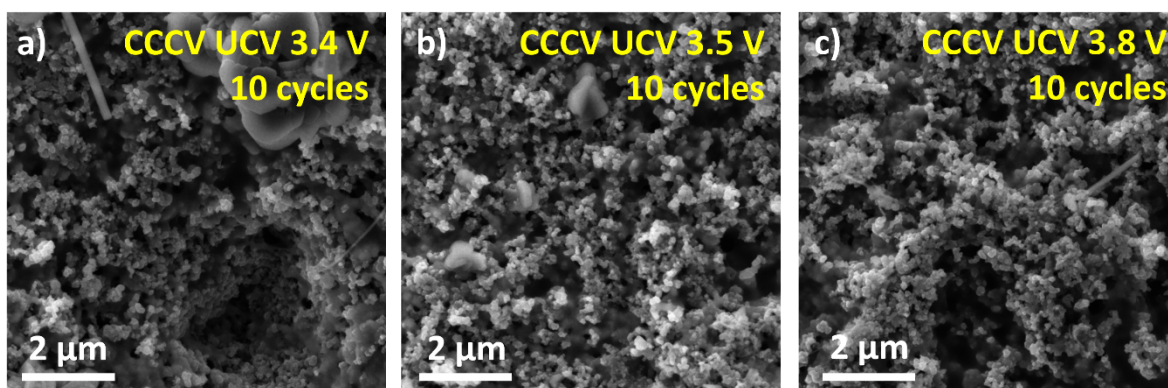


Figure S3 SEM images of electrodes from Li-O₂ cells containing LiI in the electrolyte after 10 cycles cycled with a CCCV protocol at varying upper-cut-off voltages (UCVs); **a)** 3.4 V, **b)** 3.5 V and **c)** 3.8 V.

Additional Cycling Data

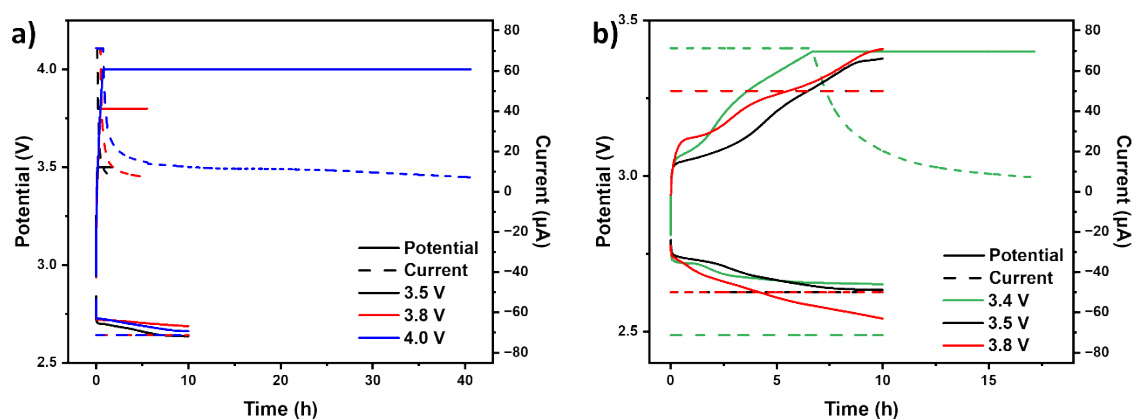


Figure S4 Potential (solid line) and current (dashed line) vs time for cells cycled with a CCCV protocol at a range of UCVs; 3.4 V (green), 3.5 V (black), 3.8 V (red) and 4.0 V (blue). **a)** Cells without LiI and **b)** containing LiI as a redox mediator in the electrolyte.

References

- [1] L.G. Cota, P. de La Mora, *Acta Crystallographica Section B*, **2005**, *61*, 133-136
- [2] L.W. Alcock, *Acta Crystallographica B (24,1968-38,1982)*, **1971**, *27*, 1682-1683
- [3] R. W. G. Wyckoff, *Crystal Structures*, **1963**, *1*, 85-237