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Supporting Information

High Resolution Visualization of the Redox Activity of Li_2O_2 in Non-Aqueous Media: Conformal Layer vs. Toroid Structure

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References

S1. Further experimental details

Materials. The electrolyte was prepared using dimethyl sulfoxide (DMSO) (Sigma-Aldrich, analytical reagent). Before use, the DMSO was dried for several days using freshly activated molecular sieves (4 Å). A concentration of 0.1 M lithium perchlorate ($LiClO_4$) (Sigma-Aldrich, 99.99 %) was prepared in DMSO after bubbling through O_2 gas (saturated, BOC Gases, U.K., 99.5 %) for 30 min prior to transferring the solution to an Ar-filled glovebox. A gel polymer electrolyte containing the cross-linker (4, 7, 10-trioxa-1, 13 tridecanediamine, Sigma-Aldrich, 97 %), and polymer matrix (in-house poly-glycidyl methacrylate (PGMA)), tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Sigma-Aldrich, $\geq$ 99 %) was used for SECCM imaging.

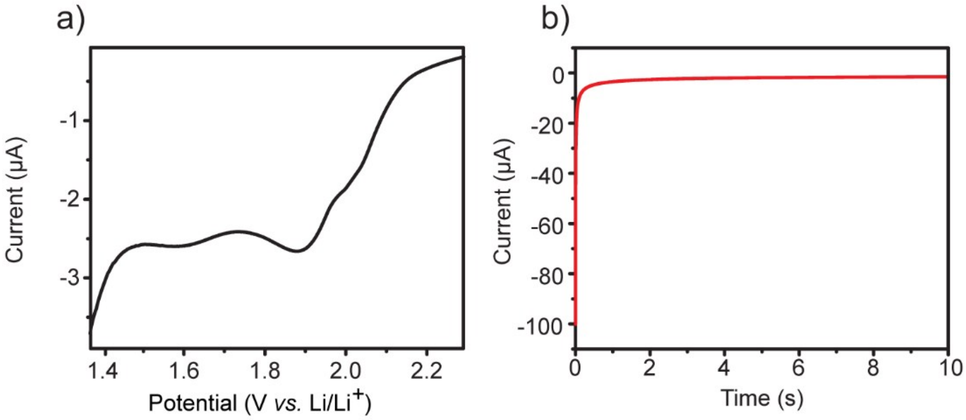

Figure S1. (a) Typical LSV recorded in O_2 saturated 0.1 M $LiClO_4$ DMSO on a gold substrate. The scan rate was 100 mV s^{-1}. (b) Typical current-time curves recorded at a substrate potential of 1.87 V_{Li/Li^+} for 10 s.

Li_2O_2 growth. A typical linear sweep voltammogram (LSV) in O_2-saturated 0.1 M $LiClO_4$ DMSO on a gold working electrode (area 1.05 cm^2), with a platinum wire counter

electrode and an AgCl-coated Ag wire quasi-reference electrode, against which all potentials are quoted ($E_{Ag/AgCl}$= 2.82 V vs. Li/Li^+), is shown in Figure 1a. There is a broad peak at 1.87 V_{Li/Li^+} and a distinct shoulder at 1.62 V_{Li/Li^+}. The peak at 1.87 V_{Li/Li^+} is attributed to surface electrochemical growth of Li_2O_2 layer and the peak at 1.62 V_{Li/Li^+} is attributed to solution-mediated growth of Li_2O_2 toroid.[1] A typical current-time curve for a 10 s deposition at 1.87 V_{Li/Li^+}, as used to grow the substrate studied in the main paper, is shown in Figure S1b. This potential was required to generate the requisite current density to produce the Li_2O_2 conformal layer and toroids and was more cathodic than expected, attributed to some O_2 loss during electrolyte transfer (into the glovebox), and the use of a smooth Au surface was used to grow Li_2O_2 products, unlike rough porous carbon matrices commonly reported (papers, carbon nanotube fibres etc.). This smooth gold substrate facilitated SECCM. Note that these Au surfaces were used as prepared, without any further treatment.

FE-SEM, Micro-Raman and AFM experiments. The Li_2O_2 sample was characterized before and after SECCM imaging using field emission-scanning electron microscopy (FE-SEM, Zeiss Supra 55-VP, 1 kV acceleration voltage). Micro-Raman spectroscopy (InVia Reflex Raman, Renishaw, UK) equipped with a solid state 633 nm laser and a 50× lens was used to determine the composition of the Li_2O_2 surface. AFM imaging of the Li_2O_2 surface was carried out in air using a tapping mode scan (Innova, Bruker).

Probe electrolyte. A solution of glycidyl methacrylate monomer (50 mL, 0.376 mol) and AIBN initiator (400 mg, 2.44 mmol) in MeCN (50 mL) was deoxygenated by bubbling with N_2 for 30 min. Concurrently, a vessel containing the CoBF (1 mg) catalyst was similarly evacuated of oxygen by purging with N_2 for 30 min. The solution of the monomer and initiator was cannulated into the vessel containing CoBF and the resulting solution was heated at 65 °C and stirred for 23 hours. Samples were taken periodically for conversion and molecular weight analysis. The resulting polymer was purified by dialysis against MeCN and finally isolated by concentration in vacuo.

Gel-polymer. The cross-linker, 4,7,10-trioxa-1,13-tridecanediamine (50 mol% with respect to epoxide) was added to a solution of poly(glycidyl methacrylate) (10 % *w/w*) in 0.1 M $LiClO_4$/DMSO electrolyte solution. The resulting solution was added to both barrels of a dual barrel nanopipette (Figure S3), which was suspended in an empty glass vial prior to curing by indirect heating at 80 °C in an oil bath. Gel formation and conductivity were confirmed by microscopy and using a conductivity sensor (1063 $\mu S\ cm^{-1}$, Mettler Toledo), respectively.

Hopping SECCM-CV experiments. Dual channel borosilicate theta capillaries (ID = 1.0 mm, OD = 1.5 mm, Harvard Apparatus, UK) were pulled using a laser pipette puller (P-2000, Sutter Instrument Co., USA) to produce nanopipettes with a diameter of ca. 140 nm (70 nm each channel; Figure S2). The dual barrel nanopipettes were filled with the gel polymer electrolyte and an Ag/AgCl wire was inserted in the back of each channel. These wires act as quasi-reference counter electrodes (QRCEs). The polymer was cured as described in the main paper. Electrolyte residues from the SECCM meniscus were inspected after experiments using FE-SEM (Supra 55-VP, Zeiss) to provide detailed information about the droplet size and location.

Defined control of the meniscus contact with the substrate was achieved by applying a bias voltage (V_2, 200 mV) between the two QRCEs to produce a direct ion current (I_{IC}) across the meniscus. The nanopipette was oscillated perpendicular to the surface (276 Hz frequency and 14 nm peak-to-peak amplitude) to induce an alternating component (AC) to the ion current between the two barrels which became detectable when the meniscus came into contact with the surface. This change in AC signal was detected using a lock-in amplifier (SR380, Stanford

Research System). A substrate voltage (V_1) was applied to one of the QRCEs to control the working electrode potential ($E_s = -(V_1 + V_2/2)$ *vs*. Ag/AgCl), and the working electrode current (I_{EC}) was measured using a custom built current-to-voltage converter. The voltammetric scan rate at each pixel was 1 V s^{-1}. Data analysis was performed in Matlab (R2014b, Mathworks Inc.) to produce I_{EC} spatial maps over a set of potentials that can be presented as a movie.[2, 3]

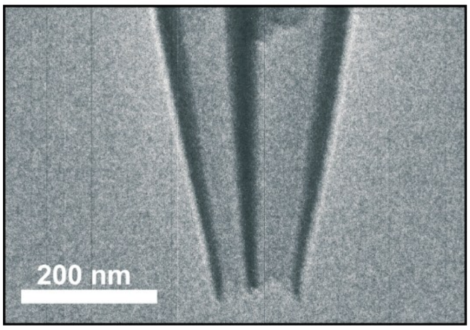

Figure S2. High resolution transmission electron microscopy (HR-TEM) image of pulled dual channel nano pippette for SECCM imaging.

S2. Movies

The experimental protocol enabled data to be reconstructed as a series of snapshots of spatially-resolved current as a function of applied potential. Movie S1 represents the behavior in the first CV cycle and Movie S2 is the behavior in the second CV cycle.

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