

Supplementary Information

Materials and methods

1,2-dimethoxyethane (DME, Aldrich) was distilled under Ar and diethylene glycol dimethyl ether (diglyme, Aldrich) and tetraethylene glycol dimethyl ether (tetraglyme, Aldrich) were distilled under vacuum. All solvents were further dried for several days over freshly activated molecular sieves (type 4Å, Aldrich) in an Ar-filled glovebox before use. Lithium bis(trifluoromethylsulphonyl)imide (LiTFSI, Aldrich) and sodium triflate (NaSO_3CF_3 , Aldrich) were dried under vacuum at 70 °C for several days prior to use. The prepared electrolyte solutions contained < 4 ppm water content (determined by Karl Fischer titration). Super P carbon black was obtained from Timcal. Deionized water for wet measurements was obtained from Sigma. The $^{18}\text{O}^{18}\text{O}$ isotope gas (> 97 atom %, 99.9 % pure) and $^{16}\text{O}^{16}\text{O}$ (99.9 % pure) was obtained from BOC. $^{16}\text{O}^{18}\text{O}$ impurity in the $^{18}\text{O}^{18}\text{O}$ gas was determined by mass spectrometry and this was corrected for in all subsequent measurements. $^{16}\text{O}^{16}\text{O}$ gas was 99.76 % pure, and the abundance of $^{16}\text{O}^{18}\text{O}$ was negligible.

Differential electrochemical mass spectrometer (DEMS) cells were constructed as described previously.^{1,2} The carbon cathodes were fabricated by making a slurry of 9:1 (m/m) Super P and PTFE binder with dry isopropanol. The electrodes were dried under vacuum and transferred to an Ar-filled glove box prior to use. A glass fibre filter (Waterman) was used as the separator. 0.25 M LiTFSI in tetraglyme served as the electrolyte, and we note that tetraglyme was used for all measurements with the exception of discharge of Na-O₂ cells. O₂ gas flow was dried using an in-line moisture trap filled with activated 3 Å molecular sieves. Cells were assembled and placed in glass tubes filled with the dry O₂ and the discharge process was performed inside an Ar-filled glove box. During DEMS experiments, cells were discharged at 0.15 mA cm⁻² for 1 h in a mixture of $^{16}\text{O}^{16}\text{O}$, $^{18}\text{O}^{18}\text{O}$ and Ar gas with the ratio of 1:1:4. The flow of gas was 1.2 ml min⁻¹. A partially oxidised two-phase Li_xFePO₄ electrode was used as the anode, which has a fixed potential of 3.45 V vs. Li⁺/Li. The isotope oxygen gas consumption and evolution were analysed by mass spectrometer, by monitoring the $^{16}\text{O}^{16}\text{O}$ (m/z=32), $^{18}\text{O}^{18}\text{O}$ (m/z=36) and $^{18}\text{O}^{16}\text{O}$ (m/z=34) channels. The total O₂ consumption was calculated from the sum of integrated flux of $^{16}\text{O}^{16}\text{O}$ (m/z=32), $^{18}\text{O}^{18}\text{O}$ (m/z=36) and $^{18}\text{O}^{16}\text{O}$ (m/z=34). The e⁻/O₂ ratio was calculated with the following equation: $e^-/\text{O}_2 = (\Delta Q/F)/\Delta n_{\text{O}_2, \text{total}}$, where ΔQ is the total charge passed during discharge and $\Delta n_{\text{O}_2, \text{total}}$ is the net O₂ consumed. For Na-O₂ systems, Swagelok Na-O₂ cells were first constructed as above with sodium metal as the anode and 0.5 M NaSO₃CF₃ in diglyme served as the electrolyte.³ During DEMS experiments, the cell was discharged at 0.1 mA cm⁻² for 1 h in a mixture of $^{16}\text{O}^{16}\text{O}$, $^{18}\text{O}^{18}\text{O}$ and Ar gas in a ratio of 1:1:4. The flow of gas was 1.2 ml min⁻¹.

For the chemical disproportionation experiments, on-line mass spectrometry measurements were performed by adding 300 µl of a Li⁺ containing electrolyte (0.25 M LiTFSI in tetraglyme) into a vial containing NaO₂ through which an Ar carrier gas (1 ml min⁻¹) was passed and fed into a mass

spectrometer. NaO₂ was obtained from cathodes after discharging Na-O₂ cells under pure ¹⁶O¹⁶O and ¹⁸O¹⁸O gases. To study the impact of water on scrambling during the disproportionation process, identical on-line mass spectrometry measurements were performed using Li⁺ electrolytes containing different amounts of water.

For post-cycling characterization, the cells were disassembled in a glovebox and the cathode was rinsed with DME and dried under vacuum prior to further characterization. The morphologies of discharge electrodes were observed by field emission scanning electron microscopy FE-SEM (Zeiss-Merlin). Fourier-transform infrared (FTIR) spectra were collected with a Thermo IR spectrometer (Nicolet 6700) in a N₂-filled glove box. Powder X-ray diffraction (PXRD) was carried out with a Rigaku Smartlab X-ray diffractometer equipped with a 3 kW rotating anode X-ray generator with Cu K α 1 radiation in an air-sensitive holder. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) data were collected using an ION-TOF GmbH instrument utilizing a 25 kV Bi³⁺ primary ion source in ToF-SIMS5-Qtac100 LEIS instrument. In order to acquire the data for this relatively large area (0.5 x 0.5 mm²), a stage scanning function was employed with 20 shots per pixel and a resolution of 256 pixels/mm. The ToF-SIMS signals cannot be directly compared between different measurements and require a calibration step. Here we use the ToF-SIMS signal from Li₂¹⁸O¹⁸O as internal reference, and the procedure is described in the following. The intensity of the Li₂¹⁸O¹⁸O signal is first corrected to account for different ¹⁸O¹⁸O amounts in the two gas mixtures, i.e., 1:1 or 1:2 ¹⁶O₂:¹⁸O₂. This signal is then used as an internal standard to normalise the Li₂¹⁶O¹⁸O signal, allowing for comparison between measurements. We take an average of three measurements and the error bars represent one standard deviation. Finally, we simplify the numbers by normalising to the Li₂¹⁶O¹⁸O amount in the 1: 1 mixed gas. The data at each step of the calibration can be found in Table S1.

To generate ¹O₂, O₂ is passed into a sealed cuvette containing 2 mL of the electrolyte solution with 10 μ M Rose Bengal (RB, Sigma) dissolved as the photosensitizer. The cuvette is placed in a cuvette holder with a built-in beam aligner and mirror located on the front and back side of the holder. A 532 nm LED light source (M530F2, Thorlabs) is connected to the beam aligner through a 400 μ m core fiber cable. When the LED is turned on, RB is excited to its triplet state (³RB*) and then the energy is transferred from ³RB* to dissolved oxygen to form singlet oxygen, converting ³RB* back to its ground state: RB + $h\nu$ + ³O₂ $\rightarrow$ ³RB* + ³O₂ $\rightarrow$ RB + ¹O₂. For detecting ¹O₂ on discharge, 0.25 M LiTFSI-tetraglyme containing 30 mM of 9,10-diphenylanthracene (DPA, Sigma), an effective ¹O₂ trap, was used as the cell electrolyte. A DEMS cell was first discharged in a mixture of ¹⁸O¹⁸O, ¹⁶O¹⁶O and Ar gas (1: 1: 4). After discharge, the cell was purged with Ar thoroughly to remove O₂ in the cell. The cell was then heated to 90 $^{\circ}$ C to release the trapped ¹O₂ and the gas evolution was recorded by mass spectrometer.

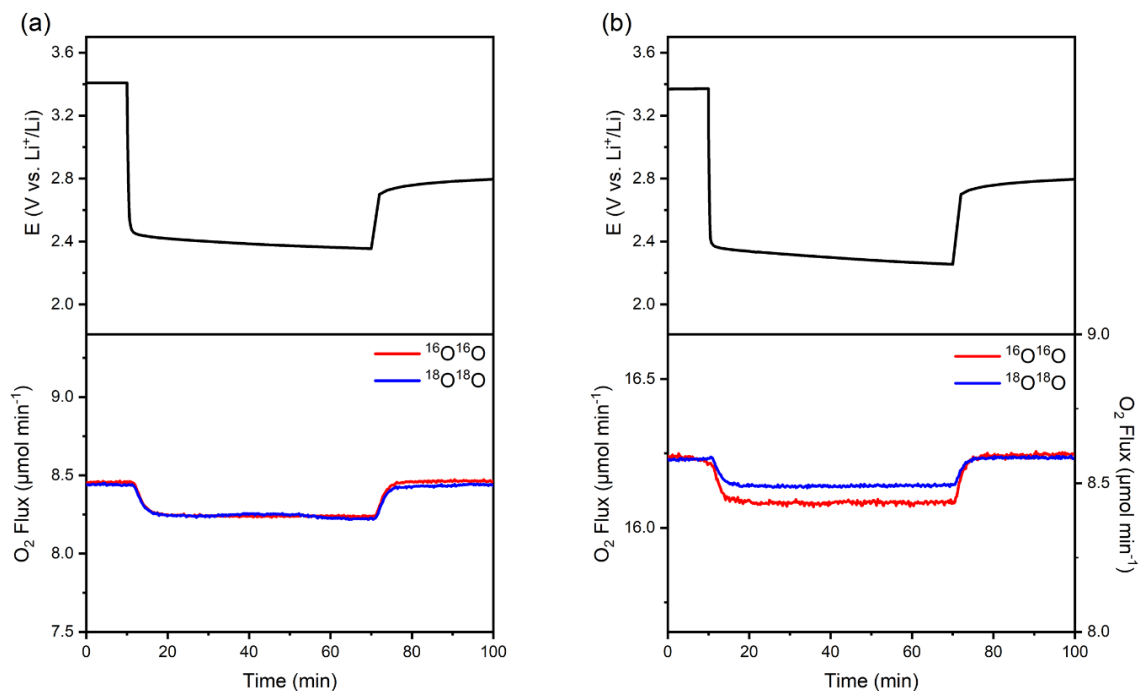


Figure S1. Load curves of oxygen reduction and the corresponding gas consumption rate of Li- O_2 cells discharged in a gas mixture of $^{16}\text{O}^{16}\text{O}$: $^{18}\text{O}^{18}\text{O}$: Ar with ratios of (a) 1: 1: 4 and (b) 1: 2: 4. The Li- O_2 cells were discharged in 0.25 M LiTFSI-tetraglyme electrolyte at a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$.

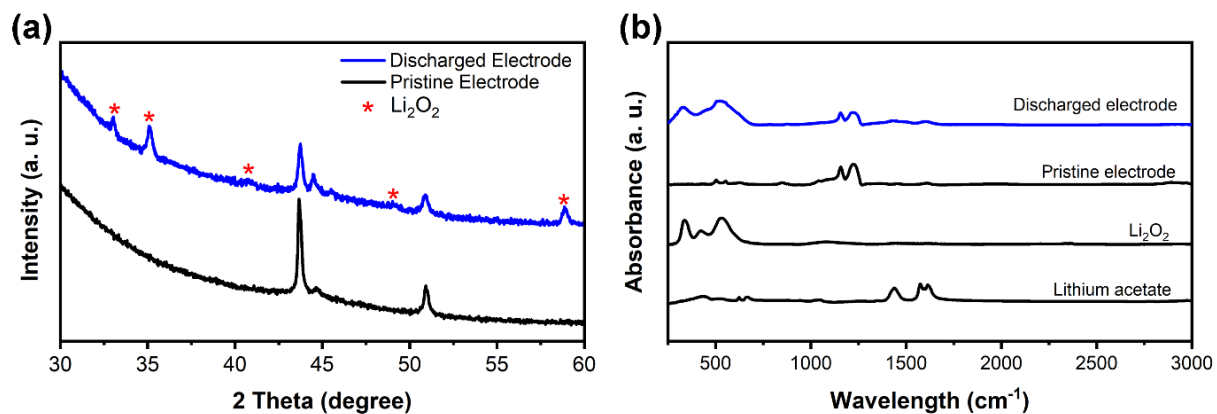


Figure S2. (a) PXRD pattern and (b) FTIR spectra of the pristine and discharged carbon electrodes from the Li- O_2 cell with the electrolyte 0.25 M LiTFSI-tetraglyme.

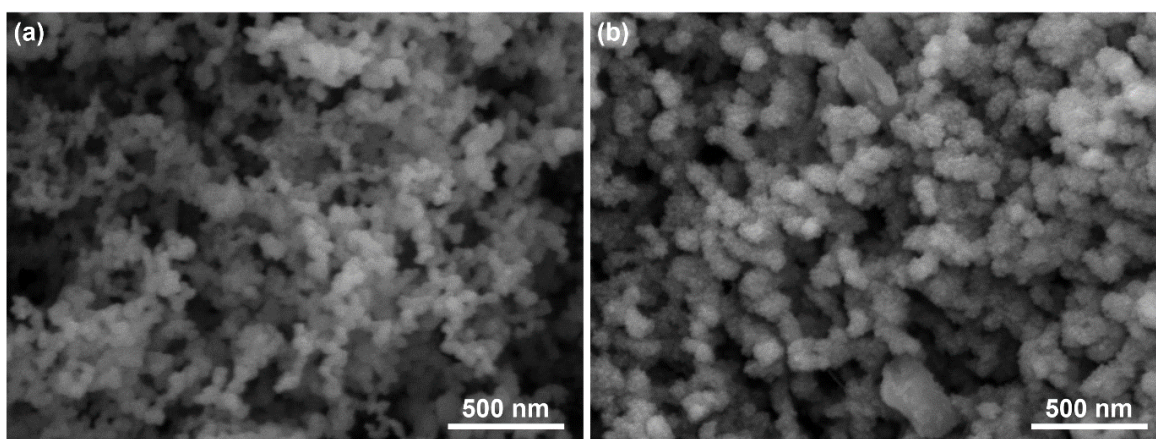


Figure S3. SEM images of (a) pristine and (b) discharged carbon electrodes from the Li-O₂ cell with the electrolyte 0.25 M LiTFSI-tetraglyme.

Table S1. Integration of ToF-SIMS ionic current results of the electrodes discharged in mixed gases with different $^{16}\text{O}^{16}\text{O} : ^{18}\text{O}^{18}\text{O}$ ratios. Error bars in Figure. 1 are defined as one standard deviation.

	Discharged in 1:1 $^{16}\text{O}^{16}\text{O} : ^{18}\text{O}^{18}\text{O}$	Discharged in 1:2 $^{16}\text{O}^{16}\text{O} : ^{18}\text{O}^{18}\text{O}$
Average $\text{Li}_2^{16}\text{O}^{18}\text{O}$ Signal	4.18×10^{-4}	5.81×10^{-4}
Average $\text{Li}_2^{18}\text{O}^{18}\text{O}$ Signal (corrected for gas ratio)	1.43×10^{-3}	1.82×10^{-3}
Average $\text{Li}_2^{16}\text{O}^{18}\text{O} / \text{Li}_2^{18}\text{O}^{18}\text{O}$ ratio	0.358	0.319
$\text{Li}_2^{16}\text{O}^{18}\text{O} / \text{Li}_2^{18}\text{O}^{18}\text{O}$ normalised to $\text{Li}_2^{16}\text{O}^{18}\text{O} / \text{Li}_2^{18}\text{O}^{18}\text{O}$ ratio (1:1)	1	0.89

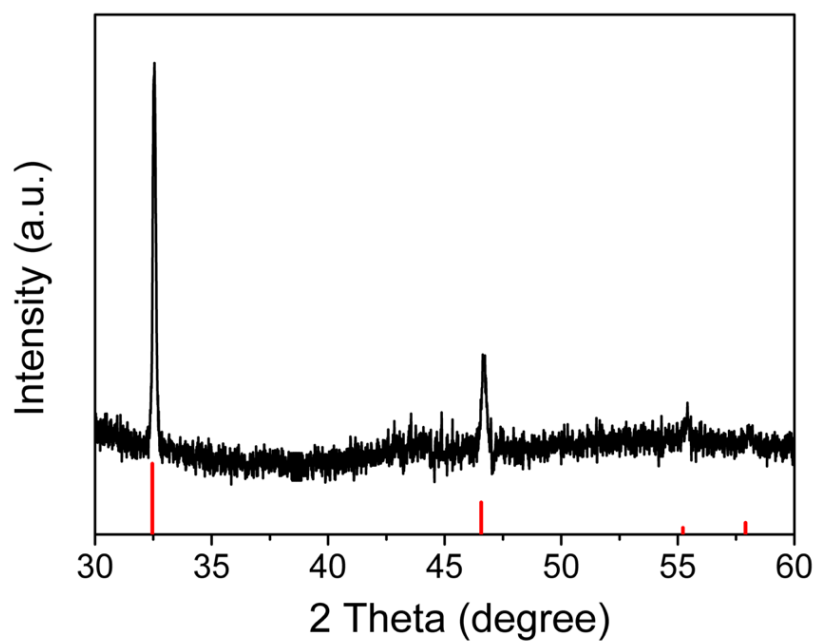


Figure S4. PXRD pattern of the discharged carbon electrode in the Na-O₂ cell in 0.5 M NaSO₃CF₃ in diglyme (black) and a reference pattern for NaO₂ (red).

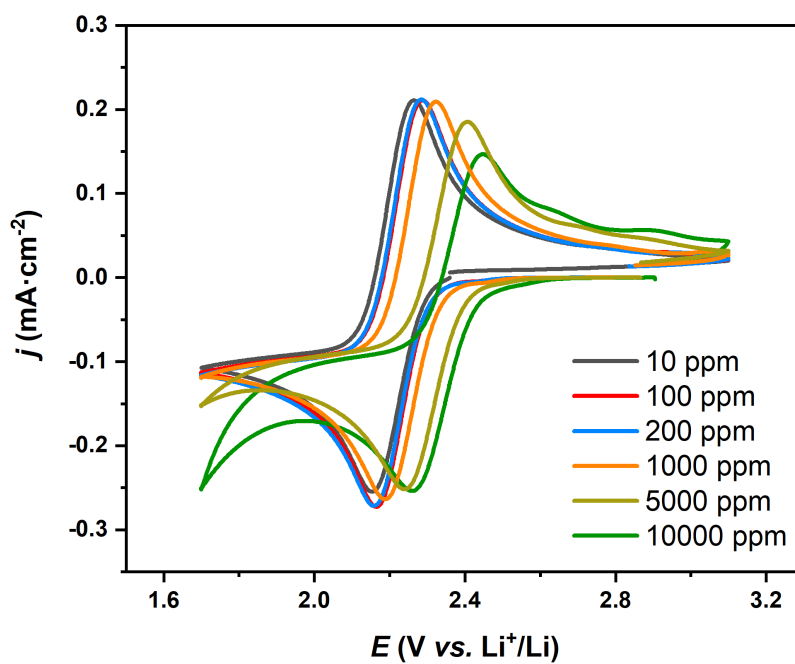


Figure S5. CVs of oxygen reduction in 0.5 M TBATFSI in tetraglyme with varying amounts of water with a scan rate of 10 mV s⁻¹.

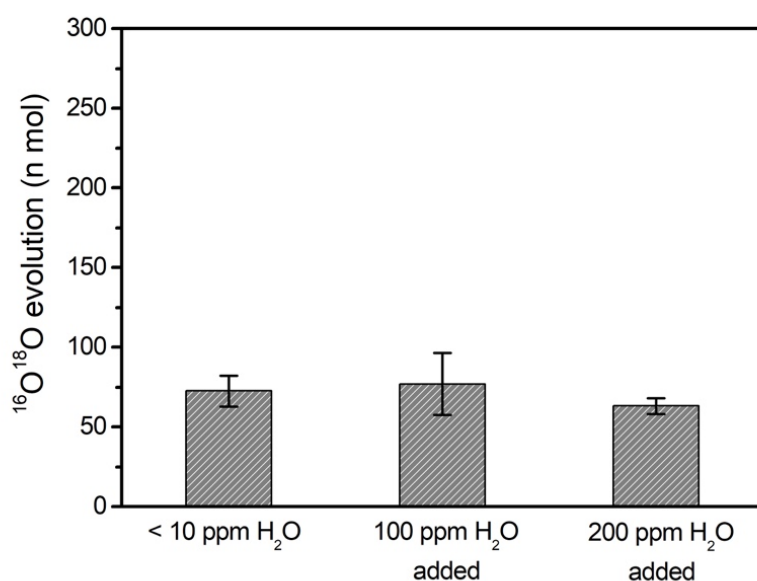
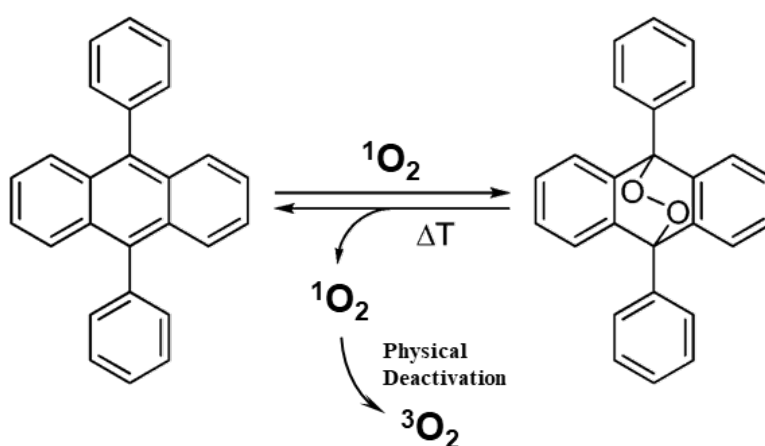


Figure S6. The total amount of the evolved $^{16}\text{O}^{18}\text{O}$ after immersing mixed isotope NaO_2 into Li^+ solutions with different H_2O concentration. $^{16}\text{O}^{18}\text{O}$ gas evolution measured using on-line mass spectrometry after injecting a solution of LiTFSI-tetraglyme with different concentration of H_2O into the vial containing NaO_2 collected from Na-O_2 cells after discharge in $^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}$, and thus containing both $\text{Na}^{16}\text{O}^{16}\text{O}$ and $\text{Na}^{18}\text{O}^{18}\text{O}$.



Scheme S1. Reaction mechanism of DPA trapping singlet oxygen under room temperature and releasing molecular oxygen upon heating.

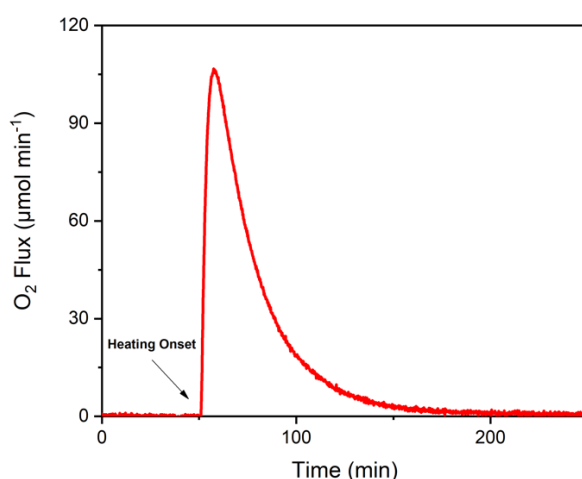


Figure S7. O₂ evolution demonstrating DPA-O₂ releasing O₂ upon heating. O₂ evolution measured using on-line mass spectrometry after heating a solution containing DPA-O₂ to 90 °C.

Supplementary Note 1: Calculation of the scrambled oxygen and disproportionation percentage

The amount of ¹⁶O¹⁸O measured by mass spectrometry was 2.25 % of the total O₂ evolved. However, this does not account for scrambling between dioxygen molecules that contain only one isotope, for example between ¹⁸O¹⁸O and ¹⁶O¹⁶O, as this results in no overall change in gas composition. Considering a bimolecular reaction and simple probabilities for collision in a 1:1 mixture, the detected scrambling is doubled to provide the overall scrambling percentage, 4.5%. An equivalent calculation is used to determine the percentage of scrambling during DEMS measurements. The amount of disproportionation during discharge is derived by comparing the quantity of ¹⁶O¹⁸O evolution observed in the mass spectrometry during chemical disproportionation to that obtained during DEMS measurements. The amount of scrambled O₂ as a percentage of the total O₂ evolved during disproportionation is 4.5%. The scrambled oxygen amount detected during electrochemical discharge in Figure S1(a) is 0.88 μmol. Assuming that disproportionation is the only route to scrambling (direct electron transfer is highly unlikely and we show in the paper doesn't occur for O₂ to O₂⁻) and taking the value above, this then represents 4.5% of the total disproportionation during discharge. Scaling 0.88 μmol to 100% of the disproportionation suggests that 19.55 μmol of Li₂O₂ out of a total 27.98 μmol undergo disproportionation. As a percentage this gives ca. 70%.

Supplementary Note 2: Influence of side reactions on singlet oxygen generation mechanism

It is well known that parasitic reactions occur in the discharge process of Li-O₂ cells. We can confirm that the e⁻/O₂ ratio on discharge is 2.04 consistent with stoichiometry of the reaction for reduction of O₂ forming predominant Li₂O₂, which is in line with the reports of others.^{4,5} It is also known that the yield of Li₂O₂ is less than 100%. Together, these results point to the surface of Li₂O₂ as the source of

the degradation and formation of the by-products such as carbonate and formate.^{4,6,7} As the routes to formation of these degradation products do not involve formation of O₂ and hence of course ¹O₂ they are not expected to impact the studies described here.⁸⁻¹⁰ The breaking of O-O bond in the scrambling pathway can in principle lead to the formation of atomic oxygen radicals and/or ozone. However, the atomic oxygen radical is reported to be highly reactive towards ether molecules¹¹. Hence if atomic oxygen radicals are formed as intermediate during discharge, they will inevitably react with the electrolyte solvent (tetraglyme) and this is not consistent with the 2.04 e⁻/O₂ value seen in our experiments, indicating the formation of atomic oxygen radical is very unlikely to occur.

References

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