Supporting information

Dynamic Oxygen Shield Eliminates Cathode Degradation in Lithium-Oxygen Batteries

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Supplementary Note 1

The simulation models a 1-D system consisting of four phases: gas | deposition layer | cathode, and the electrolyte, which contains O_2 , Li_2O_2 , DBBQ, DBBQLi, TEMPO and TEMPO⁺, flooding the deposition layer and the cathode. The flooded part is divided into small grids (4 μ m by default), and the evolution of the grid properties is simulated by iterated calculation of the changes between small time gaps (2 ms by default).

The simulation models the following processes:

- 1. Electrochemical reduction of O₂ and DBBQ, and oxidation of Li₂O₂ and TEMPO on the cathode
- 2. Diffusion of the soluble species, including O_2 , DBBQ, DBBQLi, TEMPO and TEMPO⁺, in the electrolyte
- 3. Chemical reaction between DBBQLi and O₂, and between TEMPO⁺ and Li₂O₂ in the electrolyte
- 4. Sedimentation of Li_2O_2 in the deposition layer
- 5. Dissolution and escape of O_2 at the gas/electrolyte interface

These processes are discussed in detail as follows:

Electrochemical reduction of O_2 and DBBQ, and oxidation of Li_2O_2 and TEMPO on the cathode: in cathode grids O_2 and DBBQ are reduced into Li_2O_2 and DBBQLi during discharge, while Li_2O_2 and TEMPO are oxidized into O_2 and TEMPO⁺ during charge:

$$\begin{array}{c} O_2+2Li^++2e^-\rightarrow Li_2O_2\\\\ DBBQ+Li^++e^-\rightarrow DBBQLi\\\\ Li_2O_2\rightarrow O_2+2Li^++2e^-\\\\ TEMPO\rightarrow TEMPO^++e^- \end{array}$$

These reactions are coupled with Faradaic current:

$$\mathbf{i} = F \frac{dn}{dt}$$

Where i is current, F is Faraday constant, n is the amount of species in mole and t is time. Since the limiting process in this system is diffusion instead of reaction, for simplicity these electrochemical reactions are assumed to finish instantly.

Diffusion of the soluble species, including O₂, DBBQ, DBBQLi, TEMPO and TEMPO⁺, in the electrolyte: these species diffuse in the liquid phase following Fick's law of diffusion:

$$J = -D\frac{\epsilon_{int}}{\tau}\frac{dc}{dx}$$

Where J is the flux, D is the diffusion coefficient, $\epsilon_{int} = \frac{2}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2}}$ is the average porosity of adjacent grids, $\tau = \frac{2}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2}}$

 ϵ_{int} ^{-0.5} is the tortuosity between grids, c is the concentration of species and x is position.

The concentration and diffusion of Li⁺ is omitted.

Chemical reaction between DBBQLi and O₂, and between TEMPO⁺ and Li₂O₂ in the electrolyte: chemical reactions occur when DBBQLi and O₂ or TEMPO⁺ and Li₂O₂ are present in the same grid.

$$2DBBQLi + O_2 \rightarrow 2DBBQ + Li_2O_2$$
$$2TEMPO^+ + Li_2O_2 \rightarrow 2TEMPO + O_2$$

As Li₂O₂ formation and decomposition changes the porosity in grids, the concentrations of soluble species are modified with their total amounts in the grids kept constant.

Sedimentation of Li_2O_2 in the deposition layer: when Li_2O_2 is generated at the ORR zone in the electrolyte, it deposits on nearby fibres of the deposition layer, while some particles which are not closed to any fibres sediment due to gravity. Because of the existence of the deposition layer, each Li_2O_2 particle eventually stops on a fibre of the deposition layer. This process is simulated as follows:

1. Generating a sedimentation distribution on a quartz fibre deposition layer which only contains fibres of 4 μ m diameter. Firstly, an array of grids is filled with randomly distributed '1's (standing for fibres) according to the porosity of the deposition layer. For example, a 138-element (0.55 mm / 4 μ m \approx 138) array containing randomly distributed 91 (138 * 0.658 \approx 91) '1's and 47 (138 - 91 = 47)) '0's is generated. Secondly, the index of the first nonzero element is recorded, considered as the position where a falling particle first meets a fibre. Thirdly, the first and second steps are repeated 100,000 times to obtain a distribution of the sedimentation probability. Below shows a sedimentation distribution of Li₂O₂ in a deposition layer which only contains fibres of 4 μ m diameter:



2. Generating a sedimentation distribution for mixed fibre diameters. According to SEM image of the deposition layer, the fibres can be roughly categorized as following: 4 μm (5%), 2 μm (6%), 1 μm (6%), 0.8 μm (9%), 0.5 μm (14%), 0.25 μm (6%). The sedimentation distribution obtained above is scaled to obtain distributions with different fibre diameters. Their linear weighted sum represents the sedimentation distribution in the real deposition layer (and the cathode as well, for simplicity):



 Simulate Li₂O₂ sedimentation according to the distribution. The Li₂O₂ generated in any grids is relocated according to the above distribution right after generation. About 91% of Li₂O₂ sediments within the grid it is generated, while about 8% sediments in the next 16 µm.

Dissolution and escape of O₂ at the gas/electrolyte interface: at the first grid (the one with depth = 0 mm) of the electrolyte, the concentration of O_2 is set as constant at the saturation concentration under the specified O_2 pressure, regardless the diffusion of O_2 from or to the second grid. In this way, the first grid acts as a O_2 source or sink. The amount of O_2 that diffuses into or out of this grid is plotted verses time to give the O_2 evolution or consumption profile to simulate the OEMS results.





Discussion of Figure S1: The anode side of the cell was assembled by placing a quartz fibre filter (Ø 16 mm, for preventing side reaction between lithium and the solid-state electrolyte¹) onto a piece of lithium (\emptyset 16 mm), then added with 120 μ l of anolyte. A bow comprising a quartz ring (outer \emptyset 19 mm, inner \emptyset 16 mm) sealed on a solid electrolyte (LAGP, Ø 19 mm) using silicone glue served as the separator between the anode and cathode sides to prevent cross-over of redox mediators. The cathode side, which was assembled by stacking a stainless steel (SS) ring (outer Ø 16 mm, inner Ø 14 mm) and a quartz fibre filter (Ø 14 mm, deposition layer) onto a piece of carbon paper (Ø 16mm, cathode), was placed into the bow, then added with 120 μ l of catholyte. Other porous materials can also be used for the deposition layer, while we choose quartz fibre for its stability. In addition, the structure (e.g. pore size, porosity, thickness etc.) of the deposition layer will affect the morphology of the deposited Li₂O₂ cluster. Since Li₂O₂ precipitates on deposition layer after they are generated in liquid electrolyte, a porous framework with fibers that are more evenly distributed leads to a more even distribution of Li₂O₂. On the SS ring stacks a SS mesh (\emptyset 16 mm) and a SS spring. This ring + mesh + spring structure provide electric contact between the cell top and the carbon paper with minimum disturbance on the reaction (the edge of the electrolyte layer may have different concentration profiles compared to the centre areas), making the cathode side closer to the one-dimentional model in simulation study.



Figure S2. Cyclic voltammetry on a glassy carbon electrode in a diglyme solution of 10 mM DBBQ, 10 mM TEMPO and 1M LITFSI.



Figure S3. Amount of Li_2O_2 in the discharge Non-protected and Protected cells determined using TiOSO₄ assay. The amount of Li_2O_2 is translated into equivalent mAh and normalized by the net discharge capacity. Details of the quantification experiments is described in the Methods section.

Discussion of Figure S3: To allow complete reaction of DBBQLi with O_2 , the cells are rested for at least 4 hours before Li_2O_2 quantification. The complete reaction is supported by the OCV after discharge (2.81V in Fig. 3), which is much higher than the reversible potential of DBBQ/DBBQLi (2.55 V) and indicates the absence of remaining DBBQLi. We note that the total Li_2O_2 yield (~ 60%) is lower than the OEMS-based (72%) and pressure-based OER (81%), which could be attributed to the missing solid samples attached to the surfaces of the quartz ring and stainless-steel ring (Figure S1).



Figure S4. XRD characterization of the cathodes and deposition layers in the Non-protected and Protected cells after the first discharge. The discharge product is confirmed to be Li₂O₂.



Figure S5. SEM images showing Li₂O₂ distribution along the depth in a discharged Non-protected cell.







Figure S6. SEM images showing Li₂O₂ distribution along the depth in a discharged Protected cell.



Figure S7. Simulation profiles of DBBQ concentration and O_2 consumption rate during discharge at 250 µA to 1 mAh for (a-b) the Non-protected cell, (c-d) the Protected cell and (e-f) the Protected cell in the initial 5 min. The DBBQ profiles (a, c, e) complements the DBBQLi profiles (Fig. 6, panel d, g, j). In the Protected cell, as DBBQ is consumed in the cathode and regenerated at the ORR zone, a DBBQ concentration gradient is established which supplies DBBQ back to the cathode to support continuous discharge (c). The simulation predicts a gradual increase in O_2 uptake rate to the ideal value of $1 O_2/2e^-$ at the beginning of discharge (d, 0 - 40 min), because the O_2 concentration gradient does not reach maximum until the ORR zone approaches its equilibrated position.



Figure S8. Simulated concentration profiles of O_2 , Li_2O_2 , DBBQLi and DBBQ as well as O_2 consumption rate near the end of a discharge in the Protected cell at 250 µA to 1 mAh (Zoom in on the end of Figure 7f, 7g, 7h). The ORR zone moves back to the cathode after current termination, as O_2 reacts with accumulated DBBQLi (b) and re-saturates the electrolyte (a). The O_2 consumption profile (c) shows the O_2 uptake lag, as the ORR zone moves back, during which O_2 reacts with accumulated DBBQLi and re-saturates the electrolyte. In experiment (Fig. 3b), we observed this O_2 uptake lag as expected, as well as a voltage slope from 2.62 V to 2.72 V which originates from the gradual oxidation of the accumulated DBBQLi.



Figure S9. O2 evolution of the Non-protected and Protected cells measured by pressure transducer.

Discussion of Figure S9: The pressure-based OER quantification is justified by the OEMS finding that the only gas evolved during charging below 4 V is O_2 . The $O_2/2e^-$ ratio obtained based on pressure transducer (controlled below 4.0 V) was 0.81 for both cells, which is comparable with reported conventional dual-RM cell measured by pressure transducer (0.86).² The pressure-based value is higher than the OEMS-based result; we believe it is associated with the deposition layer: it slows down the rate at which O_2 bubbles escape from the liquid phase into the gas phase, making some small O_2 signal drops below our OEMS detection limit of about 0.52 nmol/s, resulting in negative measurement error. On the contrary, O_2 bubbles are reflected in pressure changes instantly upon their generation in the deposition layer.

Protected, 10 cycles



Figure S10. Distribution of by-products in the Protected cell after 10 cycles.



Figure S11. Concentration profiles of O₂, DBBQLi and Li₂O₂ at selected times during discharge.



Figure S12. Simulated concentration profiles of O_2 , Li_2O_2 , TEMPO⁺ and TEMPO, as well as O_2 evolution rate during charging the (a-e) Non-protected and (f-j) Protected cells at 500 μ A. Li_2O_2 in both cells can be completely oxidized upon charge. The simulated gas evolution profiles (c and h) closely resemble the O_2 evolution profiles obtained via OEMS (Fig. 3c and Fig. 3d).



Figure S13. The amount of Li_2O_2 in the cathodes and deposition layers as determined by $TiOSO_4$ assay^{2,6} after discharge at various rates compared to the original Protected cells (i.e. 80%, 100% and 200% of original currents).



Figure S14. Simulation result of a modified Protected cell with 20% deposition layer thickness discharging at 5 times of the original current. (a) the simulated concentration profiles. (b) Effectiveness of protection of this cell at various currents.



Figure S15. Effect of tuning simulating parameters on the effectiveness of protection, which is defined by the distance between Li_2O_2 layer and the cathode (vertical axis). The horizontal axis denotes the ratio of tuned simulating parameters to baseline (the original value in the Protected cell). Note that although a larger DBBQLi diffusion coefficient does not influence the steady-state ORR position, it improves the effectiveness by accelerating the move of ORR layer out of the cathode.

Table S1. Comparison of the cycling performance between the Protected cell in this work and the reported
work on conventional dual redox mediator Li-O ₂ battery. ³

Performance indicators	Conventional dual-	This work, the Protected Cell
	mediator cell ³	
Absolute capacity (mAh)	0.32	1.00
Absolute current (mA)	0.16	0.25
Absolute shuffled capacity (mAh)*	16.00	84.00
Gravimetric capacity (mAh/g)	66.67	274.89
Gravimetric current (mA/g)	33.33	68.72
Gravimetric shuffled capacity (mAh/g)	3,333.33	23,091.13
Volumetric capacity (mAh/cm ³)	31.75	64.99
Volumetric current (mA/cm ³)	15.87	16.25
Volumetric shuffled capacity (mAh/cm ³)	1,587.30	5,459.51
Areal capacity (mAh/cm ²)	2.00	0.65
Areal current (mA/cm ²)	1.00	0.16
Areal shuffled capacity (mAh/cm ²)	100.00	54.60

*Note: shuffled capacity is defined as the capacity per cycle multiplied by the cycle number.

Properties		Value	Source
Deposition layer	Thickness	0.45 mm	Measured
	Porosity	0.658	Measured
	Diameter	14 mm	Measured
Cathode	Thickness	0.1 mm	Manufacturer
	Porosity	0.75	Manufacturer
Oxygen	Solubility at 1 bar O_2	5.2 mM	Reference 4
	Diffusion coefficient	4.4×10 ⁻⁵ cm ² /s	Reference 5
DBBQ	Initial concentration	100 mM	-
	Diffusion coefficient	1.2×10 ⁻⁵ cm ² /s	Measured
DBBQLi	Initial concentration	0 mM	-
	Diffusion coefficient	2.23×10 ⁻⁶ cm ² /s	Measured
ΤΕΜΡΟ	Initial concentration	100 mM	-
	Diffusion coefficient	1.4×10 ⁻⁵ cm ² /s	Reference 4
TEMPO ⁺	Initial concentration	0 mM	-
	Diffusion coefficient	1.4×10 ⁻⁵ cm ² /s	Assumed to be the same as TEMPO

Table S2. Material properties used in simulation

References:

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