

## Supplementary information

### Dissolved LiO<sub>2</sub> or Adsorbed LiO<sub>2</sub>? The Reactive Superoxide during Discharging Process in Lithium-Oxygen Batteries

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## Experimental Details

### Materials

Lithium bis(trifluoromethane)sulfonamide (LiTFSI), lithium (Li) were purchased from Sigma-Aldrich. Lithium iron phosphate (LiFePO<sub>4</sub>), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), potassium phosphate (K<sub>3</sub>PO<sub>4</sub>), N,N-Diethyl-1,4-benzenediamine, hydrogen peroxidase, potassium ferricyanide (K<sub>3</sub>Fe(CN)<sub>6</sub>), potassium chloride (KCl), Titanium oxysulfate (TiOSO<sub>4</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased from the Aladdin. Tetraethylene glycol dimethyl ether (4G) was purchased from TCI Chemicals and was distilled under vacuum. Carbon paper were purchased from SGL group Co. Ltd..

### Electrochemical active surface area (ECSA)

We employed the electrochemical double-layer approach to determine the carbon paper's actual active area in the experiment. Glassy carbon with a diameter of 2 mm and 1.5 cm<sup>2</sup> carbon paper were utilised as working electrodes in three round-bottom flasks, while Ag wire served as the reference electrode and Li as the counter electrode. The electrochemical workstation examined the CV at various sweep rates to match the relationship between current density and sweep rate, with the slope being the specific capacitance. The electrolyte employed was 0.1 M LiTFSI 4G. The following is the precise calculation equation:

$$ECSA = C_{pap} * A / C_{gla}$$

where  $A$  is the area of the glassy carbon,  $C_{gla}$  is the capacitance of the glassy carbon electrode, and  $C_{pap}$  is the capacitance of the fitted carbon paper.

### Flow cell measurement

A schematic diagram of the home-made flow cell, as shown in Figure S1. By driving convection and keeping the surface and solution pathways as separate as possible throughout the experiment, we created a self-made flow cell to measure the product lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) and by-products (Li<sub>2</sub>CO<sub>3</sub>) in order to better understand the differences in the activity of surface LiO<sub>2</sub> and solution LiO<sub>2</sub>. The working electrode of the self-made flow cell is a 2\*6 cm Ni sheet, with Ag wire serving as the reference electrode and a no-free standing LiFePO<sub>4</sub> electrode serving as the counter electrode, prior to the experiment.<sup>1</sup> We added 1 mM K<sub>3</sub>Fe(CN)<sub>6</sub> to a 1 M KCl aqueous solution to evaluate the limiting steady-state current at various flow rates. The theoretical values

were calculated using the following equation and were used to verify the validity of the self-made flow cell:

$$j = n F C_o D_o / \delta$$
$$\delta = D_o^{1/3} \nu^{1/6} y^{1/2} (Q / 60A)^{-1/2}$$

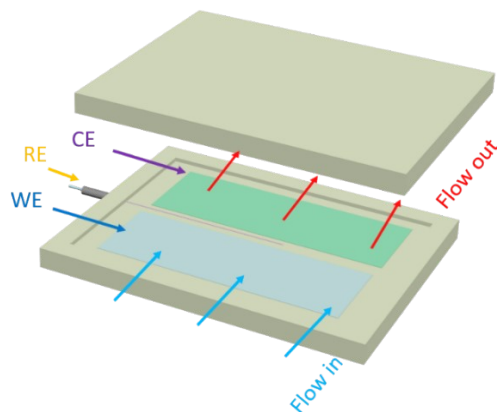
where  $n$  is the number of electrons transported by  $K_3Fe(CN)_6$ , in this case 1, and  $F$  is the Faraday constant,  $96485 \text{ C mol}^{-1}$ .  $D_o$  is the  $K_3Fe(CN)_6$  diffusion coefficient in a solution of 1 M KCl,  $7.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Kinematic viscosity ( $\nu$ ) is  $0.01 \text{ cm}^2 \text{ s}^{-1}$ , and liquid film layer thickness ( $y$ ) is 0.1 cm. The units of flow rate  $Q$  are  $\text{mL min}^{-1}$ .  $C_o$  is  $0.001 \text{ mol L}^{-1}$  and  $A$  is the working electrode's area, which is assumed to be  $12 \text{ cm}^2$ .

### Lithium peroxide measurement by UV-Vis spectrophotometer

Lithium peroxide was evaluated in the experiments at 1 atm and 0.2 atm of  $O_2$  with constant voltage and current. Li was employed as the reference electrode, while carbon paper served as the counter electrode, and  $6.2 \mu\text{Ah cm}^{-2}$  served as the cut-off condition. After performing a coloured reaction with  $Li_2O_2$  and adding  $TiOSO_4$  to the experiment, the absorbance was measured using a UV-Vis spectrophotometer to determine the amount of lithium peroxide present in the carbon paper. The particular steps were followed by consulting prior literature.<sup>2</sup> We examined the  $Li_2O_2$  that the cell in the flow cell had deposited on the Ni sheet by using a different colour development process. The deposited  $Li_2O_2$  on Ni sheet was added with 3 mL  $H_2O_2$ , 5  $\mu\text{L}$  hydrogen peroxidase, and 40  $\mu\text{L}$  buffer solution, where the buffer solution was 1 M potassium dihydrogen phosphate and 1 M potassium phosphate in a volume ratio of 7:1.

### Quantification of the lithium carbonate by Mass Spectrometry (MS)

To quantify the by-product lithium carbonate after the discharge process. The carbon paper and Ni sheet after the discharge cut-off were placed in a vial that is connected to the MS and 0.5 mL of 2 M  $H_3PO_4$  was injected into the vial to react with  $Li_2CO_3$ , forming  $CO_2$ . The released  $CO_2$  was quantified by MS



**Figure S1.** Schematics of the home-made flow cell.

### References

1. D. Cao, C. Tan and Y. Chen, *Nat Commun*, 2022, **13**, 4908.
2. X. Gao, Y. Chen, L. Johnson and Peter G. Bruce, *Nat Mater*, 2016, **15**, 882-888.