

Electronic Supplementary Information

H₂O Wash: A Simple Method Toward Eliminating Discharge Products and Regenerating the Cathodes of Li–O₂ Batteries

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Experimental Section

Material preparation

CNT (>95%), CB (99%), polyvinylidene fluoride (PVDF; M.W.=534,000), TEGDME (99%), and LiTFSI (99.95%) were purchased from Sigma–Aldrich. N-Methyl-2-pyrrolidone (NMP; 99%) was purchased from Macron. All samples were used without further purification. CNT slurry was prepared by mixing 180 mg of CNT, 20 mg of PVDF, and 9 mL of NMP. CB slurry was prepared by mixing 320 mg of CB, 80 mg of PVDF, and 7 mL of NMP. Both slurries were ball milled for 15 min at 300 rpm to form uniform slurries. The concentration was tuned by viscosity to facilitate the subsequent spray coating. The CNT and CB slurries were spray-coated onto stainless-steel meshes (d=1 cm; thickness=50 μm) to obtain air cathodes, which were then dried in a vacuum oven at 80°C overnight. The weight of CNT and CB cathodes was 0.3–0.6 and 0.4–0.8 mg, respectively.

Battery assemblies and electrochemical tests

Li–O₂ batteries were assembled inside an Ar-filled glove box with O₂<1 ppm and H₂O<1 ppm. All batteries were assembled as half cells, where components other than air cathodes were excess. Air cathodes were soaked in 1 M LiTFSI/TEGDME for 1 h to ensure the electrolyte covering the surfaces of active materials. Soaked cathodes were then assembled in 2032 coin cells in the order of cathode, separator, Li foil (d=16 mm; 20 mg), and spring. About 200 μL of the electrolyte was dropped onto the separator before putting Li foil upon it. Bottom caps with 15 holes (d=1 mm) were used to assemble the batteries. The assembled coin cells were then transferred to homemade bottles and filled with 99.9% O₂ for 10 min with a flow rate of 5 L min⁻¹, which were then sent for further electrochemical tests at room temperature. All batteries were rested for at least 8 h before any electrochemical measurements. Discharge/cycle tests were conducted by using BAT-750B cycling machines from AcuTech. The potential range was held within 2.0–4.5 V. Current densities of 50–100 and 100–200 mA g⁻¹ were applied for CB and CNT cathodes, respectively. The current densities were all normalized to the weight of conductive carbons (i.e., CB and CNTs). CV and EIS

measurements were performed with Autolab PGSTAT302N from Metrohm. C_{dl} was obtained as shown in Note S3. EIS data were collected within the frequency range of 0.1–10⁶ Hz. R_{ct} value was obtained by fitting the semicircles with Zview software. All regeneration tests, except those that underwent a cycle test, were conducted using four batteries. Error bars were presented at a 68% confidence level.

H₂O-wash and HCl-wash treatment

Discharged/cycled batteries were disassembled carefully to obtain used cathodes. The cathodes were then placed beneath a needle that supplied DI water/1 M HCl at a flow rate of 1 mL min⁻¹, which was controlled to avoid damaging the coated active materials. Each cathode was washed with DI water for 10 min to ensure complete removal of discharge products. Various measurements, which were detailed as follows, were performed to characterize electrochemical, chemical, and structural properties at discharged/washed states. For the optimized H₂O wash treatment, only 0.5 mL of H₂O is used at a flow rate of 0.1 mL min⁻¹.

Physical Characterization

A D2 phaser diffractometer from Bruker with Cu K_α radiation was used for XRD measurements. An airtight holder was used to obtain XRD patterns without the interference of moisture. SIGMA Essential from ZEISS was used to obtain SEM images and conduct EDS analysis, where the accelerating voltage was held at 5 and 15 kV, respectively. Philips Tecnai F30 Field Emission Gun Transmission Micro-scope (FEG-TEM) was used to obtain TEM images. Contact-angle measurement was performed with an FTA 1000 B from Pentad Sci. Co. The contact angle of pristine samples was measured manually because the baseline of the droplet can not be identified using the software. XAS was conducted at TLS 20A1 at the National Synchrotron Radiation Research Center in Hsinchu City, Taiwan. TEY was utilized in signal-collection mode.

Note S1. Calculation of weight of Li₂O₂ formed after discharge.

The calculation assumes that the cathodic reaction follows $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2$ with 100% yield. The weight of the formed Li₂O₂ can be calculated as follows:

$$W_{\text{Li}_2\text{O}_2} = \frac{Q \times W_{\text{Cathode}} \times 3.6 \left(\frac{\text{C}}{\text{mAh}} \right) \times M_{\text{O}_2}}{n \times F}$$

$W_{\text{Li}_2\text{O}_2}$ is the weight of formed Li₂O₂ (g); Q is the discharge capacity (mAh g_c⁻¹); W_{Cathode} is the weight of the cathode, which is 4×10^{-4} (g); n is the number of electron transfer in the cell equation and is equal to 2; F is the Faraday constant (C mol⁻¹, 96 485 C mol⁻¹); and M_{O_2} is the molecular weight of Li₂O₂, which is 45.881 (Da). The formed Li₂O₂ is 1 mg, and its weight ratio in the cathode is 71%.

Note S2. The least amount of H₂O required for H₂O-wash treatment.

Some assumptions are made to calculate the least amount of H₂O required for H₂O-wash treatment. We first assume that the rinsing agent (H₂O) is used repetitively until it is saturated with LiOH so that no H₂O is wasted. While the discharged product, Li₂O₂, can react with H₂O easily and form LiOH, we assume that all Li₂O₂ transforms into LiOH after reacting with H₂O. The reaction follows $2\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH} + \text{O}_2$. The amount of H₂O required to dissolve LiOH can be calculated as follow.

$$V_{\text{H}_2\text{O}} = \frac{2 \times Q \times W_{\text{Cathode}} \times 3.6 \left(\frac{\text{C}}{\text{mAh}} \right) \times M_{\text{LiOH}}}{n \times F \times s}$$

$V_{\text{H}_2\text{O}}$ is the volume of H₂O required to dissolve LiOH (mL); Q is the discharge capacity (7000 mAh g_c⁻¹); W_{Cathode} is the weight of the cathode, which is 4×10^{-4} (g); n is the number of electron transfers in the cell equation and is equal to 2; F is the Faraday constant (96485 C mol⁻¹); s is the solubility of LiOH at 20°C (0.113 g mL⁻¹) and M_{LiOH} is the molecular weight of LiOH, which is 23.95 (Da). 2 stands for the reaction coefficient as 1 Li₂O₂ forms 2 LiOH.

The amount of H₂O required for the reaction with Li₂O₂ can be calculated as follow.

$$V'_{\text{H}_2\text{O}} = \frac{Q \times W_{\text{Cathode}} \times 3.6 \left(\frac{\text{C}}{\text{mAh}} \right) \times M_{\text{H}_2\text{O}}}{n \times F \times D}$$

$V'_{\text{H}_2\text{O}}$ is the volume of H₂O required to form LiOH (mL); Q is the discharge capacity (7000 mAh g_c⁻¹); W_{Cathode} is the weight of the cathode, which is 4×10^{-4} (g); n is the number of electron transfer in the cell equation and is equal to 2; F is the Faraday constant (96485 C mol⁻¹); D is the density of

H₂O at 25°C (1 g mL⁻¹) and M_{H_2O} is the molecular weight of H₂O, which is 18.02 (Da).

Adding V_{H_2O} and V'_{H_2O} , we have the least amount of H₂O required which is calculated to be 23 μL.

The least amount of H₂O is far less than that we used to regenerate air cathodes, implying that there is room for further optimization.

Note S3. Obtaining C_{dl} from CV.

$$i = \frac{A}{\Delta V \times 2} = C_{dl} \frac{d\phi}{dt}$$

i is the current density (A g_c⁻¹) charging C_{dl}; A is the area enclosed by the CV cycle (A V g_c⁻¹); ΔV is the potential range, which is 0.2 (V); C_{dl} is the double-layer capacitance; and $\frac{d\phi}{dt}$ is the scan rate of CV, which is measured at 2, 4, 5, 6, 8, and 10 mV s⁻¹. To obtain the corresponding C_{dl}, ($i; \frac{d\phi}{dt}$) was plotted for each cathode.

Table S1. EDS analysis of cathodes at different stages.

	Pristine	Discharged	Washed
Carbon (at. %)	91.82	22.40	91.61
Oxygen (at. %)	4.04	74.67	5.67

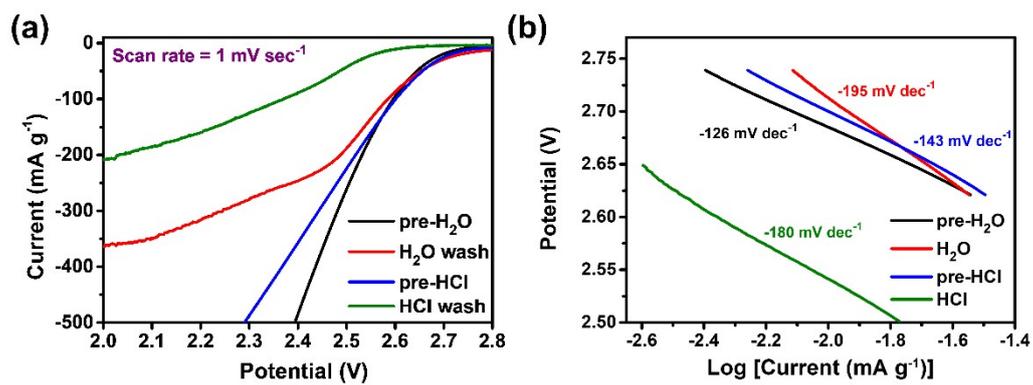


Fig. S1. (a) Linear sweep voltammetry (LSV) and (b) Tafel plot of CNT cathodes before and after H₂O/HCl-wash treatment.



Fig. S2. Contact angle of water droplet on (a) pristine, (b) discharged, and (c) washed CNT cathode.

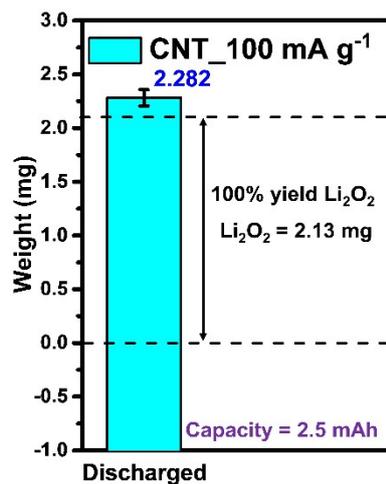


Fig. S3. The average increased weight of discharged CNT cathodes. The calculation of Li_2O_2 formed assumes 100% conversion from O_2 to Li_2O_2 .

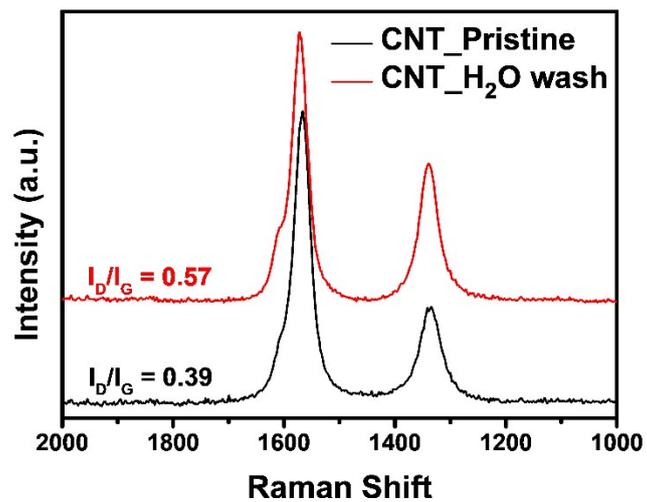


Fig. S4. Raman spectra of pristine and H₂O-washed CNT cathodes.

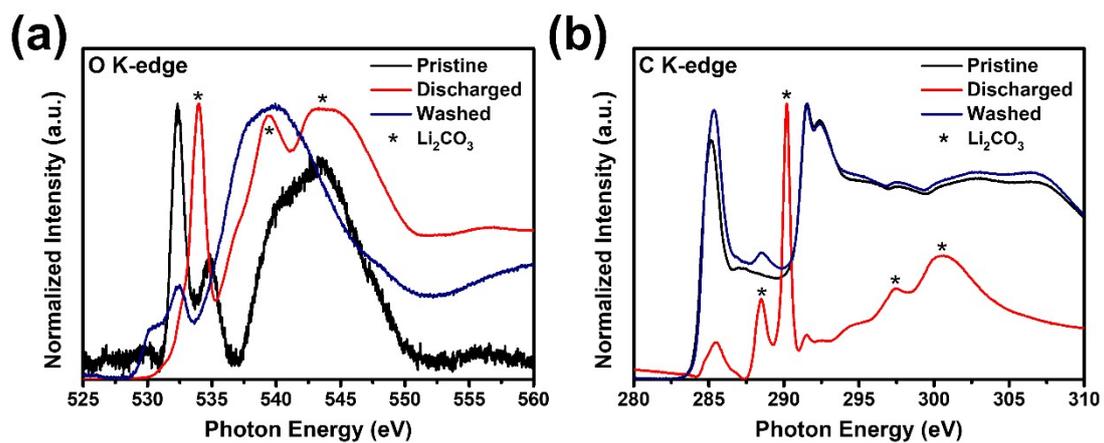


Fig. S5. XAS profiles of CNT cathodes at different stages in (a) O K-edge and (b) C K-edge.

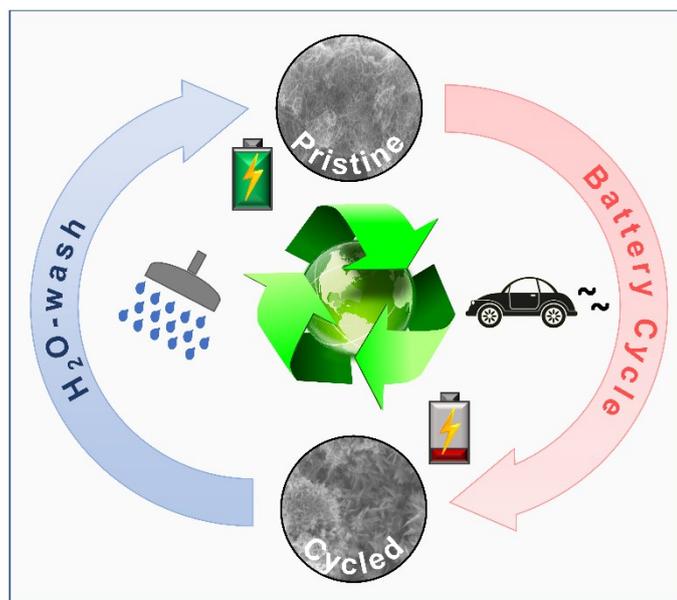


Fig. S6. Schematic diagram of the regeneration process. Characterization was done on the cathodes at their discharged/washed states.

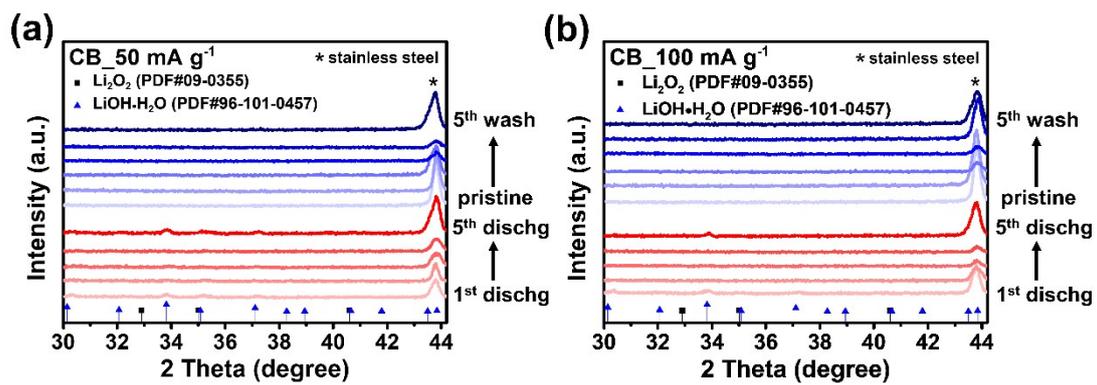


Fig. S7. XRD patterns of CB cathodes at different stages with current densities of (a) 50 and (b) 100 mA g^{-1} , respectively.

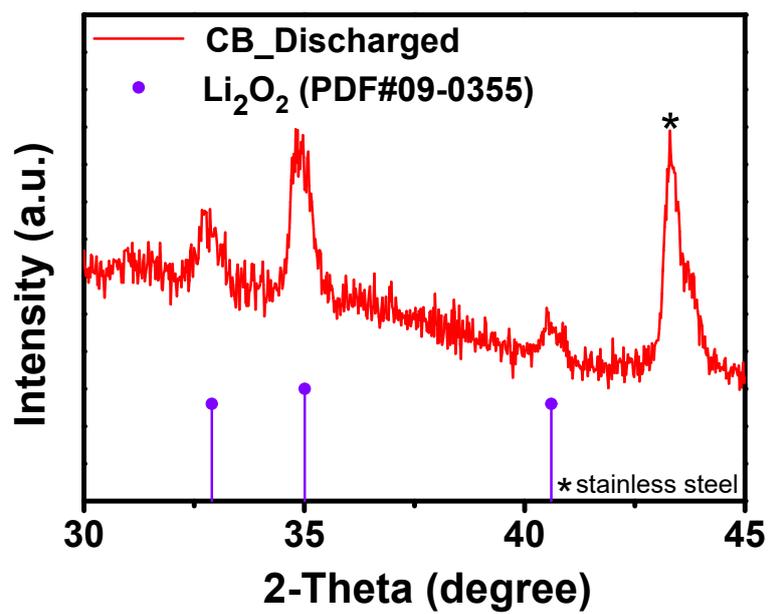


Fig. S8. XRD pattern of fully discharged CB cathode measured with an airtight holder.

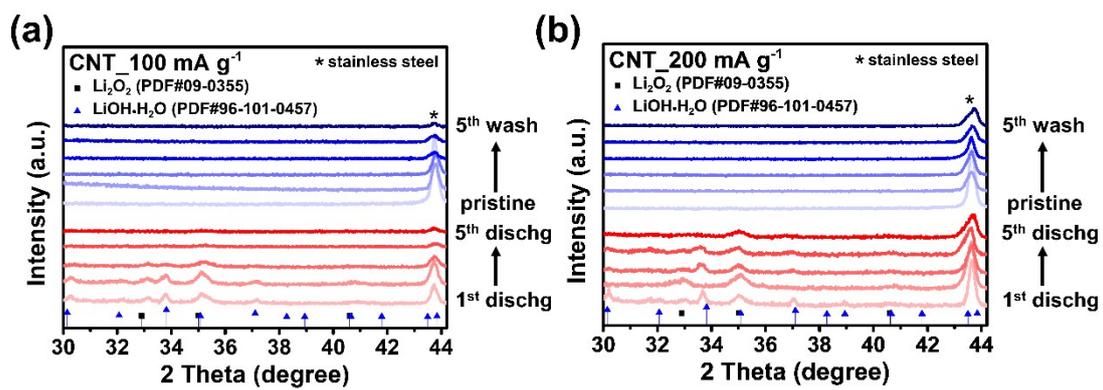


Fig. S9. XRD patterns of CNT cathodes at different stages with current densities of (a) 100 and (b) 200 mA g⁻¹.

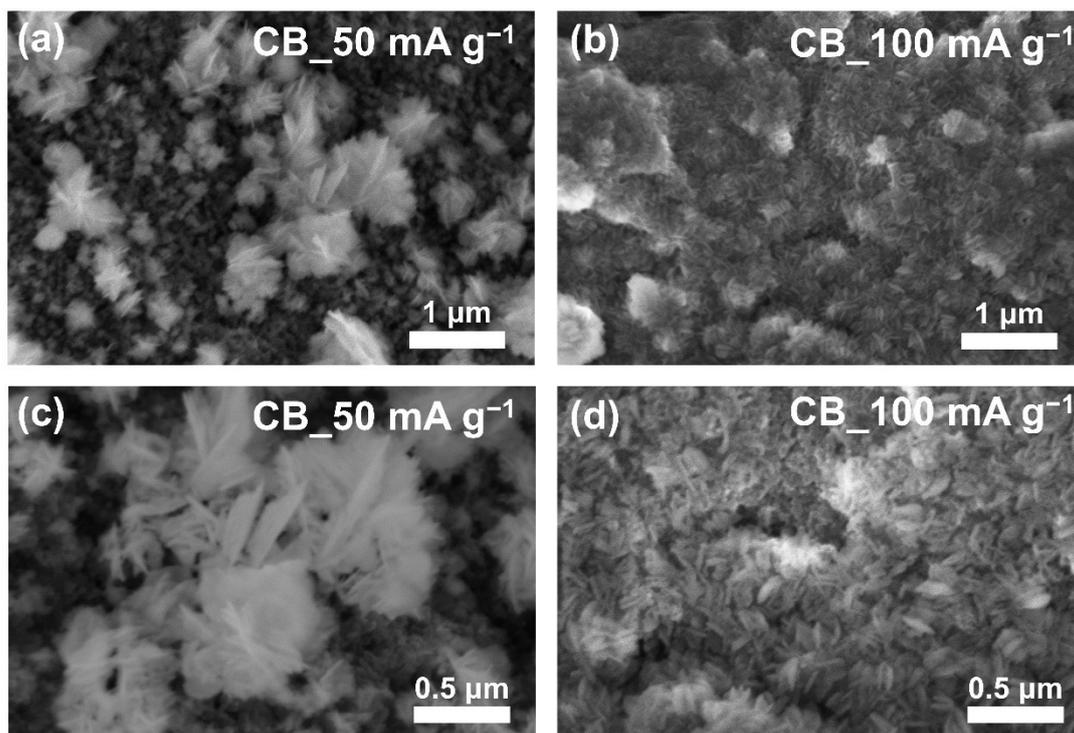


Fig. S10. SEM images of CB cathodes with current densities of (a,c) 50 and (b,d) 100 mA g⁻¹. Both cathodes were discharged to a capacity of 1000 mAh g⁻¹.

Different current densities reportedly affect the morphology, so we investigated the effect of regeneration at higher current density. The SEM images of CB cathodes at different current densities are shown in Fig. S10. Larger grains formed when using 50 mA g⁻¹ because the discharge process followed the solution route more.

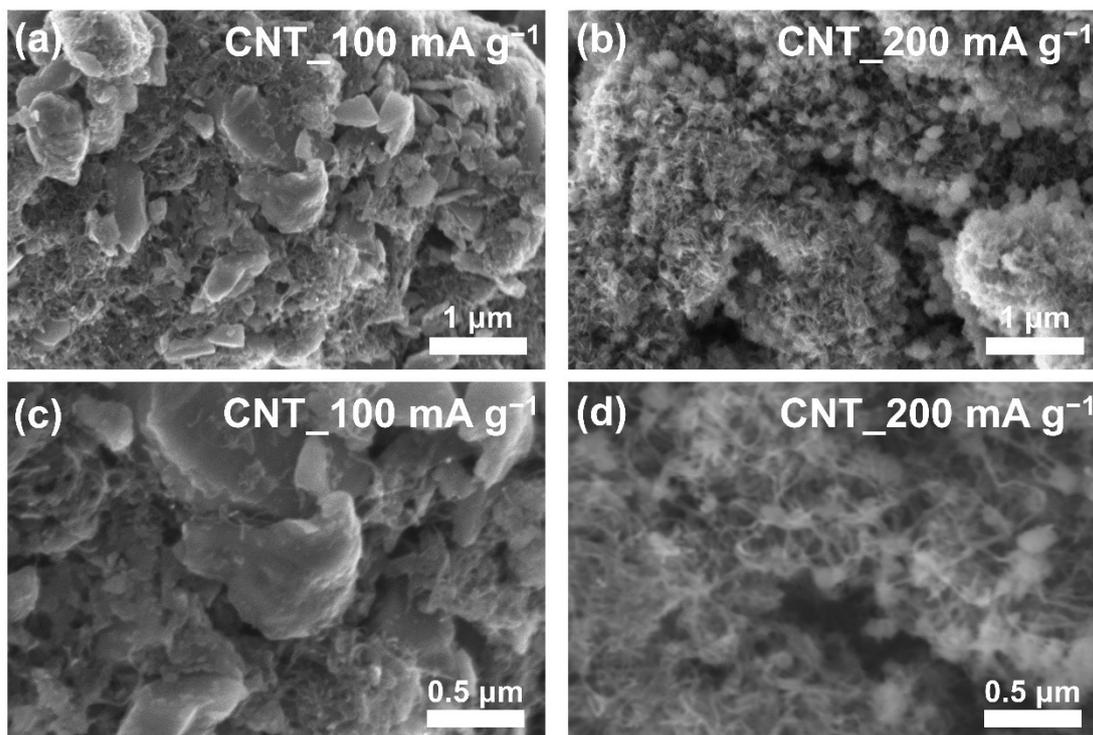


Fig. S11. SEM images of CNT cathodes with current densities of (a,c) 100 and (b,d) 200 mA g⁻¹. Both cathodes were discharged to a capacity of 1000 mAh g⁻¹.

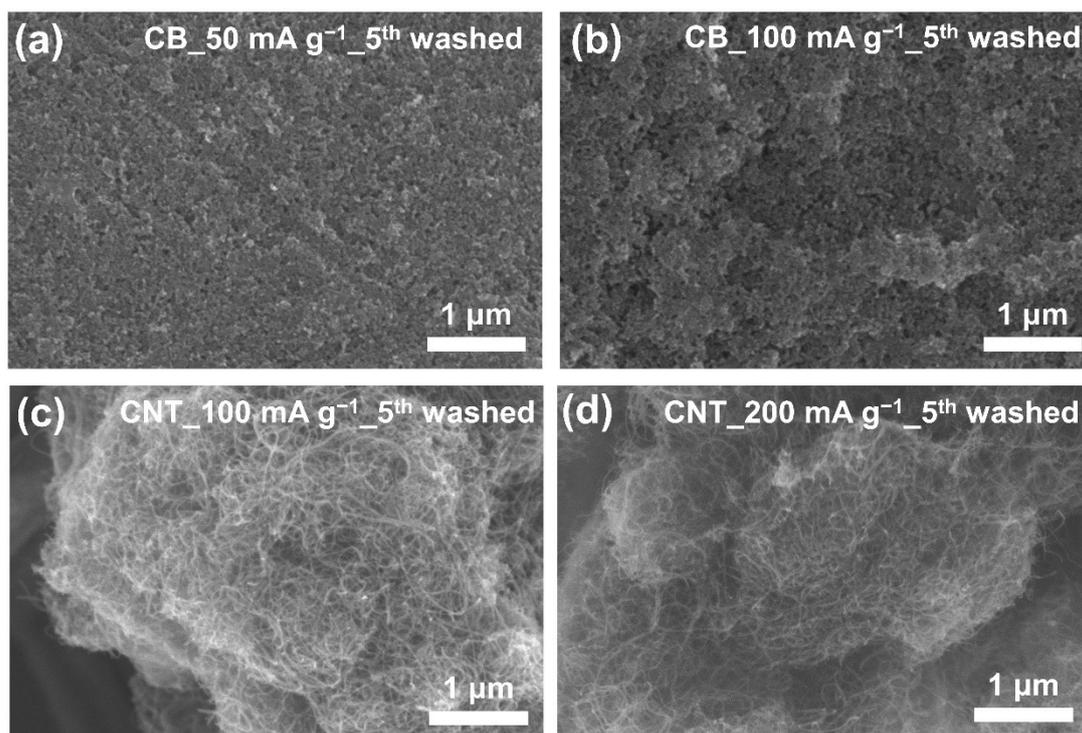


Fig. S12. SEM images of washed CB cathodes after five rounds at current densities of (a) 50 and (b) 100 mA g⁻¹. SEM images of washed CNT cathodes after five rounds at current densities of (c) 100 and (d) 200 mA g⁻¹.

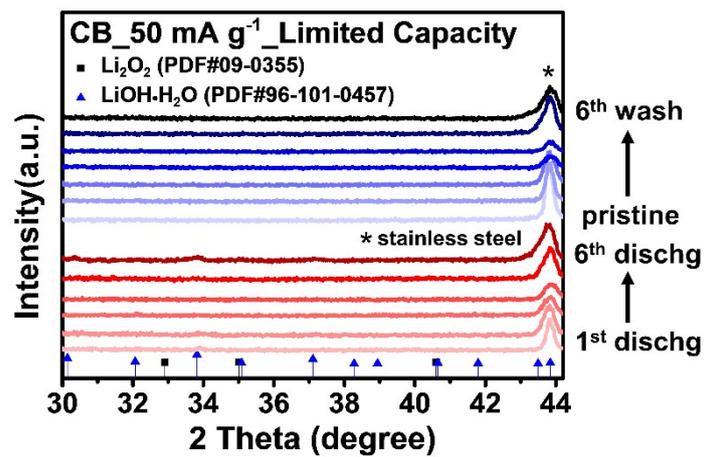


Fig. S13. XRD patterns of limited discharged CB cathodes at different stages with a current density of 50 mA g⁻¹.

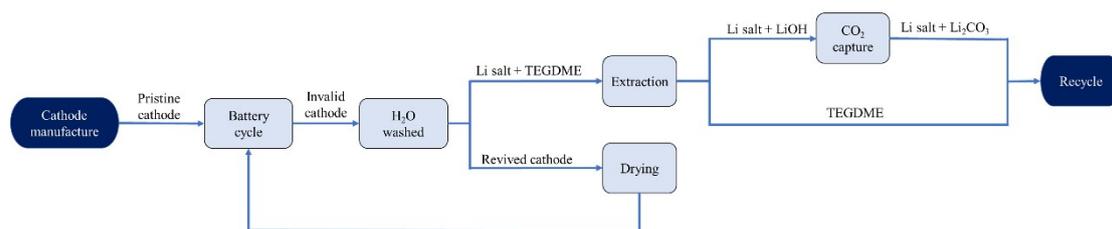


Fig. S14. Proposed recycling process for Li–O₂ batteries.

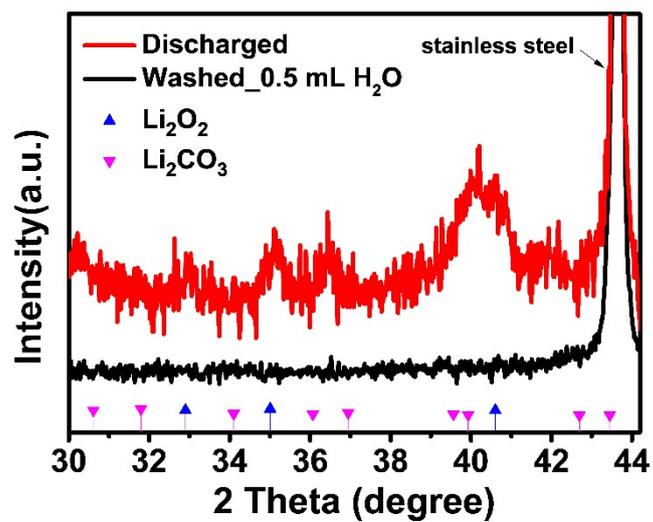


Fig. S15. XRD patterns of full discharged and washed CNT cathodes at a current density of 100 mA g^{-1} . The amount of water used for rinsing is 0.5 mL .