Supporting Information

Co-deposition of conductive additives and lithium peroxide during discharge to boost the performance of lithium-oxygen batteries

Yu-Long Liang,‡[a,b] Yue Yu,‡[c] Zi-Wei Li,[a,b] Jin Wang,[b] Jun-Min Yan,[a] Gang Huang,*[,b] Xin-Bo Zhang*[,b]

[a] Key Laboratory of Automobile Materials, Ministry of Education, Department of Materials Science and Engineering, Jilin University, Changchun 130022, China
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[c] Department of Chemistry and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, ON N2L 3G1, Canada

‡ Yu-Long Liang and Yue Yu contributed equally to this work.

E-mail: ghuang@ciac.ac.cn (G. Huang); xbzhang@ciac.ac.cn (X.-B. Zhang)

Experimental

Materials and chemicals

Tetraethylene glycol dimethyl ether (TEGDME), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), sodium dodecyl benzene sulfonate (SDBS), and lithium peroxide (Li_2O_2) were purchased from Aladdin Reagent. Carbon paper (CP) was ordered from Cetech Co., Ltd. Li foils (Li content ≥99.9%) were ordered from China Energy Lithium. Carbon nanotubes (CNTs) were bought from Macklin Incorporated. Ketjen black (KB, ECP-600JD) was purchased from Lion Corporation. Super P (SP) carbon black was bought from TIMCAL. Before use, the TEGDME was dried with 4 Å molecular sieve for at least two weeks, and LiTFSI, CNT, KB, SP, and CP were vacuum dried at 80 °C for 24 hours. The electrolyte used in this research was 1 M LiTFSI in TEGDME. All materials were stored in an Ar-filled glovebox.

Preparation of Ru@CNT and Li_2O_2 samples

The synthesis of Ru nanoparticles decorated CNTs (Ru@CNT) was referenced from our previous work.[1] In a typical synthesis process, the CNTs were immersed into a 10 mmol $RuCl_3$ ethanol solution followed by drying in air at 60 °C, and then conducting a calcination process at 250 °C for 1 h in Ar/H_2 atmosphere. The samples of Li_2O_2 and CNTs were prepared by grinding them for half an hour, putting them into molds, and pressing them into samples . This process was conducted in an argon-filled glove box.

LOBs assembly

The electrolyte with CNTs additive was prepared by adding 300 mg CNTs to 100 mL TEGEDME (with 1 M LiTFSI and 20 mg SDBS). After one hour of sonication, the solution was diluted to the desired concentrations. The electrolyte was sonicated for another thirty minutes before the assembly of batteries. The LOBs were assembled in an argon-filled glove box by stacking a lithium foil, a separator (with 100 μL electrolyte), and a CP in sequence.

Electrochemical tests

Electrochemical impedance spectroscopy (EIS) test was conducted with a perturbation amplitude of 10 mV from 0.1 Hz to 5 MHz. Cyclic voltammetry (CV) test was carried out using a scan rate of 0.1 mV s^{-1}. The EIS and CV measurement were all conducted on the Biologic VMP3 electrochemical workstations. Discharge and cycle tests were carried out on LAND test systems at room temperature.

Characterization

Powder X-ray diffraction (XRD) measurement was conducted using a Bruker D8 Focus Powder X-ray diffractometer. Scanning electron microscopy images were obtained using a Hitachi S4800 field emission scanning electron microanalyzer. X-ray photoelectron (XPS) spectrum was collected on an ESCALABMKLL X-ray photoelectron spectrometer using an Al K_α source. The conductivity of samples was obtained using a 2450 SourceMeter from KEITHLEY.

Theoretical calculation

The percolation model was simulated based on python 3.10. In the model, the CNTs were treated as spheres, and the radius of the sphere was estimated via the random coil model.[2] The percolation threshold could be obtained from Figure S6. Figure S7 supports the view that the CNTs appear in the form of sphere, as well as the work of Liu et al.[3] Figures S8 and S9 depict aspects of the calculation process. The specific code used for simulation was adapted from the open source repositories of users 'Songyosk' and 'amv213' on GitHub.

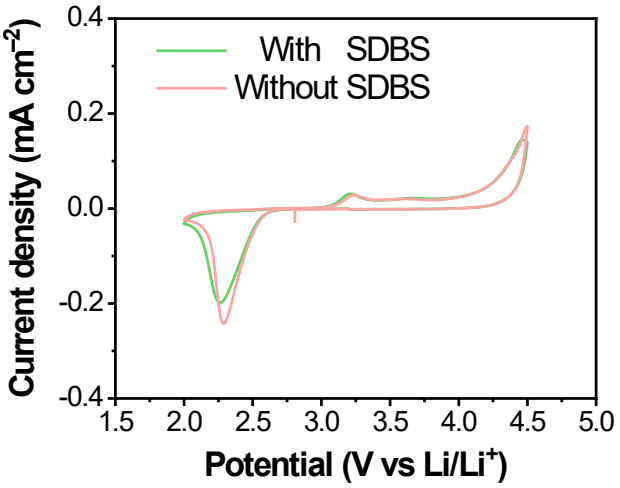

Fig. S1 The CV curves of LOBs with and without SDBS.

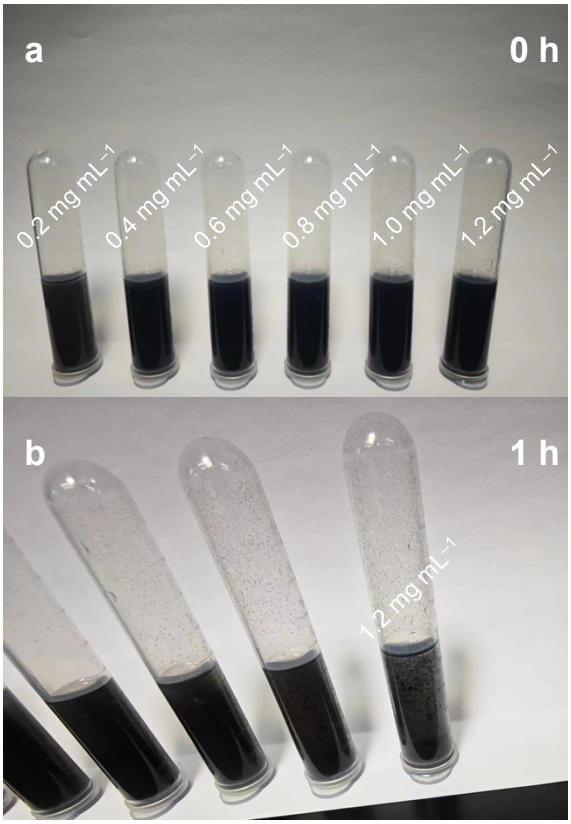

Fig. S2 Optical images of the electrolytes containing different CNT contents. (a) After ultrasonic dispersion. (b) after 1 hour of stewing.

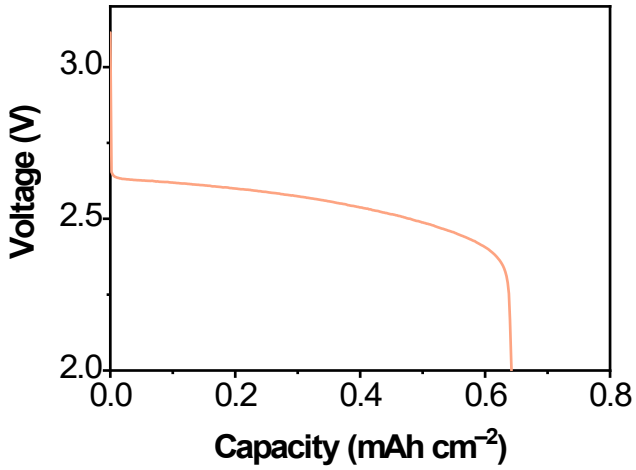

Fig. S3 Discharge curve of the LOB with 0.1 mg CNTs sprayed on the cathode.

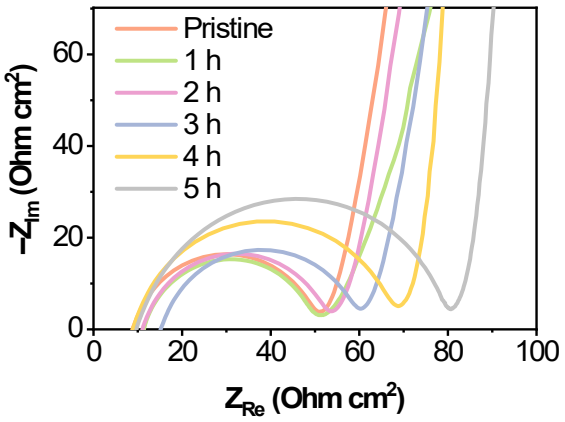

Fig. S4 EIS curves of the LOBs without CNTs discharged for 1 to 5 hours at a current density of 0.05 mA cm^{-2}.

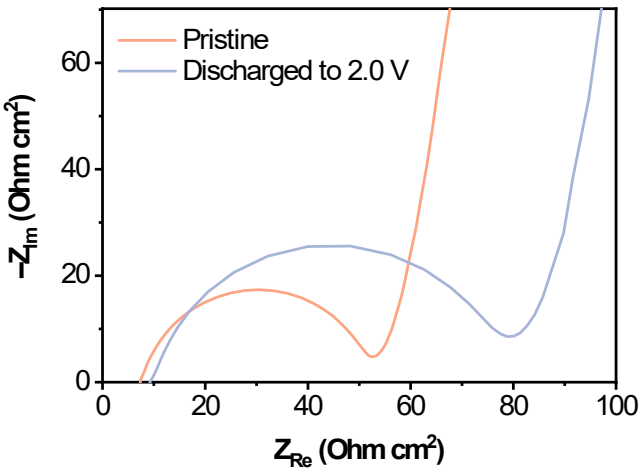

Fig. S5 EIS curves of the pristine LOB and LOB discharged to 2 V.

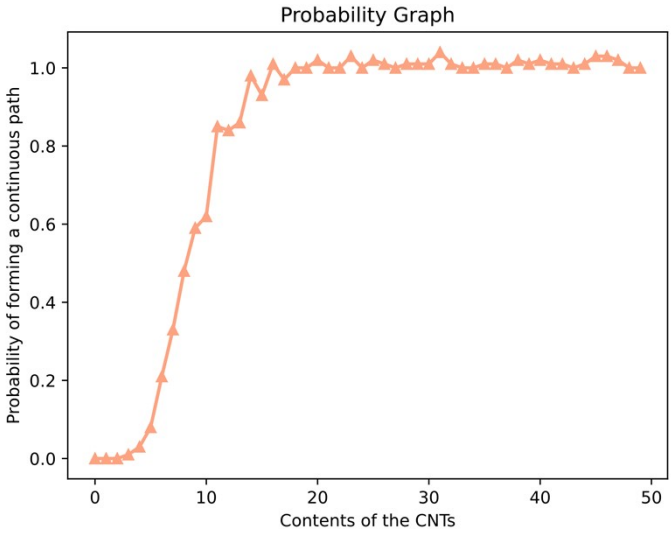

Fig. S6 The relationship between the probability of forming a continuous path and the contents of CNTs.

The following is a typical calculation process: First, a random function is used to generate the coordinates of the spheres' centers in the defined space. After the diameter of the sphere is given, the program will calculate the distance between the two centers. If the distance is less than the diameter, the two spheres are considered to overlap. At this time, the overlapping spheres are regarded as a whole, and other spheres are checked to see if they overlap with the whole. If so, the overlapping spheres are also incorporated into the whole, and so on. After this step is completed, several groups connected as a whole will be obtained. These groups are checked to see if they are in contact with the left and right end faces at the same time (assuming that the left and right directions are the conductive directions). If they are in contact at the same time, it is considered that there is a conductive path in the system, otherwise there is no conductive path (as shown in Figure S8). At each CNT content, the program will repeat the above process 100 times. Finally, the number of times for forming a conductive path is divided by the totally running number of the program to obtain the probability of forming a conductive path at the corresponding CNT content.

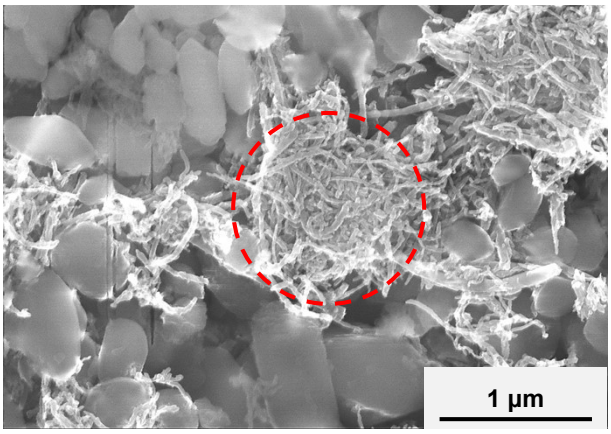

Fig. S7 SEM image of the morphology of CNTs in the 10 wt% sample, which are roughly spherical and closely packed with Li_2O_2.

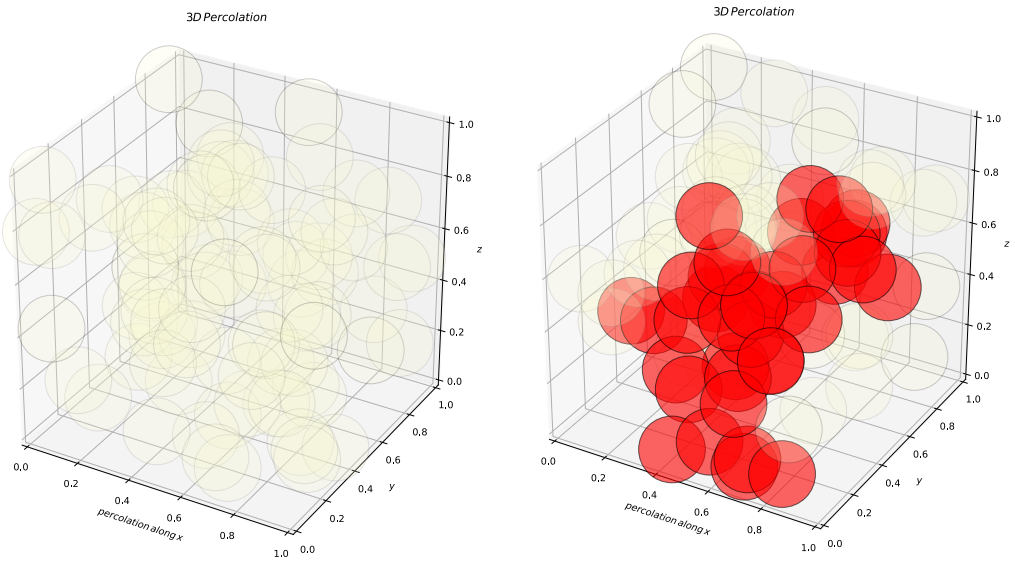

Fig. S8 A non-conductive path (left) and a conductive path (right).

Fig. S9 The relationship between the average number of spheres for spanning cluster and the radius of spheres.

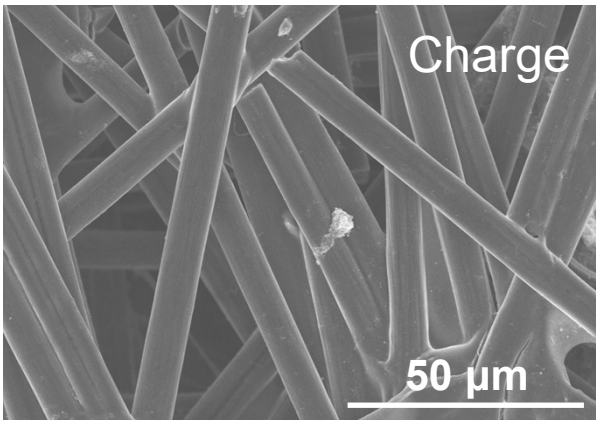

Fig. S10 SEM image of the cathode of LOB with 1.0 mg mL^{-1} CNTs after the first charge process.

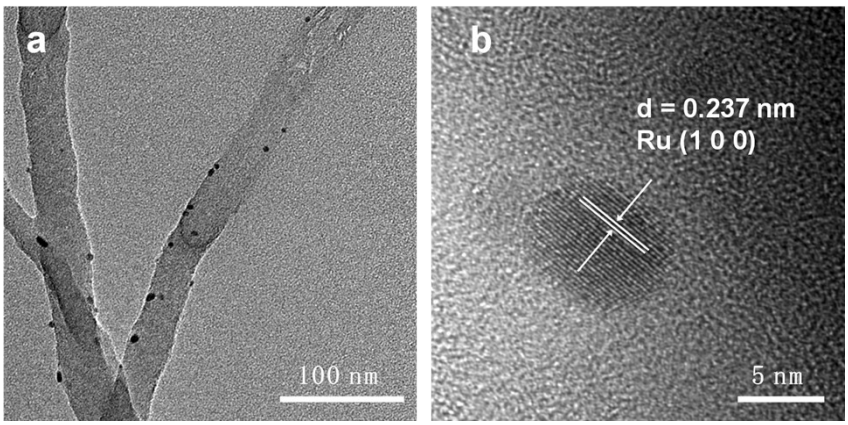

Fig. S11 (a) Transmission electron microscope (TEM) image of the Ru@CNT. (b) The corresponding HRTEM image of a Ru particle.

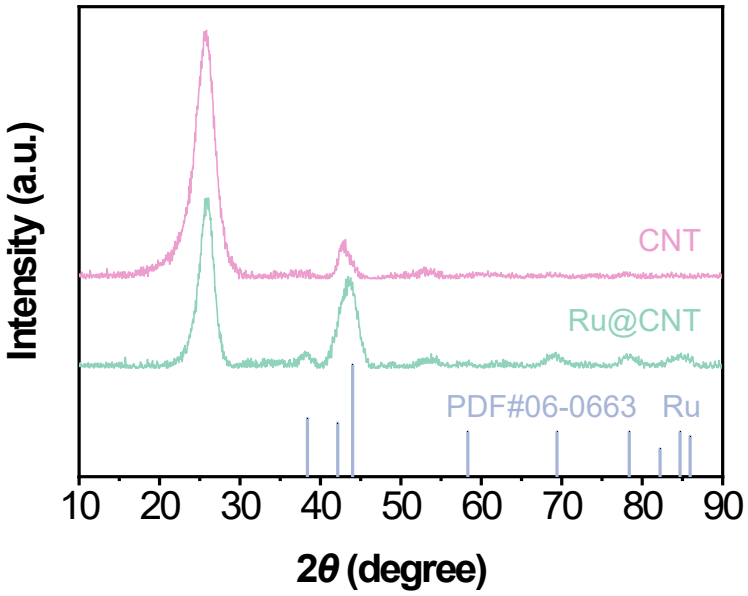

Fig. S12 XRD patterns of the Ru@CNT, CNT, and Ru.

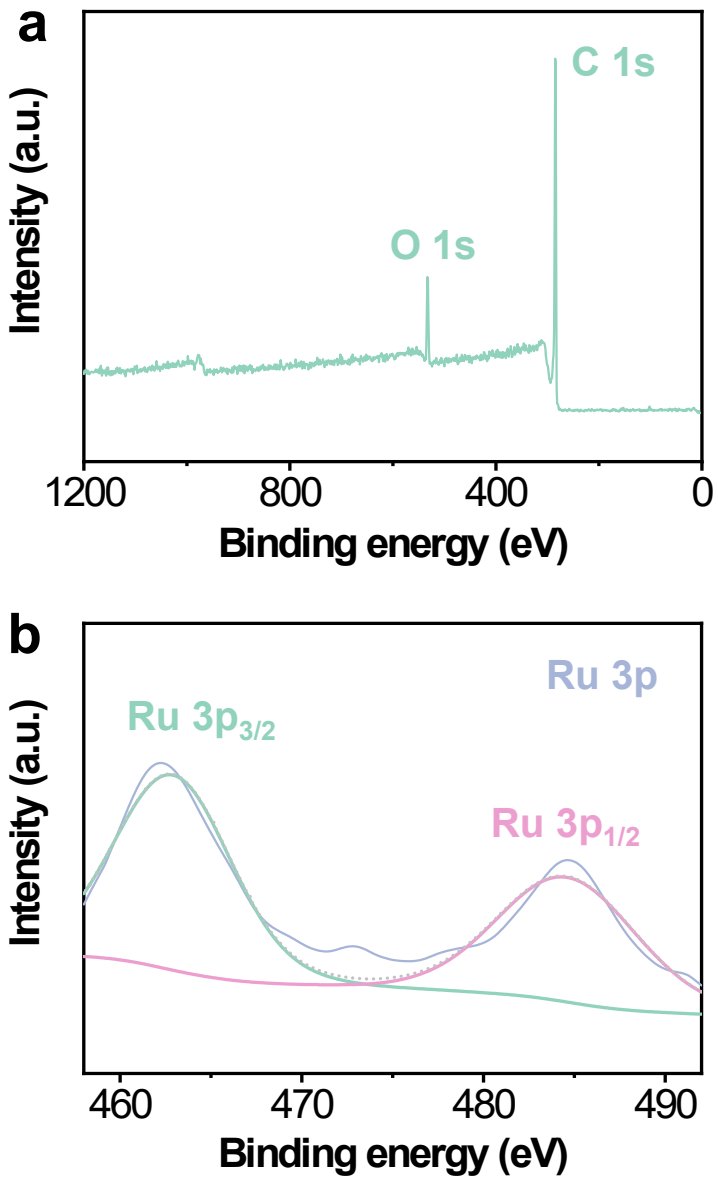

Fig. S13 X-ray photoelectron spectroscopy (XPS) spectra of the Ru@CNT. (a) Full survey scan. (b) Fine scan of Ru 3p.

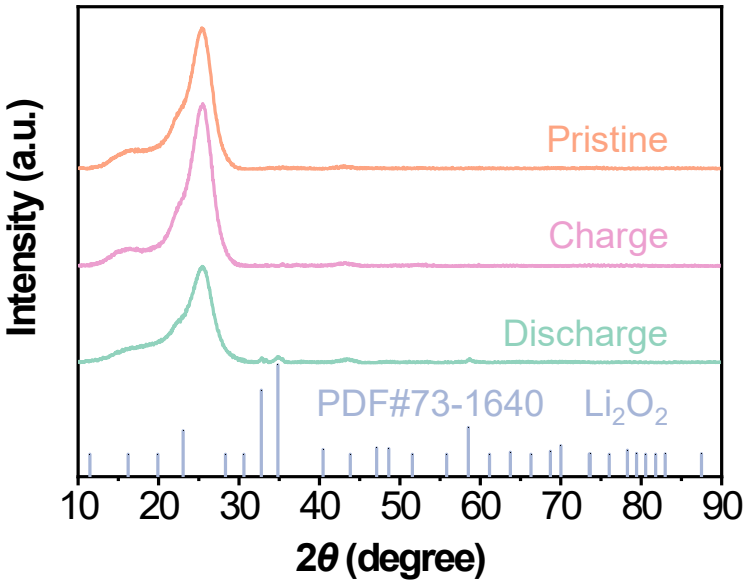

Fig. S14 XRD patterns of the cathodes of LOBs at different states.

Table S1 The specific data of the conductivity calculations.

Sample	Content (wt%)	Cross-sectional area (mm^2)	Conductivity (S cm^{-1})
1	0	31.8	1.503×10^{-11}
2	1	26.4	2.052×10^{-11}
3	3	24.7	3.024×10^{-11}
4	5	25.2	2.801×10^{-6}
5	10	24.0	8.263×10^{-3}
6	15	25.8	4.277×10^{-2}
7	20	26.9	1.594×10^{-1}
8	100	11.2	53.210

References

1. Q. C. Liu, L. Li, J. J. Xu, Z. W. Chang, D. Xu, Y. B. Yin, X. Y. Yang, T. Liu, Y. S. Jiang, J. M. Yan and X. B. Zhang, *Adv. Mater.*, 2015, **27**, 8095-8101.
2. R. Zallen, *The physics of amorphous solids*, John Wiley & Sons, 2008.
3. D. Liu, J. Wang, W. Peng, H. Wang and H. Ren, *Compos. Sci. Technol.*, 2022, **221**, 109300.