Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

A New Type of Sealed Rechargeable Lithium-Lithium oxide Battery based on Reversible LiO_2/Li_2O_2 Interconversion

Libin Chen [a], *Jian Yang* [b], *Zhixuan Lu* [b], *Peng Dai* [a], *Xiaohong Wu* [a], *Yuhao Hong* [b], *Liangping Xiao* [d], *Ling Huang** [b], *Hua Bai** [c], *Shi-Gang Sun** [a,b]

[a] State Key Laboratory of Physical Chemistry of Solid Surfaces, [b] College of Chemistry and Chemical Engineering, [c] College of Materials, Xiamen University, Xiamen 361005, P. R. China. Department of Physics, Research Insitute for Biomimetics and Soft Matter, Xiamen 361005, P. R. China

Experiment

Electrode preparation

5 mL 4 mg mL^{-1} GO aqueous solution was mixed with 5 mL 0.13 mol L^{-1} alkali (LiOH) aqueous solution. The mixed solution was sealed in a hydrothermal reactor, and then carried out at 180 °C for 5 h.[1] Then the achieved OR-rGO was dialyzed with pure water for two days. Afterwards, the OR-rGO was shrinked in air for 30h and then

freeze-dried. As shown in Figure 1B, the area of OR-rGO we prepared was about 1.1 cm^2 (±0.1), the weight of it was about 8 mg (±1).

The heat treatment process is as follows: put OR-rGO in a glass tube of a tube furnace, replace the air in the glass tube with Ar, and then increase the temperature of the tube furnace from room temperature to 400 ˚C at a rate of 5 ˚C min^{-1}. Keep it at 400 ˚C for 5 hours, then cool to room temperature. The OR-rGO conducted with heat treatment was named as h-rGO.

Cell assembly

At first, the cathode was preloaded with $Li_2O_2/LiO_2/O_2^-$ through a discharging process in a semi-open cell filled with O_2 gas, the operation process is shown in Figure 1A. The semi-open battery was assembled by stacking Lithium (diameter:16 mm, thickness: 2mm) /separator/OR-rGO/carbon fabric into a 2025 coin cell with punched hole on the positive shell and then pressing. The electrolyte solution was 1 M $LiCF_3SO_3$ dissolved in tetraethylene glycol dimethyl ether (TEGDME). Then the battery was transferred into a vessel filled with O_2. Afterwards, it was carried out with discharge process at 0.1 mA cm^{-2}. Then the battery was disassembled and the cathode preloaded with discharge product was sealed into a 2025 coin cell stacked between Lithium/separator and carbon fabric. $LiCF_3SO_3$/TEGDME or LiTFSI–2% $LiNO_3$/1,3-dioxolane–dimethoxy ethane (DOL–DME) was used in sealed batteries. All battery assembly and disassembly operations were performed in a Ar-filled glove box.

Characterization of OR-rGO

SEM was taken with Hitachi S-4800 Scanning electron microscope. OR-rGO was fixed on a sample stage by conducting resin and the image was obtained under 15 kV. N_2 adsorption-desorption test was performed on Autosorb-iQ to further characterize the specific surface area and pore size distribution of OR-rGO. The XPS measurement was displayed on ESCALAB 250Xi X-ray Photoelectron Spectrometer. FTIR was performed on Nicolet iS50 in the transmittance mode. OR-rGO was mixed with KBr and ground in an agate mortar. Then the mixture was pressed into flakes for FTIR measurement.

In situ Raman spectra

The in situ Raman spectra were recorded using a Witec instrument conducted with a laser at 632.75 nm wavelength which was focused on the cathode surface through a ×50 long working distance lens. The OR-rGO cathode which had been discharged in a Li-O_2 battery for 22h was assemble with Li anode into a battery case with a big hole on the cathode side to permit the Raman laser. Then the cell was transferred to a homemade in situ Raman cell (Renbin Group) and the cathode was placed on the face of the quartz window for laser to pass through. The power of the laser beam delivered to the cathode surface was roughly 2.5 mW and the Raman spectrum acquisition time was typically 30s with two accumulations. The spectral resolution of the Raman spectra in the study was approximately 1.0 cm^{-1}. Then the in situ Raman was observed during the charge-discharge test at a current density of 0.1 mA cm^{-2} and a cutoff capacity of 0.8 mAh cm^{-2}.

Online electrochemical mass spectrometry

Gas generation from the sealed Lithium-superoxide battery during charge-discharge process was determined through an online electrochemical mass spectrometry (OEMS). We use He flow (5 mL min^{-1}) to purge the gas generated during charge-discharge process at a current density of 0.1 mA cm^{-2} from the test cell to the mass spectrometer (Agilent 5975C).

Computation method

All spin-polarized computations were carried out by ORCA in this study. [2-3] The 6-31G(d,p) basis set and the B3LYP functional were applied to optimize geometries and obtain Raman intensities. [4-6] The dispersion correction was considered for all the computations.[7-8]The dipole correction was carried out. The $C_{42}H_{15}$ graphene fragment was used to represent the basic structure of graphene. The adsorption energy was calculated according to the equation:

$$E_{ads} = E_{*LiO_2} - E_{*} - E_{LiO_2} \tag{1}$$

Where * were related to the graphene models for the LiO_2 adsorption.

A Structure visualization software named vesta was applied.[9]

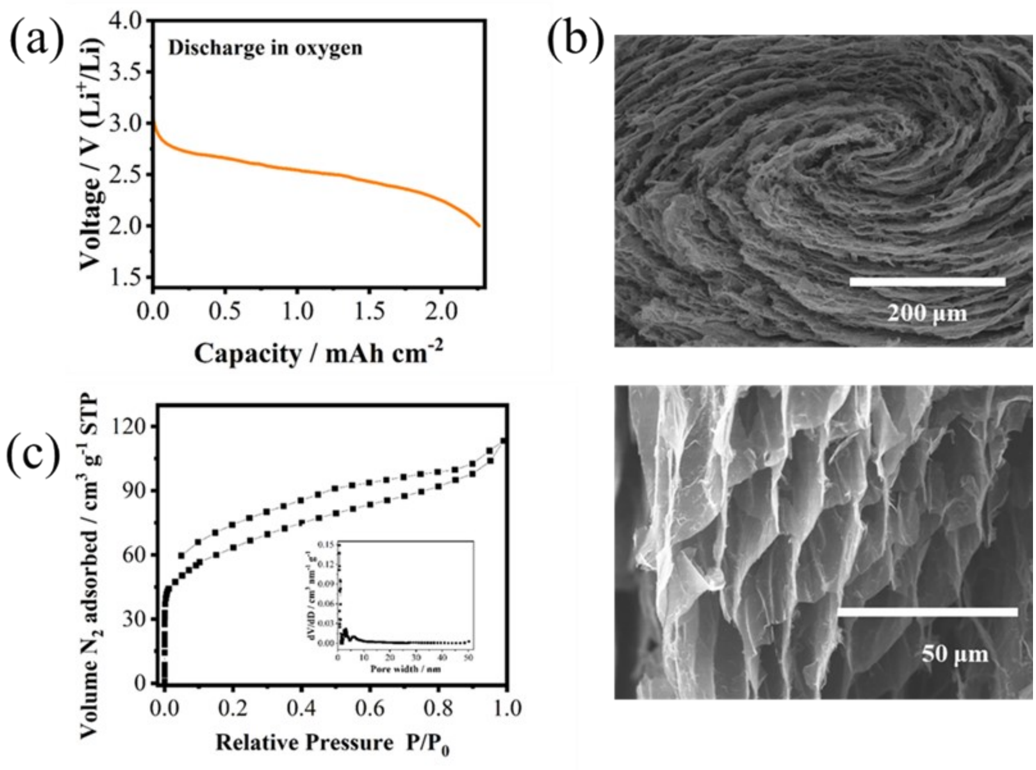

Figure S1. (a) Discharge curve of the semi-open Li-O_2 battery with OR-rGO as cathode at current density of 0.1 mA cm^{-2} for 22 h; (b) SEM image of OR-rGO; (c) BET N_2 adsorption/desorption isotherm of OR-rGO, the insert is the corresponding pore distribution of OR-rGO.

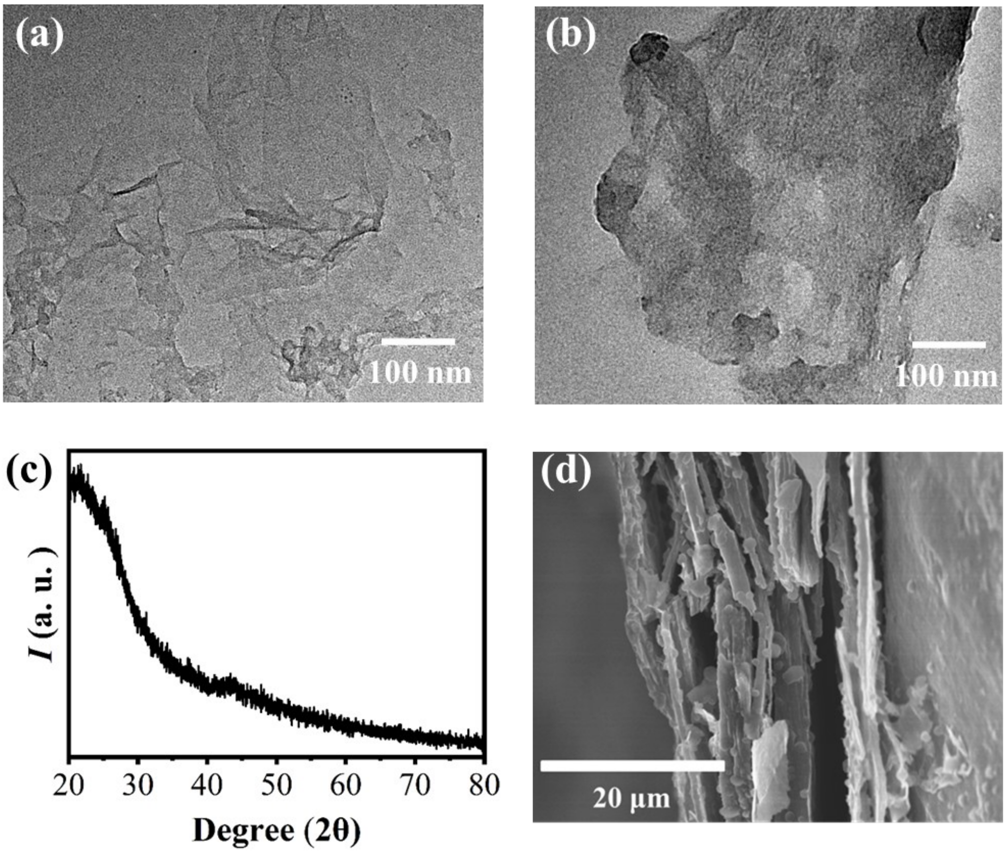

Figure S2. TEM image of (a) OR-rGO and (b) LiO$_x$/OR-rGO; (d) X-ray diffraction (XRD) pattern of LiO$_x$/OR-rGO cathode; (e) SEM image of LiO$_x$/h-rGO cathode.

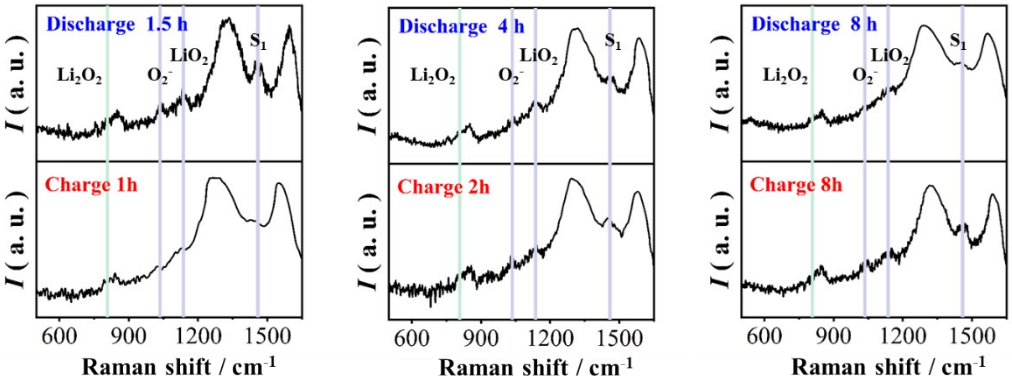

Figure S3. Full spectrum of in-situ Raman spectra of the LiO_x/OR-rGO cathode during discharge charge process respectively at 1.5h/4h/8h and charge process respectively at 1h/2h/8h.

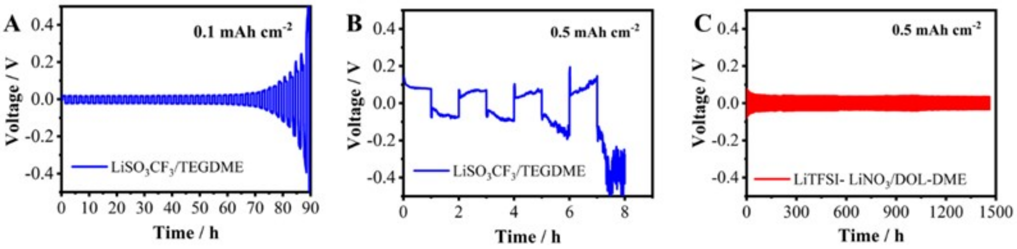

Figure S4. Voltage–time profiles of Li/Li symmetric cells with $LiSO_3CF_3$/TEGDME as electrolyte (a) at a current density of 0.1 mA cm^{-2} and (b) at a current density of 0.5 mA cm^{-2}; (c) Voltage–time profiles of Li/Li symmetric cell with LiTFSI-2%$LiNO_3$/DOL-DME as electrolyte at a current density of 0.5 mA cm^{-2}.

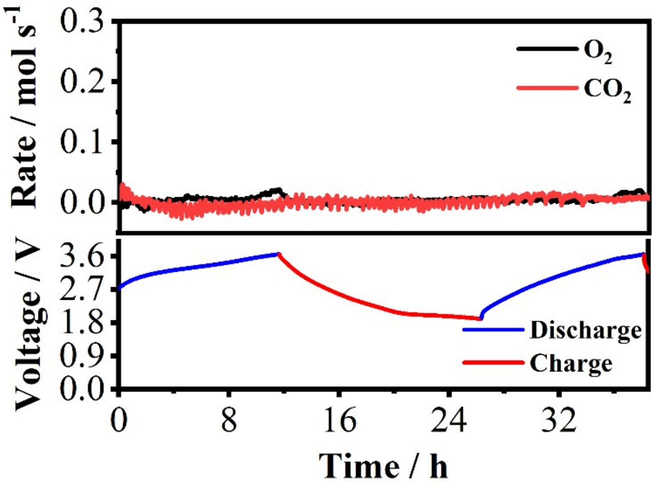

Figure S5. OEMS results of gas evolution rate (Rate) in discharge-charge processes within a voltage window (1.9 V-3.65 V) of a Li-LiO_x battery with a LiO_x/OR-rGO cathode predischarged in O_2 for 24h with binary electrolyte of $LiCF_3SO_3$/TEGDME and LiTFSI-2%$LiNO_3$/DOL-DME.

REFERENCES:

(1) Yao, B.; Chen, J.; Huang, L.; Zhou, Q.; Shi, G., Advanced Materials 2016, 28 (8), 1623-1629.

(2) Neese, F., The ORCA Program System. WIREs Comput. Mol. Sci. 2012, 2 (1), 73-78.

(3) Weigend, F.; Ahlrichs, R., Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. Phys. Chem. Chem. Phys. 2005, 7 (18), 3297-3305.

(4) Hehre, W. J.; Ditchfield, R.; Pople, J. A., Self—consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. J. Chem. Phys. 1972, 56 (5), 2257-2261.

(5) Becke, A. D., Density ‐ functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. 1993, 98 (7), 5648-5652.

(6) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti Correlation-energy Formula into a Functional of the Electron Density. Phys. Rev. B 1988, 37 (2), 785-789.

(7) Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the Damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem. 2011, 32 (7), 1456-1465.

(8) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A Consistent and Accurate Ab initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. J. Comput. Chem. 2010, 132 (15), 154104.

(9) Momma, K.; Izumi, F., Vesta 3 for Three-dimentional Visualization of Crystal, Volumetric and Morphology data. J. Appl. Cryst. 2011, 44, 1272-1276.