Supporting Information

Extending Cycling Life of Lithium-Oxygen Batteries Based on Novel

Catalytic Nanofiber Membrane and Controllable Screen-Printed

Method

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. Experimental Section

Synthesis of Ru-rGO catalyst: GO was purchased from Institute of Coal Chemistry. Ru-rGO and rGO were obtained through the hydrothermal method. In a brief process, 14 mL GO (6.0 mg mL⁻¹) was first dispersed in 60 mL deionized water with ultrasonic wave pulverizer for 5 min, further an ultrasound treatment for 30 min, 1 mL RuCl₃ solution (10 mg mL⁻¹) was mixed with the suspension with ultrasonic wave pulverizer for 5 min, ultrasonic for 30 min and stirring for 8-12 h. After, 5.3 mL 80 wt% hydrazine hydrate was added into the mixture dropwise under drastic stirring for another 15 min. The obtained mixture was transferred into 100 mL Teflon-lined autoclave, and kept at 180 °C for 12 h. The product was washed with deionized water for several times. After that it was frozen-dried for over 24 h in vacuum at 0.026 Pa, and then was dried under vacuum at 120 °C for another 12 h. Finally, the sample was annealed under Ar at 400 °C for 1 h to get Ru-rGO. rGO was prepared according to the same procedure only without adding RuCl₃.

Synthesis of Ag nanowires: 0.425 g PVP (Mw=40,000) was dissolved in 10 mL ethylene glycol (EG). After Stirring for 1-2 h, 90 µL NaCl (0.1 M in EG) was added into the PVP solution, as denoted A. 0.17 g AgNO₃ was dissolved in 10 mL EG and continuously stirred for 10 min, as named B. B was added into A drop in drop in one minute completely and stirred for another 3 min. Finally, the solution was transferred into 50 mL Teflon-lined autoclave, and kept at 160 °C for 5.5 h. The obtained product was precipitated with acetone for two times. After that, the gray product was washed with ethanol by centrifugation, then dispersed in ethyl alcohol. The concentration of Ag

nanowires dispersed in ethanol was about 1.2 mg/ml.

Preparation of PAN/Ag/Au catalytic membrane: PAN nanofiber membranes were synthesized by an electrospinning method. Briefly, 2.1 g polyacrylonitrile (PAN, Mw=150,000) powder was added to 15 mL N, N-dimethylformamide (DMF) with vigorous stirring to form a homogeneous solution. Then the obtained solution was loaded in a plastic syringe with a metal needle (24 gauge). The feeding rate was kept to be 0.6 ml/h during electrospinning and the distance was positioned 15-20 cm between a rotating belt of aluminum foil and needle. The applied positive voltage and negative voltage was 20.0 kV and -2.0 kV, respectively. Firstly, the glass fiber paper as separator with a diameter of 47 mm was stick on the rotating roller and the electrospinning time was kept for only one minute. Then the composite separator was obtained. Secondly, Ag nanowires solution was sprayed on the surface of PAN membrane and then was dried at 60°C for 8 h under vacuum. Finally, the above separator was sputtered gold for 1 minute under 20 μ A. Then final functional separator was successfully obtained.

Materials Characterization: The crystal structures were analyzed by X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5418$, 40 kV, 40 mA) in the 2 θ range of 10-80°. Morphologies were used by field-emission scanning electron microscope (FESEM, NOVA NANOSEM 450) and transmission electron microscope (TEM, Tecnai G2 F20) to characterize. Thermogravimetric analysis (TGA) was performed on a TG instrument (Mettler) with a heating rate of 10 °C /min from room temperature to 600 °C under Ar/O₂ (V:V=1:1) atmosphere to measure the weight percent of Ru. The contact angle was measured by an XG-CAM Contact Angle Meter.

Electrochemical Measurement: The electrochemical performance were characterized by typical 2032 coin cells with holes on the positive side in an argon-filled glove box with water and oxygen levels less than 0.5 ppm. The oxygen cathodes were a homogenous slurry, consisting of 80 wt% rGO or Ru-rGO and 20 wt% polyvinylidene fluoride (PVDF). Then the electrode ink was screen-printed on the carbon paper. After that, the carbon papers were dried in an oven at 80 °C for 2 h, then dried at 120 °C for 12 h under vacuum. Finally, the loading mass of Ru-rGO on the electrodes is 0.4±0.05 mg cm⁻². 1 M lithium bis-(trifluoromethanesulfony)-imide (LiTFSI) in tetraethlene glycol dimethyl ether (TEGDME) was used as electrolyte and the functional catalytic membrane was close to oxygen electrode. Lithium foils were used as counter electrode. The Li-O₂ cells were tested in a dry plastic box filled with pure oxygen atmosphere. Galvanostatic discharge-charge tests were carried out in the voltage range of 2.2~ 4.4 V (vs. Li⁺/Li) after 4-6 hours rest period using a battery testing system (LANDIAN, BTS3000) at room temperature. The specific capacity of the electrodes were calculated based on the mass of Ru-rGO or rGO. Cyclic voltammetry (CV) and linear sweep voltammograms (LSV) measurements were carried out with a CHI 660E electrochemical workstation at a scan rate of 1 mV s⁻¹. EIS (electrochemical impedance spectra) measurements were also performed on CHI 660E electrochemical workstation in the frequency range from 0.01 Hz to 10^6 Hz .



Fig. S1 The synthesis process of PAN/Ag/Au membrane.



Fig. S2 The optical photographs of the lightweight feature of PAN membrane (a) and PAN/Ag/Au membrane (b); The resistance of decorated separator, the optical photographs of PAN/Ag membrane (c) and PAN/Ag/Au membrane (d); The optical photographs of designable electrode via screen-printing method.



Fig. S3 (a) The TGA curve of Ru-rGO; (b, c) The SEM images of rGO and Ru-rGO; (d-f) Element mapping images of C, O and Ru of Ru-rGO.



Fig. S4 (a) Initial discharge-charge profiles of Ru-rGO catalyst with PAN/Ag membrane and PAN/Au membrane for Li-O₂ cells at a current density of 50 mA g^{-1} ; (b) Representative CV curves of the cells with the rGO, Ru-rGO and D-Ru-rGO electrodes, respectively, in the voltage range of 2.0-4.4 V (vs. Li⁺/Li) at a scan rate of 1 mV s⁻¹.



Fig. S5 EIS patterns of rGO, Ru-rGO and D-Ru-rGO based cathodes before discharge-charge for Li-O₂ batteries (a, b), Ru-rGO and D-Ru-rGO based cathodes after 8th (c) and (d).



Fig. S6 XRD patterns of Ru-rGO based cathode of Li-O₂ cells after the first discharge and charge

(a); Cross-sectional morphology of D-Ru-rGO electrode after discharge (b).



Fig. S7 The surface of Li metal after being cycled for 8 cycles without (a) and with (b)

PAN/Ag/Au membrane.