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Supporting Information

A hybrid gel/solid-state polymer electrolyte for long-life lithium oxygen batteries

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Experimental Section

Cathode material synthesis: Graphene oxide (GO) was synthesized from graphite (Aldrich, powder, < 20 nm, synthetic) by the Hummers method,[1] the details of which have been described elsewhere. RuO_x decorated on the nitrogen-doped reduced graphene oxide (N-rGO@RuO_x) composite was prepared via the microwave hydrothermal route from the raw materials RuCl3, graphene oxide, and urea as the nitrogen source. First, the graphene oxide aqueous solution (2 mg ml^{-1}) was mixed with urea (GO: urea = 1:400 wt%) and $RuCl_3$ (rGO: RuO_x = 7:3 molar) under vigorous agitation and ultrasonication for 1 h. The mixed solution was transferred into a microwave autoclave (inside volume 100 ml), and then reacted at 180 °C for 30 min. After the reaction, the resultant precipitate was collected, washed with water and ethanol for several times, and dried at 80 °C in vacuum.

Gel-solid polymer electrolyte synthesis: gel-polymer electrolyte was prepared bymixing 1 M $LiCF_3SO_3$ in tetraethylene glycol dimethyl ether (TEGDME) liquid electrolyte. Ethoxylated trimethylolpropane triacrylate (ETPTA, Mw = 428, trivalent acrylate monomer), 2-hydroxy-2-methyl-1-phenyl-1-propanon (HMPP, photo-initiator), and vacuum-dried Al_2O_3 nanoparticles (average particle size = 50 nm, Sigma) were mixed with the above liquid electrolyte in an argon filled glove box. The weight-based composition ratio of the (ETPTA/liquid electrolyte = 15/85 w/w)/ Al_2O_3 = 35/65 w/w, in which the concentration of HMPP was fixed at 1.0 wt% of the ETPTA. The solution was then subjected to vigorous mixing via ball milling for 0.5 h at 400 rpm under argon protection, to yield a uniform dispersion of Al_2O_3 nanoparticles.

Air electrode preparation: A piece of gas diffusion layer (2.5 cm × 7 cm) was placed on a hotplate (100 °C), and the obtained N-rGO@RuO_x in an ethanol dispersed solution was coated on the surface of the gas diffusion layer (composite coating weight = 1.5 mg cm^{-2}, composite coating area = 2.5 cm × 5 cm) by brushing it on layer by layer. Then, the whole electrode was dried at 140 ^{o}C in a vacuum oven overnight. In the second step, the obtained gel polymer electrolyte was brushed on the surface of the gas diffusion layer (catalyst side) to a depth of about 1-2 mm, following by UV lamp irradiation to solidify the gel to form a solid layer. The entire process was carried out in an argon-filled glove box. For the liquid electrolyte, the same procedure was used to make a N-rGO@RuO_x coated gas diffusion layer, following by cutting it into 12 mm disks for the electrodes.

Anode electrode preparation: nickel foam (2.5 cm × 5 cm) was filled with the obtained gel-polymer electrolyte, and a layer about 1 mm thick was brushed on the side of the nickel foam. At the same time, lithium foil (2.5 cm × 5 cm) was attached on the other side of the nickel foam. An extended nickel tip was attached as the current collector.

Lithium oxygen battery assembly: For the gel-solid state polymer electrolyte, the assembly steps are shown in the schematic diagram in Figure 1. As for the liquid electrolyte cell, electrochemical experiments were performed using CR2032 type coin cells with holes in the cathode shell. The electrolyte consisted of a solution of 1 M $LiCF_3SO_3$ in tetraethylene glycol dimethyl ether (TEGDME). Pure lithium foil was used as the counter electrode. The cells were assembled in an argon-filled glove-box (Mbraun, Unilab, Germany). Galvanostatic discharge-charge cycling was conducted witha fixed 1000 mAh g^{-1} cut-off discharge capacity, with discharging followed by charging to 4.5 V vs. Li^+/Li. All tests were carried out on LAND CT 2001A multi-channel battery testers at room temperature in oxygen atmosphere using our specially designed facility. Linear sweep voltammetry (LSV) was conducted between 2.5 and 6 V at the scanning rate of 10 $mV \cdot s^{-1}$ (Princeton Applied Research PARSTAT 2273) to evaluate the stability of the gel-solid electrolyte, using lithium as reference and counter electrode and a piece of stainless steel as the working electrode. The ionic conductivity (σ) of the gel-polymer electrolyte was determined by AC impedance spectroscopy using two pieces of stainless steel (Princeton 2273). The electrolyte was sandwiched between two parallel stainless steel discs (d = 1 cm). The thicknesses of the films were measured using a micrometer screw gauge. Temperatures were controlled with a home-made oven and were kept constant during each measurement. The frequency ranged from 1 Hz to 106 Hz at a perturbation voltage of 10 mV. The ionic conductivity was calculated from the electrolyte resistance (Ra), obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (L), and the electrode area (S) according to Equation (1). The temperature dependence of the conductivity shows classical Arrhenius behaviour according to

Equation (2):

$$\sigma = \frac{L}{R_a\, S} \qquad (1)$$

Meanwhile, the activation energy of the ionic conductivity of the gel-polymer electrolyte samples with various polymerization times was examined according to Equation (2):

$$\sigma = \sigma_0 exp(-E_a/RT) \qquad (2)$$

Where σ is the ionic conductivity, σ_o is a constant, E_a is the activation energy, R is the gas constant, and T is the temperature.

Characterization: The particle size and morphology of the samples were examined using transmission electron microscopy (TEM, 200 kV JEOL 2011 instrument). Raman spectroscopy was performed on a Jobin Yvon HR800 Raman spectrometer employing a 10 mW neon laser at 632.8 nm. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a VG Scientific ESCALAB 2201XL instrument using aluminium Kα X-ray radiation. XPS spectral analysis was conducted using XPS Peak-fit software.

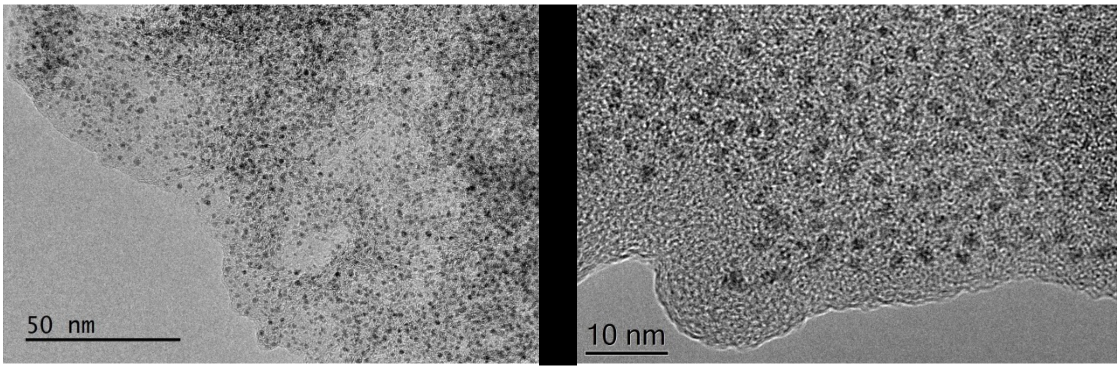

Figure S1. HRTEM images of the N-rGO@RuO$_x$ composite.

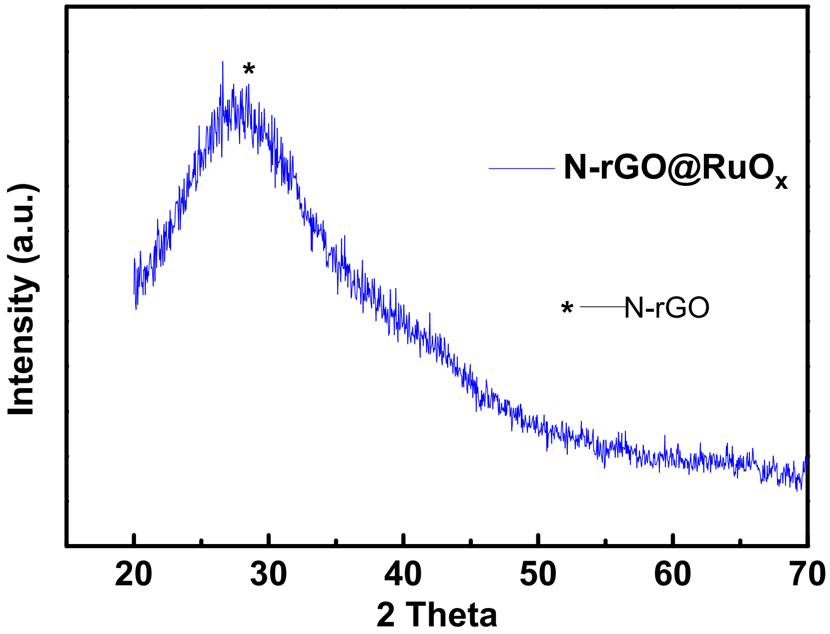

Figure S2. XRD pattern for the N-rGO@RuO$_x$ composite.

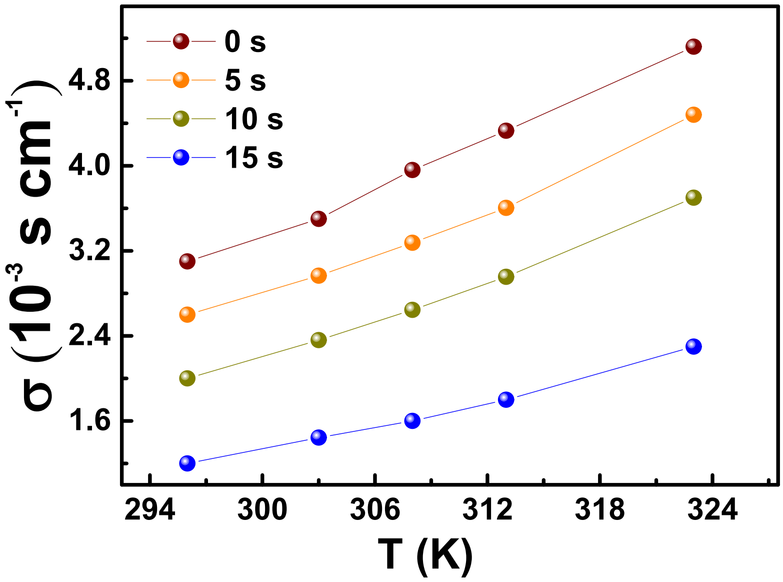

Figure S3. Temperature dependence of the ionic conductivity of electrolyte samples with different polymerization times.

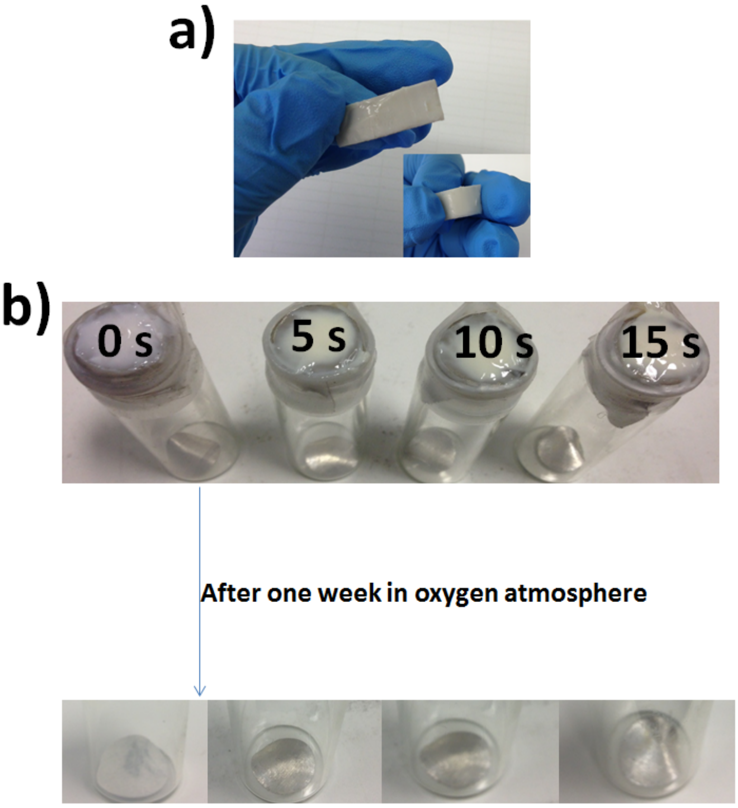

Figure S4 a) free-standing electrolyte and membrane after 15s irradiation by UV lamp; b)Home-made simple system to detect the oxygen permeability of GPE electrolyte samples with different polymerization times.

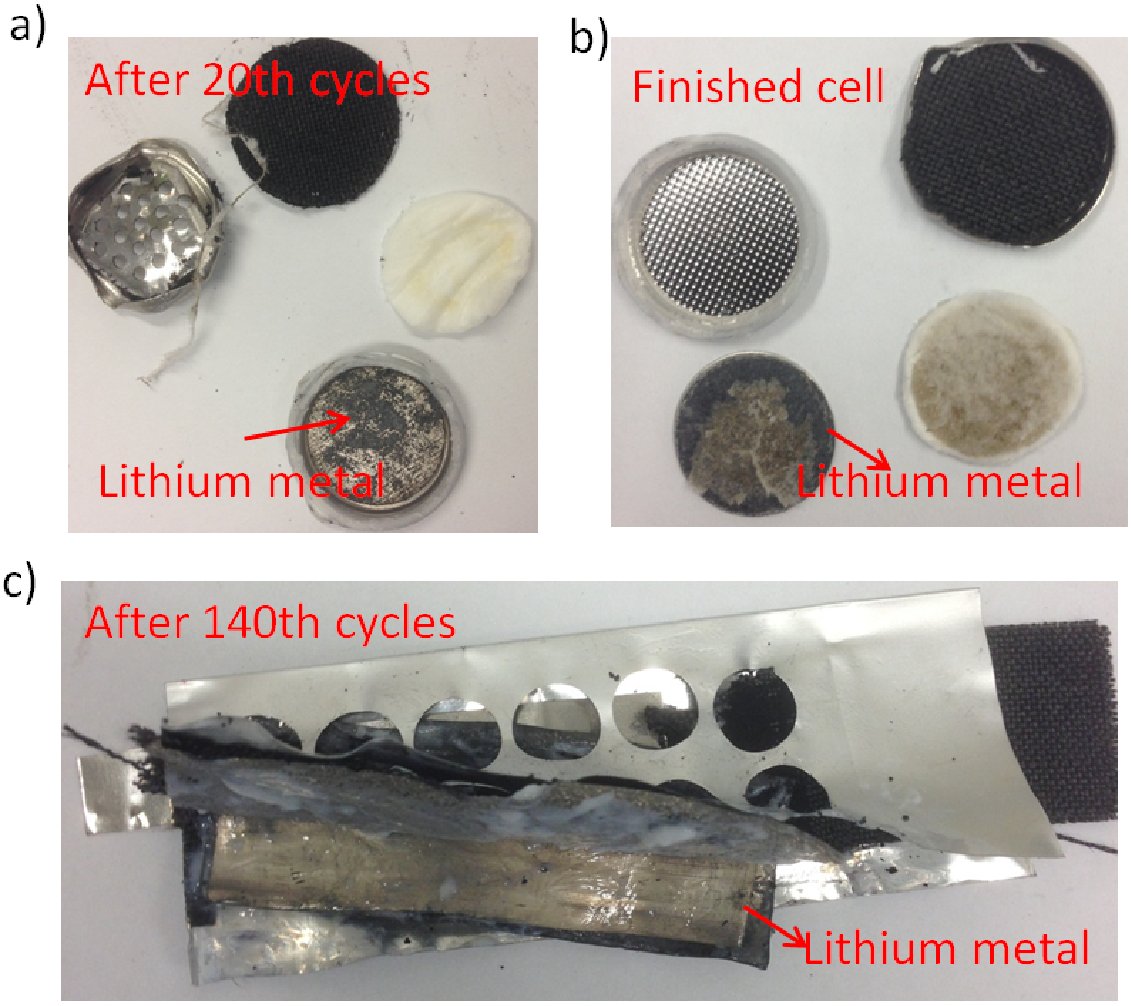

Figure S5. Disassembled batteries: (a, b) ordinary liquid cells. (c) gel-solid-state polymer electrolyte.

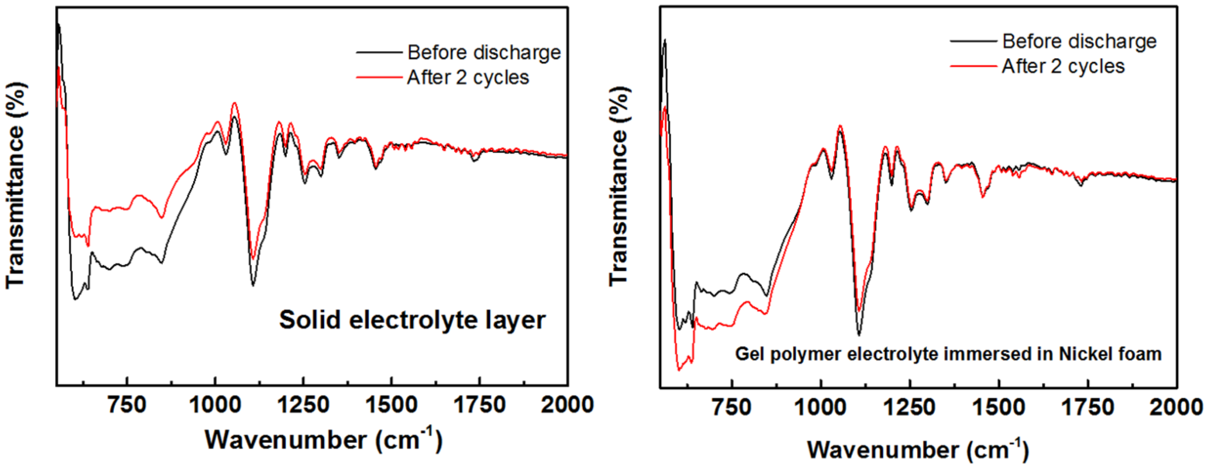

Figure S6 FT- IR spectra of the solid electrolyte layer and gel polymer electrolyte immersed in nickel foam before and after 2 cycles.

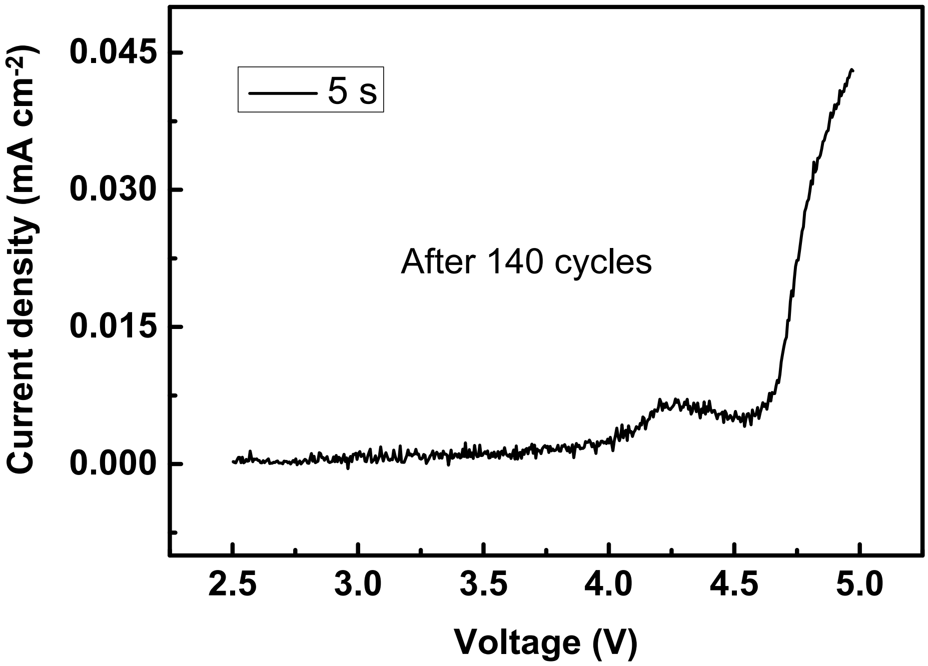

Figure S7. Stability of the gel-solid-state polymer electrolyte with 5 s polymerization time after 140 cycles.

1. W. S. Hummers and R. E. Offeman, *J Am Chem Soc*, **1958**, 80, 1339.