

Supplementary Information

***In Situ* Synthesis of Amorphous Titanium Dioxide Supported RuO₂ as a Carbon-free Cathode for Non-aqueous Li-O₂ Batteries**

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Experimental details

Preparation of TiO₂/RuO₂ composites

TiO₂/RuO₂ composites were prepared by a simple sol-gel method using TiOSO₄ (titanium (IV) oxide sulfate sulfuric acid hydrate, TiOSO₄·xH₂O + H₂SO₄, Alfa Aesar), RuCl₃·xH₂O (ruthenium chloride hydrate, ReagentPlus®, Sigma-Aldrich), NH₄OH (ammonium hydroxide, 28.0-30.0%, Junsei Chemical) and urea (ACS reagent, 99.0-100.5%, Sigma-Aldrich). The *in situ* synthesis process is as following: 2.5 g of TiOSO₄ was dissolved in 250 ml of D.I. water with vigorous stirring to get a transparent solution. A 0.6823 g of RuCl₃·xH₂O was dissolved into the above solution and stirred for 2 h, followed by the 0.1567 g of urea addition as a dispersant. Then, NH₄OH was added dropwise to the above solution to obtain precipitates until the pH reached 7. The precipitates were thoroughly rinsed with D.I. water and dried in a convection oven at 120°C. The resultant precursors were annealed at 300 and 600°C for 2 h under vacuum, respectively. For *ex situ* synthesis, amorphous TiO₂ and crystalline RuO₂ were synthesized separately. To prepare amorphous TiO₂, 2.5 g of TiOSO₄ was dissolved in 250 ml of D.I. water to obtain a transparent solution, followed by the addition of 0.1567 g of urea. White precipitate was achieved by adding NH₄OH until the pH reached 7 and were then rinsed and dried. The resultant TiO₂ precursor was annealed at 300°C for 2h under vacuum. To prepare crystalline RuO₂, 0.6823 g of RuCl₃·xH₂O was dissolved in 250 ml of D.I. water with vigorous stirring to form a dark-brown solution with vigorous stirring, followed by the addition of NH₄OH until the pH reached 7. After rinsing and drying, the RuO₂ precursor was annealed at 600°C for 2h under vacuum. This separately prepared amorphous TiO₂ and crystalline RuO₂ were mixed together in an agate mortar in a weight ratio of 2.24:1.

Measurements

An X-ray powder diffractometer (XRD, Rigaku) with a graphite-monochromator equipped with Cu K α radiation (40 kV and 40 mA) was used on the as-synthesized samples to investigate their crystal structures. The particle size and morphology were observed using field-emission scanning electron microscopy (FE-SEM, Tescan Mira 3 LMU FEG, 20kV) and transmission electron microscopy (TEM, Tecnai G2 T-20S, FEI) equipped with energy-dispersive X-ray spectroscopy (EDS). Raman spectroscopy was performed using NT-MDT NTEGRA Spectra C. High-resolution X-ray diffraction (HR-XRD) measurements were performed using a Rigaku SmartLab with Cu radiation (9kW).

The cathode was fabricated by spreading the as-synthesized sample with a binder (PTFE, poly-(tetrafluoroethylene)) on a circular disk of SUS (steel use stainless) mesh with diameter of 11 mm, which is a gas diffusion layer as well as a current collector. The weight ratio of the sample and PTFE was 8:2. The solvent was a mixture of isopropanol and deionized water (1:1 v/v). The total mass loading of the cathode (*a*-TiO₂/*c*-RuO₂ and PTFE) was approximately 0.8 to 1 mg, and the mass of the TiO₂ loaded on the cathode was approximately 0.5 to 0.7 mg. The resultant cathode was dried at 120°C for 12 h under vacuum. CR2032 type coin cells were assembled in an argon-filled glove box with an electrolyte of 1 M LiTFSI in TEGDME, and Li foil as an anode material. The water concentration in the electrolyte was <30 ppm as determined by a Mettler-Toledo Karl Fischer titration. Electrochemical properties were measured by a battery cycler (WBCS-3000, WonAtech) with an applied current density of 100 mA g⁻¹. The energy efficiency was determined as the ratio between the integrated areas of charge and discharge profiles.

Results

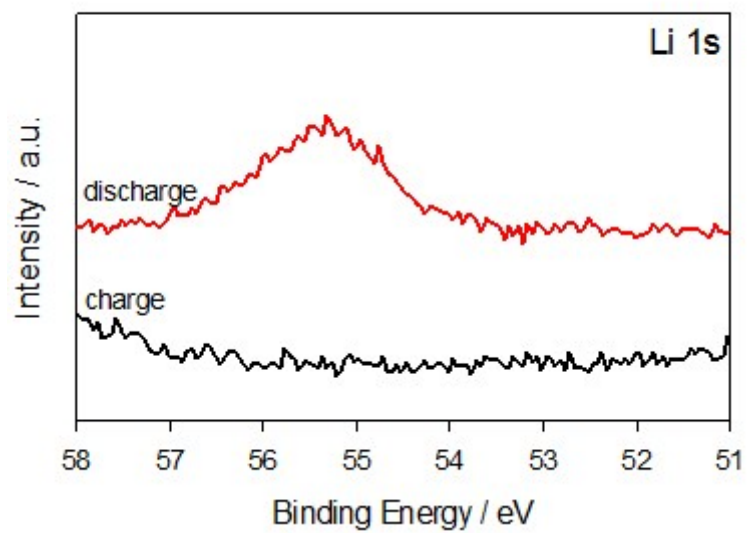


Fig. S1 XPS Li 1s spectra after the first discharge and recharge