

Supporting Information

**An oxygen cathode with stable full discharge-charge
capability based on 2D conducting oxide**

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1. Experimental Section

Synthesis of the RuO₂ nanosheet: Layered sodium ruthenate precursor (NaRuO₂) synthesized by a solid-state reaction by heating a mixture of Na₂CO₃, Ru and RuO₂·H₂O (2:1:3 molar ratio) at 900 °C for 12 h under a flow of argon. Then, 1 g of layered NaRuO₂ precursor was treated with 1 mol L⁻¹ aqueous HCl solution for 3 days at room temperature to trigger the extraction of Na ions and result the formation of hydrated layered protonic ruthenate. Note that the exhausted acid needs to be updated every day. The acid-treated sample was added into 250 ml tetramethylammonium hydroxide (TMAOH, 0.5 wt %) aqueous solution under vigorously shaken for 2 days at room temperature to form a TMA-layered ruthenic acid intercalation compound, and then exfoliated to single or few layered ruthenic acid (HRO) nanosheets by ultrasonication treatment in water bath for 2 h (300 W L⁻¹). The delaminated HRO suspension with

dark-green color and a small amount of sediment was separated by centrifuging at 8000 rpm for 20min. The solid product was centrifugally collected (13000 rpm) and washed with deionized water and then followed by freeze-dried for one day. Finally, rutile RuO₂ nanosheets with blue-black color can be obtained by heating treatment of the pre-prepared HRO nanosheets at 250 °C for 4h in flowing dry air to remove water and proton, giving a yield of ~40% (the yield is calculated based on the amount of Ru). In above typical synthesis, the mole ratio of TMAOH/H⁺ was adjusted to 0.5, 3, 5, 10, 20 for optimizing the delamination, where H⁺ is the ion-exchangeable proton in the protonated ruthenate. At TMAOH/H⁺ = 0.5, it was found the powder of the protonated H_{0.2}RuO₂·nH₂O deposits on the bottom of the reaction vessel when the shaking is stopped. At TMAOH/H⁺ = 3, very stable colloidal suspensions with dark-green color can be obtained. A visible but little amount of precipitate is observed when the shaken solution is allowed to stand for a longer period of time. The amount of precipitate seems smallest when TMAOH/H⁺ ≥ 5.

Battery assembly: Dimethyl sulfoxide (DMSO) was dried over 4 Å molecular sieve and then distilled over NaOH pellets before use. LiClO₄ was dried in a vacuum oven at 150 °C. The electrolyte was prepared in an Ar-filled glove box by dissolving 1 mol L⁻¹ LiClO₄ (Wako) in DMSO and stored in the presence of a piece of Li foil, where Li metal are quite stable in dried and purified DMSO even for three months. However, the Li metal stored in commercial DMSO changed partially to black, accompanied with a color change of the DMSO (colorless to light yellow) just for one week, suggesting the reaction between Li metal and impurities in the DMSO (Figure S13, Supporting information). The cathode paste was prepared by dispersing 8.5 mg of RuO₂ nanosheet in 300μL of isopropanol containing 1.5 mg of lithiated Nafion (LITHionTM Dispersion). The paste was coated onto an Al mesh (φ =10 mm), and the mass loading of the RuO₂ is

$\sim 0.8 \text{ mg/cm}^2$. A Li-O₂ cell was assembled with a nanosheet RuO₂ cathode, a glass fiber separator (Whatman GF/A) encapsulated with appropriate electrolyte, and a Li foil (0.4mm thickness) in a coin cell with 7 holes in the glove box. After assembling, the cell was put into a gas-tight glass chamber with Swagelok gas valves for the entrance and exit of oxygen gas. In addition, a 100-ml beaker containing 10ml of the DMSO was also put into the glass chamber to keep appropriate vapor pressure. The oxygen pressure in the glass chamber was 1 atm.

Measurements and characterization: Thermogravimetry (TG) was conducted on a 2020S TG Analyzer (MAC Science, Japan) in a temperature range from 25 to 400 °C at a heating rate of 5 °C min⁻¹. X-ray diffraction was performed on a Bruker D8 Advanced diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. Chemical state and composition was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi). Galvanostatic discharge/charge was conducted on a Hokuto discharging/charging system. AFM image was obtained on atomic force microscopy (AFM, JEOL JSPM-5200). Electrochemical impedance spectroscopy (EIS) was obtained on Solartron 1640 with a voltage amplitude of 10 mV and frequency of from 0.1MHz to 0.1Hz. All electrochemical measurements were conducted at 25 °C under 1atm oxygen atmosphere. Electrical conductivity of the RuO₂ nanosheet was measured on Keithley 2400, and I-V curve of a single RuO₂ nanosheet was carried out on the *in situ* TEM (JEOL JEM-3100 FEF). Scanning electron microscopy (SEM, LEO Gemini Supra 35) and transmission electron microscopy/selected area electron diffraction (TEM/SAED, JEOL JEM-3000F) were obtained with an accelerating voltage of 5kV and 300kV, respectively. The discharged/charged cathodes were taken out from a coin cell, and washed with dried dimethoxyethane (Wako, DME) before the SEM, XPS and TEM analyses.

2. Supplementary Figures

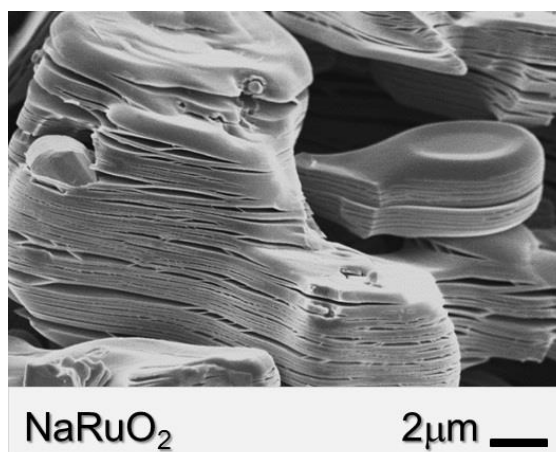


Figure S1. SEM image of the pristine layered precursor at high magnification.

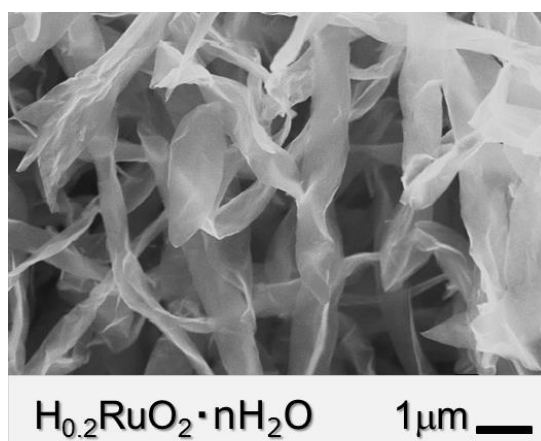


Figure S2. SEM image of the delaminated ruthenic acid at low magnification.

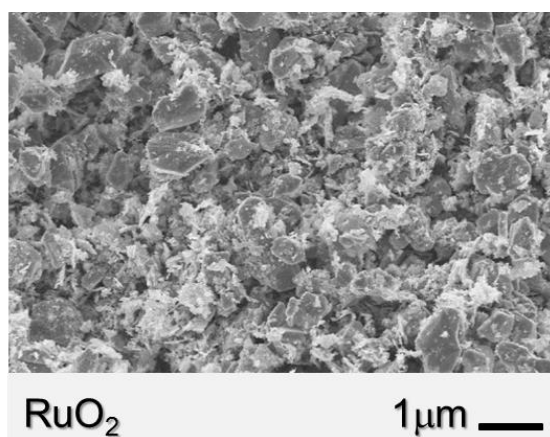


Figure S3. SEM image of the RuO₂ obtained at 400 °C in the flowing air.

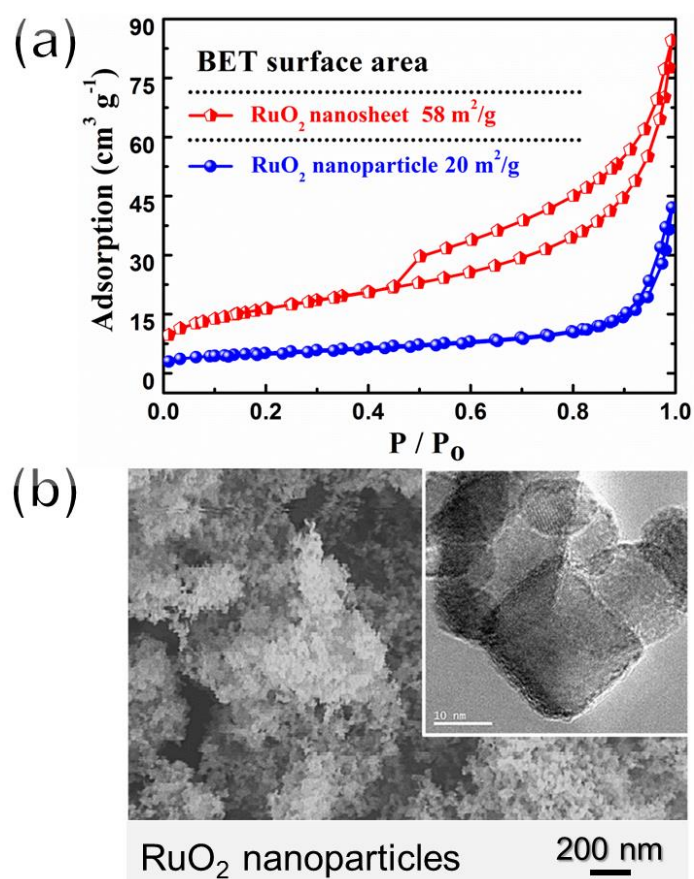


Figure S4. (a) Nitrogen-adsorption-desorption isotherms of the RuO_2 nanosheets and nanoparticles, respectively. (b) SEM and TEM (see the inset) images of the commercial RuO_2 nanoparticles.

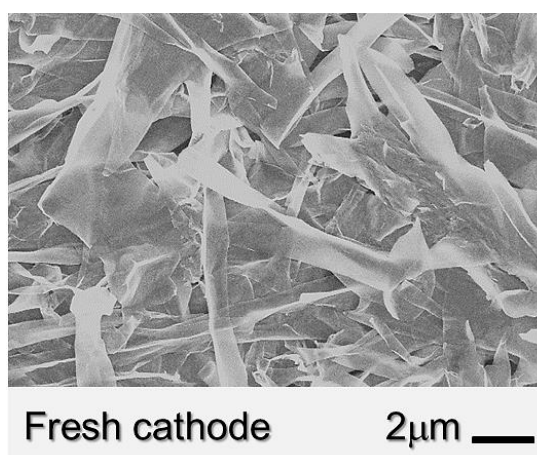


Figure S5. SEM image of the fresh RuO_2 nanosheet cathode at low magnification.

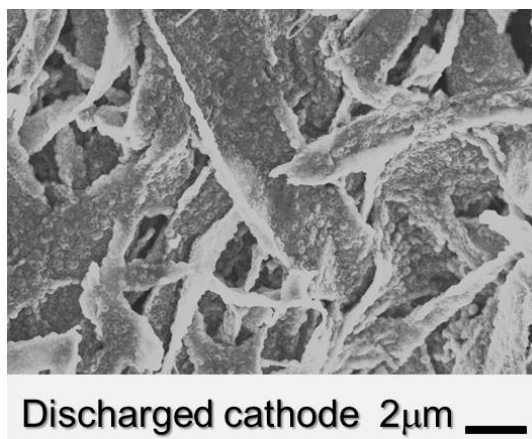


Figure S6. SEM image of the discharged RuO₂ nanosheet cathode at low magnification.

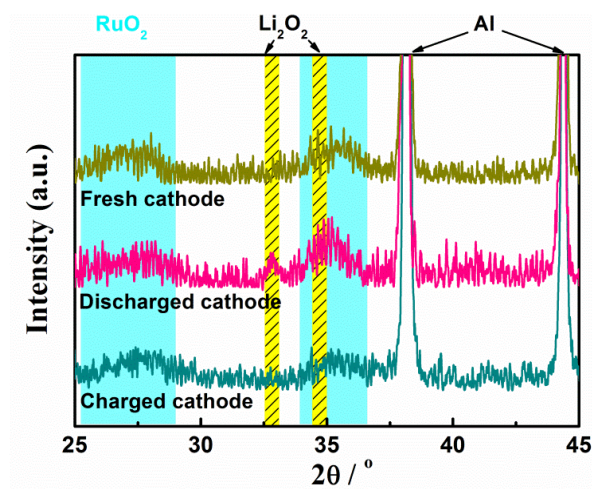


Figure S7. XRD patterns of the RuO₂ nanosheet cathode at states of pristine, 1st discharge, and 1st recharge, respectively.

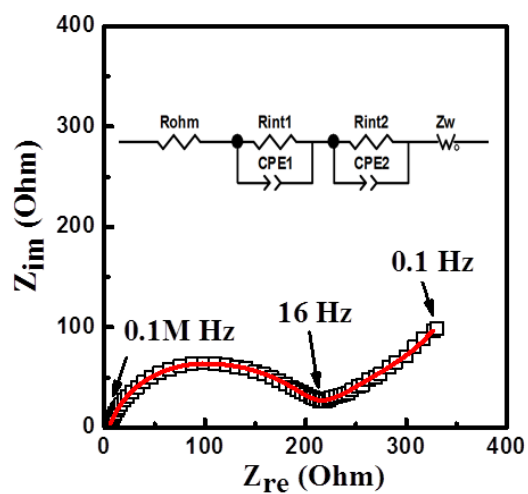


Figure S8. Impedance spectra of the Li-O₂ cell with RuO₂ nanosheet cathode. An equivalent circuit was set up to analysis the impedance spectra. Experimental data

shown as black circles, and the red line was the fitting line based on the equivalent circuit.

Rohm: Ohmic resistance of the Li-O₂ cell, giving a value of 3.9 Ohm;

Rint1: Interfacial resistance between the Li anode and the electrolyte;

Rint2: Interfacial resistance between the RuO₂ nanosheet and the electrolyte;

Zw: Warburg impedance arising from the presence of Li⁺ concentration gradients.

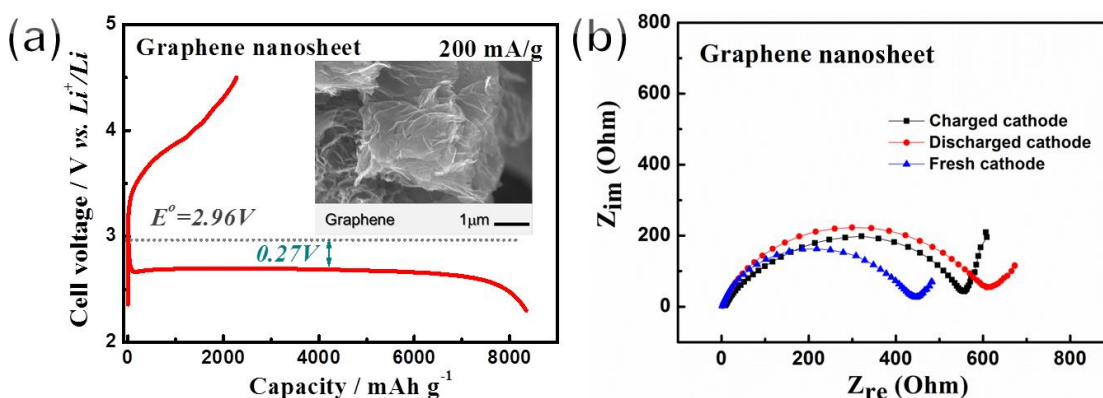


Figure S9. (a) The first cycle discharge/charge behavior of the 2D graphene cathode at a current density of 200 mA g⁻¹. The potential cut-off values are at 2.3 and 4.5 V for discharge and charge processes, respectively. (b) The EIS results of 2D-graphene cathode at states of pristine, 1st discharge, and 1st recharge, respectively.

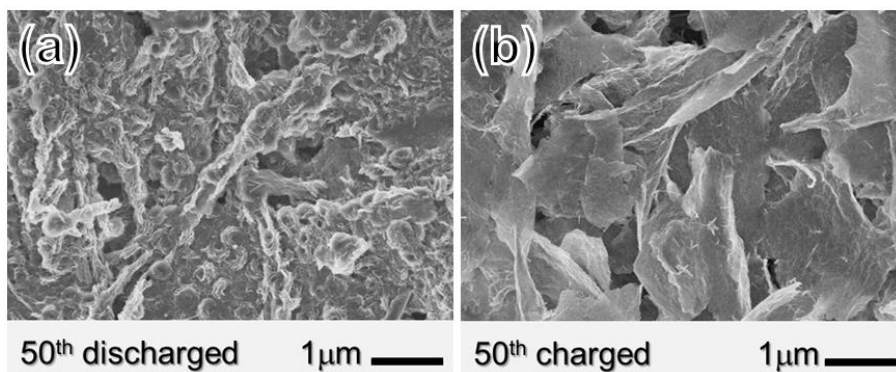


Figure S10. SEM images of cathode at states of 50th discharge (a) and 50th recharge (b), respectively.

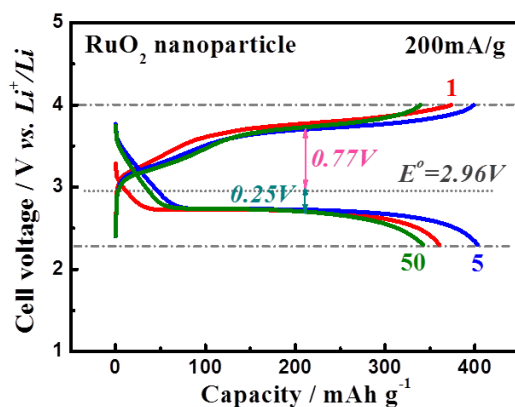


Figure S11. Full discharge/charge profiles of the Li-O₂ battery with commercial RuO₂ nanoparticle cathode over 50 cycles controlled by potential limits from 2.3 to 4.0 V at 200 mA g⁻¹.

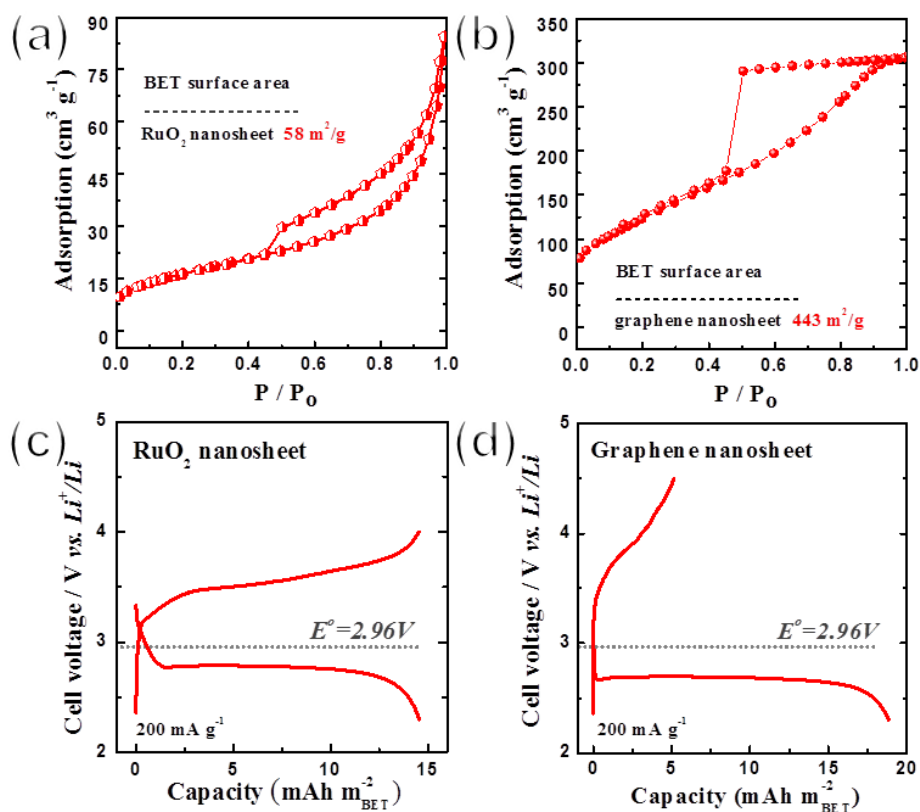


Figure S12. (a-b) Nitrogen-adsorption-desorption isotherms of the RuO₂ nanosheet and graphene, respectively. (c-d) Galvanostatic discharge and charge profiles of the RuO₂ nanosheet and graphene cells in the 1st cycle at the same current densities of 200 mA g⁻¹, respectively. The obtained capacities of the 2D RuO₂ and graphene are normalized by the BET surface areas.

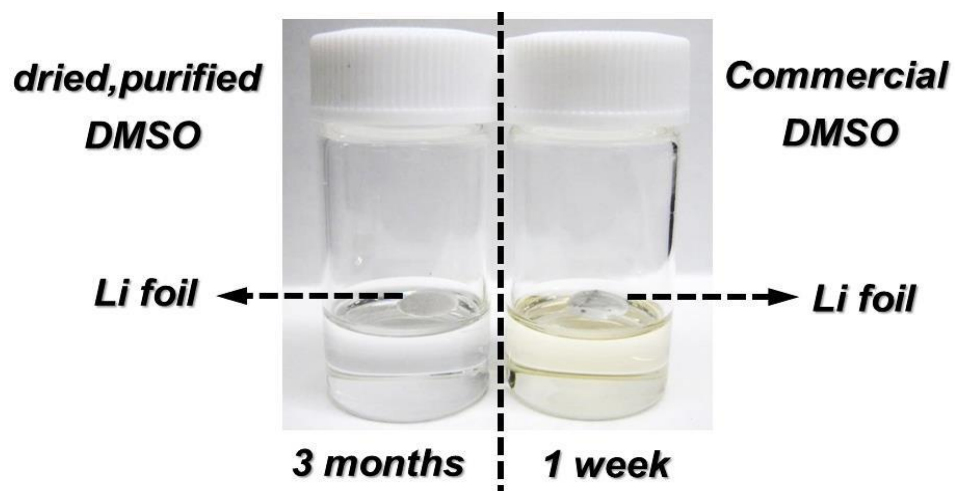


Figure S13. Photographs of the Li foil stored in dried and purified DMSO, and in commercial DMSO, respectively.