

Electronic Supplementary Information

Equilibrium Voltage and Overpotential Variation of Nonaqueous Li-O₂ Batteries Using Galvanostatic Intermittent Titration Technique

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Experimental Methods

Prior to preparing the electrolytes, the ionic liquid of PP13TFSI (Kanto Chemical Corporation) in battery grade was degassed by baking at 80°C for 72 h in vacuum. They were further dried by stirring over lithium foil in an M-Braun glove box with purified Ar under conditions of the moisture as well as the oxygen content less than 0.1 ppm. The final water content of PP13TFSI solvent in the electrolyte was below 5 ppm, measured by a Metrohm 831 KF Coulometer. LiClO₄ (99.99% trace metals basis, Aldrich) as the Li salt was baked under vacuum at 90°C for 60 h. Then the electrolytes were prepared by dissolving of 0.4 M LiClO₄ into the PP13TFSI with stirring at room temperature for 12 h.

The air cathodes were purchased from Microphase Co. LTD in Japan, composed of vertically aligned carbon nanotubes (VACNTs) grown on stainless-steel meshes. The mass of carbon nanotubes was approximately 2.0 mg cm⁻² and their specific surface areas are approximately 80 m² g⁻¹ as measured by ASAP 2010 system. Before cell assembly, the VACNT electrodes were dried at 80°C under vacuum for 48 h.

Each Li-O₂ cell in Swagelok-type was assembled in an Ar-filled glove box with oxygen and moisture levels below 0.1 ppm, consisting of a lithium foil anode (0.5 mm thick), a VACNT cathode and a glass fiber (GF/B, Whatman) separator soaked with the electrolyte. Then the cells were sealed in the in-house built chambers with the inlet and outlet tubes for oxygen flowing, transferred into an incubator which was maintained at a constant temperature of 60°C. With an oxygen flow of 20 sccm, the cells were firstly rested for 4 h with the stabilized open circuit voltage (OCV) of approximately 3.0 V. Then the discharge and charge measurements were conducted by

a battery tester (Arbin BT2000).

For X-ray diffraction (XRD) measurement, the discharged or charged VACNT cathodes were taken out from the cells in the Ar-filled glove box, washed with CH₃CN and dried on a filter paper under vacuum, and mounted in the sample holder which was sealed by two silicon-glue rings together with a stainless-steel plate and a Be window. The XRD scans were carried out using a diffractometer (D8 Discover, Bruker) with Cu K_{α} radiation in a reflection mode. Detection of the morphology variation upon cycling was conducted by scanning electron microscope (SEM, FEI Magellan 400). For all the above measurements, the samples during transfer were carefully protected with Ar atmosphere without exposing to ambient air.

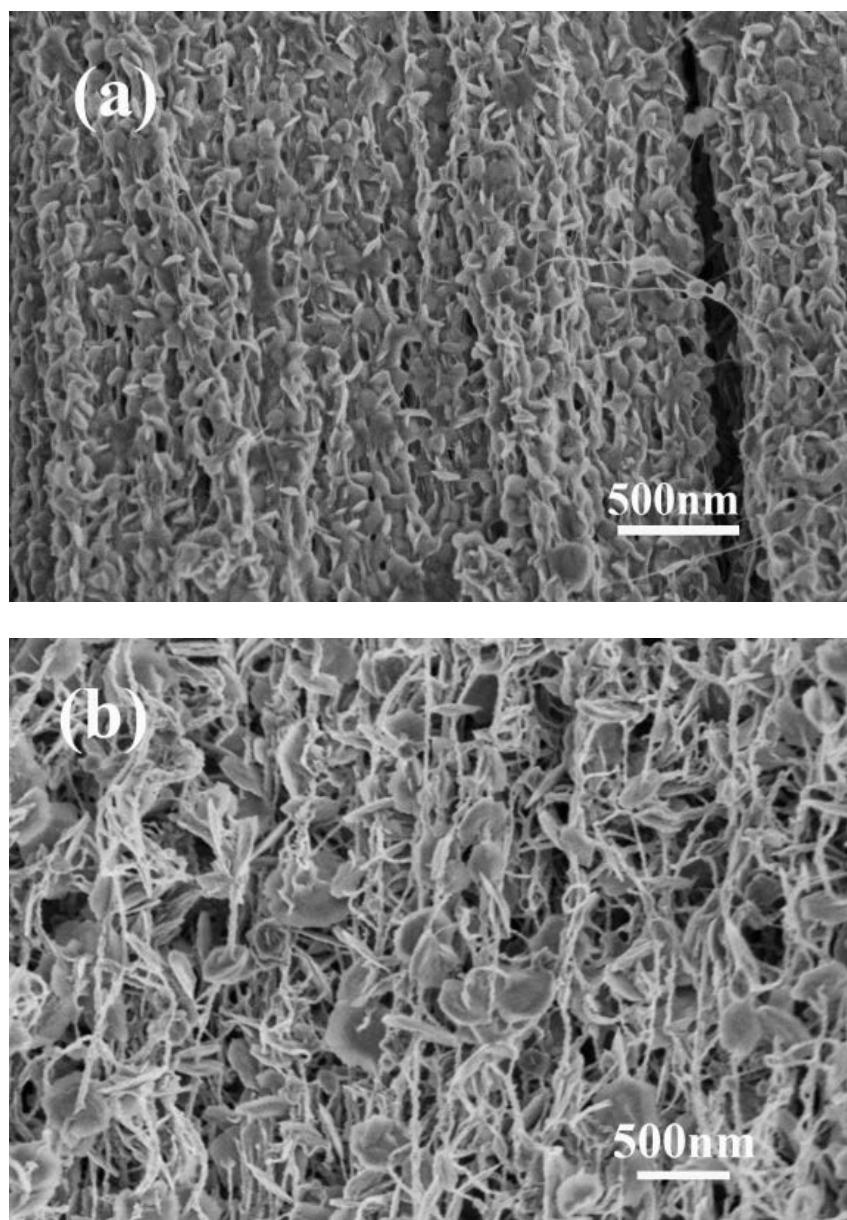


Fig. S1: Scanning electron microscopy (SEM) images for (a) the carbon-nanotube cathode discharged at the current density of 0.3 mA cm^{-2} under GITT, and (b) the carbon-nanotube cathode discharged at the current density of 0.3 mA cm^{-2} under the continuous condition. It is revealed that the Li_2O_2 grows like the abacus balls around the carbon nanotubes for both cases. Nevertheless, the particles in the GITT case are smaller in size ($\sim 100 \text{ nm}$) while larger in density than those in the other case.

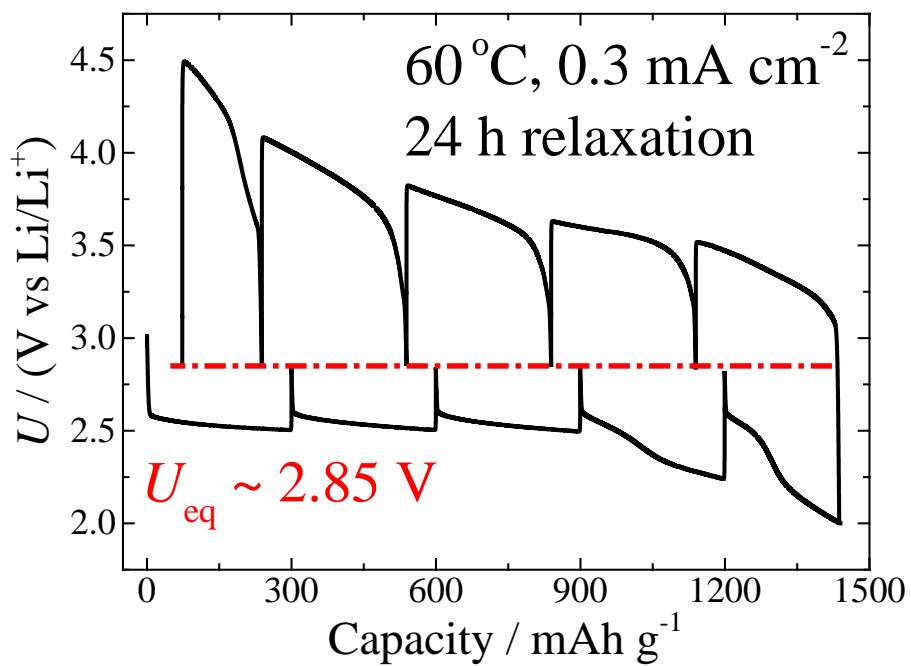


Fig. S2: GITT curves measured at 60°C and the current density of 0.3 mA cm^{-2} with the relaxation time of 24 h.

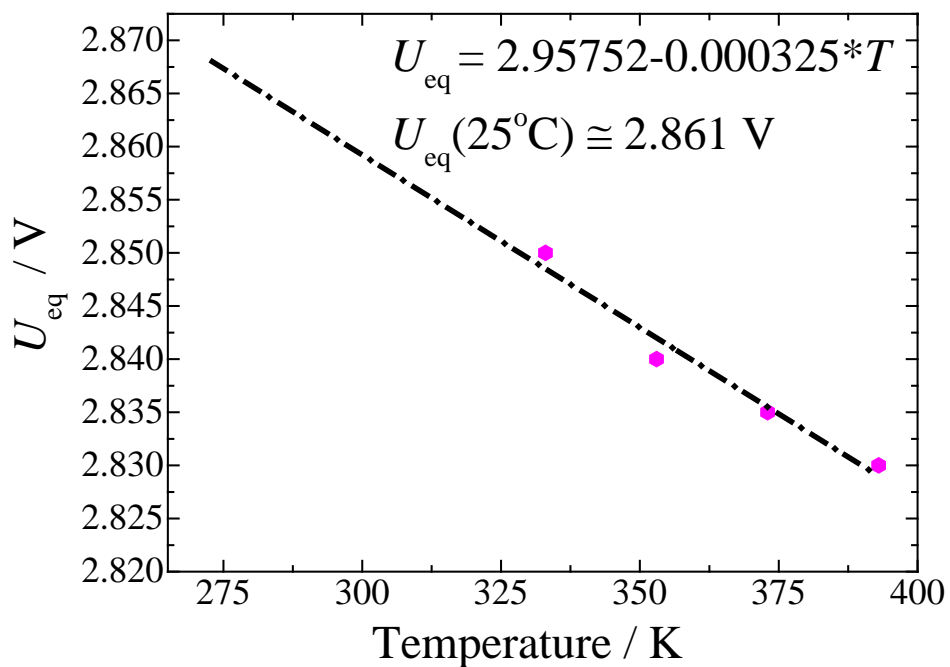


Fig. S3: U_{eq} as a function of temperature. $\Delta_r S$ of the measured Li-O₂ battery is -62.6 ($-3.25 \times 10^{-4} nF$, with $n = 2$) $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The simulated U_{eq} at 25°C is 2.861 V.

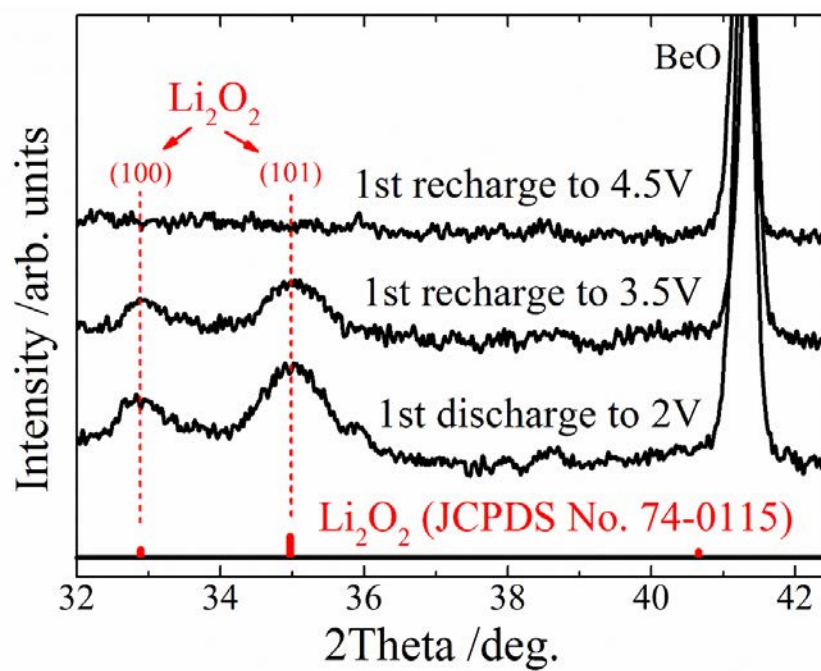


Fig. S4: XRD scans for the cathodes after the discharge to 2 V and the recharge to 3.5 V. It can be seen that Li_2O_2 is the only detectable crystalline product in both discharge and charge processes.

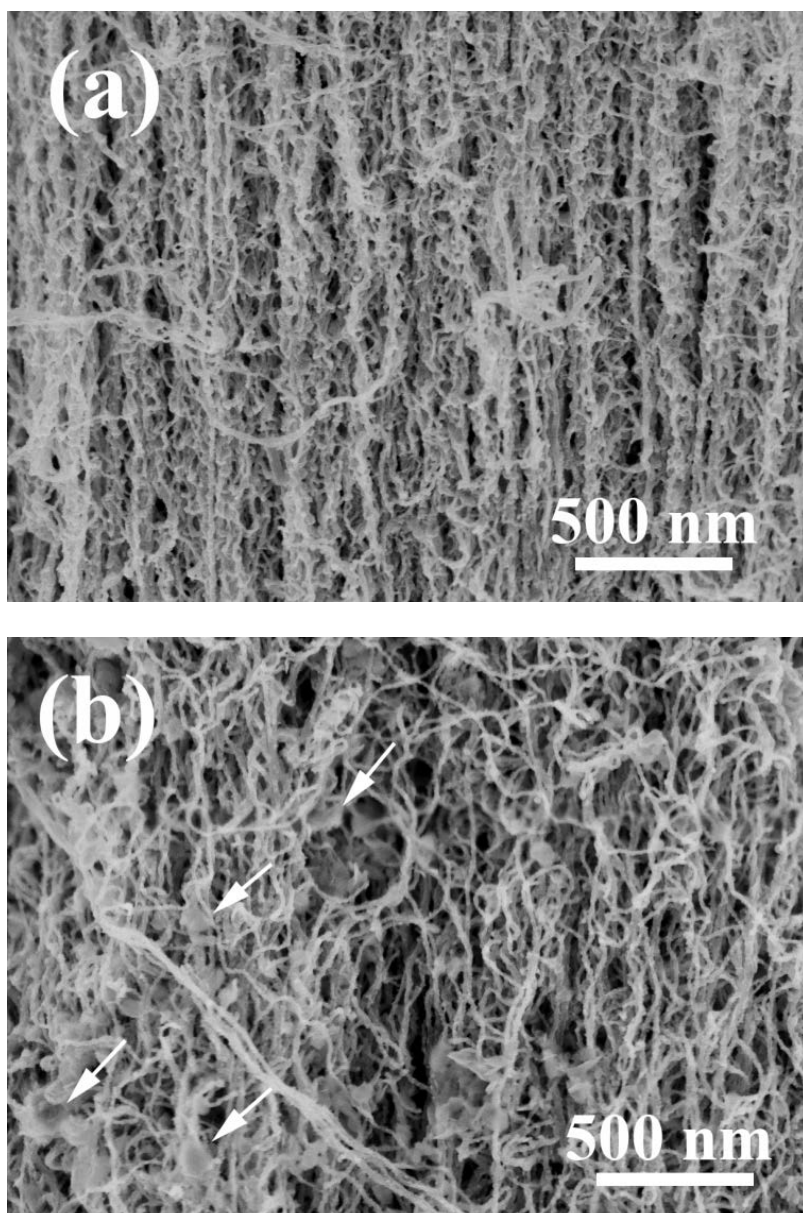


Fig. S5: Scanning electron microscopy (SEM) images for (a) the carbon-nanotube cathode discharged at the current density of 0.4 mA cm^{-2} to 1000 mAh g^{-1} and (b) the carbon-nanotube cathode discharged at the current density of 0.1 mA cm^{-2} to 1000 mAh g^{-1} . It is revealed that at the larger current density [as shown in (a)] the Li_2O_2 particles grow like the films around the carbon nanotubes, while some abacus balls of the Li_2O_2 particles grown around the carbon nanotubes can be found at the smaller current density [as shown in (b)].

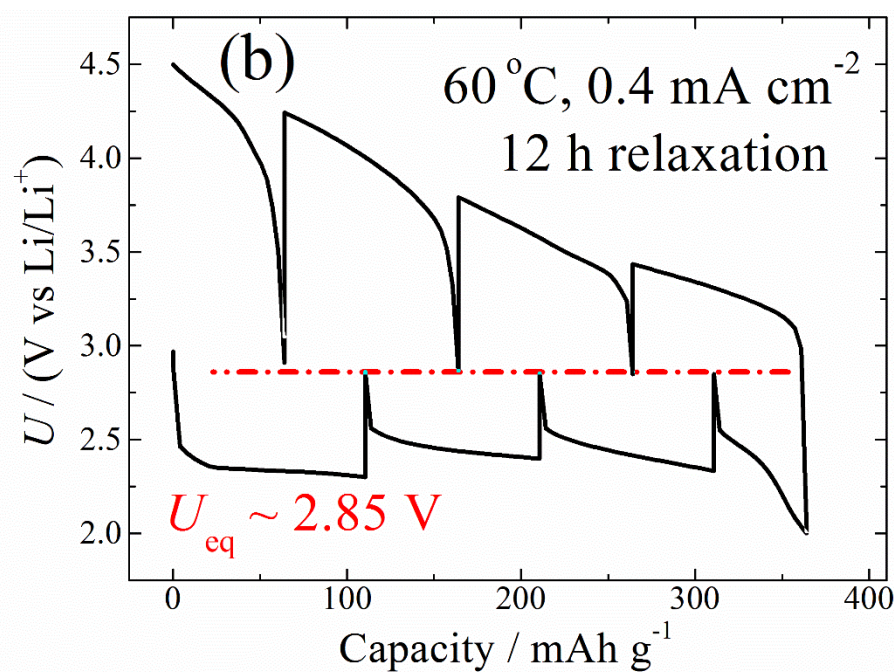
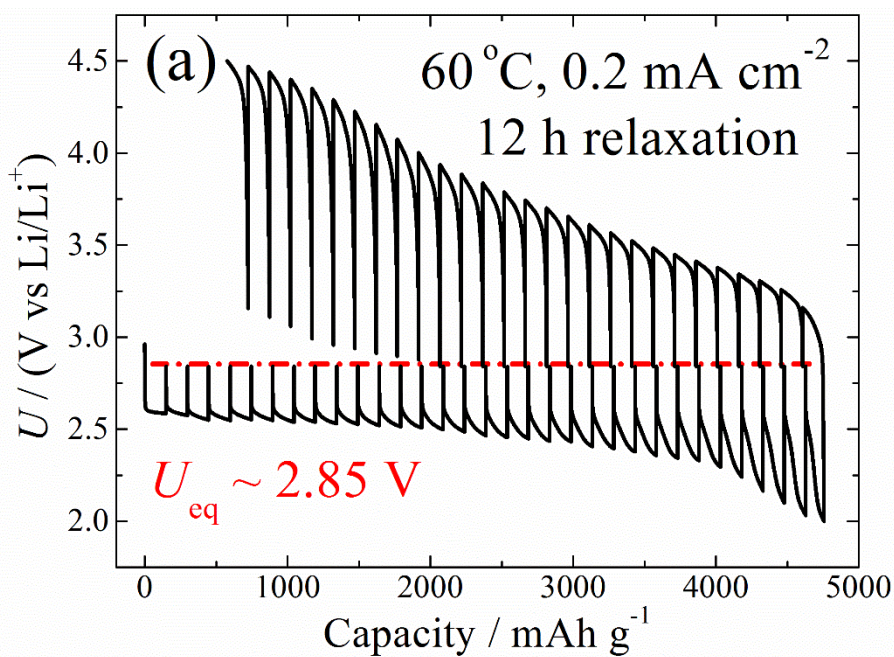


Fig. S6: GITT curves measured at 60°C and the current density of (a) 0.2 mA cm^{-2} and (b) 0.4 mA cm^{-2} with the relaxation time of 12 h.

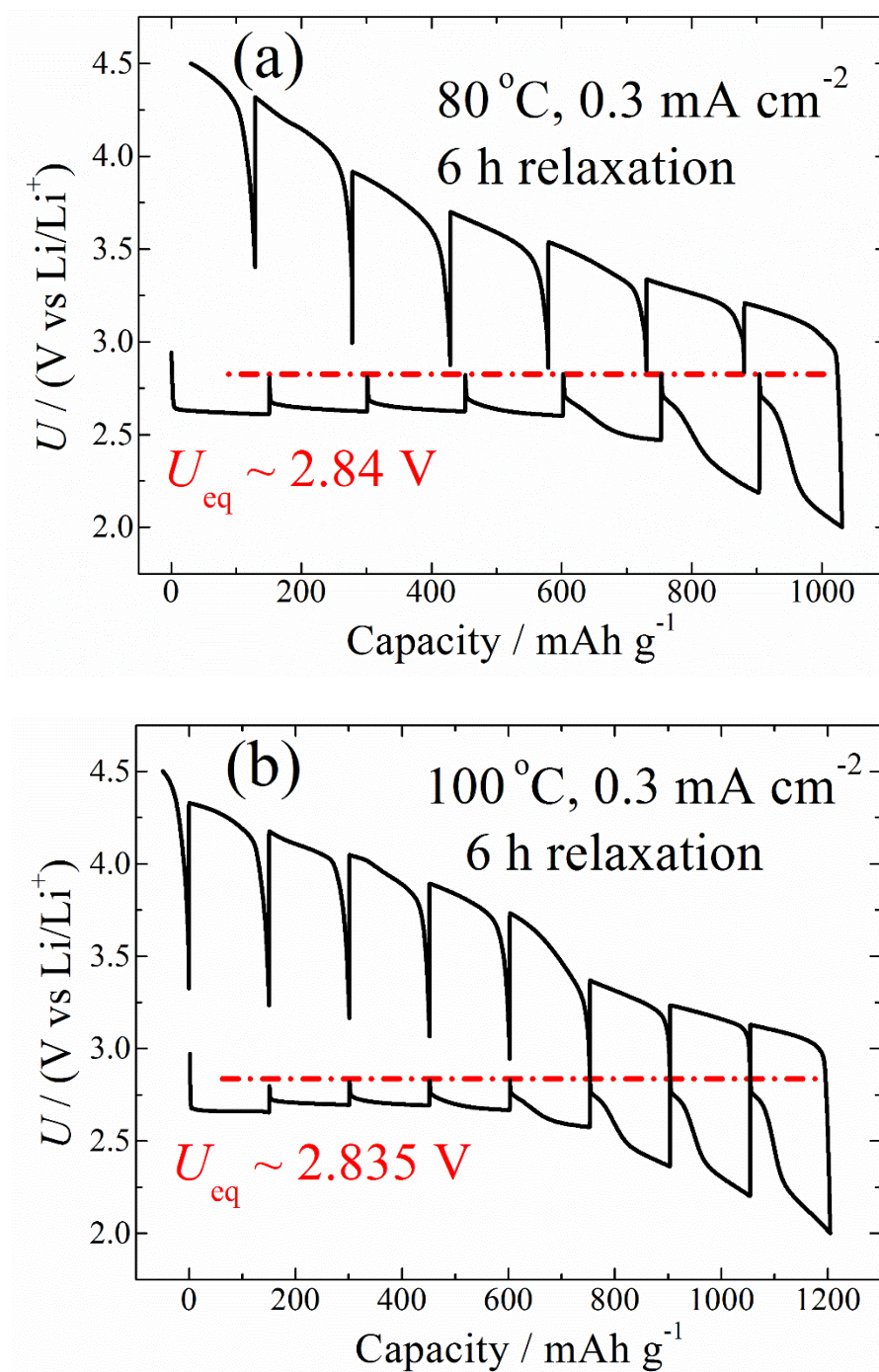


Fig. S7: GITT curves measured at (a) 80°C and (b) 120°C and the fixed current density of 0.3 mA cm^{-2} with the relaxation time of 6 h.