

Supporting Information

A Transmission Electron Microscopy study of the electrochemical process of lithium-oxygen cells

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1. Experimental Procedures

1.1. *Li-O₂ cell preparation and electrochemical measurements*

A carbon material (Super P) and a polyvinylidene fluoride binder (PVDF) were intimately mixed in a N-methyl-2-pyrrolidone (NMP) solution with a weight ratio of 8:2. Then, the resulting slurry was

coated on a gas-diffusion layer (TGP-H-030 carbon paper, Torray) with carbon loading density of $1.0 \pm 0.1 \text{ mg}_{\text{carbon}} \text{ cm}^{-2}$. The prepared electrode was dried for 12 hours at 100°C under vacuum to remove the residual solvent. For electrochemical test of Li-O₂ cells, The R2032 coin type cells were assembled in an argon-filled glove box (MBRAUN, H₂O < 0.1 ppm, O₂ < 0.1 ppm). The positive top cover was machine-drilled to evenly distributed $21 \times 1.0 \text{ mm}$ dia. holes to provide the oxygen flow. The cell consists of metallic lithium foil anode (400 μm thick), the aforementioned carbon cathode and glass filter (Whatman®) separator. A solution of LiCF₃SO₃ (Aldrich) in a tetra (ethylene glycol) dimethyl ether (TEGDME) solvent and propylene carbonate (PC) with a molar ratio of 1:4, respectively, was used as the electrolyte. The LiCF₃SO₃ (Aldrich) salt was vacuum-dried at 100°C for 24 hours prior to use. All solvents were also dried for several days over activated molecular sieves. The prepared electrolytes had a moisture contents of < 10 ppm determined using a Mettler-Toledo Karl Fischer.

The fabricated Li-O₂ cell was electrochemically tested by using galvanostatic cycling with a VMP3 Biologic-instrument. The charge-discharge test was carried out on the time-controlled mode at current density of $500 \text{ mA g}_{\text{carbon}}^{-1}$ for 20 hours ($10,000 \text{ mAh g}_{\text{carbon}}^{-1}$). For these tests, the cell was placed in an oxygen-filled chamber with a pressure slightly higher than 1 atm.

1.2. Characterization of oxygen electrode after cycling

A High-resolution transmission electron microscopy (HR-TEM, model JEM-2010, JEOL) was employed to observe the morphology of the air electrode samples after cycling. The samples were protected from exposure to air during the transfer to the TEM chamber by conductive tape and carbon grid applied in the glove box. To examine the product on each discharge and charge state after cycling using TEGDME, these vacuum-dried electrodes were measured by using the X-ray diffraction (XRD, Rint-2000, Rigaku) with Cu-K α radiation source.

2. Results

2.1. XRD analysis of the SP electrode at different cycling stage

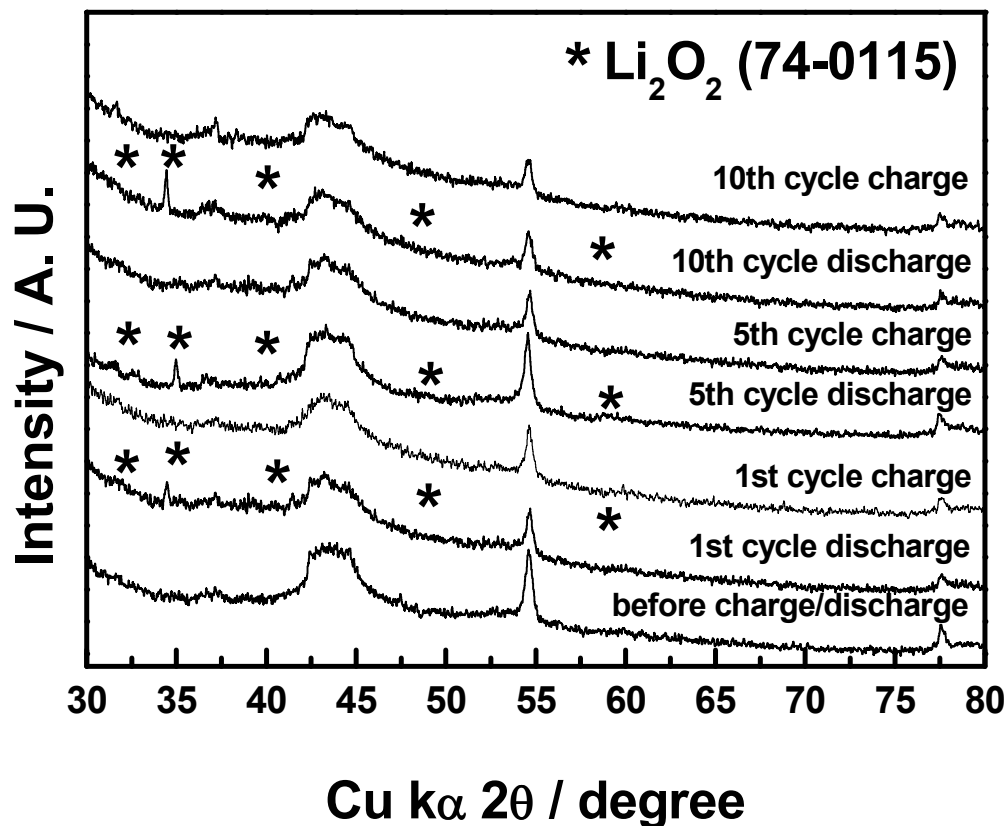


Figure S1. XRD analysis run on the oxygen electrode before and after charging at 1st, 5th and 10th cycles

The Figure shows that the presence lithium peroxide, Li_2O_2 is detected as the main product of all discharges of the lithium-oxygen cell while no traces of it were observed in the following charges.

2.2. TEM analysis of the SP electrode at discharge stage

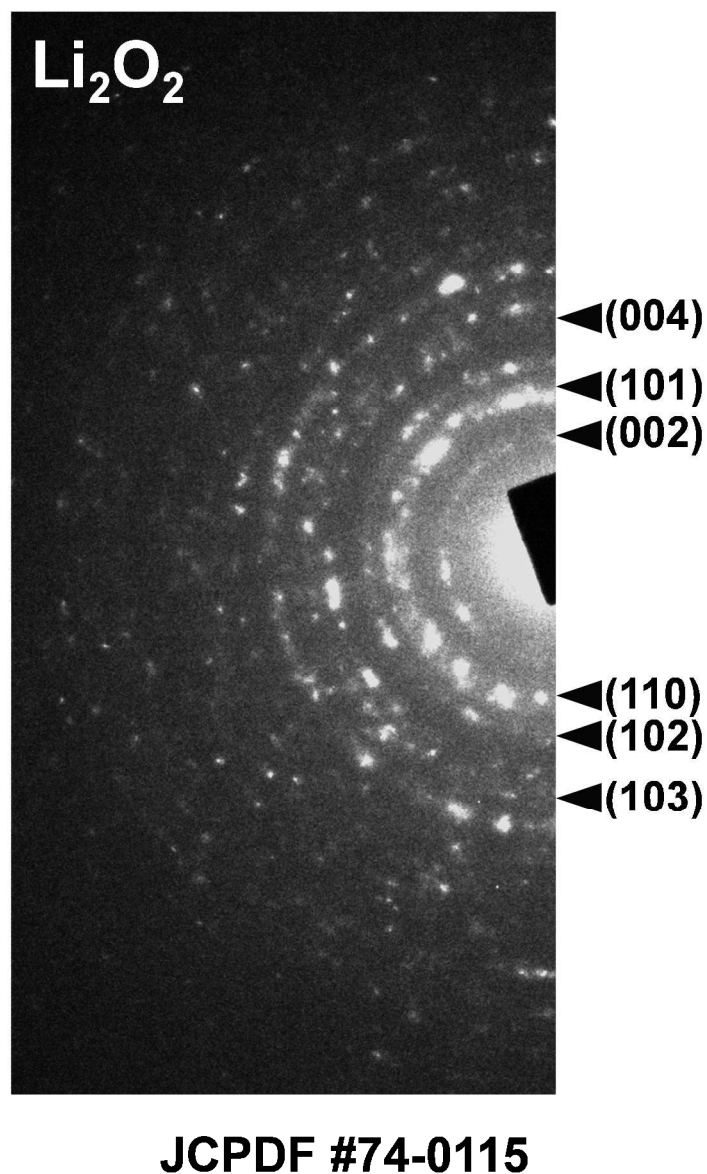


Figure S2. Polycrystalline electron diffraction pattern of a crystalline particle formed on a discharged oxygen electrode. The pattern is indexed to hexagonal Li_2O_2 .

Figure S2 shows the electron diffraction pattern of Li_2O_2 nanoparticles found on the solid surface of the oxygen electrode after full cell discharge. The polycrystalline structure is clearly revealed.

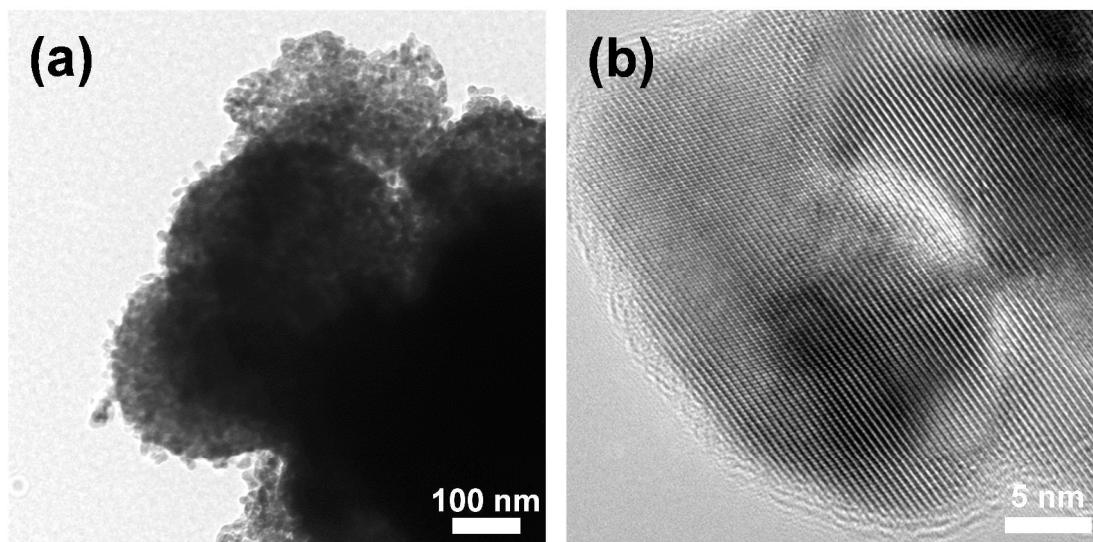


Figure S3. (a) TEM image of a discharged oxygen electrode showing that the deposited Li_2O_2 particles are formed by primary crystalline particles. (b) High resolution TEM image of a primary Li_2O_2 particle.

The high-resolution TEM image shown in the Figure confirms the crystalline nature of some of the Li_2O_2 particles formed on the positive electrode substrate following the discharge process of the Li-air cell

2.3. XRD analysis of the SP electrode at different discharge capacity

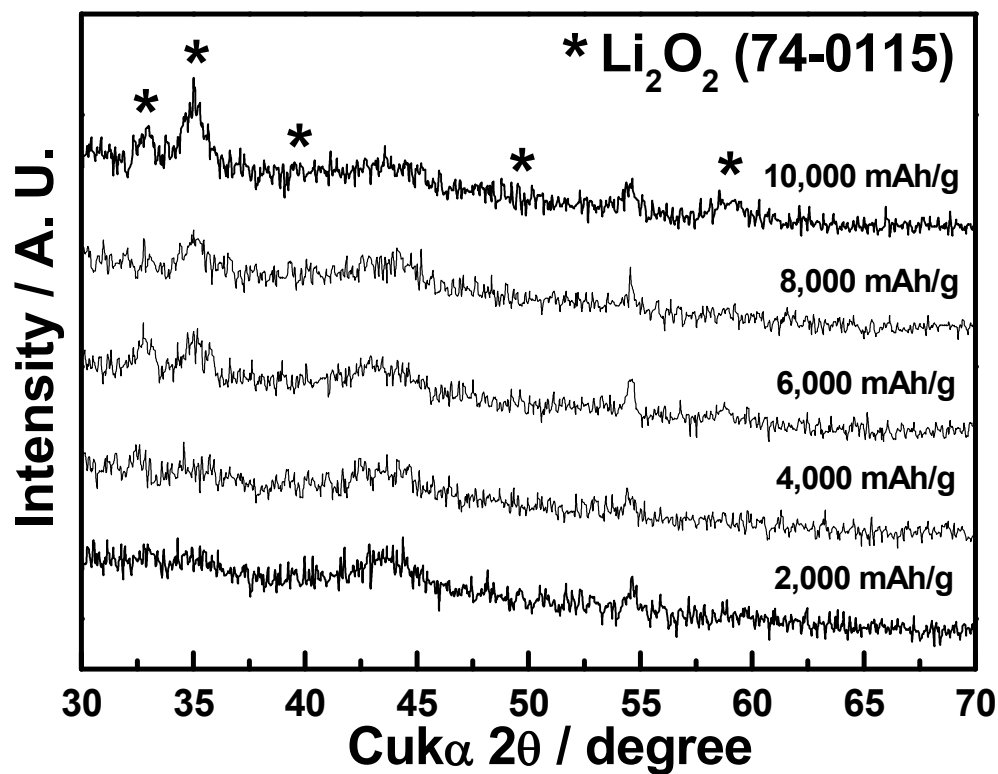


Figure S4. XRD analyses of an oxygen electrode taken at progressive stages of the discharge process in the lithium cell.

The XRD spectra reported in Figure S4 reveals a passage from an amorphous to a crystalline state upon proceeding with the discharge process, confirming the TEM analysis reported in Figure S3.

2.4. TEM analysis of the SP electrode at discharge stage

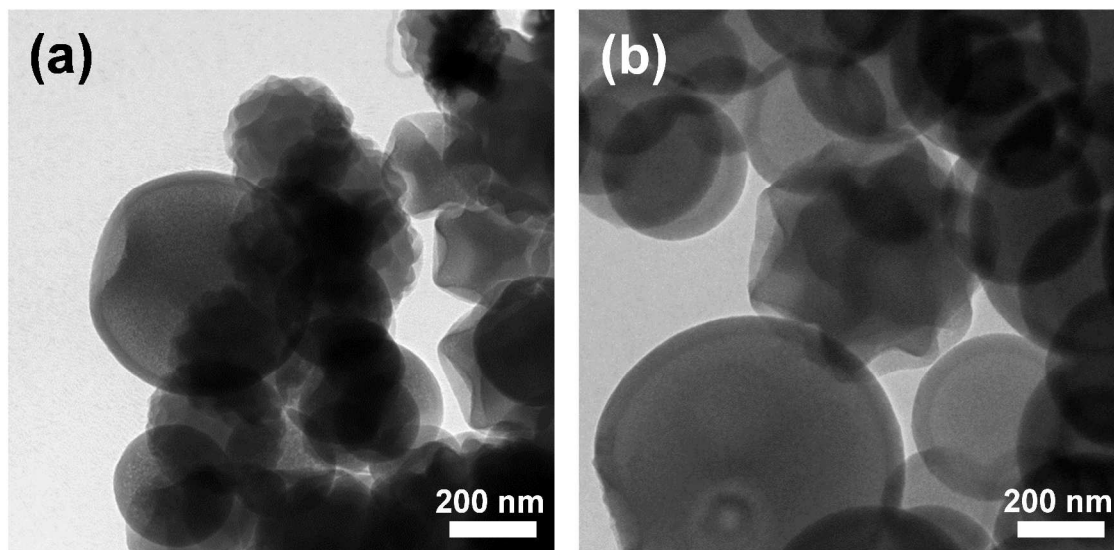


Figure S5. TEM images of Li_2O_2 particles taken on the oxygen electrode after cell discharge.

Figure S5a reveals that some Li_2O_2 particles are broken or in part collapsed due to the pressure build-up inside the hollow structures. These broken particles appear similar in appearance to the “doughnut”-shaped Li_2O_2 particles often imaged with SEM. In addition to the hollow particles, both solid and collapsed particles were found among the discharge product (b).