Electronic Supplementary Information

Platinum catalyst deposited on zirconia support for the design of lithium-oxygen battery with enhanced cycling ability

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Experimental Details

Preparation of platinum deposited onto a zirconia support (Pt/ZrO_2) 10 wt% of platinum precursor ($H_2PtCl_6 \cdot 6H_2O$, Sigma-Aldrich) was added to 0.05 g ZrO_2 (Sigma-Aldrich) in distilled water (100 ml). The solution was stirred for 1 h and sonicated for 1 h. A $NaBH_4$ solution (0.15g, 50ml, Sigma-Aldrich) was slowly added drop-wise to the sample solution to reduce the platinum. The solution was aged for 12 h and washed with distilled water. The sample was dried in a 60 ˚C oven for 12 h. Commercial platinum black (Alfa Aesar) was used for the platinum catalyst for comparison.

Characterization The morphology and surface properties were measured by transmitted electron microscopy (TEM, JEOL, JEM-2100), X-ray diffraction (XRD, Rigaku, D/max-2200), BET analysis (Micrometrics, ASAP2010) and X-ray spectroscopy (XPS, Thermo Scientific, Sigma Probe)

Electrochemical characterization The Swagelok-type Li-O_2 cells were assembled using lithium metal as an anode, 1 M Bis(trifluoromethane) sulfonamide lithium salt (Sigma-Aldrich) dissolved in tetraethylene glycol dimethyl ether (Sigma-Aldrich) was used as an electrolyte and gas-diffusion layer (SGL carbon, GDL 10BC) with the catalyst as a cathode. All cells were fabricated in an argon-filled glove box. Catalysts were applied via a spray gun using catalyst ink. 10 mg of catalyst was added into 5 ml 2-propanol (SAMCHUN chemicals) for catalyst ink. The amount of loaded Pt/ZrO_2 was 0.5 mg cm^{-2}. To equalize the amount of active material without support, the mass density of Pt particle electrode was adjusted to 0.05 mg cm^{-2}. Before the electrochemical characterization, cells were transferred to an oxygen-filled chamber. Charge/discharge tests were conducted with a multichannel automatic battery cycler (WonATech, WBCS3000). Cyclic voltammetry and galvanostatic tests were carried out using a potentiostat (WonATech, ZIVE 2). In galvanostatic reduction/oxidation test, a three-electrode configuration was used with a glassy carbon electrode with a diameter of 5 mm as the working electrode and platinum meshes as counter and pseudo-reference electrodes. Seven μl of catalyst ink was fabricated by mixing 10 mg catalyst, 5 mg Nafion (NanoBest Corp.) and 0.8 ml 2-propanol, which was dropped onto a glassy carbon and dried. 0.5 M tetrabutylammonium perchlorate (Sigma-Aldrich) dissolved in dimethyl sulfoxide (SAMCHUN chemicals) was used for the electrolyte and O_2 purge for 1h before the test.

Computational Details Periodic DFT calculations were conducted using a Vienna ab initio simulation package (VASP). Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was applied to a generalized gradient approximation (GGA).[1,2] Ionic cores were calculated under the projector augmented wave (PAW) method.[3] The

energy cutoff for the plane wave basis was 520 eV. A brillioun zone was described by 1 × 1 × 1 Monkhorst-Pack k-point mesh. DFT+U calculation was introduced with U_{eff} = 4 eV for zirconium. This U value was obtained from the construction of electronic and geometric structures of bulk zirconia.[4] This U_{eff} is also used to calculate the stability of zirconia nanoparticle with various shapes.[5] The van der waals interactions are described using a DFT+D2 method established by Grimme. The source of the parameters for grimme's potential was studies by F. Picaud[6] and G. Kresse.[7]

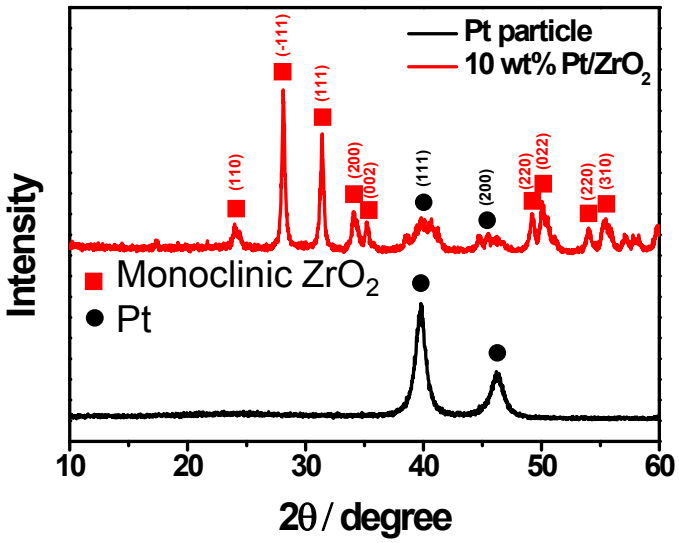

Figure S1. XRD patterns of Pt/ZrO_2 and Pt particle

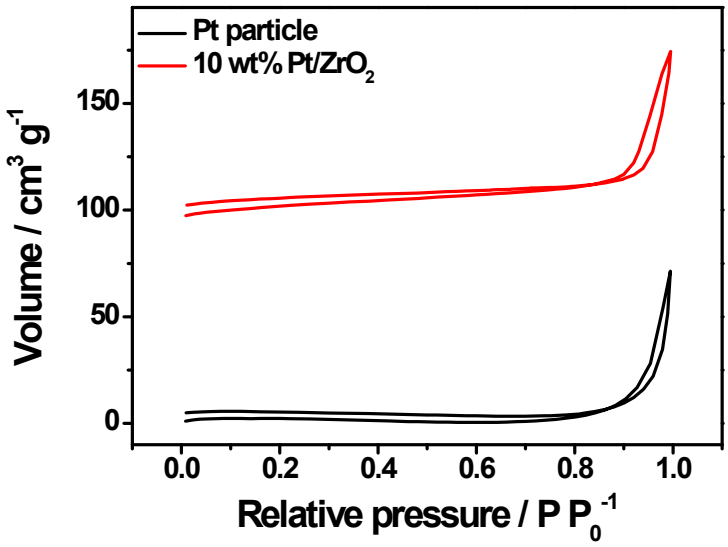

Figure S2. N_2 adsorption-desorption isotherms of Pt particle and Pt/ZrO_2

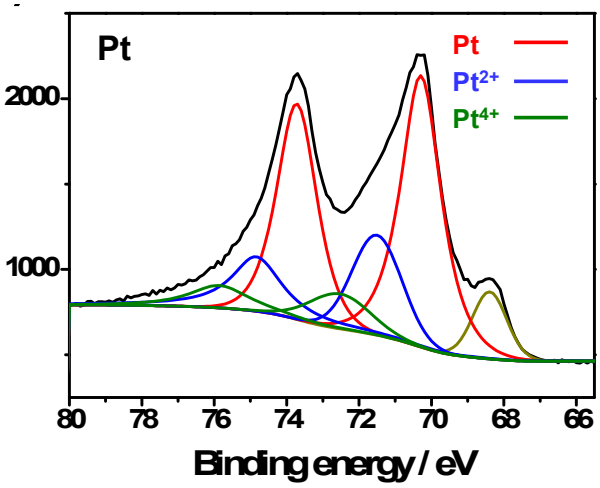

Figure S3. XPS analysis of Pt/4f of Pt/ZrO_2. Olive line is background.

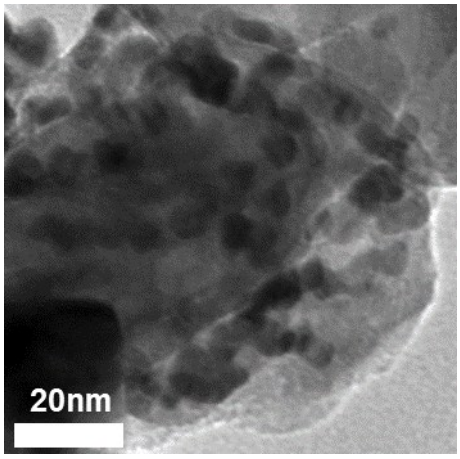

Figure S4. TEM image of 20 wt% Pt/ZrO_2

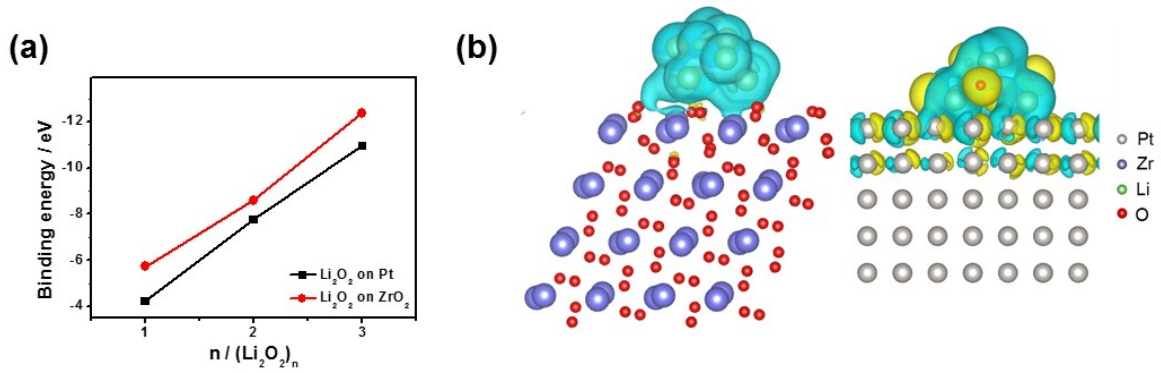

Figure S5. Calculated binding energy of $(Li_2O_2)n$ (n = 1,2,3) adsorbed on platinum (200) and zirconia (111) planes. Binding energy calculated by $E_{Li2O2} + E_{surface} - E_{ad}$. E_{Li2O2} is energy of Li_2O_2 monomer, dimer and trimer, $E_{surface}$ is energy of clean surface of Pt and ZrO_2 and E_{ad} is energy of Li_2O_2 adsorbed on Pt and ZrO_2. (b) Charge density difference of Li_2O_2 adsorbed on Pt and ZrO_2. The isosurfaces are 0.01 ea_0^{-3} and plotted at positive (yellow) and negative (blue) values.

References

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