Supporting Information

A Study on the Catalytic Activity of Noble Metal Nanoparticles on Reduced Graphene Oxide for Oxygen Evolution Reactions in Lithium-Air Batteries

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EXPERIMENTAL METHODS

Material Synthesis: GO was prepared by modified Hummers method.^{1,2} Pt-rGO, Pd-rGO, and Ru-rGO hybrid were synthesized by modified polyol method.³ GO dispersion (1 mg ml⁻¹) in ethylene glycol (EG) was first prepared with the aid of horn sonication for 1 hr. Proper amount of noble metal salt (H₂PtCl₆, Na₂PdCl₄, and RuCl₃) was added to 100 ml of GO colloidal dispersion and incubated for 2 hrs. Solution pH was then adjusted to pH 13 with NaOH (2.5 M in EG). The reaction temperature was increased to 120 °C, and NaBH₄ reducing agent dissolved in EG was injected slowly. The solution remained reacted for 1 hr at this temperature and cooled to room temperature. The precipitates were filtered, washed and dried under vacuum.

Characterization: The microstructure of supported catalysts was analyzed with Transmission Electron Microscopy (JEOL JEM-2100F) and Scanning Electron Microscopy (Hitachi S-4800). X-Ray Diffraction (XRD) was done using a Rigaku D/Max-2500 powder diffractometer with Cu K α radiation. Thermo Gravimetric Analysis (TGA) was carried out using a Netzsch TG209F3 apparatus at a heating rate of 10 °C min⁻¹ in air flow. X-ray Photoelectron Spectroscopy (XPS) was measured on ThermoVG K-alpha. For Nuclear Magnetic Resonance (NMR) analysis, the electrolyte were extracted from the electrode and separator of disassembled tested cells in argon filled globe box. Then, NMR experiments were conducted in DCCl₃ (chloroform-d₆) as solvent, and tetramethylsilane (TMS) as a reference on a VNMRS 600 MHz instrument. Raman spectra of the discharged cathode were obtained using a Renishaw 2000 or inVia microscope spectrometer with a HeNe laser at exciting wavelength of 633 nm. The sample was loaded to a gas-tight Raman cell with glass or quartz window in a glove box.

Electrochemical Test: To prepare the oxygen electrode, noble metals-rGO hybrids and pristine rGO were intimately mixed in a N-methyl-2-pyrrolidone (NMP) solution and a polyvinylidene fluoride binder (PVDF) with a weight ratio of 8:2. The slurry was coated on a gas-diffusion layer (TGP-H-030 carbon paper, Torray) with loading density of 0.157 mg cm⁻², and dried for 12 hrs at 100 °C under vacuum to remove the residual solvent. The electrochemical cells were based on a R2032 coin type cells that the positive top cover were machine-drilled to evenly distributed 21 $\times$ 1.0 mm dia. holes for the oxygen intake). The cells were assembled in an argon-filled glove box (MBRAUN, H₂O < 0.1 ppm, O₂ < 0.1 ppm) with metallic lithium foil anode (400 μ m thick), rGO hybrids cathode, glass filter (Whatman®) separator and TEGDME-LiCF₃SO₃ electrolyte. The electrolyte was a solution of LiCF₃SO₃ (Aldrich) in a tetra

(ethylene glycol) dimethyl ether (TEGDME, a moisture contents of < 10 ppm) solvent with a molar ratio of 1:4. 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 with a fixed capacity of 2000 mAh g⁻¹ at current density of 200 mA g⁻¹ for 10 hrs. For these tests, the cell was placed in an oxygen-filled chamber with a pressure slightly higher than 1 atm. The capacity was normalized by the total weight of oxygen electrodes (rGO or rGO + catalyst).

Figure S1. Microstructural analysis of noble metal catalyst-rGO hybrids (a) XRD pattern of Pt-rGO hybrid (b) particle size distribution and high resolution TEM image of Pt-rGO hybrid, (c) XRD pattern of Pd-rGO hybrid (d) particle size distribution and high resolution TEM image of Pd-rGO hybrid (e) XRD pattern of Ru-rGO hybrid, and (f) particle size distribution and high resolution TEM image of Ru-rGO hybrid.

Figure S2. TGA curves of (a) Pt-rGO hybrid, (b) Pd-rGO hybrid and (c) Ru-rGO hybrid.

Figure S3. XPS spectra of (a) C1s peaks of GO, (b) C1s peak of rGO after modified polyol process, (c~e) survey scan of (c) Pt-rGO hybrid, (d) Pd-rGO hybrid and (e) Ru-rGO hybrid.

Figure S4. High resolution XPS spectra of noble metal-rGO hybrids. (a) Pt4f peaks of Pt-rGO, (b) Pd3d peaks of Pd-rGO and (c) Ru3p_{3/2} peak of Ru-rGO.

Figure S5. TEM images showing (a) Pt-rGO hybrid, (b) Pd-rGO hybrid and (c) Ru-rGO hybrid.

Figure S6. SEM and EDX of (a) Pt-rGO hybrid, (b) Pd-rGO hybrid and (c) Ru-rGO hybrid.

Figure S7. Discharge voltage curves in an enlarged voltage scale for Figure 3. (a) 1st cycle of catalyst free and catalyst loaded rGO electrodes. (b~d) (b) Pt-rGO hybrid, (c) Pd-rGO hybrid and (d) Ru-rGO hybrid.

Figure S8. Cycling profiles of Li-air cells after 6th cycle (a) Pt-rGO, (b) Pd-rGO, and (c) Ru-rGO.

Figure S9. Cyclic voltammetry results of rGO, Ru-rGO and Pt-rGO hybrid cathodes at a constant scan rate of $100 \mu\text{V s}^{-1}$ for 4 cycles. (a) rGO electrode, (b) Ru-rGO hybrid electrode, (c) Pt-rGO hybrid electrode, and (d) enlarged anodic scan in CV curves of Ru-rGO and rGO cathodes.

Figure S10. (a) Typical discharge-charge profile of rGO electrode at a limited capacity of 10,000 mAh g⁻¹. (b)~(d) SEM images of rGO electrodes at different charge capacities at points indicated in (a).

Figure S11. (a) Typical discharge-charge profile of Pt- rGO electrode at a limited capacity of 10,000 mAh g⁻¹. (b)~(d) SEM images of Pt-rGO electrodes at different charge capacities at points indicated in (a). Red circles: discharge products.

Figure S12. Raman spectra of discharge products from rGO only, Pt-, Pd- and Ru-rGO hybrid electrodes.

Figure S13. FT-IR spectra of the (a) rGO only, (b) Pt-rGO, and (c) Ru-rGO electrodes at 15th cycles.

Figure S14. SEM images of pristine, 15th discharged, and 15th charged electrodes. (a) rGO only, (b) Pt-rGO, and (c) Ru-rGO hybrid electrodes.

References

1. Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, 80, 1339-1339.
2. Xu, Y.; Sheng, K.; Li, C.; Shi, G. *ACS Nano* **2010**, 4, 4324-4330.
3. Ha, H.-W.; Kim, I. Y.; Hwang, S.-J.; Ruoff, R. S. *Electrochem. Solid State Lett.* **2011**, 14, B70-B73.