High cycle stability of Li-O_2 batteries enabled by RuO_2 loaded Metal-organic framework-derived Co-based catalysts

Yajun Zhao[a,*], Guocai Zheng[a], Guofei Li[a], Hanqing Liu[a], Xiaojing Li[a]

[a] School of Automotive Engineering, Hefei Technology College, Hefei 230012, Anhui, China.

* Corresponding authors: zyj@htc.edu.cn

Synthesis of Co_3O_4: The synthesis method of ZIF-8@ZIF-67 is obtained by the previous literature.[1] Under stirring, pour 20 mL of methanol solution containing 1.85 g of zinc nitrate into 30 mL of methanol solution containing 1.67 g of dimethylimidazole, stir for 5 min, then add 50 mL methanol solution containing 1.47 g cobalt nitrate under stirring, and then quickly add 50 mL methanol solution containing 1.67 g dimethylimidazole, stirring for 30 minutes, stand and aged the solution for 24 hours, the precipitate was collected by centrifugation and dried under vacuum at 60 °C. The obtained powder is calcined at 900 °C for 3 h in an Ar atmosphere, and then annealed at 350 °C for 4 h in a muffle furnace to obtain Co_3O_4 material.

Synthesis of Co_3O_4/RuO_2:

Disperse 0.1 g Co_3O_4 particles in 40 mL deionized water, then, add 0.03 g $RuCl_3 \cdot H_2O$, mix well, add 0.2 M NaOH solution to adjust the pH to 10, 180 ℃ hydrothermal reaction for 16 h, centrifuge to collect the precipitate, wash it with water and ethanol for 3 times, and dry it under 60 °C. The obtained powder is annealed in a muffle furnace at 350 °C for 3 hours to obtain Co_3O_4/RuO_2 material.

Material Characterization

The D/MAX2500V X-ray diffractometer (XRD) is selected to test the phase of the prepared material, the scanning speed is 10º/min, and the scanning range is 20-90º. The Gemini 500 field emission scanning electron microscope (SEM, Carl Zeiss Jena) is used to study the microscopic morphology of the sample. The internal structure and element distribution of the material is characterized by a transmission electron microscope (TEM, JEM-2100F, Hitachi), combined with selected area electron diffraction (SAED) and energy dispersive X-ray (EDX) spectroscopy tools. The ESCALAB250 X-ray photoelectron spectrometer (XPS) is used to analyze the surface composition of the sample and the valence of each element. The specific surface area of the material is calculated through the N_2 adsorption and desorption test of the material at 77 K.

ORR/OER performance test

Use the ATA-1B rotating disk electrode (RDE) to test the ORR/OER performance of the material. RDE uses a glassy carbon electrode (GCE) as the working electrode, a saturated calomel

electrode (SCE) (V vs RHE=V vs SCE+1.068)[2] as the reference electrode, and platinum electrode as the auxiliary electrode. Weigh 10 mg catalysts and 2 mg Vulcan-XC72 carbon into isopropanol water (2 mL) mixed with 40 μL Nafion solution (5 wt%), the volume ratio of isopropanol to deionized water is 1:5, ultrasonically disperse for 1 hour, pipette 7 μL of catalyst suspension and drop it on the polished glassy carbon electrode surface (electrode diameter is 3 mm), and test after the solvent evaporates naturally and dries.

Test conditions: 0.1 mol/L KOH solution saturated with oxygen is the electrolyte; the scanning speed is 10 mV/s; the potential scanning interval of the ORR polarization curve is: 0 ~ -0.6 V, and the disk electrode speed is 400 ~ 2000 rpm; The potential scanning interval of the OER polarization curve is: 0 ~ 1 V, and the rotating speed of the disk electrode is 1600 rpm.

the Koutecky-Levich equation as follow:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{dl}} \quad (1)$$

$$j_k = nFkC_o \quad (2)$$

$$j_{dl} = 0.62nFD_o^{2/3}v^{-1/6}C_o\omega^{1/2} \quad (3)$$

j_k represents kinetic current density, j_{dl} is the diffusion-limiting current density. n represents the number of electron transfer; F is the Faraday constant; D_O is the diffusion coefficient of oxygen; C_O is oxygen concentration dissolved in the electrolyte solution; k represents Boltzmann constant; ω represents the angular velocity and v is the kinetic viscosity of the electrolyte.

Battery performance test

Use CT-3008 Neware battery test system to test the battery performance of materials. The battery uses lithium sheet as the negative electrode, glass fiber filter membrane (Whatman grade GF/D) as the diaphragm, 1 mol/L LiTFSI solution (with TEGDME as the solvent) as the electrolyte, and the catalyst-loaded carbon paper as the oxygen electrode. Assemble 2032-type button batteries in an argon glove box. The oxygen electrode was prepared by KB, catalysts, and PVDF with a weight ratio of 6: 3: 1. The load of catalyst and KB on the carbon paper was about 0.5±0.1 mg cm^{-2}.

Battery charge and discharge performance test: current density is 100 mA g^{-1}; voltage range is 2.0-4.5 V (vs. Li^+/Li). Battery cycle performance test: The current density is 500 mA g^{-1}; the voltage range is 2-4.5 V (vs. Li^+/Li); the specific charge-discharge capacity is limited to 1000 mA h g^{-1}.

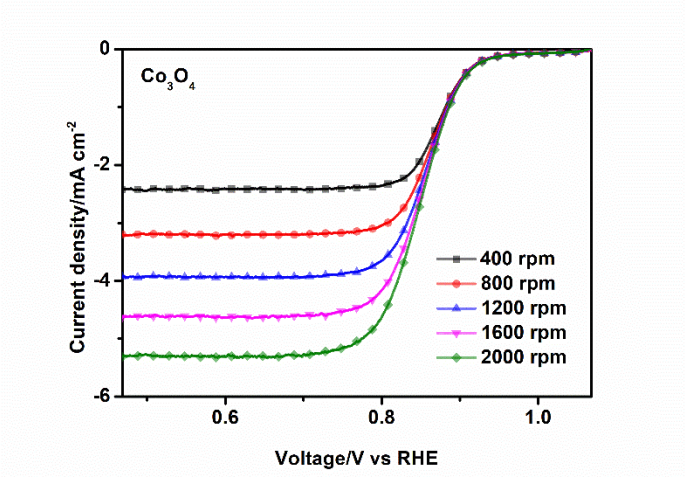

Fig. S1 The ORR curves at different rotating speed of Co_3O_4.

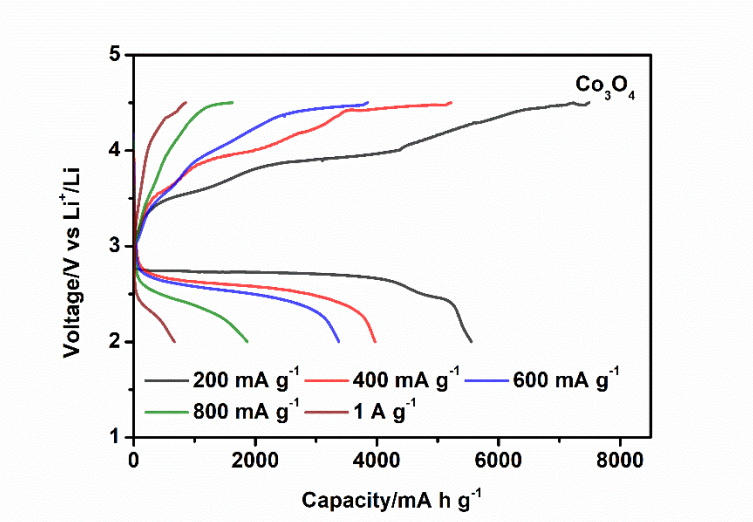

Fig. S2 The rate performance of Co_3O_4.

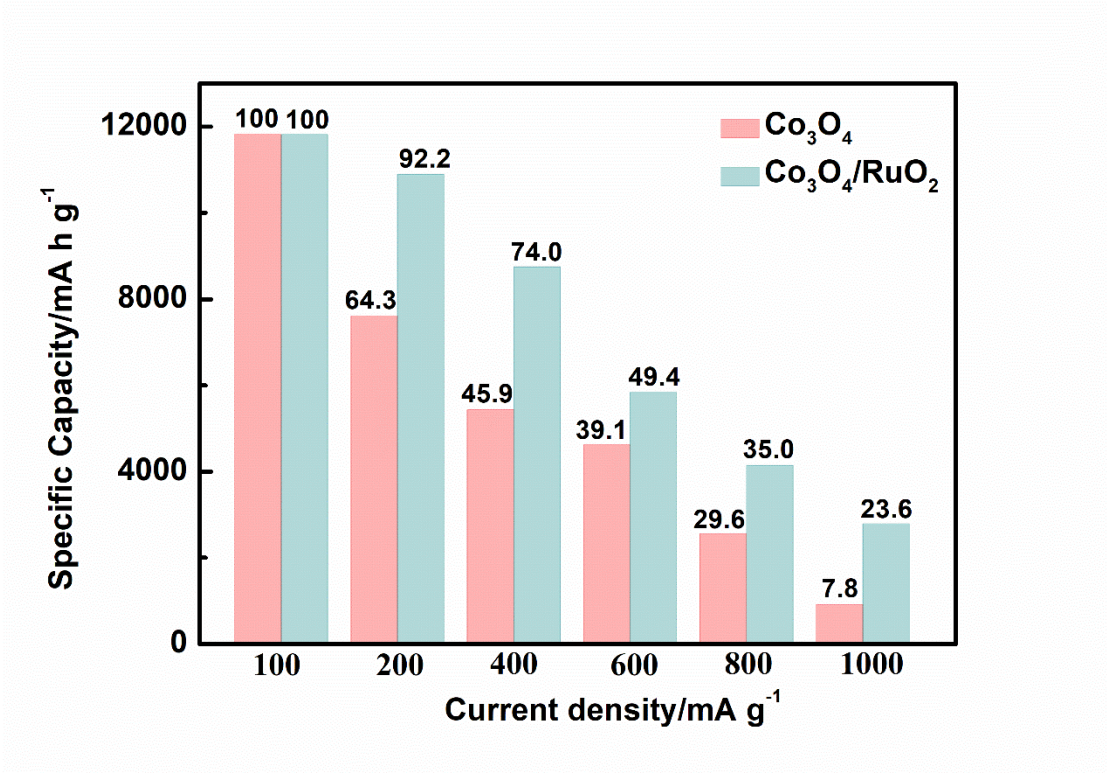

Fig. S3 The capacity retention of Co_3O_4/RuO_2.

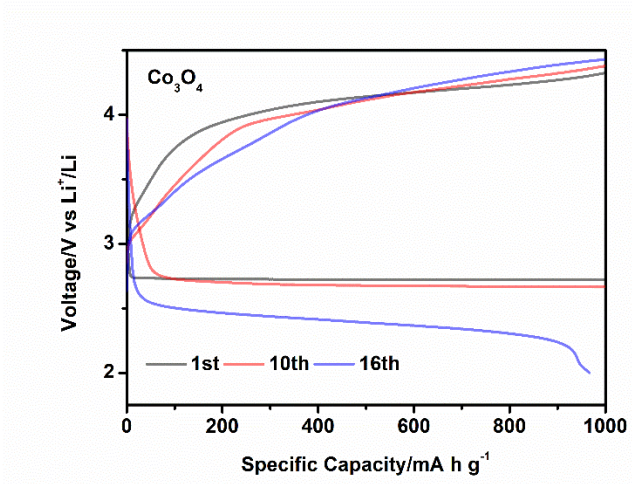

Fig. S4 The cycle performance of Co_3O_4.

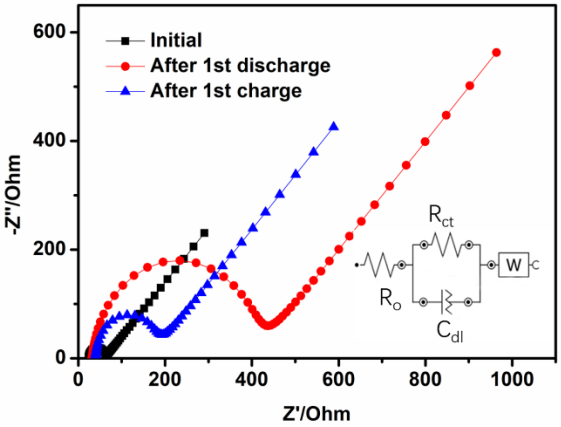

Fig. S5 Nyquist plots of Co_3O_4 cathode in Li-O_2 batteries proposed at different stage.

[1] Y. Zhao, L. Ding, X. Wang, X. Yang, J. He, B. Yang, B. Wang, D. Zhang, Z. Li, Yolk-shell ZIF-8@ ZIF-67 derived Co_3O_4@ $NiCo_2O_4$ catalysts with effective electrochemical properties for Li-O_2 batteries, Journal of Alloys and Compounds, (2020) 157945.

[2] H. Hu, B. Guan, B. Xia, X.W. Lou, Designed formation of Co_3O_4/$NiCo_2O_4$ double-shelled nanocages with enhanced pseudocapacitive and electrocatalytic properties, Journal of the American Chemical Society, 137 (2015) 5590-5595.