

Lanthanide-Driven Electronic and Defect Engineering in Spinel Co_3O_4 : Unraveling the Structure-Activity Synergy for Bifunctional Oxygen Electrocatalysis

Tianqi Cao ¹, Hongyu Cui ¹, Junyi Liu ¹, Chuanhui Zhang ^{1, 2, *}

¹ Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China

² Faculty of Chemical Engineering and Energy Technology, Shanghai Institute of Technology, Shanghai 201418, China

* Correspondence: zhangch@qdu.edu.cn

1. Catalyst characterization

Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7800F) was used to characterize the morphology features of the catalysts. X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (Rigaku Ultima IV, 40 kV) with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). Nitrogen adsorption-desorption isotherms were measured on a Quantachrome Autosorb-IQ3 automated sorption system. The specific surface areas were computed using the Brunauer-Emmett-Teller (BET) method. Raman spectra were recorded on a Renishaw inVia plus Micro-Raman spectrometer using a 50 mW DPSS laser with 532 nm excitation wavelength. The temperature-programmed desorption of oxygen (O_2 -TPD) technique was employed to conducted on a chemisorption analyzer (Quantachrome, Chembet Pulsar). A sample was pretreated under the conditions of 3 vol.% O_2 in Helium at 300 °C for 2 h. Then, the sample was cooled to room temperature followed by heating to 900 °C at a ramp of 10 °C min^{-1} in He. The X-ray photoelectron spectroscopy (XPS) technique was used to analyze the chemical composition and metal valances with the C 1s binding energy (284.6 eV) of adventitious carbon as an internal standard to calibrate all spectra on a PHI 5000 Versa Probe III equipment using Al $\text{K}\alpha$ radiation (1486.6 eV) as the radiation source flow.

2. Electrochemical measurements

Electrochemical measurements of the catalysts were conducted using the three-electrode testing system on an Autolab Potentiostat PGSTAT 302N at room temperature. First, 5 mg of catalyst powder and 2.5 mg of Cabot Vulcan carbon (XC-72) were dispersed into a mixed solution containing 750 μL of deionized water, 250 μL of isopropyl alcohol, and 20 μL of Nafion (5 wt.%). The mixture was subjected to ultrasonic treatment for 30 min to prepare a homogeneous catalyst ink. The working electrode was fabricated by depositing 10 μL of the catalyst ink onto the glassy carbon surface of the rotating ring-disk electrode (RRDE) with an area of 0.19625 cm^2 , resulting in a catalyst loading value of 0.25 mg cm^{-2} . The Hg/HgO was used as the reference electrode and platinum foil (1 cm^2) served as the counter electrode. The electrolyte was employed by 0.1 mol L^{-1} KOH solution. For comparison, commercial Pt/C and RuO_2 were also evaluated in ORR and OER under the same testing conditions, respectively. The potential data obtained from the Hg/HgO electrode ($E_{\text{Hg/HgO}}$) was converted to potentials vs. the reversible hydrogen electrode (E_{RHE}) using the following formula:

$$E_{RHE} = E_{H_2/H_2O} + 0.059 \times \text{pH} + 0.098 \quad (\text{S1})$$

In an oxygen-saturated KOH electrolyte, high-purity oxygen (99.99%) was continuously bubbled for 30 min. The linear sweep voltammetry (LSV) curves were collected with a scanning speed of 2 mV·s⁻¹ under rotating speeds ranging from 400 to 2500 rpm. The transferred electron number (n) was calculated by the Koutecky-Levich (K-L) equations:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}} \quad (\text{S2})$$

$$B = 0.2nFD_0^{2/3}v^{-1/6}C_0 \quad (\text{S3})$$

$$J_K = nFKC_0 \quad (\text{S4})$$

where J (mA cm⁻²) is the measured current density, J_L (mA cm⁻²) and J_K (mA cm⁻²) are the diffusion- and kinetic- limiting current densities, ω (rpm) is the electrode rotation rate, F is the Faraday constant (96,500 C mol⁻¹), C_0 is the bulk concentration of oxygen (1.2×10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of oxygen in the electrolyte (1.9×10⁻⁵ cm² s⁻¹), v is the kinematic viscosity of the electrolyte and K is the electron-transfer rate constant.

The rotating ring-disk electrode (RRDE) curves were recorded at a scanning rate of 2 mV s⁻¹ in an oxygen-saturated 0.1 M KOH electrolyte. The HO₂⁻ % and n are determined according to the following formulas:

$$\text{HO}_2^- \% = 100 \frac{2 I_r/N}{I_d + I_r/N} \quad (\text{S5})$$

$$n = 4 \frac{NI_d}{NI_d + I_r} \quad (\text{S6})$$

where I_d (mA) is the disk current, I_r (mA) is the ring current and $N = 0.249$ is the current collection efficiency of the platinum ring.

Tafel slopes were analyzed by the Tafel equations:

$$\eta = a + b \times \log |j| \quad (\text{S7})$$

$$a = \frac{RT}{\alpha F} \log j^0 \quad (\text{S8})$$

$$b = -\frac{RT}{\alpha F} \quad (\text{S9})$$

Where η (V) is the overpotential, j^0 (A) is the exchange current density, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T (K) is the absolute temperature, α is the transfer coefficient, and F is the Faraday constant (96,500 C mol⁻¹).

The LSV curves were acquired at a scanning rate of 2 mV s⁻¹ in an oxygen-saturated KOH electrolyte to evaluate the OER performance of the catalysts. The electrochemical impedance spectroscopy (EIS) measurements were conducted at 1.55 V (vs. RHE).

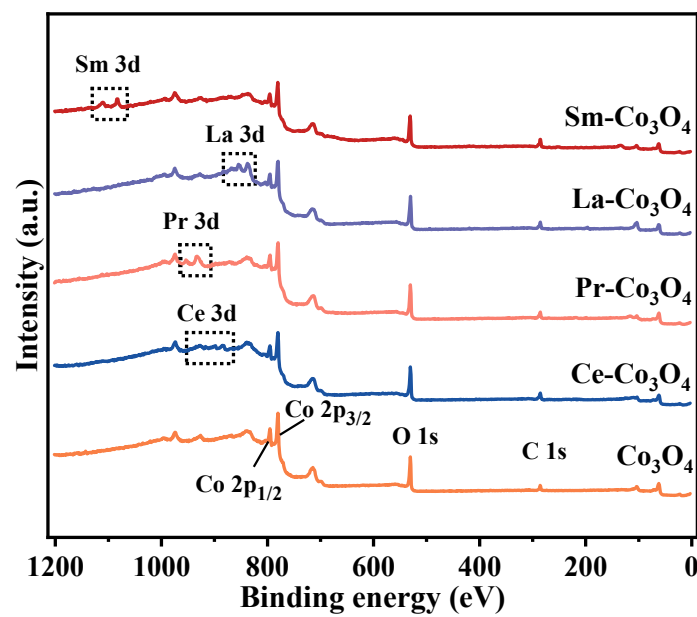


Figure. S1 Wide-scan XPS spectra of Co_3O_4 and $\text{M-Co}_3\text{O}_4$

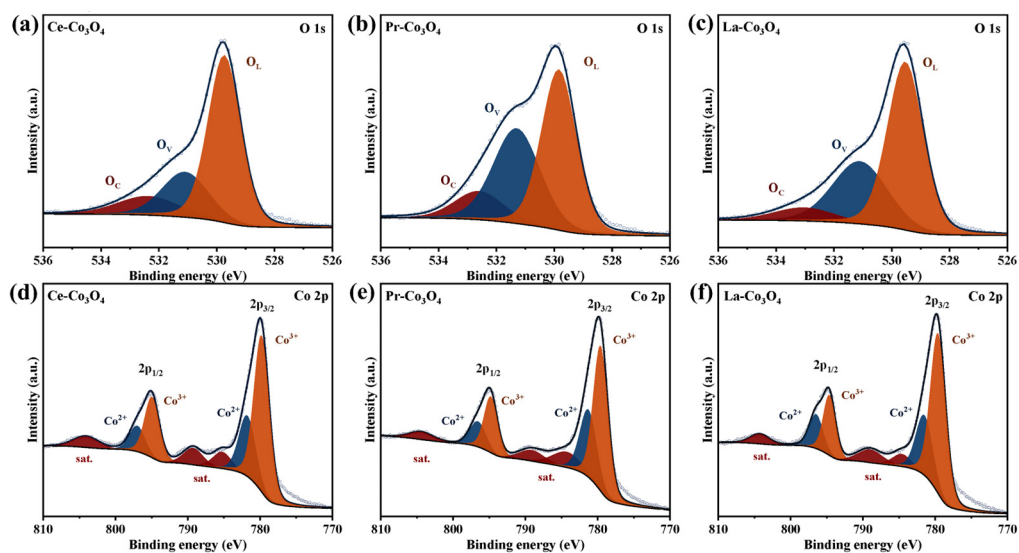


Figure. S2 O 1s XPS spectra of (a) Ce-Co₃O₄, (b) Pr-Co₃O₄ and (c) La-Co₃O₄, Co 2p XPS spectra of (d) Ce-Co₃O₄, (e) Pr-Co₃O₄ and (f) La-Co₃O₄

Table S1 Textural properties of the catalyst derived from the nitrogen physisorption measurements

Catalysts	Specific Surface Area ^a (m ² g ⁻¹)	Total Pore Volume ^b (cm ³ g ⁻¹)	Pore Diameter ^c (nm)
Co ₃ O ₄	19.2	0.12	34.6
Ce-Co ₃ O ₄	32.6	0.16	18.1
Pr-Co ₃ O ₄	58.4	0.17	13.8
La-Co ₃ O ₄	56.9	0.15	12.1
Sm-Co ₃ O ₄	67.2	0.19	10.2

^a Determined by the Brunauer-Emmett-Teller method.

^b Estimated from the volume adsorbed at the relative pressure $p/p_0 = 0.99$.

^c Determined by the Barret-Joyner-Halenda method.