Poly-active centric Co_3O_4 - CeO_2 /Co-N-C composites as superior oxygen reduction catalysts for Zn-air batteries

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ABSTRACT Zinc-air battery is one of the most promising next-generation energy conversion and storage systems. Green and low-cost catalysts with high oxygen reduction reaction (ORR) catalytic activity are desired to meet the requirements of Zinc-air batteries. Herein, poly-active centric Co_3O_4 - CeO_2 /Co-N-C (ketjenblack carbon) catalysts were prepared by a facile method. The Co_3O_4 and CeO_2 nanoparticles are uniformly anchored on the surface of Co and N doped carbon support. The half-wave potential of Co_3O_4 - CeO_2 /Co-N-C in the rotating disk electrode testing is close to that of Pt/C. The Zn-air battery using Co_3O_4 - CeO_2 /Co-N-C as the cathode catalyst can provide a high specific capacity of 728 mA h g^{-1} at 20 mA cm^{-2} and maintain a stable discharge voltage. The remarkable catalytic performance is mainly attributed to the synergistic effect among Co_3O_4 , CeO_2 and Co-N-C, the outstanding electrical conductivity and the large surface area. Benefitting from the high catalytic activity, environmental friendliness and the facile synthesis process, Co_3O_4 - CeO_2 /Co-N-C catalyst lends itself well to a great prospect in the application of metal-air batteries.

Keywords: electrocatalyst, Zn-air battery, oxygen reduction reaction, cobalt oxide, cerium oxide

INTRODUCTION

With the increasing demands of energy and the growing public concerns about excessive consumption of fossil

fuels, it is very imperative to develop alternative and sustainable energy conversion and storage systems such as fuel cells, metal-air batteries, lithium ion batteries and supercapacitors with low cost, environmental friendliness and high efficiency [1–4]. Among them, metal-air batteries and fuel cells have great potentials for next-generation electric vehicles if the sluggish kinetics of oxygen reduction reaction (ORR) can be enhanced significantly [5–8]. To date, platinum (Pt) and its alloys are considered as the most efficient catalysts for ORR, but their prohibitive cost, scarcity and insufficient durability hinder their wide application [9–12]. Therefore, it is highly desirable and still challenging to develop non-precious metal ORR catalysts with comparable catalytic performance and higher stability. Over recent years, a series of non-precious metal catalysts (NPMCs) have been exploited for ORR [13–16], including metal-free nitrogen-doped carbon materials [17–19], nanocarbon/transition-metal compound hybrids [20–22] and metal oxides [23–25]. Among metal oxides, cobalt trioxide (Co_3O_4) shows good ORR performance but low electrical conductivity. Liu *et al.* [26] reported Co_3O_4 anchored on N-doped ketjenblack (Co_3O_4 /N-KB) as an ORR electrocatalyst for Al-air battery. They considered that the improved electrical conductivity and the synergetic chemical coupling effect between Co_3O_4 and N-KB boosted the performance of Co_3O_4 /N-KB. Huang *et al.* [27] utilized the nitrogen-

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doped partially exfoliated multiwall carbon nanotubes as support to greatly improve the performance of Co_3O_4 nanoparticles. In this work, we synthesized a highly efficient ORR electrocatalyst consisting of Co_3O_4 and CeO_2 nanoparticles supported on Co and N doped KB. The addition of CeO_2 with the “oxygen buffer” ability greatly increases the catalytic performance of Co_3O_4 .

EXPERIMENTAL SECTION

Chemicals

The KB carbon (ECP600JD) used in this work was purchased from the Lion King Co. Ltd. (Japan). $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ ($\geq 99.5\%$), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.5\%$), melamine ($\geq 99\%$) and Nafion emulsion (5 wt%) were from Sigma-Aldrich (China). Potassium hydroxide ($\geq 96\%$) was bought from Sinopharm Chemical Reagent Co. Ltd. (China). Ethanol and ammonia ($\geq 99.8\%$) were from Tianjin Rgent® Chemicals Co. Ltd. (China). Commercial 20% Pt/C catalyst from Johnson Matthey (HISPEC3000, USA) was used as a benchmark. All aqueous solutions were prepared with deionized water.

Sample preparation

The synthesis process of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-C}$ catalyst is

shown in Scheme 1. Firstly, KB and melamine with a mass ratio of 1:1 were added in 200 mL of anhydrous ethanol under stirring to form a uniform suspension. The mixture was dried at 80°C for 8 h under stirring and at 60°C vacuum oven overnight. The obtained sample was ground and denoted as MMKB. Cobalt acetate (1.0 mmol) and 0.5 mmol of cerium nitrate were added to 70 mL of deionized water under stirring before regulating the pH of the solution to 8.0 with ammonia. After that, the above solution and MMKB were moved to a 100-mL Teflon autoclave after stirring at 80°C for 30 min and the mixture reacted at 150°C for 12 h. After the reaction, the precipitate was filtrated and washed several times to remove the impurities and dried at 80°C overnight. Finally, it was calcined in a muffle furnace at 320°C for 2 h with a heating rate of 5°C min^{-1} and the obtained sample was noted as $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$. For comparison, the $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ and $\text{CeO}_2/\text{N-KB}$ were prepared in a similar way without cerium nitrate/cobalt acetate, respectively.

Materials characterization

The structural information was examined by X-ray powder diffraction (XRD) with Cu K α radiation (Bruker D8 Advance, $\lambda=1.5418 \text{ \AA}$) over the 2θ range of $10^\circ\text{--}80^\circ$

Scheme 1 Schematic illustration of the synthetic procedure for $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-C}$.

with a scan speed of 8° min^{-1} at room temperature. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were attained from field emission scanning electron microscope (Hitachi, SU8220) and spherical aberration correction transmission electron microscope (STEM, Titan G2 60-300 with image corrector), respectively. Raman spectroscopy was performed on a LabRAM HR800 microscope using a 632.81-nm excitation laser. The specific surface area was tested by a specific surface & pore size analysis instrument (Beishide Instrument, 3H-2000PS1). The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) on an Escalab 250Xi photoelectron spectrometer (Thermo Fisher) at 2.4×10^{-10} mbar using a monochromatic Al K α X-ray beam (1486.60 eV). All binding energies were referenced to the C 1s peak (284.60 eV). The thermal gravimetric analysis (TGA) was conducted to quantify the carbon material by an SDT 2960 simultaneous DSC-TGA in the air from room temperature to 900°C with a heating rate of $10^\circ\text{C min}^{-1}$. The Co and Ce elemental analyses in the metal oxide were carried out through the Thermo Fisher ICAP RQ inductively coupled plasma mass spectrometry (ICP-MS) spectrometer.

Electrochemical measurements

The electrochemical characterization was carried out in O_2 -saturated 0.1 mol L^{-1} KOH by a CHI 750E electrochemical workstation. The three-electrode system consists of an Ag/AgCl electrode (filled with 3.5 mol L^{-1} KCl) as the reference electrode, a graphite rod as the counter electrode, and a glassy carbon (GC) electrode loaded with the catalyst as the working electrode. The catalyst ink was prepared by dispersing the active material (5 mg) in a solution containing ethanol (1000 μL), deionized water (900 μL) and 100 μL of 5 wt% Nafion (Nafion 117, DuPont). To prepare the working electrode, 15 μL of the catalyst ink was drop-casted onto a polished GC ($\varphi = 4.0 \text{ mm}$) of the rotating ring-disk electrode (RRDE) device (RRDE-3A) and was dried at room temperature to get the catalyst loading of 0.3 mg cm^{-2} . The linear sweep voltammetry (LSV) curves were recorded at a scan rate of 2 mV s^{-1} with 1600 rpm and corrected with iR -drop compensation. All potentials reported in this study were referenced to the reversible hydrogen electrode (RHE) according to the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.205. \quad (1)$$

Koutecky-Levich (K-L) plot (J^{-1} vs. $\omega^{-1/2}$) was used to calculate the number of electrons transferred (n). The

rotating disk electrode measurement (ALS Co., Ltd) was conducted at a scan rate of 2 mV s^{-1} under various rotation speeds (400, 625, 900, 1225, 1600, 2025 and 2500 rpm). The number of electrons transferred (n) can be obtained from the slope of the K-L plot based on the K-L equation [28,29]:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\sqrt{\omega}}, \quad (2)$$

$$B = 0.62nFD^{2/3}\nu^{-1/6}C_0.$$

J is the measured current density. J_L and J_K are the diffusion limiting current density and the kinetic limiting current density, respectively. B is gotten from the slope of the K-L curve and ω is the rotation speed in rpm. F , D , ν and C_0 represent the Faraday constant ($96,485 \text{ C mol}^{-1}$), the oxygen diffusion coefficient in 0.1 mol L^{-1} KOH ($1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), the kinetic viscosity ($10.09 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$) and the bulk concentration of oxygen ($1.26 \times 10^{-6} \text{ mol cm}^{-3}$), respectively.

RRDE measurement was performed to acquire the total electron transfer number (n) and hydrogen peroxide yield ($\%\text{H}_2\text{O}_2$) based on the following equations [30]:

$$n = \frac{4I_{\text{disk}}}{I_{\text{ring}}/N + I_{\text{disk}}}, \quad (3)$$

$$\%\text{H}_2\text{O}_2 = \frac{2I_{\text{ring}}/N}{I_{\text{ring}}/N + I_{\text{disk}}} \times 100\%. \quad (4)$$

I_{disk} and I_{ring} are the voltammetric currents at the disk and ring electrode, respectively. N is the RRDE collection efficiency whose value is determined to be 0.43.

Zn-air battery measurements

Zn-air battery was assembled with the air diffusion cathode, Zn anode and 6 mol L^{-1} KOH electrolyte. The air diffusion cathode was prepared through dripping 300 μL of catalyst ink (5 mg mL^{-1}) onto carbon cloth (W1S1009, Ce Tech Co., Ltd) with the loading of 1.5 mg cm^{-2} . The galvanostatic discharge was carried out with a LAND testing system.

RESULTS AND DISCUSSION

The XRD patterns of $\text{CeO}_2/\text{N-KB}$, $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ and $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ are shown in Fig. 1a. The sharp diffraction peaks of $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ are indexed to Co_3O_4 (PDF#42-1467) and only CeO_2 is observed in $\text{CeO}_2/\text{N-KB}$ except carbon. The four sharp diffraction peaks of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ at approximate 28.6° (111), 32.3° (200), 48.2° (220) and 56.4° (311) are consistent with CeO_2 (PDF#34-0394), and the diffraction peaks at 31.3° , 36.9° , 44.8° , 59.4° and 65.2° are assigned to

Figure 1 XRD patterns of $\text{CeO}_2/\text{N-KB}$, $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ and $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ composite with the standard diffraction card of Co_3O_4 (PDF#42-1467) and CeO_2 (PDF#34-0394).

Co_3O_4 (PDF#42-1467). The local magnification of the XRD pattern of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ is shown in Fig. S1 and a broad peak in the range of $20^\circ\text{--}25^\circ$ is ascribed to carbon. According to the Scherrer equation [31], the crystal sizes of CeO_2 and Co_3O_4 in $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ were calculated to be 9.3 and 4.9 nm respectively, which are slightly smaller than those in $\text{CeO}_2/\text{N-KB}$ (10.3 nm) and $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ (6.7 nm).

The SEM, TEM and high-resolution TEM (HRTEM) images of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ are presented in Fig. 2. The size of the $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ aggregates is about 100 nm with a porous structure that is beneficial to the exposure of active sites (Fig. 2a and b). Fig. 2c and e are the TEM images of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ and the electron diffraction pattern corresponding to Fig. 2c is shown in Fig. S2. On account of the observation of some electron diffraction spots and rings in the electron diffraction pattern, the Co_3O_4 and CeO_2 in the catalyst are in the form of nano size polycrystals. The concentric rings correspond to the crystal planes of Co_3O_4 ((220), (422), (531)) and CeO_2 ((111), (220), (222)). In addition, the corresponding HRTEM images of the two red square regions marked in Fig. 2c and e are exhibited in Fig. 2d and f. The fringe spacings of 0.286 and 0.202 nm belong to the (220) and (400) planes of Co_3O_4 (PDF#42-1467). Meanwhile, the lattice distances of 0.163, 0.312 and 0.191 nm are well in accordance with the (311), (111) and (220) crystal planes of CeO_2 (PDF#34-0394), respectively. According to the STEM-EDS mapping analysis (Fig. 3), the C, N, O, Co and Ce elements distribute uniformly on the carbon support. The existence of N element provides an evidence for the successful doping of N.

TGA/DSC analysis (Fig. S3) was conducted to quantify

the oxide loading on KB carbon in the $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ catalyst. The composites were heated from room temperature to 900°C in air with a ramp rate of $10^\circ\text{C min}^{-1}$. A slight mass loss below 100°C is due to the release of the adsorbed water. A drastic weight loss of approximately 87.89 wt% was observed over the temperature range between 330 and 550°C , corresponding to the combustion of the carbon material. When the temperature exceeded 550°C , the weight kept stable with only oxides left.

In order to measure the specific surface area of the hybrid catalyst, the specific surface and pore size analyses were applied. The N_2 adsorption-desorption curve (Fig. 4a) presents a H3-type of hysteresis loop at relative pressures of P/P_0 ranging from 0.45 to 1, indicating the presence of abundant mesoporous [32]. The pore size of the $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ is mainly centered at 2.3 nm (Fig. 4a inset), which demonstrates the mesoporous characteristic, consistent with the result of the N_2 adsorption-desorption curve. The specific surface area, average pore size and pore volume of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$, MMKB and KB are compared in Table S1. The specific surface area of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ ($869.5 \text{ m}^2 \text{ g}^{-1}$) is lower than that of KB ($1369.4 \text{ m}^2 \text{ g}^{-1}$) but higher than that of MMKB ($643.8 \text{ m}^2 \text{ g}^{-1}$). The high specific surface area of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ facilitates the exposure of active sites and the transfer of reactants and products, which are beneficial for the ORR.

Raman spectroscopy (Fig. 4b) was used to further identify the structural information of the catalysts. Two characteristic peaks at approximately 1320 cm^{-1} (D band) and 1600 cm^{-1} (G band) were observed in all four samples ($\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$, $\text{Co}_3\text{O}_4/\text{N-KB}$, $\text{CeO}_2/\text{N-KB}$ and KB) [33]. The D band represents a disordered carbon and the G band is attributed to sp^2 hybrid graphite carbon. Moreover, the relative intensity ratio of the peaks (I_D/I_G) provides a gauge for the degree of disorder of the material [34]. Obviously, the I_D/I_G value of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ ($I_D/I_G=1.53$) is higher than the others (KB ($I_D/I_G=1.34$), $\text{CeO}_2/\text{N-KB}$ ($I_D/I_G=1.32$) and $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ ($I_D/I_G=1.35$)). The high I_D/I_G ratio for $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ is due to the structural defects caused by nitrogen atom doping onto the carbon materials. These kinds of defects may improve the ORR performance [35,36]. In addition, the prominent peaks at 457 and 675 cm^{-1} are derived from Co_3O_4 and CeO_2 nanoparticles, respectively, which confirms the coexistence of these nanoparticles [37,38].

To further identify the valence states and surface compositions of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$, XPS measurements were conducted (Fig. 5). The corresponding fitting

Figure 2 SEM (a, b), TEM (c, e) and HRTEM (d, f) images of the prepared $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$.

results of the spectra are presented in Tables S2–S6. The signals of C, N, O, Co and Ce elements were detected in the survey spectrum (Fig. 5a). The C 1s spectrum in Fig. 5b shows the peak at 284.8 eV for the C–C/C=C bonds [39] and the peaks at 285.5, 287.5 and 289.0 eV originated from C–N, C=N and C=O bonds, respectively [40,41]. The lone pair electrons of N atom can form a delocalized conjugated system with the sp^2 -hybridized carbon frameworks to strengthen the interactions be-

tween the carbon base and metal [42]. Similarly, the bonding configurations of nitrogen atoms in N 1s spectra (Fig. 5c) can be divided into five peaks at 398.6, 399.5, 400.4, 401.2 and 406.7 eV, corresponding to pyridinic-N, Co–N, pyrrolic-N, graphitic-N and nitrate-N species, respectively [43–45]. The nitrogen atoms primarily exist in the form of pyridinic-N (44.0%) and Co–N (28.0%) (Table S3), which play a key role in ORR. The high content of pyridinic-N and Co–N can effectively

Figure 3 STEM and elemental mapping analyses of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ composite: (a) STEM image. (b) STEM image taken from the middle selected region marked in (a). (c–j) The corresponding elemental mapping images of (c) C-K, (d) N-K, (e) O-K, (f) Co-K, (g) Co-L, (h) Ce-K, (i) Ce-L and (j) Ce-M.

Figure 4 (a) N_2 adsorption-desorption isotherm of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$. The inset is the corresponding pore size distribution curve. (b) Raman spectra of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$, $\text{Co}_3\text{O}_4/\text{Co-N-KB}$, $\text{CeO}_2/\text{N-KB}$ and KB.

strengthen the electron-transfer of the Co_3O_4 and CeO_2 through a change in the electronic delocalization effect of the carbon atoms and a decrease in the loss of electron transfer energy [46]. The graphitic-N can improve the mobility and conductivity of the catalyst [47]. Moreover, the O 1s spectrum could be clearly deconvoluted into three typical peaks at 530.0, 532.1, and 533.6 eV (Fig. 5d). The binding energy at 530.0 eV corresponds to the O atoms in metal-oxygen bonds (denoted as O_a) and 533.6 eV is due to chemically bonded water and adsorbed water (denoted as O_y) [48]. The peak at 532.1 eV might be assigned to the defect oxygen or the surface oxygen (denoted as O_β) [49]. As shown in Fig. 5e, the Co 2p_{3/2} spectrum can be deconvoluted into five peaks and the peaks at binding energies of 779.8, 780.8 and 782.5 eV

correspond to Co^{3+} , Co^{2+} and Co-N active sites, respectively [50,51]. Meanwhile, the satellite peaks are located at 785.0 and 788.4 eV [52]. Based on Table S5, the average valence of Co_3O_4 is about 2.35 which is lower than the normal average of 2.67, implying the presence of oxygen vacancies in Co_3O_4 . In addition, the binding energy of Co-N in Co 2p_{3/2} spectrum for $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ is 1.3 eV higher than that of $\text{Co}_3\text{O}_4/\text{Co-N-C}$ reported by Li *et al.* [29], while the binding energy of N species in N 1s spectrum for $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ is similar to that of $\text{Co}_3\text{O}_4/\text{Co-N-C}$. Therefore, the CeO_2 interacts with Co-N-KB through the Co, not the N in Co-N-KB. Two kinds of peaks (3d_{3/2} and 3d_{5/2}) were detected in the Ce 3d spectrum (Fig. 5f). The peaks marked as B4, B3, B1, A4, A3, and A1 are assigned to Ce^{4+} , whereas the peaks denoted as

Figure 5 XPS spectra of (a) $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$, (b) C 1s, (c) N 1s, (d) O 1s, (e) Co 2p and (f) Ce 3d for $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$.

B2 and A1 are attributed to Ce^{3+} [53]. Owing to the presence of Ce^{3+} , oxygen vacancies and unsaturated chemical bond are introduced in CeO_2 nanoparticle to create a charge imbalance. Furthermore, the Co and Ce elemental analyses in the metal oxides and the atomic ratio of each element in $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ are shown in Tables S7 and S8, respectively.

Cyclic voltammetry curves in O_2 - (solid line) and Ar-saturated (dot line) 0.1 mol L^{-1} KOH solutions within the potential ranging from 0.17 to -1.17 V (vs. RHE) are presented in Fig. 6a. The CV curves in the Ar-saturated

electrolyte have invisible peaks for all the metal oxide-based samples. Conversely, when the electrolyte is saturated with O_2 , there is a well-defined cathodic ORR peak that highlights the significant electrocatalytic activity for ORR. $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ displays an oxygen reduction peak at 0.81 V, which is much more positive than those of $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ (0.76 V) and $\text{CeO}_2/\text{N-KB}$ (0.71 V) and comparable to that of Pt/C (0.83 V). The remarkably improved ORR performance of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ compared with $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ and $\text{CeO}_2/\text{N-KB}$ may be attributed to the synergistic interaction among

Figure 6 (a) CV curves of the fabricated catalysts and commercial Pt/C in O_2 -solid line and Ar-saturated (dot line) 0.1 mol L⁻¹ KOH within the potential ranging from 0.17 to -1.17 V (vs. RHE) at a scan rate of 10 mV s⁻¹. (b) LSV curves of blank, fabricated catalysts and commercial Pt/C in O_2 -saturated 0.1 mol L⁻¹ KOH solution with a scan rate of 2 mV s⁻¹ and a rotation speed of 1600 rpm. (c) LSV curves of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ in O_2 -saturated 0.1 mol L⁻¹ KOH solution at a scan rate of 2 mV s⁻¹ with different rotating speeds and (d) the corresponding K-L plots at different potentials.

Co_3O_4 , CeO_2 and Co-N-C active sites. To gain insight into the ORR catalytic performance, the LSV curves of the different materials in O_2 -saturated 0.1 mol L⁻¹ KOH at 1600 rpm are compared in Fig. 6b. The MMKB, $\text{CeO}_2/\text{N-KB}$ and $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ show much lower ORR activities than Pt/C. On the other hand, the $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ sample has an onset potential of 0.93 V similar to Pt/C (0.95 V). Remarkably, the half-wave potential of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ (0.80 V) is only 10 mV lower than that of Pt/C, where the voltage gap is lower than that of Co-N-C reported by Wu *et al.* [54]. Hence, the significantly improved ORR performance of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ is ascribed to the synergistic interaction among CeO_2 , Co_3O_4 and Co-N-C active sites. In addition, the LSV curves of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ with different rotating rates from 400 to 2500 rpm were carried out to study the ORR kinetics (Fig. 6c). The K-L plots are given in Fig. 6d, which show good linear relationship. The linearity of the K-L plots manifests a diffusion-limited reaction on $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ electrode. Through

the K-L Equation (2), the electron transfer numbers (n) of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ at 0.50, 0.55, 0.60, 0.65, 0.70 and 0.75 V vs. RHE were calculated to be 3.7–3.8, respectively. The peroxide yield (% H_2O_2) derived from the RRDE measurements in Fig. 7a reaches 10.18% between 0.5 and 0.7 V, which is lower than that of $\text{CeO}_2/\text{N-KB}$ (18.40%) and $\text{Co}_3\text{O}_4/\text{Co-N-KB}$ (17.84%) and close to that of Pt/C (7.25%). The corresponding RRDE curves are shown in Fig. S4. The average electron transfer numbers of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ ($n = 3.80$) and Pt/C ($n = 3.86$) are both close to 4, proving that the four-electron reaction dominates the pathway of ORR. The Tafel slopes (Fig. S5) were calculated to further understand the ORR kinetic performance of catalysts. The Tafel slope of $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ (83 mV dec⁻¹) is close to that of Pt/C (75 mV dec⁻¹), indicating the good kinetic behavior for ORR.

The long-time stability of the $\text{Co}_3\text{O}_4\text{-CeO}_2/\text{Co-N-KB}$ catalyst was investigated by accelerated life test (ALT) with a scanning rate of 100 mV s⁻¹ in the range of 0.2–0.8 V in an O_2 -saturated 0.1 mol L⁻¹ KOH solution. After

Figure 7 (a) Peroxide yield (HO₂⁻%) and electron transfer number (*n*) of different catalysts in a potential range of 0.5–0.7 V (vs. RHE) attained through RRDE. LSV curves of Co₃O₄-CeO₂/Co-N-KB (b) and Pt/C (c) before and after 500, 1000, 5000 cycles CV at 0.2–1.0 V (vs. RHE) in O₂-saturated 0.1 mol L⁻¹ KOH. (d) Chronoamperometric of Co₃O₄-CeO₂/Co-N-KB and Pt/C in O₂-saturated 0.1 mol L⁻¹ KOH electrolyte at 0.65 V (vs. RHE) and 1600 rpm.

5000 cycles, the half-wave potential of Co₃O₄-CeO₂/Co-N-KB is only negatively shifted by 27 mV (Fig. 7b) which is similar to that of Pt/C (28 mV, Fig. 7c). The stability of Co₃O₄-CeO₂/Co-N-KB and Pt/C was also investigated by a chronoamperometry test (*i*-*t* relationship) at 0.65 V in the same electrolyte. As shown in Fig. 7d, Co₃O₄-CeO₂/Co-N-KB remains 90% of the initial current after 10 h of testing, while Pt/C only remains 65%.

Zn-air battery measurements

The Zn-air battery performance of Co₃O₄-CeO₂/Co-N-KB was tested in a battery illustrated in Fig. 8a. Fig. 8b compares the Nyquist plots of the Zn-air battery with Co₃O₄-CeO₂/Co-N-KB and Pt/C as the catalysts at open circuit voltage. The semicircle on the Nyquist plot of Co₃O₄-CeO₂/Co-N-KB is lower than that of Pt/C. The galvanostatic discharge curves of the two batteries at different current densities are shown in Fig. 8c. The open circuit voltage of the battery containing Co₃O₄-CeO₂/Co-N-KB is 1.44 V, which is slightly lower than that of the one containing Pt/C (1.47 V). In the larger current density regions (5–20 mA cm⁻²), the voltage of the two bat-

teries are rather similar. In Fig. 8d, the battery with Co₃O₄-CeO₂/Co-N-KB could run stably until the Zn anode is completely consumed during the long-term galvanostatic discharge producing high specific capacities (772 mA h g⁻¹ at 5 mA cm⁻² and 728 mA h g⁻¹ at 20 mA cm⁻², calculated by the consumed Zn mass). The excellent electrochemical performance and the long-term stability of the Co₃O₄-CeO₂/Co-N-KB catalyst make it a promising candidate for fuel cells and metal-air batteries.

CONCLUSIONS

In summary, the poly-active centric Co₃O₄-CeO₂/Co-N-KB catalyst with a good electronic conductivity and large surface area was prepared. Due to the synergistic effect among Co₃O₄, CeO₂ and Co-N-KB, Co₃O₄-CeO₂/Co-N-KB favors the four-electron pathway of ORR and presents good long-time stability. The half-wave potential of Co₃O₄-CeO₂/Co-N-KB (0.80 V vs. RHE) is close to that of Pt/C (0.81 V vs. RHE). The Zn-air battery with Co₃O₄-CeO₂/Co-N-KB as the catalyst provides a high specific capacity of 728 mA h g⁻¹ at 20 mA cm⁻². The low cost, good ORR performance and long-term stability make

Figure 8 (a) Schematic of a Zn-air battery with Co₃O₄-CeO₂/Co-N-KB catalyst. (b) Nyquist plots of Co₃O₄-CeO₂/Co-N-KB-battery and Pt/C-battery at open circuit state. (c) Galvanostatic discharge curves of Zn-air batteries with Co₃O₄-CeO₂/Co-N-KB and Pt/C as cathode catalysts at different current densities. (d) Long-term galvanostatic discharge curves of the Zn-air battery with Co₃O₄-CeO₂/Co-N-KB catalyst at 5 mA cm⁻² and 20 mA cm⁻².

Co₃O₄-CeO₂/Co-N-KB a promising catalyst for fuel cells and metal-air batteries.

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Author contributions Li G and Mu Y synthesized the material, did the SEM test, collected the electrochemical data and wrote the manuscript. Chen Y and Liu G did the XRD and XPS tests. Huang Z and Wang N analyzed the experimental data. Liu J conducted the TGA and electrochemical tests. Li OL and Shao M analyzed the experimental data and modified the manuscript. Shi Z conceived and supervised the experiments, and modified the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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多活性中心 Co_3O_4 - CeO_2 /Co-N-C复合材料作为锌空气电池的优良氧还原催化剂

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摘要 为了满足新一代金属空气电池对绿色、低成本且具有高氧还原催化活性催化剂的迫切需求, 本文通过简便方法制备了具有多活性中心的 Co_3O_4 - CeO_2 /Co-N-C(科琴黑)氧还原催化剂。其中, Co_3O_4 和 CeO_2 纳米颗粒均匀地固定在Co、N共掺杂的碳载体表面。 Co_3O_4 - CeO_2 /Co-N-C在旋转圆盘电极测试中的半波电位与Pt/C接近。以 Co_3O_4 - CeO_2 /Co-N-C作为阴极催化剂的锌空气电池可以在 20 mA cm^{-2} 下提供 728 mA h g^{-1} 的高比容量并能够维持稳定的放电电压。其优异的催化性能主要归功于 Co_3O_4 、 CeO_2 和Co-N-C之间的协同作用、高导电性和大比表面积。 Co_3O_4 - CeO_2 /Co-N-C催化剂具有催化活性高、环境友好、合成工艺简单等优点, 在金属空气电池中具有广阔的应用前景。