Insight on the active sites of CoNi alloy embedded in N-doped carbon nanotubes for oxygen reduction reaction

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ABSTRACT Transition metal alloy electrocatalysts have sparked intense interest for their use in oxygen reduction reaction (ORR). However, there is almost no corresponding research on the alloy active sites. In this study, CoNi alloy nanoparticles embedded in bamboo-like N-doped carbon nanotubes (CoNi-NCTs) as catalysts constructed by a facile pyrolysis of Prussian blue analogs were investigated. The density functional theory calculation reveals that the oxygen molecules are more easily adsorbed on the Ni sites in these catalysts, while the Co sites favor the formation of OOH* intermediates during ORR. In addition, the cooperation of the CoNi alloys with the N-doped carbon benefits electron transfer and promotes electrocatalytic activity. The optimized CoNi-NCT shows remarkable ORR catalytic activity with an half-wave potential ($E_{1/2}$) of 0.83 V, an onset potential (E_{onset}) of 0.97 V, and superior durability, all of which surpass the commercial Pt/C catalysts. The assembled zinc-air battery delivers a small charge/discharge voltage gap of 0.86 V at 10 mA cm⁻², a high-power density of 167 mW cm⁻², and good stability (running stably over 900 cycles).

Keywords: N-doped carbon nanotube, CoNi alloy, active site, oxygen reduction reaction, Zn-air battery

INTRODUCTION

With the increasing pressure from energy consumption levels and environmental problems, various energy storage and conversion systems have been extensively developed by using economical and sustainable clean energy to replace traditional fossil fuels [1–3]. Proton exchange membrane fuel cells and zinc-air batteries (ZABs) are the most promising devices due to their clean energy con-

version pathways and high efficiency [4]. Oxygen reduction reaction (ORR) is kinetically sluggish pivotal half-reaction in which the four-electron reaction pathway is much more popular [5]. Pt-based precious metal catalysts are consistently used to drive the effective four-electron process (rather than the ineffective two-electron pathway). However, the disadvantages of these Pt-based catalysts that limit their commercial application are high cost, scarcity, and poor stability [6]. Recently, lots of studies have focused on discovering highly effective non-precious materials to replace Pt-based catalysts [7–9]. Transition metal-based compounds (i.e., nitrides, carbides, oxides, and alloy electrocatalysts [10–13]) are promising candidates due to the advantages of their abundance, excellent activity, and durability [14–16]. Additionally, N-containing carbon nanostructures (coupled with transition metal species) can form metal-nitrogen-doped carbon catalysts that increase active centers and improve the stability of ORR [17–22].

Alloys consisting of two or more metal species are much more complex, and they are worth investigating in comparison with single-metal electrocatalysts [23]. The electrons of different metal species transfer due to the differences in electronegativity, resulting in high electrocatalytic activity due to electron rearrangement [24–26]. Therefore, the synergy originating from the difference in electronegativity can be controlled by adjusting the size, morphology, and alloy microstructure. The alloy structure decreases the formation barrier of the oxygen intermediates and promotes the ORR four-electron process. The component also affects the electrocatalytic activity of the alloy electrocatalyst [27–30]. Multiple studies have

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researched the interaction between the alloy and its support, as well as the electron transfer between the metals that compose the alloy nanostructures [31]. However, the role of different metal sites within alloy electrocatalysts is rarely studied. Our group's previous work investigated the change in bond length, coordination number, and valence state of the Fe-Fe bond in FeCo alloy catalysts by *in-situ* X-ray absorption spectroscopy, revealing that the Fe sites were the active centers during the ORR process [32]. It was also confirmed that the Co-N and Co-Co bond in the single-metal Co-N-C catalyst were the active sites for the ORR reaction. These findings provided new insight into the active centers of alloy electrocatalysts toward ORR [33]. In the case of bimetallic alloy catalysts based on the earth-abundant Fe, Co, and Ni elements, FeCo and FeNi alloy electrocatalysts have been studied more than CoNi alloy electrocatalysts, including the synthetic strategies and the mechanism of their synergy [34]. In addition, carbon nanotubes (CNTs) improve ORR activity due to their efficient electron transfer property. The metal nanoparticles encapsulated in CNTs not only promote ORR activity but also exhibit good corrosion and oxidation resistance. Therefore, precise control of the growth of CNTs is beneficial to the exposure of active sites and the promotion of ORR activity [35]. With the consideration of these results, this study designed a CoNi-based catalyst for ORR, in which the embedding of N-doped carbon further improved the activity and stability of the catalyst. The density functional theory (DFT) calculation was conducted to clarify the active sites and electrocatalytic mechanisms.

N-doped carbon nanotubes, embedded with CoNi alloy particles (CoNi-NCTs), were synthesized through a simple pyrolytic strategy. First, CoNi Prussian blue analogs (PBAs) were formed by reacting Co salt with Ni salt that further coordinated with melamine. The PBAs were then pyrolyzed to form CoNi alloys and catalyzed with melamine to form CNT structures. DFT shows that the Ni sites in CoNi alloys facilitate O₂ adsorption, while the Co sites decrease the reaction barrier of the rate-determining step (RDS) (the process of OOH* formation) and promote the four-electron process of the ORR. In addition, the embedded NCT structures could expose more active sites and enhance the mass and electron transfer. They may also prevent the accumulation of alloy nanoparticles. In alkaline electrolytes, the CoNi-NCTs exhibit much better activity and durability when compared with the commercial Pt/C catalysts for ORR. In addition, it shows much better performance than the corresponding benchmark precious metal-based battery when used as an

air-cathode to assemble primary and secondary ZABs.

EXPERIMENTAL SECTION

Synthesis of CoNi-NCT samples

The PBAs were formed by dissolving 1.3 mmol of potassium hexacyanocobaltate(III) and 3.0 mmol of nickel chloride in 80 mL of H₂O and stirred for 20 min. Subsequently, 45 mmol of melamine was added to the above solution and stirred for 6 h. The homogenous blue powder precursor was formed after filtering, washing, and evaporation. The precursor was pyrolyzed at 600°C for 1 h in N₂ at ambient temperature, and then the temperature was continuously raised to 800°C and kept steady for 2 h. The CoNi-NCT samples were obtained after treatment with acid (to remove the extra metal species). For comparison, Co-N-doped carbon (Co-NC) and Ni-NCT samples were also derived from potassium hexacyanocobaltate(III) and nickel chloride catalysts. The molar ratio between the cobalt and nickel salts in the structures was also investigated. The amount of K₃[Co(CN)₆] was changed to 0.75, 2, and 3 mmol, while the amount of nickel chloride was kept constant at 3 mmol to obtain CoNi-NCT-1, CoNi-NCT-2, and CoNi-NCT-3, respectively. The detailed synthetic conditions for all of the samples are listed in Table S1.

Synthesis of NiFeP/carbon cloth as the oxygen evolution reaction (OER) catalyst for assembling the ZAB

A 2 × 3 cm² hydrophilic carbon cloth (CC) was immersed in 60 mL of solution containing 1 mmol of Ni(CH₃COO)₂, 2 mmol of Fe(NO₃)₃·9H₂O, 4 mmol of NH₄F, and 5 mmol of urea. It was then transferred into a 100-mL Teflon-lined stainless-steel autoclave and heated at 100°C for 18 h to obtain NiFe-layered double hydroxide (LDH)/CC. Afterwards, the NiFe-LDH/CC and 0.3 g of NaH₂PO₂ were heated at 400°C for 2 h in N₂ at ambient temperature, to obtain NiFeP/CC.

Characterizations

X-ray diffraction (XRD) patterns were tested by a Rigaku D/max-IIIIB diffractometer using Cu Kα (λ = 1.5406 Å) with the accelerating voltage of 40 kV and the applied current of 20 mA. Raman spectra were performed on a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. Thermogravimetric analyses were recorded on a TA Q600 under a stream of air at a heating rate of 10°C min⁻¹. Scanning electron microscopy (SEM) images were performed on a Hitachi S-4800 instrument operating at 5 kV. Transmission electron microscopy (TEM)

images were measured on a JEOL JEM-2100 electron microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG ESCALABMK II with a Mg KR achromatic X-ray source.

Electrochemical test

The ORR measurements were performed on a Pine instrument (Pine Instrument Company, US) by a modulated speed rotator rotating ring-disk electrode (RRDE) with a glassy carbon disk (diameter: 5.61 mm) and a Pt ring (inner/outer ring diameter: 6.25/7.92 mm). The ORR electrocatalytic activities were measured by a typical three-electrode system, in which a Pt foil (1.0 cm²) and a reversible hydrogen electrode were employed as the counter electrode and reference electrode, respectively. A catalyst ink was prepared by mixing 5 mg of catalyst powder and 2 mL of 0.5% Nafion ethanol solution in an ultrasonic bath for 1 h. Then, 30 μ L of the catalyst ink was slowly dropped onto the glassy carbon disk surface of the RRDE for preparation of the working electrode. The electrocatalytic performance was tested in O₂-saturated 0.1 mol L⁻¹ KOH electrolytes. The linear scan voltammetry (LSV) curves were recorded at a scan rate of 5 mV s⁻¹. The ORR kinetics were analyzed by using the Koutecky-Levich (K-L) equation as follows:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}, \quad (1)$$

$$B = 0.62nFC_0(D_0)^{3/2}\nu^{-1/6}, \quad (2)$$

$$j_K = nFkC_0, \quad (3)$$

where j , j_K , and j_L correspond to the measured, kinetic, and diffusion-limiting current densities, respectively; ω is the angular velocity of the rotating disk ($\omega = 2\pi N$, where N is the linear rotating speed in r min⁻¹); n is the overall number of electrons transferred in the ORR; F is the Faraday constant (96,485 C mol⁻¹); C_0 is the bulk concentration of O₂ (1.22×10^{-6} mol cm⁻³); D_0 is the diffusion coefficient of O₂ (1.93×10^{-5} cm² s⁻¹); ν is the kinematic viscosity of the electrolyte (1.00×10^{-2} cm² s⁻¹); k is the electron transfer rate constant. For the Tafel plot, the j_K was calculated from the mass-transport correction by the following equation:

$$j_K = \frac{j \times j_L}{(j_L - j)}. \quad (4)$$

The electron transfer number (n) was determined by the following equation:

$$n = 4 \times \frac{I_d}{I_d + I_r/N}, \quad (5)$$

where I_d is the disk current, and I_r is the ring current. The RRDE current collection efficiency of N was 0.37. The OER performance was evaluated by a three-electrode system in 1 mol L⁻¹ KOH electrolyte on a CHI660 instrument. The LSV polarization curve was obtained at a sweep rate of 5 mV s⁻¹.

Assembly and test of the ZABs

A homemade liquid ZAB was assembled by using zinc foil as the anode and 6 mol L⁻¹ KOH + 0.2 mol L⁻¹ Zn(CH₃COO)₂ as the electrolyte. The air-cathode was prepared as follows: 5 mg of the catalyst was uniformly dispersed in a mixed solution of 1.5 mL of ethanol and 0.5 mL of 0.5% Nafion solution. The catalyst slurry was then loaded on blank CC and NiFeP/CC with a loading of 1 mg cm⁻² to construct the primary and rechargeable ZABs. The ZABs were tested by a LAND CT2001A model battery test system (LANHE Company, Wuhan) in air atmosphere.

RESULTS AND DISCUSSION

Structural characterizations

Cobalt and nickel salts reacted to form CoNi PBAs. Following this reaction, they were coordinated with melamine. During the pyrolysis process at the relatively low temperature of 600°C, the PBAs were transferred to CoNi alloy nanoparticles, and the melamine was converted into graphitic carbon nitride structures [36,37]. When the temperature increased to 800°C, the graphitic carbon nitride decomposed into a carbon and nitrogen source that formed the bamboo-like NCTs under the catalytic effect of the CoNi alloy [38,39]. As the SEM image shows in Fig. 1a, the CoNi-NCT consists of a bamboo-like NCT with a diameter of ~50 nm. Its hollow structure is clearly observed in Fig. 1b. The Co-NC and Ni-NCT samples were also prepared and derived from cobalt and nickel salts, respectively. The Co-NC sample shows a structure of Co nanoparticles loaded with nanosheet structures (Fig. S1a), while the Ni-NCT sample exhibits CNT structures without bamboo-like morphology. This indicates that cobalt and nickel had a synergistic catalytic effect on the formation of the bamboo-like NCTs. Additionally, the ratio between the cobalt and nickel salts affects the structure of the bamboo-like NCTs. As is demonstrated in Fig. S2, the CoNi-NCT-1, CoNi-NCT-2, and CoNi-NCT-3 samples derived from different ratios of cobalt and nickel salts exhibit CNTs without bamboo-like structures. Therefore, only a specific ratio of the cobalt and nickel salts could catalyze the formation of

Figure 1 (a, b) SEM images, (c) TEM and (d) HRTEM images of the CoNi-NCT. (e) The HAADF-STEM image and (f) the corresponding energy dispersive X-ray spectroscopy elemental mapping images of Co, Ni, C, and N.

perfect bamboo-like NCT structures.

The TEM image confirms that the alloy nanoparticles are located on the top of the CNTs (Fig. 1c). The CoNi nanoparticles were embedded in the graphitic carbon layer, as shown in the high-resolution TEM (HRTEM) image (Fig. 1d). The lattice fringes with distances of 0.34 and 0.204 nm correspond to the graphitic carbon (002) plane and the CoNi alloy (111) plane, respectively [40]. The high-angle annular dark-field scanning TEM (HAADF-STEM) image and the corresponding elemental mapping show that the Co and Ni elements are concentrated in the area of nanoparticles, while the C and N elements are dispersed in the whole area of the nanotube, further demonstrating how the CoNi alloy nanoparticles are embedded in the NCT structures (Fig. 1f).

In Fig. 2a, the XRD patterns of Co-NC and Ni-NCT samples both exhibit the characteristic diffraction peaks of Co (JCPDS#15-0806) and Ni (JCPDS#04-0850). The three diffraction peaks of the CoNi-NCT are located at 44.3° , 51.7° , and 76.1° . They are situated between the characteristic diffraction peaks of Co and Ni, further confirming the existence of the CoNi alloy. The D-band and G-band in Raman spectra are located at 1360 and 1580 cm^{-1} , respectively (Fig. 2b) [41]. The CoNi-NCT exhibits a higher intensity ratio (0.96) between the dis-

ordered carbon and graphitic carbon (I_D/I_G) than Co-NC (0.66) and Ni-NCT (0.53). These ratios indicate that the incorporation of CoNi alloy nanoparticles induces more effective formations that benefit the electrocatalytic activity. As the N_2 adsorption-desorption isotherms show in Fig. 2c, all of the samples exhibit a type IV hysteresis loop. The Brunauer-Emmett-Teller specific surface areas of CoNi-NCT, Co-NC, and Ni-NCT are about 293.8 , 162.5 , and $150.9\text{ m}^2\text{ g}^{-1}$, respectively. The mediate value of the CoNi-NCT facilitates the proper exposure of active sites and electron transfer, thereby enhancing the electrocatalytic activity [42].

XPS further uncovers the surface structure and chemical valence of the samples. The survey XPS spectrum shown in Fig. S3a confirms that the CoNi-NCT is composed of Co, Ni, C, N, and O elements. The Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks in the high-resolution Co 2p spectrum are deconvoluted into Co^0 (778.4 and 793.7 eV) and oxidized Co (785.2 and 801.1 eV) (Fig. 2d). The high-resolution Ni 2p spectrum is divided into Ni^0 , high-valence Ni, and satellite peaks (Fig. 2e). The oxidation of Co and Ni is attributed to the existence of the oxidized layer on the surface of the CoNi alloy nanoparticles. The C 1s spectrum shows four peaks concentrated around 284.6 eV (C-C), 285.5 eV (C-N), 287.6 eV (C=O), and 290.7 eV (π -

Figure 2 (a) XRD patterns, (b) Raman spectra, and (c) N_2 adsorption-desorption isotherms of CoNi-NCT, Co-NC, and Ni-NCT. (d) Co 2p XPS spectra, (e) Ni 2p XPS spectra, and (f) the contents of different N-doping for CoNi-NCT, Co-NC, and Ni-NCT.

π^*) (Fig. S3b). The asymmetric peak of C–N indicates the N-doping in the graphitic carbon nanostructures. As is illustrated in Fig. S3c, the high-resolution N 1s spectrum is mainly deconvoluted into pyridinic-N (398.3 eV), metallic-N (398.9 eV), and graphitic-N (400.7 eV). Both pyridinic-N and metallic-N could serve as the ORR active sites, while the graphitic-N favors electron transfer. The CoNi-NCT has significantly more N content when compared with the Co-NC and the Ni-NCT (Fig. 2f and Fig. S3d, e). This indicates that the existence of CoNi alloy is beneficial in preserving N species due to the strong interactions between metal and nitrogen atoms. Because the N species can coordinate with the metal species [43], the N species play an important anchoring role for the CoNi alloy on the CNT.

Theoretical calculations and the catalytic mechanism

DFT calculations were used to predict the origin of the ORR active sites for the CoNi alloy coupled with N-doped carbon nanostructures. Previous studies demonstrated that the metal sites, not the N-doped carbon nanostructures, were the main active sites of the ORR. To gain insight into the Co or Ni active sites, the CoNi-NCT model was built based on the N-doped carbon nanostructure supporting the CoNi alloy on the main exposed (111) plane (calculation methods and the corresponding data are described in Tables S2 and S3). The Co-C/N and

Ni-C/N models were built by the same method. Fig. 3 shows the free energy pathways of the ORR, including (I) the initial oxygen adsorption step and (II–V) the subsequent four-electron reduction processes. By calculating the O_2 adsorption energy values of the Co-N/C (O_2 adsorbed on Co), the Ni-N/C (O_2 adsorbed on Ni), and the CoNi-N/C (O_2 adsorbed on CoNi alloy), it was discovered that the O_2 adsorption process was spontaneous for all three models (Fig. S4). Notably, the O_2 adsorption ability for the Ni-N/C model was much stronger than that of Co-N/C, demonstrating that the Ni sites in the CoNi alloy play the main role in O_2 adsorption.

All of the Gibbs reaction free energy (ΔG) values of the various intermediate formations at the metal sites for the three models are negative in the ORR direction at a 0 V equilibrium potential, implying an exothermic process. The formation of OOH^* is the RDS due to the higher ΔG value. Additionally, the CoNi-C/N shows the lowest energy barrier compared with the Co-C/N and Ni-C/N, indicating efficient ORR activity of the CoNi alloy-based catalyst. The ΔG value of every step for the Co-C/N is lower than the values for the Ni-C/N, proving that the Co sites are favorable for the four-electron transfer process. When the equilibrium potential is 1.23 V, the ΔG values of CoNi-C/N clearly drop, especially for the O^* and OH^* steps. This is more conducive to the ORR. The results reveal that the Ni sites in the N-doped carbon nano-

Figure 3 This cycle represents the four-electron transfer pathway of CoNi-C/N. The inset is the free energy diagrams of CoNi-C/N (O_2 adsorbed on CoNi), Co-C/N (O_2 adsorbed on Co), and Ni-C/N (O_2 adsorbed on Ni) at 0 and 1.23 V, respectively.

structures embedded with CoNi alloy benefit O_2 adsorption, while the Co sites promote the four-electron transfer process, resulting in an excellent ORR performance.

Electrochemical performance

The ORR activity was evaluated by using an RRDE at a speed of 1600 r min^{-1} in O_2 -saturated 0.1 mol L^{-1} KOH. As an excellent electrocatalyst, to drive a high current density at a low overpotential with a small Tafel slope value is desired. The LSV curve (Fig. 4a) of the CoNi-NCT exhibits a larger positive onset potential (E_{onset}) of 0.97 V at the current cut-off of -0.01 mA cm^{-2} (catalyst loading is 0.6 mg cm^{-2}) and a higher half-wave potential ($E_{1/2}$) of 0.83 V than the single-metal samples (Co-NC (0.86, 0.75 V) and Ni-NCT (0.87, 0.76 V)) and is comparable to Pt/C (1.0, 0.86 V). The samples derived from different pyrolytic temperatures and atom ratios of Co were also tested for comparison. Their ORR activity is worse than that of the CoNi-NCT (Fig. S5). As shown in Fig. 4b, the CoNi-NCT sample shows a smaller Tafel slope of 57.3 mV dec^{-1} compared with the Co-NC ($\sim 89.3 \text{ mV dec}^{-1}$) and the Ni-NCT samples ($\sim 76.6 \text{ mV dec}^{-1}$), which is close to that of Pt/C

($\sim 53.7 \text{ mV dec}^{-1}$). In addition, the CoNi-NCT performs a limiting current density similar to that of Pt/C (Fig. 4c). These results demonstrate that the existence of CoNi alloy promotes the ORR activity due to the synergistic effect between Co and Ni that facilitates an effective ORR process.

The CoNi-NCT displays a four-electron ORR pathway with an electron transfer number (n) of 3.9 in alkaline conditions accompanied by a low H_2O_2 yield of 2.9% (Fig. 4d, e), indicating a similar behavior to Pt/C (3.8, 4%). It has been suggested that a mixed rate control step involves an electron transfer step and a diffusion step of oxygen-containing intermediates from the active sites [44]. The kinetics of the CoNi-NCT was tested at different rotating speeds (400 to 2500 r min^{-1}) (Fig. 4f). The diffusion saturation current density increases as the rotation speed increases, demonstrating a first-order kinetic process. The corresponding K-L curves obtained at different potentials show good linearity and parallelism (Fig. 4g), proving that the n values for ORR are the same at different potentials [45]. This phenomenon is also observed for Pt/C (Fig. S6). These findings suggest that the CoNi alloy nanoparticles, coupled with the NCTs, produce more active sites and favor the direct reduction

Figure 4 (a) LSV curves of CoNi-NCT, Co-NC, Ni-NCT, and 20% commercial Pt/C in O_2 -saturated 0.1 mol L^{-1} KOH electrolyte with a sweep rate of 5 mV s^{-1} at the rotating speed of 1600 r min^{-1} . (b) The Tafel curves derived from (a). (c) The comparison of E_{onset} , $E_{1/2}$, and J_L for different catalysts. (d) LSV curves for CoNi-NCT and Pt/C on an RRDE electrode. (e) Electron transfer number (n) and H_2O_2 yield vs. potential. (f) RRDE polarization curves at different rotating rates and (g) the K-L plots at different potentials for the CoNi-NCT. LSV curves of (h) CoNi-NCT and (i) Pt/C before and after 10,000 cycles.

of O_2 into OH^- by a highly efficient four-electron process. In addition, the NCTs have a catalytic surface that weakens the binding of oxygenated intermediates, resulting in excellent ORR activity.

The stability of the electrocatalyst is also important. As shown in Fig. 4h, there is no noticeable change in the LSV curve for CoNi-NCT after 10,000 cycles. The $E_{1/2}$ only experiences a negative shift of 7 mV, whereas Pt/C exhibits a larger negative shift of 30 mV (Fig. 4i). This superior stability is attributed to the N-doped carbon embedded structures that not only improve ORR activity but also effectively avoid the dissolution and agglomeration of CoNi alloy nanoparticles. A chronoamperometric response is used to further test the durability of the catalysts. The CoNi-NCT shows a negligible current degradation of 3% at 10,000 s, while the current degradation of Pt/C is approximately 7%, demonstrating the excellent long-term stability of the CoNi-NCT (Fig. S7a). When compared with Pt/C, the CoNi-NCT also exhibits good stability after the injection of 3 mol L^{-1} CH_3OH in

0.1 mol L^{-1} O_2 -saturated KOH electrolyte (Fig. S7b). These findings indicate that the CoNi-NCT has superior CH_3OH tolerance and selectivity toward ORR.

ZABs performance

Encouraged by the efficient ORR electrocatalytic activity of the CoNi-NCT, the performance of a ZAB was further examined in 0.2 mol L^{-1} $\text{Zn}(\text{Ac})_2 + 6 \text{ mol L}^{-1}$ KOH electrolyte. Fig. 5a shows the schematic diagram of the liquid ZAB in which an aqueous primary rechargeable ZAB was constructed by using the CoNi-NCT as the air-cathode. When the current density increased from 2 to 50 mA cm^{-2} and then suddenly changed back to 2 mA cm^{-2} , there was a negligible change in the voltage for the CoNi-NCT-based ZAB, whereas the Pt/C-based ZAB showed a 10% voltage decrease (Fig. 5b). This reveals the better stability of the CoNi-NCT-based ZAB. In addition, the CoNi-NCT-based ZAB delivered the discharge capacities of 671.6 $\text{mA h g}_{\text{Zn}}^{-1}$ at 10 mA cm^{-2} and 713.2 $\text{mA h g}_{\text{Zn}}^{-1}$ at 5 mA cm^{-2} (Fig. 5c). The battery also

Figure 5 (a) Schematic illustration of the liquid ZABs. (b) Discharge curves of the primary ZABs assembled using the CoNi-NCT and Pt/C as the air-cathodes at different current densities. (c) Long-time galvanostatic discharge curves of the primary ZAB assembled by using the CoNi-NCT as the air-cathode. (d) LSV and power density curves. (e) Galvanostatic discharge-charge cycling curves of the rechargeable liquid ZABs assembled by using CoNi-NCT + NiFeP/CC and Pt/C + RuO₂ as the air-cathodes. (f) Photograph of the LED screen lit up by three ZABs in series.

exhibited significantly higher performance than the reported primary rechargeable ZABs (Table S4).

To explore the potential of the CoNi-NCT as the ORR catalyst in a rechargeable ZAB, the OER catalyst of NiFeP grown on CC (NiFeP/CC) was prepared by a facile hydrothermal synthesis combined with a subsequent process. The NiFe-LDH/CC precursor exhibits a NiFe-LDH crystalline phase same as the standard PDF#26-1286 (Fig. S8a). The representative XRD patterns and SEM images confirm that the NiFeP nanosheets have grown on CC support after a phosphating process (Figs S8b and S9). The synthetic NiFeP/CC needs an overpotential of about 0.29 V to drive a current density of 10 mA cm⁻² (Fig. S10). For constructing the rechargeable ZAB, the air-cathode was prepared by coating the CoNi-NCT with the NiFeP/CC with a loading content of 1 mg cm⁻². The CoNi-NCT + NiFeP/CC battery exhibited an open-circuit voltage of 1.39 V (Fig. S11). A mixture of state-of-the-art commercial Pt/C + Ru₂O₃ with a mass ratio of 1:1 was also used to assemble another ZAB as a reference. As shown in Fig. 5d, the CoNi-NCT + NiFeP/CC battery displayed a power density of 167 mW cm⁻², much higher than that of the Pt/C + Ru₂O₃ battery (127 mW cm⁻²). In addition, the initial discharged and charged potentials of the CoNi-NCT + NiFeP/CC battery were 1.17 and 1.91 V at 10 mA cm⁻² (as is shown in Fig. 5e), respectively. This was a smaller voltage gap of 0.74 V, whereas the Pt/C +

RuO₂ battery had a voltage gap of 0.85 V. Notably, the CoNi-NCT + NiFeP/CC battery exhibited a smaller attenuation, and the discharged voltages were 1.11 V after 200 h and 1.10 V after 300 h, respectively. For the Pt/C + RuO₂ battery, the discharged voltage decreased to 1.01 V with a large voltage gap of nearly 1.0 V after 200 h. The superior performance of the CoNi-NCT + NiFeP/CC battery is attributed to the efficient activity and stability of the CoNi-NCT, further implying that it is a potential candidate for substituting precious metal catalysts. Three CoNi-NCT + NiFeP/CC batteries connected in series lit up a 3.0 V blue light-emitting diode (LED) screen (Fig. 5f), demonstrating a promising practical application.

CONCLUSIONS

In summary, a CoNi-NCT complex was synthesized by a facile pyrolytic strategy, in which the CoNi alloy nanoparticles embedded in bamboo-like N-doped carbon nanotubes. DFT calculation results indicate that the Ni sites in the CoNi alloy promote the oxygen adsorption and electron transfer of the ORR. In addition, the Co sites in the CoNi alloy reduce the RDS reaction barrier of the formation energy for *OOH, benefiting the rapid reaction process of the four-electron ORR pathway. It also exhibits excellent activity and long-term stability due to the synergistic effect of CoNi and NCT that is favorable for the charge/mass transfer. As an air-cathode for primary and

rechargeable ZABs, it shows much better performance than the precious metal-based batteries. This study provides new insight on the role of alloy catalyst active sites in ORR. This insight is significant for constructing high-efficiency non-precious metal catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

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

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N-掺杂碳纳米管包覆的CoNi合金作为氧还原催化剂的活性位点研究

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摘要 过渡金属合金电催化剂引起了人们对氧还原反应(ORR)的强烈兴趣,但是对其活性位的研究尚不深入. 本论文中,我们通过对普鲁士蓝类似物的热解,得到将CoNi合金纳米粒子封装在竹节状N-掺杂碳纳米管中的复合物(CoNi-NCT). 通过密度泛函理论计算表明,氧分子更容易吸附在合金中的Ni位点上,而Co位点有利于降低ORR过程中OOH*中间体的形成势垒. 此外, CoNi合金与N掺杂的碳有利于电子转移,提高电催化活性. 优化的CoNi-NCT表现出卓越的ORR催化活性,半波电势为0.83 V,起始电位为0.97 V,并且具有优异的稳定性,性能优于商业Pt/C催化剂. 作为空气正极组装的锌-空气电池,在10 mA cm⁻²时充放电电压差为0.86 V,功率密度为167 mW cm⁻²,且具有良好的稳定性(可稳定运行900次).