

Bimetallic cobalt-nickel phosphide composite biomass carbon materials as efficient electrocatalysts for zinc-air batteries

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Abstract

Zinc-air batteries (ZABs) are promising energy storage devices, but their efficiency is limited by the sluggish kinetics of the oxygen reduction and evolution reactions (ORR/OER). While composites of transition metal phosphides (TMPs) and nitrogen-doped carbon (NC) are attractive bifunctional catalysts, their performance is constrained by unclear synergistic mechanisms in bimetallic sites and challenges in designing structures that balance active site exposure with stability. To address this, we synthesized a series of CoMP@NC (M = Mn, Fe, Ni) catalysts using chitosan-derived carbon. The optimized CoNiP@NC exhibits excellent ORR activity (onset potential: 0.876 V) and OER performance (overpotential: 503 mV at 10 mA cm⁻²). Theoretical calculations indicate that Ni doping modulates the electronic structure of Co sites, lowering the reaction barrier. Furthermore, a rechargeable ZAB with a CoNiP@NC cathode demonstrated stable cycling for 240 hours, outperforming the Pt/C-RuO₂ benchmark. These results highlight CoNiP@NC as a highly efficient and durable bifunctional electrocatalyst for ZABs.

1. Introduction

The consumption of fossil fuels has caused a series of severe environmental pollution issues for society, such as acid rain and the greenhouse effect [1, 2]. Significant efforts have been expended in exploring next-generation energy storage technologies for renewable clean energy supply. Rechargeable zinc-air batteries (ZABs), comprising a zinc anode, air cathode, and aqueous electrolyte, are regarded as promising candidates due to their exceptionally high theoretical energy density of 1086 Wh kg⁻¹, inherent safety conferred by the aqueous electrolyte, and the low cost associated with zinc's abundance and ease of handling [3, 4]. However, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics at the air electrode of rechargeable ZABs are sluggish [5–7]. Achieving efficient, synergistic dual-function activity for both ORR and OER remains challenging, hindering further development of rechargeable ZABs. Traditional noble metal-based materials such as Pt/C and RuO₂/IrO₂ are commonly employed catalysts in ZABs. However, their scarcity, insufficient durability, and high cost hinder large-scale and long-term application. Consequently, there is an urgent need to develop high-performance bifunctional electrocatalysts for ORR and OER to enhance cathode redox kinetics and construct high-performance rechargeable ZABs [8–10].

Transition metal phosphides (TMPs) serve as non-precious metal catalysts, wherein both phosphorus and metal sites function as active sites during electrocatalysis. Furthermore, phosphides exhibit higher electrical conductivity than their corresponding oxides, thereby facilitating charge transfer. Their excellent conductivity and low cost have garnered significant attention, particularly for their outstanding performance in the OER [11, 12]. The oxides or hydroxides formed on the surface of these phosphides can serve as active sites, significantly enhancing their OER catalytic performance. However, the intrinsic OER activity of single-metal phosphides (such as CoP) still lags behind that of precious metals [13]. Recent studies indicate that introducing a second transition metal (such as Fe, Ni, Mn) to form bimetallic phosphides can effectively modulate the electronic structure, optimise surface electron distribution, and

improve conductivity [14]. This synergistic interaction between bimetallic elements confers superior catalytic activity and stability compared to monometallic phosphides [15]. Furthermore, considering that the distinct mechanisms of the ORR and OER necessitate different active sites, the strategy of integrating two or more components into electrocatalysts offers the potential for site-specific selection.

Nitrogen-doped carbon (NC) materials are recognized as highly active sites for the ORR [16]. They possess a high specific surface area, and the construction of defect structures can yield additional catalytic active sites, thereby enhancing their catalytic efficiency [17, 18]. However, the preparation of many NC materials relies on unsustainable carbon sources and toxic nitrogen precursors, hindering their large-scale application. Therefore, this study employs Chitosan, a biocompatible and biodegradable compound, as a composite precursor for both carbon and nitrogen sources[19–21]. NC materials from Chitosan not only effectively utilizes chitin waste to reduce environmental burdens but also enables the production of high-performance electrochemical devices[22, 23]. However, integrating ORR/OER bifunctionality remains challenging with single catalysts. Composites combining bimetallic transition metal phosphides with NC materials hold promise for achieving this dual functionality.

Transition metal phosphides were composited with biomass carbon materials to integrate ORR and OER properties by modulating their active elements and electronic structures. In this paper, a series of CoMP@NC (M = Mn, Fe, Ni) transition metal phosphides were prepared by two-step hydrothermal method and CVD. In the CoMP@NC composite material, the nitrogen-doped carbon support exhibits multiple synergistic functions that surpass those of a mere support: it serves as both a highly conductive network and porous mass transfer channel, while directly providing active sites for pyrrole nitrogen ORR; simultaneously, through strong electronic interactions with CoMP, it optimizes the electronic structure of the metal centers and acts as a stabilizing framework ensuring long-term durability of the catalytic system. Meanwhile, Co and Ni bimetals existed on the materials as M-P, which better enhanced the utilization efficiency of the catalytic active sites. Electrochemical tests were conducted on the catalyst. For CoNiP@NC, the ORR exhibited an onset potential of 0.876 V, and the OER showed an overpotential of 503 mV at a current density of 10 mA cm⁻². DFT calculations were employed to reveal the mechanism of the role of its electronic structure in ORR and OER. The results indicated that the coexistence and synergistic effect of the active sites of Co and Ni could effectively reduce the overpotential during the catalytic process, thereby enhancing the catalytic activity. Additionally, the CoNiP@NC-based rechargeable zinc-air battery could cycle for 240 h at a current density of 2 mA cm⁻², demonstrating better cycle stability performance compared to the Pt/C-RuO₂ battery (110 h).

2. Experiments

Materials

Chitosan ((C₈H₁₃NO₅)_n, deacetylation degree ≥ 95%), hydrochloric acid (HCl, 36 ~ 38%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, AR), potassium hydroxide (KOH, AR), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), isopropanol (C₃H₈O, AR), and propanetriol (C₃H₈O₃, AR), Sodium hypophosphite

(NaH_2PO_2 , AR) were purchased from Shanghai McLean Biochemical Technology Co. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, AR) was purchased from Tianjin Fuyu Fine Chemical Co. Nafion solution (5% wt%) was provided by DuPont, and the experimental water was deionized water (H_2O). All chemical reagents were used as received without any additional purification.

Sample Preparation

NC preparation: 5 g of chitosan was added to 75 mL of hydrochloric acid (1 M) solution, heated and stirred at 60 °C for 2 h and then dried at 120 °C, and finally ground to obtain the powder. Subsequently, the powder was heated up to 800 °C under Ar atmosphere at a heating rate of 2 °C min^{-1} for 10 h. The calcined powder was washed several times with 1 M hydrochloric acid, deionized water and ethanol, respectively, and dried, and the product was recorded as NC.

Preparation of CoMAMSs nanorods: 0.468 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to 160 mL of isopropanol, which was recorded as solution A. 0.418 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 32 mL of glycerol, which was recorded as solution B. The obtained cobalt-to-nickel molar ratio is approximately 1.12:1. To ensure comparability of the effects of the second metal, both CoMnAMSs and CoFeAMSs were prepared using the same cobalt-to-manganese (or iron) molar ratio. The product was mixed with CoNiAMSs in an oven at 180 °C for 6 h. The product was washed with deionized water and ethanol several times and dried. Solution A and solution B were mixed in an oven at 180 °C for 6 h. The product was washed several times with deionized water and ethanol and dried, and the product was recorded as CoNiAMSs. Similarly, CoMnAMSs and CoFeAMSs were prepared as above.

Phosphatization: 0.25 g of CoNiAMSs, 0.25 g of NC, 0.5 g of PVP were dissolved in 70 mL of isopropanol and 16 mL of propanetriol, stirred and ultrasonicated for 30 min and then placed in an oven at 180 °C for 6 h. CoNi@NC was obtained by washing with water, ethanol, and acetone for a number of times and drying, respectively. Under the Ar atmosphere (60 sccm), the furnace was heated to 350 °C at a temperature increase rate of 2 °C min^{-1} for 2 h, and the product was recorded as CoNiP@NC. Similarly, CoMnP@NC and CoFeP@NC were prepared as above.

Characterization

The surface morphology of the catalysts was observed by scanning electron microscopy (SEM, ZEISS Sigma 300), while the specific surface area and pore size of the catalysts were observed by BET test at Micromeritics ASAP 2460 instrument. In addition, the physical phase and crystal structure of the catalysts were analyzed by X-ray diffraction (XRD, Bruker D8 Advance), and the chemical composition of the catalysts was characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB Xi⁺).

Electrochemical testing

The electrochemical evaluation was carried out on a CHI 760E electrochemical workstation connected to a rotating disk ring electrode (RRDE) test system. The system consists of a working electrode (glassy carbon substrate coated with catalyst ink), a counter electrode (glassy carbon electrode) and a reference electrode (Ag/AgCl). In the three-electrode test conducted in this study, glassy carbon electrodes were selected as the counter electrodes primarily due to their stability in alkaline electrolytes and their ability to avoid ion dissolution and migration contamination associated with precious metal counter electrodes, thereby ensuring the reliability of assessing the intrinsic activity of non-precious metal catalysts. All comparative experiments were performed under identical conditions to maintain fairness. A homogeneous catalyst ink was prepared by mixing 5 mg of catalyst powder, 5 mg of carbon black, 40 μL of 5 wt% Nafion solution, and 1 mL of anhydrous ethanol. In electrochemical testing, the loading amount of the active material on the working electrode was determined through the following steps: 20 μL of uniform catalyst ink was applied by drop coating onto the polished glassy carbon electrode surface (diameter 5 mm, geometric area 0.196 cm^2), followed by drying at room temperature. Based on the mass-accumulation relationship between the catalyst powder and the ink, the surface loading amount of the active catalyst (excluding conductive carbon black and binder) on the working electrode was approximately 0.51 mg cm^{-2} . All tested catalysts, including commercial Pt/C and RuO_2 reference samples, were loaded with identical amounts to ensure fair performance comparisons. The ORR and OER activities of the catalysts were evaluated by linear potentiometric scanning at a scanning rate of 5 mV s^{-1} under saturated O_2 or N_2 atmosphere, with the electrode speed set at 1600 rpm. To prevent O_2 bubbles from accumulating on the surface of the working electrode, the working electrode was first scanned for 20 cycles for electrode activation prior to data collection. The Ag/AgCl potentials obtained from the tests needed to be converted by a (1–1) reversible hydrogen electrode (RHE) and the potential values were corrected for iR compensation according to Eq. (1–2).

$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197 \text{ V}$	(1–1)
$E_{\text{iRcorrected}} = E - iR$	(1–2)

Calculation method

A three-dimensional periodic model of CoMP@NC was constructed using Materials Studio (MS) software. Subsequently, computational analysis based on Density Functional Theory (DFT) was performed using Vienna Ab-initio Simulation Package (VASP). In order to describe the exchange-correlation effects, the Perdew-Burke-Ernzerhof (PBE) method in the generalized gradient approximation (GGA) is used. In addition, the interactions between ions and electrons are treated by means of the projection-enhanced wave (PAW) pseudopotential method. When performing the calculations, the plane wave truncation energy is set to 550 eV. during the structure optimization process, all atoms are set in the relaxed state; whereas, when investigating the surface properties, the two layers of atoms at the bottom of the model are fixed, and the rest of the atoms are kept in a relaxed state.

Zinc-Air Battery Testing

Zinc air batteries were fabricated by using zinc foil as the anode, CoMP@NC as the air cathode, and an electrolyte consisting of a 15 mL solution of 0.2 M ZnCl_2 and 6 M KOH. The open-circuit voltage, charge-discharge curves, and power density curves were tested on a CHI 760E electrochemical workstation; the charge-discharge cycle stability tests were performed on a Blue Power battery test system CT3001A. In addition, Pt/C and RuO_2 were mechanically mixed at a ratio of 1:1 (Pt/C- RuO_2) and used as a control group for investigating the performance of Pt/C- RuO_2 -based zinc air batteries.

3. Results and discussion

3.1 Material characterization

Figure 1a shows a schematic diagram of the catalyst preparation process. Bimetallic phosphides loaded on biomass carbon materials were prepared by a two-step hydrothermal method and CVD phosphorization. The microscopic morphology of the catalysts was characterized by scanning electron microscopy (SEM) (Fig. 1). As shown in Fig. 1b, the high-temperature calcination of chitosan can obtain carbon materials with different pore sizes, whose pore size distribution is relatively uniform, and the existence of porous carbon materials can make more active sites exposed, which in turn enhances the electrocatalytic activity of the catalyst. At the same time, a series of cobalt-based bimetallic phosphides were obtained by further composite phosphorylation of bimetallic nanorods synthesized by a hydrothermal method with biomass carbon materials (Figs. 1c-g). As can be seen from Fig. S1, the nanomicrospheres on the surface of the CoNi@NC material before phosphatization have a regular shape, while after phosphatization, the shape of the nano-microspheres is slightly altered, with some of them having an irregular shape (Fig. 1f). In addition, thanks to the presence of ionic surfactants, the distribution of bimetallic phosphides is more uniform. In order to further understand the elemental distribution of the synthesized CoNiP@NC, mapping tests were performed. As shown in Figs. 1h-l, the results of its elemental mapping show that Co, Ni, P, N, and C elements are all present. It can be seen that the CVD phosphatization was only carried out on the nano-bimetallic microspheres, while the N element was uniformly distributed on the biomass carbon material.

In order to understand the specific surface area of the catalyst materials, nitrogen physical adsorption-desorption tests (BET) were performed, which showed that All samples exhibited Type IV adsorption-desorption isotherms and H3-type hysteresis loops (Fig. S2), indicating that they are primarily composed of mesoporous structures. As shown in Table S1, the BET specific surface areas of the catalyst samples were 19.4875, 16.9112, 24.4811 and 17.5437 $\text{m}^2 \text{g}^{-1}$, and the BJH desorption pore volumes were 0.0779, 0.0630, 0.0399 and 0.0889 $\text{cm}^3 \text{g}^{-1}$, respectively. Since all four samples were prepared by loading metal phosphides onto biomass char materials, the specific surface areas of the catalysts in each group showed minimal variation. As evidenced by the isotherm results in the figure, all samples exhibited mesoporous structures, further corroborating the conclusion in Fig. S2, with pore size distributions predominantly concentrated within the 2–20 nm range. The mesoporous defective structure plays a crucial role in providing more active sites, and the porous structure can provide more channels for

oxygen diffusion, which can promote the rapid diffusion and mass transport of active sites in the electrolyte, thus forming more three-phase (solid-liquid-gas) interfaces to facilitate the catalytic reaction. These BET analysis results indicate that the CoNiP@NC catalysts have a large pore volume and specific surface area, which can shorten the transport paths of reactants and products and thus improve the catalytic reaction efficiency.

The material composition and crystal structure of the catalysts were analyzed by XRD, and the relevant results are shown in Fig. 2a. Due to calcination and phosphatization, the four materials are not highly crystalline, and thus the diffraction peaks are not obvious. However, it is not difficult to see that the diffraction peaks of CoP existed in all four groups of samples, which is in good agreement with the diffraction peaks of JCPDS NO.29-0497. In addition, the element Mn cannot combine with P to form M-P bonds, but the XPS results confirm the presence of Mn element in CoMnP@NC, indicating that CoMnP@NC has been successfully prepared. Meanwhile, the FeP (JCPDS NO.71-2261) and Ni₂P (JCPDS NO.03-0953) diffraction peaks of the CoFeP@NC and CoNiP@NC samples can be seen in the figure, indicating the formation of FeP and Ni₂P phases. X-ray photoelectron spectroscopy (XPS) can be used to find more about the chemical state of the elements on the surface of the material and the composition of the sample, so the valence state of the chemical elements of the catalyst was studied by XPS. The XPS full spectrum analysis results confirm that the composition elements of the CoNiP @ NC sample include Co, Ni and P, which is consistent with the results of SEM energy spectrum analysis (EDS) (Fig. 2b).

The successful introduction of Co atoms into the catalyst could be further confirmed using XPS. In the high-resolution Co 2p region (Fig. 3a), the peaks at ~ 782 eV and ~ 800 eV present broad Co 2p_{1/2} and Co 2p_{3/2} peaks, which are back-convoluted to the Co³⁺ state, which corresponds to Co-P. The peaks located at ~ 784 eV and ~ 805 eV, on the other hand, correspond to Co-O, which belongs to the Co²⁺ state in the Co 2p_{3/2} and Co 2p_{1/2} orbitals, respectively [24]. The presence of oxygen elements in them can be attributed to surface oxidation phenomena. In addition, the signal at ~ 787 eV was identified as a relevant satellite peak [25]. Meanwhile, the molar ratio of Co²⁺/Co³⁺ was calculated based on the peak area (Table 1). It can be seen that the ratio of Co²⁺ to Co³⁺ on the surface of the CoNiP@NC catalyst was significantly higher than that of the other samples, which could be attributed to the fact that the doping of Ni altered the electronic environment of CoP@NC, thus increasing the content of Co²⁺ on the surface of the catalyst, whereas a high concentration of Co²⁺ favors the ORR.

The P 2p spectra of the four sets of samples were fitted as shown in Fig. 3b. ~131 eV is the peak belongs to M-P in the region of P 2p_{3/2}, P 2p_{1/2}, and ~ 135 eV signal corresponds to P-O. The peaks of P-O are mainly related to phosphorus bound in the carbon matrix, and the peaks of M-P are related to phosphorus on the bimetallic nanorods. As can be seen from the figure, the M-P signals of all the four groups of samples are not obvious, which may be due to the presence of carbon material that leads to the blockage of the binding of metal to P and thus manifests as P-O [26]. In addition, in the high-resolution N 1s region (Fig. 3c), the signal at ~ 398 eV corresponds to pyrrolic nitrogen (Pyrrolic-N), and the signal

at ~ 401 eV corresponds to graphitic nitrogen (Graphitic-N) [27]. The binding energies of Metal-N and Pyrrolic-N are close to each other, while the peak of Pyrrolic-N contains Metal-N, which is the active site of ORR. N is the active site of ORR [28, 29]. Compared with the other four groups of catalysts, CoNiP@NC showed the highest Pyrrolic-N/Graphitic-N ratio, indicating that the synergism of Co and Ni caused it to exhibit the best ORR activity.

In addition, the nature of oxygen in the catalyst greatly affects the catalytic activity of the catalyst. O 1s region typically originate from the natural oxidation of material surfaces, forming thin layers of cobalt oxide/cobalt hydroxide. This phenomenon is common in TMPs and is beneficial for OER activity. In the high-resolution O 1s region (Fig. 3d), the signals were M-O (Lattice-O), M-OH/OOH (Surface-O), P-O, and C-O [30]. The lattice oxygen (Lattice-O) determines the thickness of the surface oxide layer, while the surface oxygen (Surface-O) determines the catalytically active sites of the OER [31, 32]. Upon combination with elemental Ni, CoNiP@NC showed a higher Surface-O/Lattice-O ratio, suggesting that it may have a higher charge transport efficiency in the OER process.

Table 1
Surface atomic concentrations of catalysts

CoP@NC	Surface-O/Lattice-O	Pyrrolic-N/Graphitic-N	Co ²⁺ /(Co ²⁺ +Co ³⁺)
	0.52	0.17	0.42
CoMnP@NC	0.68	0.32	0.48
CoFeP@NC	0.95	0.30	0.47
CoNiP@NC	1.51	0.36	0.52

3.2 Electrocatalytic performance

The ORR performance in this experiment was tested by a typical three-electrode system. The electrocatalytic performance of CoMP@NC in oxygen-saturated KOH solution was investigated by means of LSV polarization curves (Fig. 4a). The LSV polarization curves allow access to the onset potential, half-wave potential, and limiting current density of the catalysts in order to assess the catalytic activity of ORR. The activity of a catalyst is usually measured by the overpotential required for the electrocatalytic reaction, and higher onset and half-wave potentials indicate lower overpotentials required for the ORR, suggesting that the catalyst has stronger catalytic performance. Table S2 lists the LSV test results of all catalysts, and the onset potential, half-wave potential, and limiting current density of CoNiP@NC were 0.876 V, 0.670 V, and 4.64 mA cm⁻², respectively. CoNiP@NC was higher than the other controls but slightly lower than the commercial Pt/C catalysts, and its half-wave potential is markedly superior to the other three bimetallic phosphides, being closer to that of Pt/C, indicating a higher output potential during operation. And its limiting current density was 11% higher. The limiting current density was increased by 11%. These results indicate that the introduction of Ni enhances the ORR catalytic activity of monometallic cobalt-based phosphides, while suggesting a stronger interaction between Co and Ni.

The reaction kinetics of the catalysts can be evaluated by Tafel plots, and the Tafel slope reflects the reaction kinetics rate of the catalyst materials, with smaller slopes indicating faster reaction rates and larger slopes indicating slower reaction rates. In the LSV curves of the catalysts, a significant linear relationship was shown between the potential E and $\text{Log}J_K$, and the Tafel slope values could be further calculated by curve fitting. As shown in Fig. 4b and Table S2, it can be seen that CoNiP@NC has a smaller Tafel slope with a value of only $87.42 \text{ mV dec}^{-1}$, the smaller Tafel slope indicates a faster electron transfer rate and lower overpotential, which directly explains why it exhibits a more positive half-wave potential and higher activity in Fig. 4b, which indicates that the ORR kinetics of this catalyst material is faster.

In addition, in the process of ORR catalysis, stability is also one of the key parameters to evaluate the practical feasibility of zinc-air batteries, which is directly related to the long-term performance and service life of batteries. In order to systematically evaluate the stability of the catalyst, the test is usually carried out on a high-precision rotating disk electrode (RDE) device. The constant potential method was used in the experiment. The working potential was set to 0.8 V (relative to the reversible hydrogen electrode), and the electrode rotation speed was maintained at 900 rpm to simulate the mass transfer conditions in the actual reaction. Under the condition of continuous test time of 15000 s, the current-time curve and performance attenuation of the catalyst were recorded, so as to comprehensively analyze its electrochemical stability and durability. Figure 4c shows the current-time curves of different catalysts. After continuous operation for as long as 15,000 s, the current density of CoNiP@NC still remains at 88.28%, while that of CoP@NC is only 54.14%. This indicates that this catalyst has excellent ORR stability. This may be attributed to the fact that the active centers of the composite material formed by the bimetallic phosphide of Co and Ni and the carbon material are more stable, and the electrolyte has a relatively small corrosive effect on it, thus resulting in better stability of the catalyst material.

Figure S3 records the LSV curve data for different catalysts in the rotational speed range from 100 rpm to 2500 rpm and the potential from 0.2 V to 1.2 V, respectively, which were used to obtain comprehensive information on the dynamics of ORR. As the rotation speed of the rotating disk electrode increases, the reduction current gradually increases, which is due to the fact that the oxygen in the electrolyte can diffuse more efficiently to the electrode surface, thereby promoting the interaction between oxygen and the active site of the catalyst. The larger reduction current indicates that the reduction reaction is more likely to occur, and the ORR performance of the catalyst is better. In addition, the Koutecky-Levich plots of CoNiP@NC at different reduction potentials show a good linear relationship, indicating that the oxygen dissolution process follows a first-order kinetics. The high current density of CoNiP@NC suggests that the introduction of nickel and its joint action with cobalt significantly enhance the chemical reaction rate.

The electron transfer number (n) and dynamic current density (J_K) were further investigated through the Koutecky-Levich (K-L) plots generated by RDE. Fig. S4 shows the K-L plots for the catalyst at 0.2 V voltage, where a linear correlation between j^{-1} and $\omega^{-1/2}$ is exhibited. The electron transfer number is an important indicator to determine the ORR pathway. In ORR, the catalyst may proceed in two different

pathways: one is the generation of water through a four-electron transfer reaction and the other is the generation of hydrogen peroxide through a two-electron transfer reaction. However, the four-electron reaction pathway is usually preferred due to the strong corrosive nature of hydrogen peroxide, which contributes to the stability of the catalyst and the safety of the cell. As shown in Fig. 4d, the value of n for CoNiP@NC is 3.70, which is closest to four electrons. This further indicates that CoNiP@NC predominantly undergoes a four-electron reaction process. Additionally, the significant increase in J_K for CoNiP@NC further validates that, without any substantial change in the reaction mechanism, the catalyst exhibits more excellent ORR activity.

Similarly, the OER test was also carried out in a KOH solution. Figure 5a shows the linear sweep voltammetry (LSV) polarization curves measured at 1600 rpm. The curve clearly reflects the electrochemical process of the catalyst. Through the analysis of the characteristic potential parameters, the initial potential (E_{onset}) of the catalyst and the overpotential (η_i) corresponding to the specific current density can be analyzed. These key electrochemical parameters can effectively characterize the catalytic activity of the catalyst in the OER process and are important indicators for evaluating its catalytic performance. The smaller these values are, the more it implies that the catalyst can initiate the reaction at a lower potential in the OER, and the easier the OER reaction is to proceed. As shown in Table S3, CoNiP@NC exhibited a low onset potential of 1.501 V and an overpotential of 0.503 V, which are superior to those of other catalysts and the benchmark RuO_2 , demonstrating its excellent OER activity. In addition, it further illustrates that the introduction of Ni and its interaction with Co can effectively serve as the catalytic active sites for the OER, significantly increasing the rate of molecular oxygen generation.

The Tafel slope was obtained by fitting the LSV curve of the OER test, and its value reflects the steady-state kinetic rate. A smaller Tafel slope indicates a smaller electron transfer barrier. As shown in Fig. 5b and Table S3, the Tafel value of NiP@NC is $116.26 \text{ mV dec}^{-1}$, which is significantly smaller than those of CoP@NC ($128.41 \text{ mV dec}^{-1}$) and the benchmark RuO_2 ($133.32 \text{ mV dec}^{-1}$) catalysts. This indicates that the synergistic effect between Co and Ni is conducive to promoting the OER kinetic process. The stability and durability of the catalyst material are crucial for the performance of zinc-air batteries. As shown in Fig. 5c, the OER durability and stability of the catalyst materials were evaluated using the chronoamperometry (i-t) technique. After an i-t test for 15,000 seconds, the current retention rates of CoP@NC, CoMnP@NC, CoFeP@NC, and CoNiP@NC were 51.33%, 60.04%, 63.74%, and 84.28%, respectively. The current density of CoNiP@NC can still reach 84.28% after the 15,000 s test, demonstrating its excellent stability. CoNiP@NC exhibits excellent stability both in the ORR and OER. On the one hand, it may be because the introduction of Ni has changed the electronic structure and coordination environment around CoP. On the other hand, the heterojunction formed by being supported on the carbon material may enhance the connection between the active sites of the catalyst.

The bifunctional catalytic activity of the catalyst can usually be quantified by the potential difference between ORR and OER ($\Delta E = E_j = 10 - E_{1/2}$) (Fig. 5d). The smaller the potential difference (ΔE), the more balanced the electrocatalytic efficiency of the catalyst in the two reactions, thus reflecting the higher

bifunctional catalytic activity. Therefore, ΔE is an important index to evaluate the comprehensive performance of catalysts, which is widely used in the research of energy conversion and storage. As shown in Table S4, the ΔE of CoNiP@NC is 1.063 V, which is close to that of the commercial Pt/C-RuO₂ catalyst, indicating that it has excellent bifunctional ORR/OER electrocatalytic activity. It is noteworthy that the ΔE of CoNiP@NC is lower than that of other catalysts currently reported (Table S5). This may be due to the fact that the introduction of Ni and the simple low-temperature phosphating process have improved the OER catalytic performance. Meanwhile, the biomass carbon material has promoted the conversion between O₂ and OH⁻, thus enhancing the ORR catalytic activity while maintaining high OER activity.

3.3 DFT calculations

The electrochemical test results fully demonstrate that the introduction of Ni, together with its synergistic effect with Co and the combination with carbon materials, successfully achieves the integration of ORR and OER performance and significantly enhances the reaction rate. To uncover the essence of this synergistic enhancement mechanism on the atomic and electronic scales, density functional theory (DFT) calculations were further performed on the CoMP@NC model system, providing an in-depth analysis of the effects of different elements on the catalytic activity of Co sites during the oxygen reaction processes.

Specifically, a bulk phase model was constructed based on the CoP crystal structure (JCPDS NO. 29–0497), with the second metal M (Mn, Fe, Ni) introduced by substituting partial Co atoms to form the CoMP bulk phase. The nitrogen-doped carbon (NC) carrier model was simulated using graphene fragments containing pyrrole nitrogen and graphitic nitrogen defects. The composite interface model of CoMP nanoparticles and the NC carrier was obtained by positioning specific CoMP crystal planes (e.g., the (011) plane) onto the NC carrier surface and optimizing the configuration energetically. For computational surface property analysis, representative exposed Co sites in the composite material were selected as adsorption active centers. This study focused primarily on the adsorption behavior at Co atom sites within CoMP. Free energy plots for the adsorption and transformation of O₂, H₂O, and key intermediates (OOH, O, OH) at Co sites * were simulated during both ORR and OER reaction pathways. The atomic ratios of Co to the doping metals M (Mn, Fe, Ni) in the constructed CoMP bulk and surface models were set at 1:1, consistent with the experimental precursor ratio, with emphasis placed on investigating synergistic effects under equal doping proportions.

Based on the free energy calculations of oxygen intermediates (O, OOH, and OH), Fig. 6a-d illustrate the free energy changes of each intermediate reaction step on an ideal catalyst at zero electrode potential ($U = 0$ V) and reversible potential ($U = 1.23$ V). The free energy diagrams under different catalytic systems exhibit similar trends, indicating that the rate-determining step (RDS) of the oxygen reduction reaction (ORR) is the conversion of OH to H₂O—a process that appears endothermic (uphill) at $U = 1.23$ V, implying that the catalytic material requires a certain overpotential to make all reaction steps proceed spontaneously. The maximum potential corresponding to the free energy drop of each reaction step can

serve as an evaluation metric for electrocatalytic activity. The free energy diagrams reveal that, at the equilibrium potential of 1.23 V, the conversion step from $\ast\text{OH}$ to H_2O on the Co sites in CoP@NC, CoNiP@NC, CoMnP@NC, and CoFeP@NC requires overpotentials of approximately 0.75 V, 0.63 V, 0.73 V, and 0.66 V, respectively, to render all steps thermodynamically "downhill." Among these, CoNiP@NC exhibits a lower required overpotential, confirming its superior electrocatalytic activity, which aligns with experimental results. Theoretical calculations demonstrate that, compared to CoP@NC, CoMnP@NC, and CoFeP@NC, CoNiP@NC significantly reduces the energy barrier of the RDS in ORR, thereby exhibiting more efficient ORR reaction kinetics.

Figure 7 shows the free energy of the Co sites in the CoMP@NC model during the OER. Similarly, all steps in the OER process for all models are uphill/endergonic processes. As can be seen from the figure, the formation of adsorbed $\text{O}^\ast$ from $\text{OH}^\ast$ is the RDS. At the equilibrium potential, the Co sites of CoP@NC, CoMnP@NC, CoFeP@NC, and CoNiP@NC require overpotentials of 0.53 V, 0.48 V, 0.51 V, and 0.45 V, respectively, to make all steps show a downhill trend, thus promoting the OER reaction. The above calculations further confirm that the coexistence and synergistic effect of Co and Ni active sites on the carbon material can effectively reduce the overpotentials during the ORR and OER processes, thereby enhancing the catalytic activity.

3.4 Zinc-air battery performance test

In order to comprehensively evaluate the feasibility and performance of CoNiP @ NC material in practical applications, this study used this material as an air cathode, while using a zinc plate as an anode, and a mixed solution of 6 M KOH and 0.2 M Zn (Ac) $_2$ was used as an electrolyte to assemble a zinc-air battery (ZABs). On this basis, the electrochemical performance of the battery system was further systematically tested (Figs. 8a-b). Meanwhile, under the same testing conditions, a mixed catalyst of commercial Pt/C and RuO_2 (with a mass ratio of 1:1, denoted as Pt/C- RuO_2) was selected as the control catalyst.

Figures 8c - f present the comparison data between CoNiP@NC and Pt/C- RuO_2 in terms of open - circuit voltage, charge - discharge polarization curves, power density, and charge - discharge cycle stability. The test results show (Fig. 8c) that the open circuit voltage of CoNiP@NC is 1.48 V, slightly lower than the 1.53 V of Pt/C- RuO_2 . Meanwhile, it was observed from the charge-discharge polarization curves in Fig. 8d that the voltage of CoNiP@NC was higher than that of Pt/C- RuO_2 during charging, while the voltage during discharge was lower than that of Pt/C- RuO_2 . In addition, the discharge power density of CoNiP@NC was lower than that of Pt/C- RuO_2 (Fig. 8e). In addition, the charge discharge cycling test can be used to evaluate the long-term stability of the cells. The CoNiP@NC-based zinc-air battery was cycled for 240 h at a current density of 2 mA cm^{-2} (Fig. 8f), which exhibited a longer cycle life than that of the Pt/C- RuO_2 (110 h), as well as a lower voltage decay rate than that of the Pt/C- RuO_2 . In comparison to the cycle times of other catalysts currently available, this catalyst exhibits a longer cycle time, highlighting its advantages more distinctly (Table S6). The above results indicate that the CoNiP@NC catalyst's longer cycle life suggests an advantage in terms of durability.

3.5 Investigation of Active Sites

The exceptional bifunctional catalytic activity of the CoMP@NC composite can be attributed to the multiple active sites formed through synergistic interactions among its components. For the oxygen reduction reaction (ORR), the activity primarily stems from pyrrole nitrogen sites in the nitrogen-doped carbon matrix, cobalt sites in the nickel-doped bimetallic phosphide that modulate the electronic structure, and abundant surface Co^{2+} species confirmed by XPS and DFT calculations. For the oxygen evolution reaction (OER), the activity mainly arises from the in situ formation of a metal (oxygen) hydroxide layer on the phosphide surface, highly active surface oxygen species, and synergistic sites between the cobalt-nickel bimetallic complex. The integration of these multifunctional active sites enables CoNiP@NC to efficiently catalyze both ORR and OER reactions.

4 Conclusions

Biomass carbon materials were compounded with transition metal phosphides using a two-step hydrothermal method and CVD phosphorization to obtain CoNiP@NC bifunctional catalysts. The CoNiP@NC catalysts showed onset potentials, half-wave potentials, limiting current densities, and n for the ORR of 0.876 V, 0.670 V, 4.64 mA cm^{-2} , and 3.70, respectively, and overpotentials of 503 mV for the OER. 3.70, and the overpotential of OER was 503 mV with a bifunctional characteristic $\Delta E = 1.063 \text{ V}$. The DFT results confirmed that the incorporation of Ni decreased the overpotential of Co sites during the oxygen reaction. In addition, the CoNiP@NC-based rechargeable zinc-air battery could be cycled for 240 h at a current density of 2 mA cm^{-2} , which exhibited a better cycling stability performance than that of the Pt/C-RuO₂ battery (110 h). In summary, the synergistic effect of Co and Ni dual sites and the composite with biomass carbon materials realized the integration of ORR and OER performances, which provided a feasible idea for the design of highly efficient and stable bifunctional catalysts for transition metal phosphides.

Declarations

Declarations of interest

None.

Acknowledgements

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Figures

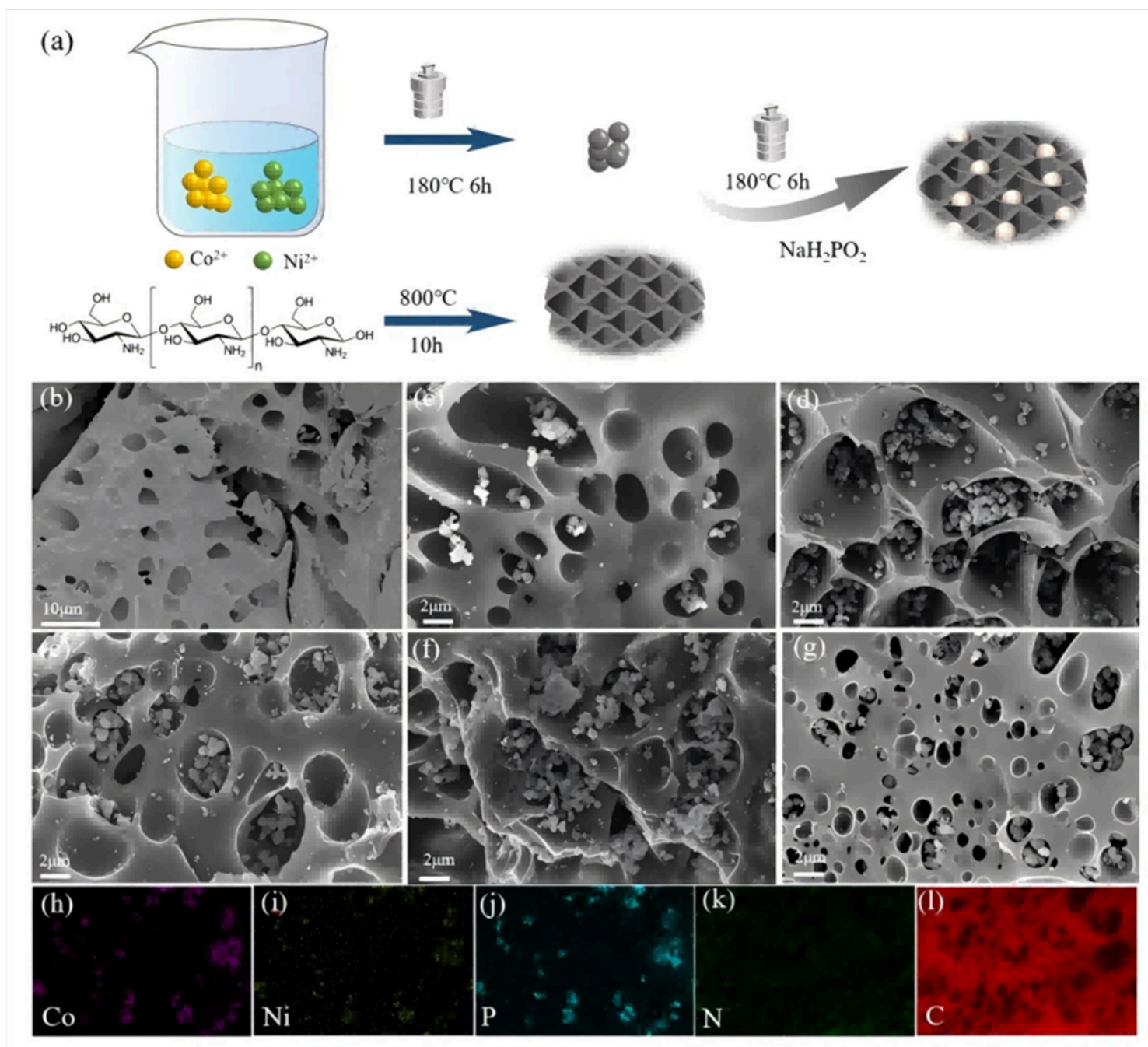


Figure 1

(a) Schematic of the preparation flow; SEM: (b) NC; (c) CoP@NC; (d) CoMnP@NC; (e) CoFeP@NC; (f-g) Co, Ni, P, N, C elemental mapping of CoNiP@NC and (h-l) CoNiP@NC

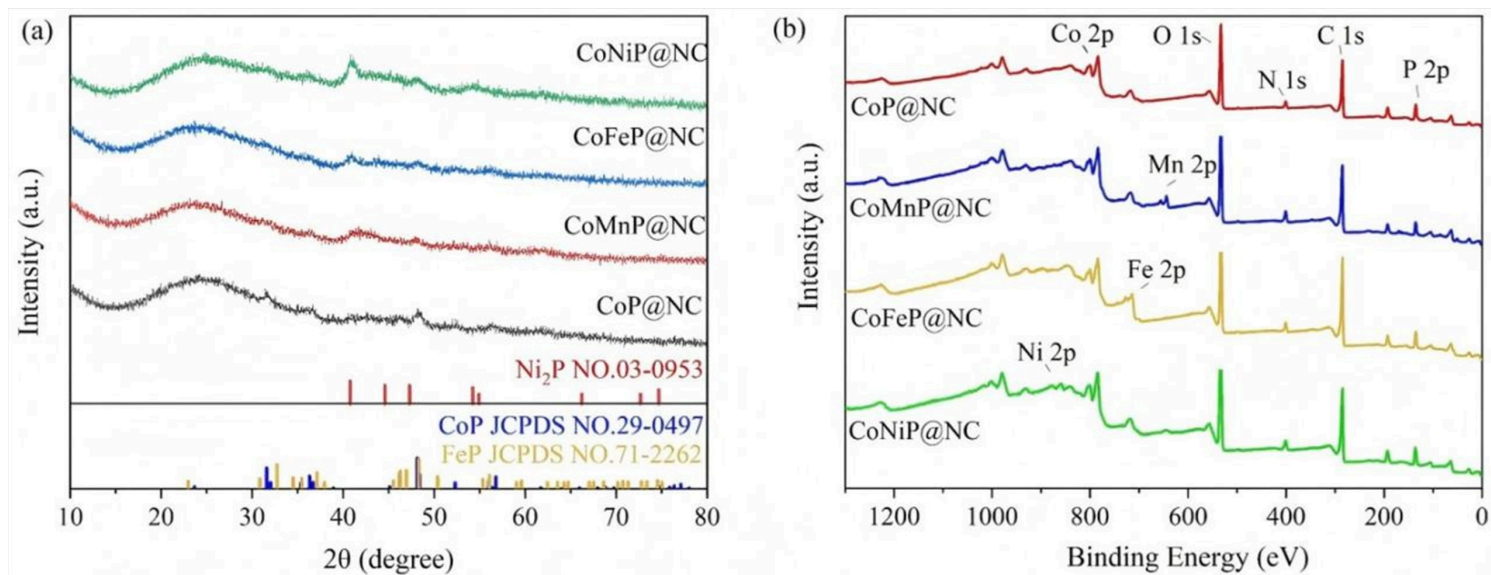


Figure 2

(a) XRD spectra; (b) XPS full spectra of CoP@NC, CoMnP@NC, CoFeP@NC and CoNiP@NC samples

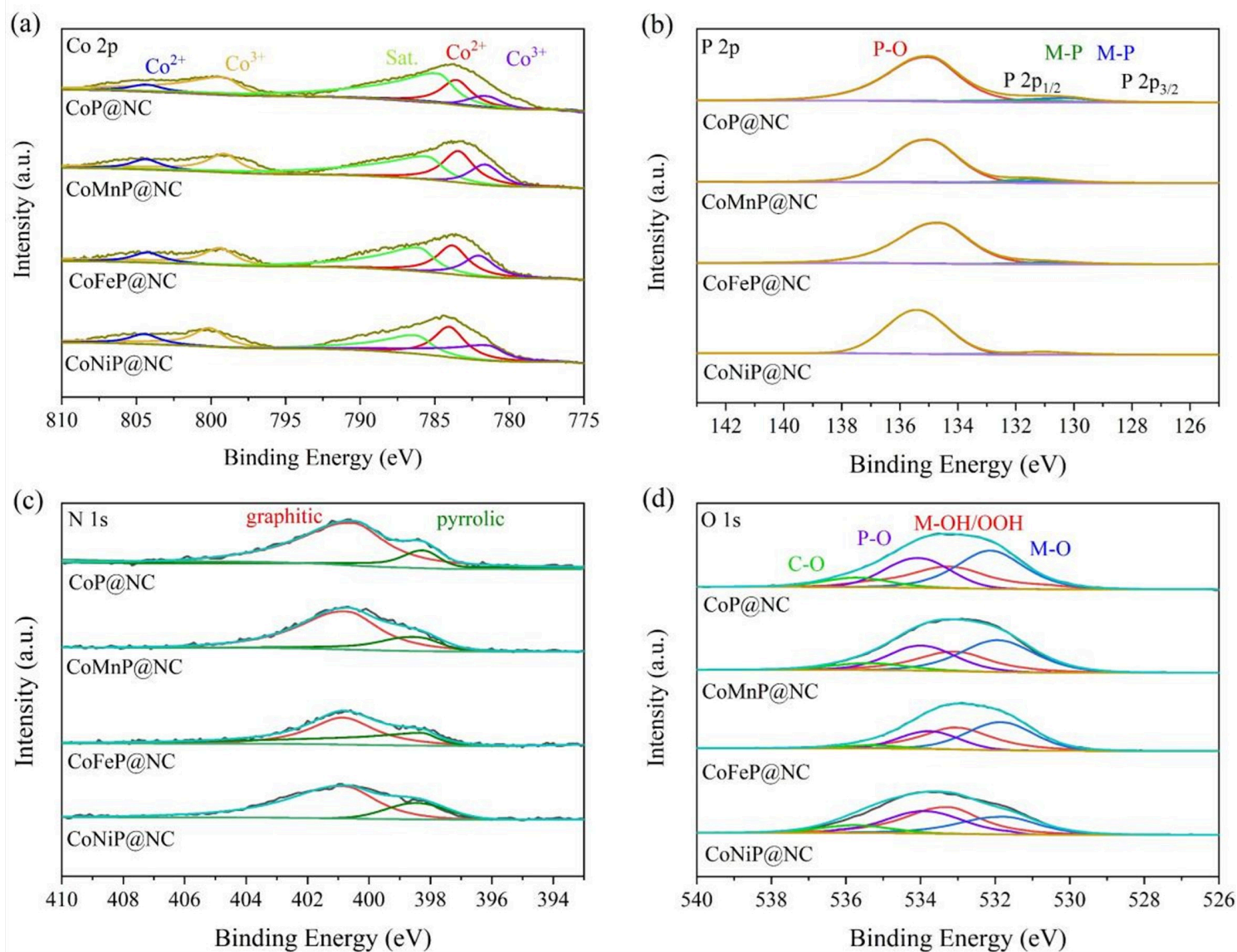


Figure 3

XPS spectra of CoP@NC, CoMnP@NC, CoFeP@NC and CoNiP@NC: (a) Co 2p; (b) P 2p; (c) N 1s and (d) O 1s

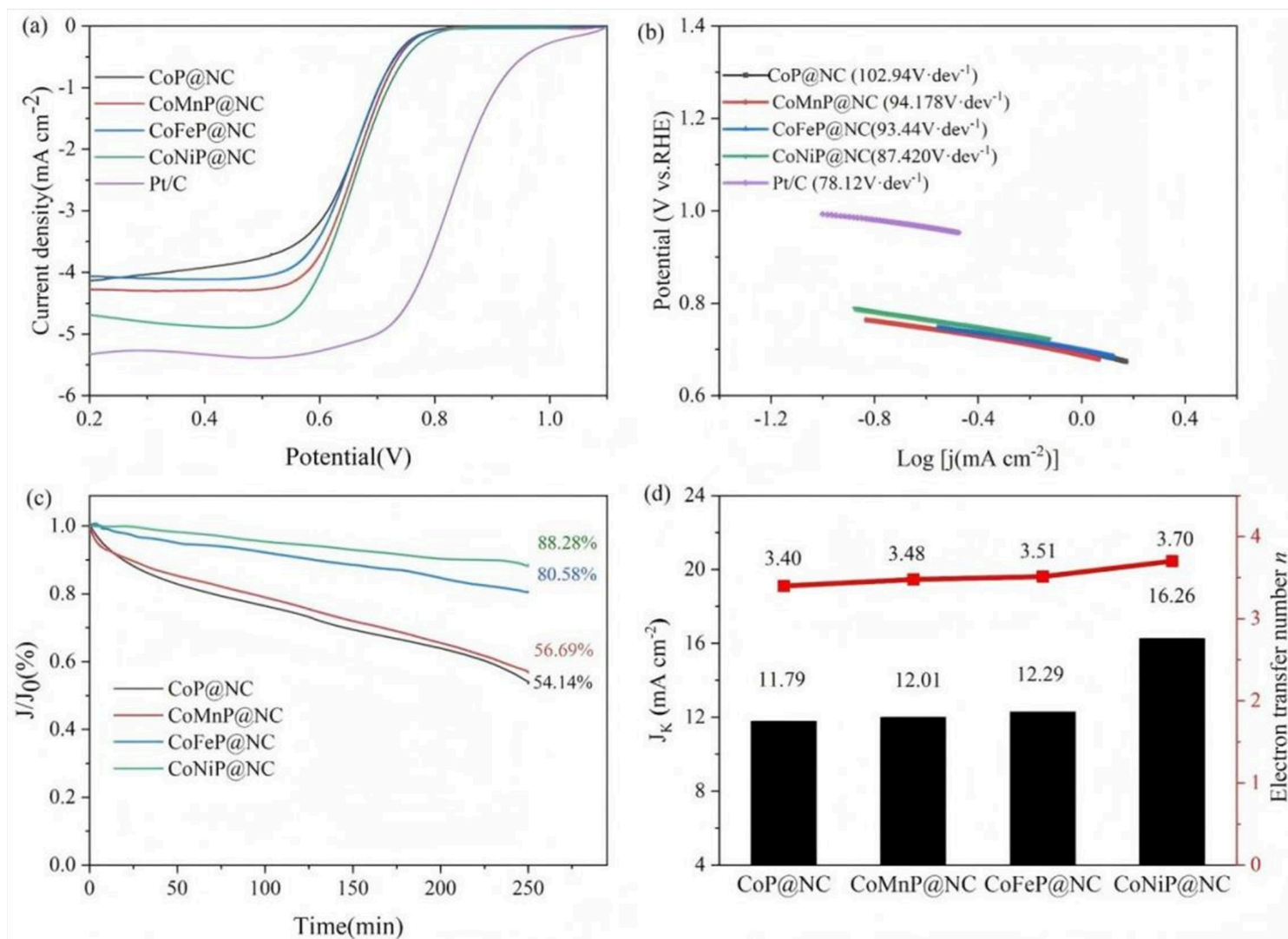


Figure 4

(a) RDE oxygen reduction polarization curves; (b) Tafel curves; (c) stability test curves; (d) electron transfer number versus dynamic current density plots for CoP@NC, CoMnP@NC, CoFeP@NC, CoNiP@NC, and Pt/C at 10 mV S⁻¹

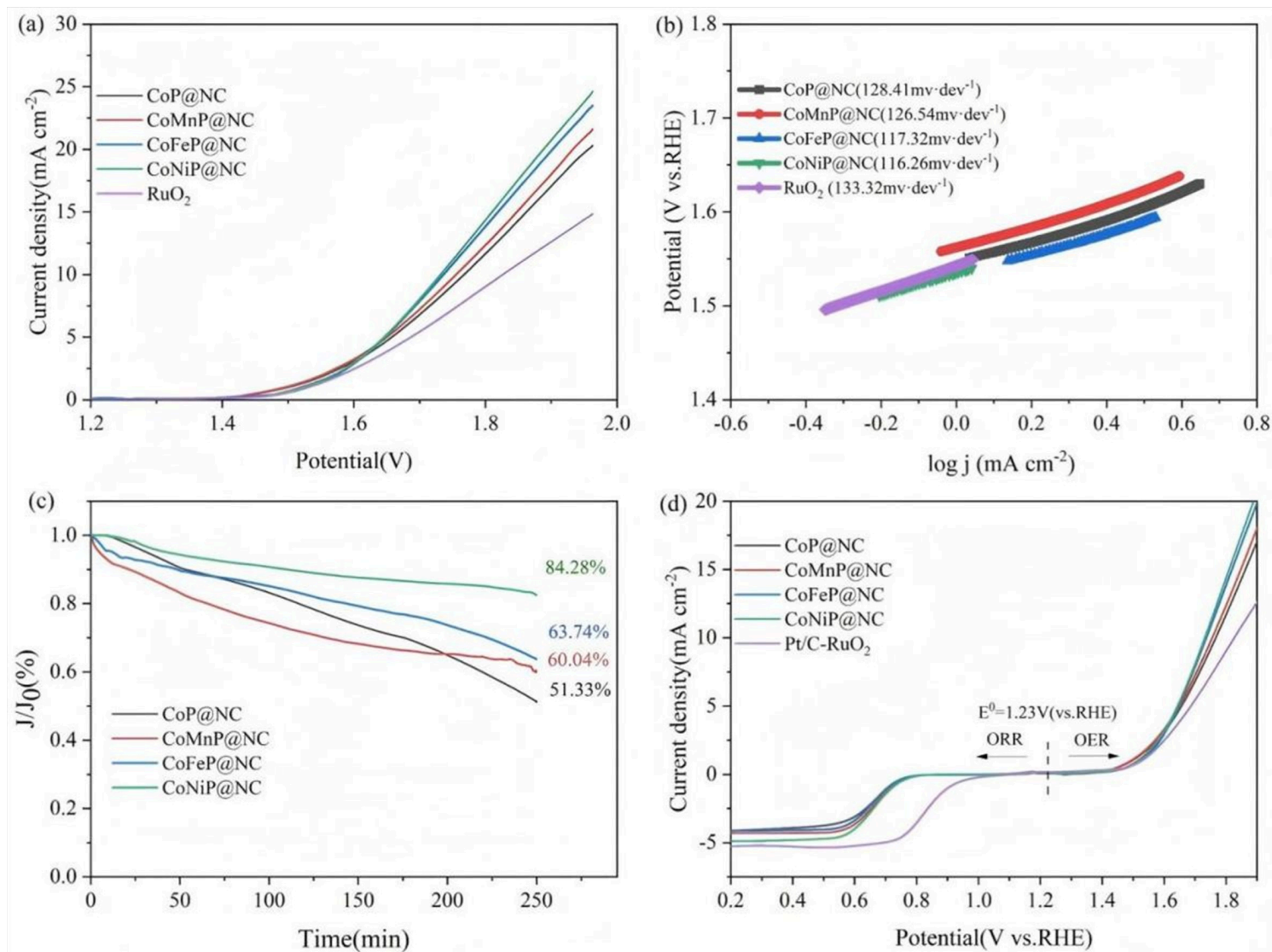


Figure 5

(a) LSV curves; (b) Tafel curves; (c) Stability test curves; (d) Bifunctional catalytic activities of ORR and OER for CoP@NC, CoMnP@NC, CoFeP@NC, CoNiP@NC, and RuO_2 in O_2 -saturated 0.1 M KOH solution at a test rate of 50 mV s^{-1}

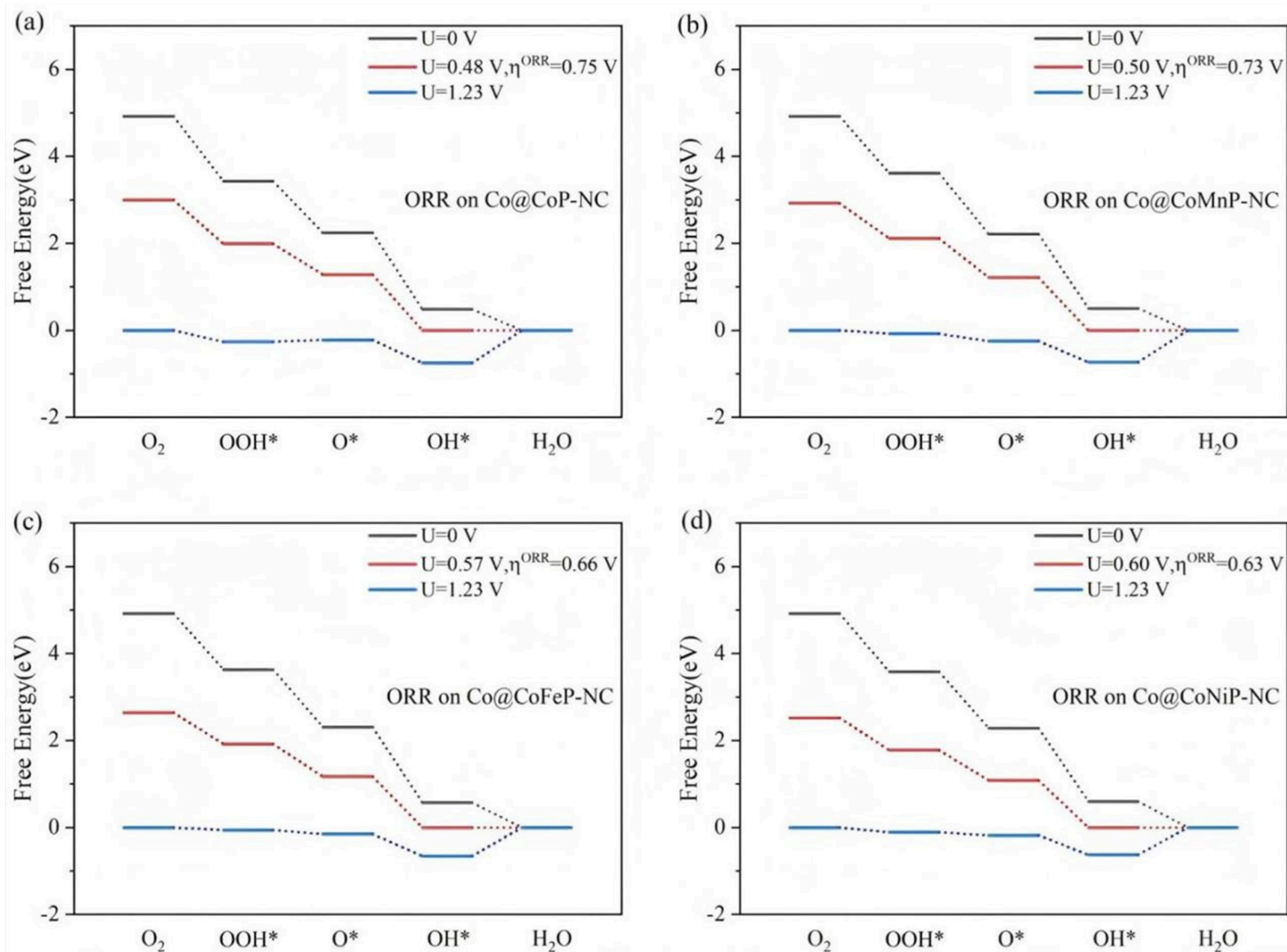


Figure 6

Free energies of Co sites of (a) CoP@NC, (b) CoMnP@NC, (c) CoFeP@NC, and (d) CoNiP@NC during the ORR process

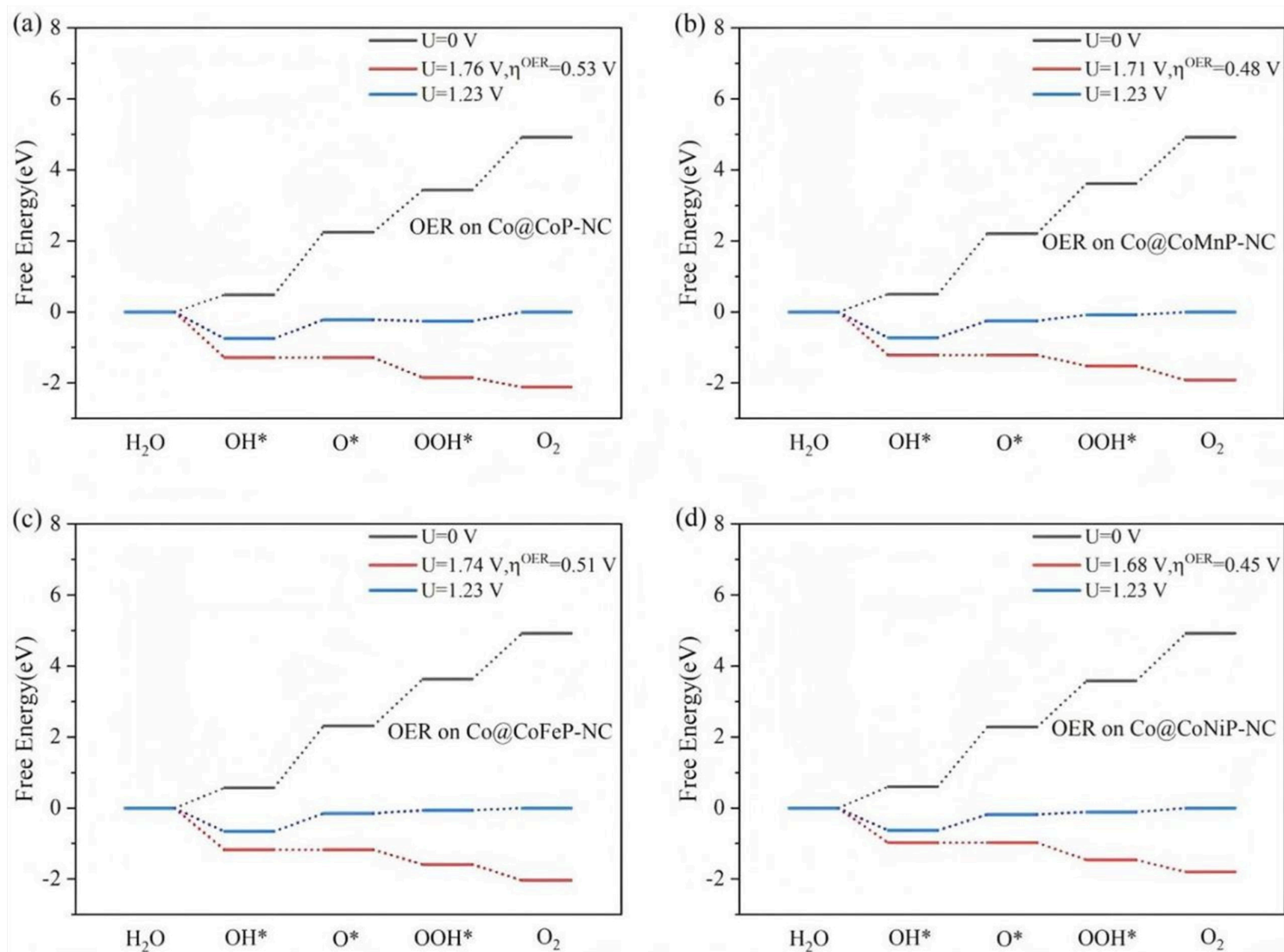


Figure 7

Free energies of Co sites of (a) CoP@NC, (b) CoMnP@NC, (c) CoFeP@NC, and (d) CoNiP@NC during the OER process.

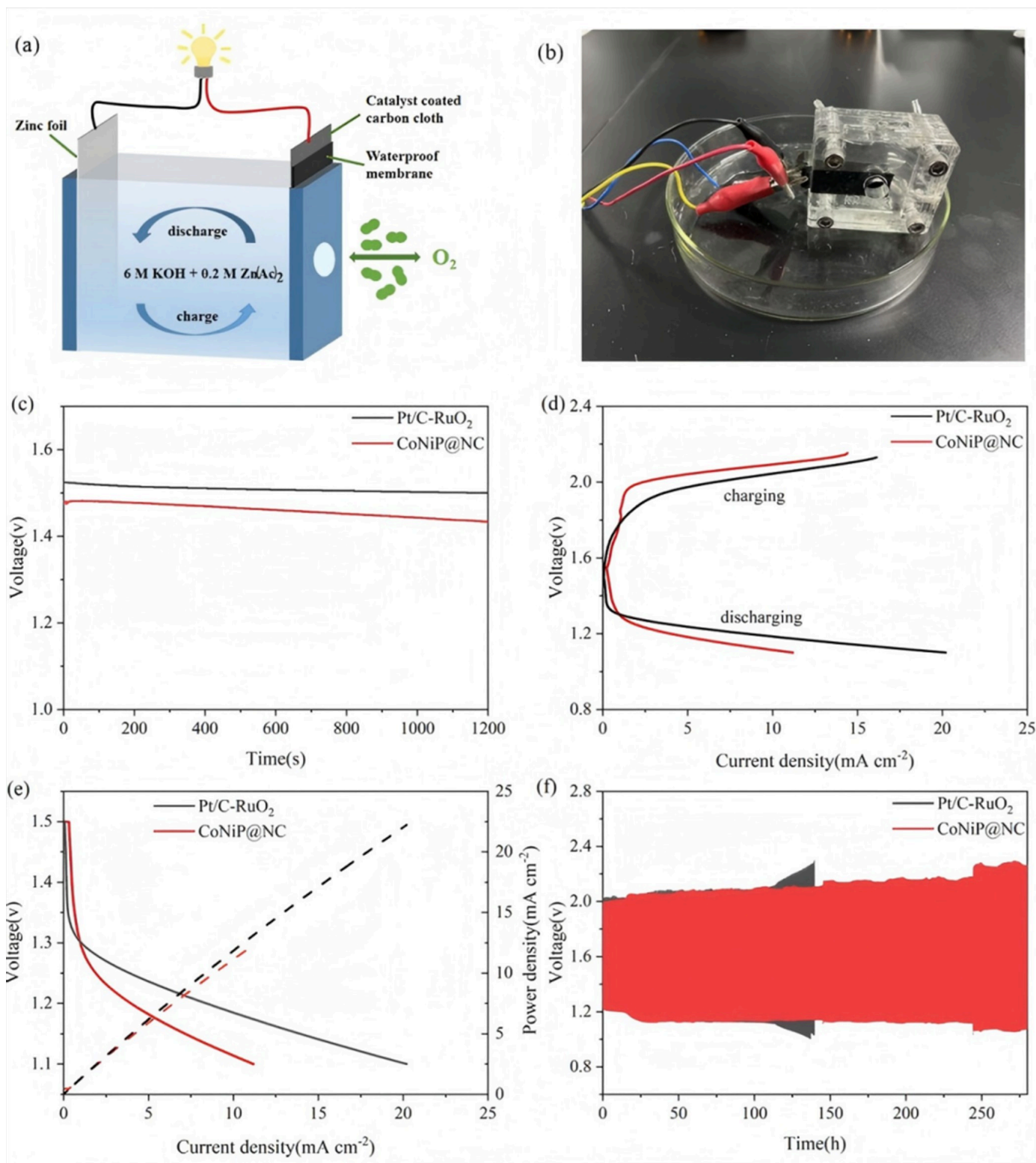


Figure 8

(a) Schematic diagram of ZABs; (b) Assembly diagram of ZABs; (c) Open-circuit voltage; (d) Charge-discharge polarization curves; (e) Power density test; (f) Charge-discharge cycling curves

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