Indiscrete metal/metal-N-C synergic active sites for efficient and durable oxygen electrocatalysis toward advanced Zn-air batteries

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Abstract
Carbon has been deemed promising electrocatalyst for oxygen reduction/evolution reaction (ORR/OER). However, most carbon materials are not stable in highly oxidative OER environments. Herein, nitrogen (N) and transition metal (TM) co-doped carbon nanosheets hybridizing with transition metal (TM/TM-N-C, TM = Fe, Co, Ni) are developed from biomass lysine by employing a NaCl template and molten-salt-promoted graphitization process. Among the as-synthesized TM/TM-N-C, the Ni/Ni-N-C with Ni nanocubes embedded in carbon demonstrates an excellent ORR-OER stability during the potential of 0.06–1.96 V. The rechargeable Zn-air battery with the fabricated Ni/Ni-N-C as the cathode catalyst produces a low voltage gap of 0.773 V, which is only slightly increased by 5 % after 150 cycles testing. Combined experimental and theoretical studies reveal that the exceptional activity and ORR-OER wide potential durability of Ni/Ni-N-C can be ascribed to highly active Ni-N4-C configuration, synergistic effect between Ni and Ni-N4-C, carbon nanosheets structure and formation of stable Ni3+-N for protecting carbon from oxidation.

1. Introduction
The growing of highly efficient energy conversion/storage devices, such as metal-air battery, water electrolyzing generator, reversible fuel cell, etc., have been triggered by the increasingly high demand for energy sources [1,2]. The oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), the crux in these energy devices, are of great academic and industrial interest [3]. However, both the ORR and OER involve complex adsorption/desorption and electron transfer processes with sluggish kinetics, which requires efficient and stable bifunctional electrocatalysts to generate high currents at the operating potentials [4].

Platinum group metals (such as Pt, Pd-based materials) and precious metal oxides (such as IrO2 and RuO2) are well-known highly active ORR and OER electrocatalysts, respectively. However, the scarcity and high price of these materials on earth greatly impede the large-scale application of the above electrochemical energy devices [5,6]. To explore potential alternatives to replace the rare and expensive the precious-metal-based catalysts, great efforts have been focused on exploring low-cost and earth-abundant catalysts and the fundamental understanding of their active sites and catalytic reaction pathways [7]. Compared to metal oxides [8–10], sulfides [11,12] and carbides [13,14], carbons are promising electrocatalysts for ORR due to the advantages of cheap resource, high intrinsic electronic conductivity, convenient surface functionalization, and tenability [15–17]. In particular, the electronic structure as well as physical and chemical properties of carbon can be engineered by co-doping of metal and nitrogen, thereby favors for modulating both the ORR and OER activity [18–21]. However, the durability of carbon toward OER still remain a great challenge because of the highly oxidative environment arose from oxygen evolution at the high potentials. It’s known that the standard Nernstian potential is 1.229 V for the OER. While the thermodynamically potential for carbon oxidation is above 0.207 V (C + 4OH− → CO2 + 2H2O + 4e−), which becomes significant above 1.0 V [3,22]. To address this challenge, the graphene tubes modified with FeCoNi alloy were developed by Wu et al. [3]. Other than this, few investigation has been reported.

Aiming to boost both the activity and long-term stability of TM-N-C toward ORR and especially OER, we report a class of nitrogen and transition metal doped carbon nanosheets modified with transition metal (TM/TM-N-C, TM = Fe, Co, Ni), which are derived from lysine by
employing NaCl crystal template and a molten-salt-promoted graphitization process. The fabrication of TM/TM-N-C is cost-effective, green and scalable. L-lysine is a kind of natural amino acids that is eco-friendly and renewable. Compared to the traditional hard templates, such as silica nanoparticles (SiO₂) [23], magnesium cube (MgO) [24], and porous anodic alumina (PAA) [25], etc., the novel and facile template of NaCl crystal, employed in this work, has the advantages of recyclability and easily removable with water, without the active site loss. Moreover, the NaCl crystal can promote the graphitization of carbon materials via a molten-salt-promoted process [26,27].

In our previous study, the possibility of employing NaCl template to synthesize nitrogen-doped carbon hollow cubes (NCHCs) was explored preliminarily [27]. The obtained NCHCs showed promising ORR activity, however, the OER activity of NCHCs was not satisfactory. Especially, the NCHCs presented inferior durability toward OER like other metal-free heteroatom-doped carbon reported [3,28]. To address the durability challenge of carbon, in this work, transition metal and N co-doped carbon hybridizing with transition metal (TM/TM-N-C, TM = Fe, Co, Ni) are thereby synthesized from biomass lysine and transition metal salts by employing NaCl template and a molten-salt-promoted graphitization process. It’s found that the addition of transition metal significantly influence the morphology, structure, and the resulting catalytic activity and long-term stability of carbon for OER and ORR. The as-fabricated Fe/Fe-N-C with Fe nanoparticles wrapped in carbon nanosheets shows an excellent catalytic activity for OER, while the Ni/Ni-N-C with Ni nanocubes embedded in carbon exhibits a superb catalytic activity for OER. Impressively, the Ni/Ni-N-C demonstrates an excellent OOR-OER stability over a wide potential of 0.06–1.96 V. Furthermore, to explore the practical applications of TM/ TM-N-C, Zn-air batteries (ZAB) have been constructed by adopting Fe/ Fe-N-C and Ni/Ni-N-C as the air cathode catalyst, respectively. The primary ZAB with Fe/Fe-N-C cathode produces a high power density of 0.181 W cm⁻², superior to that of ZAB assembled with benchmark Pt/C cathode (0.162 W cm⁻²). More importantly, the rechargeable ZAB with Ni/Ni-N-C cathode delivers excellent long-term durability. The ZAB remains stable over 210 h at a current density of 10 mA cm⁻² when repeatedly charged and discharged, which is much more stable than that of state-of-the-art Pt/C- and IrO₂-based ZAB. Combined experimental and theoretical studies reveal the electrocatalytic activity and durability origin of TM/TM-N-C.

2.2. Physical characterization

The scanning electron microscopy (SEM, Hitachi-S4700) and transmission electron microscopy (TEM, FEI Tecnai-G2 F20 operating at 200 kV) were used to study the morphology as well as microstructures of the samples. The crystal or amorphous phase of the samples was investigated with an X-ray diffractometer (XRD, Cu Kα radiation; 40 kV, 40 mA; λ = 0.154 nm). Nitrogen adsorption-desorption isotherms were acquired on the ASAP-2020M system of N₂ at 77 K. The Brunauer–Emmett–Teller (BET) specific surface area and the pore size distribution of the samples were calculated using adsorption data in a relative pressure of 0-1 and the desorption branches of the isotherms, respectively. The X-ray absorption spectroscopy (XAS) of the samples were performed at 300 mA and 2.5 GeV (Beamline 4B7B station, Beijing Synchrotron Radiation Facility). The X-ray photoelectron spectroscopy (XPS) of the samples were collected on an ESCALAB 250Xi (Thermo Fisher) by using Al Kα radiation.

2.3. Electrochemical measurement

The ORR and OER were studied with a standard three-electrode setup using the PINE electrochemical workstation (AFPBP1 bipotentiostat, and AFMSRX rotorator) at 25°C. The conventional rotating ring-disc electrode (RRDE) was comprised of glassy carbon (GC) disk (Φ55 nm) coated with catalyst surrounded by a Pt ring. The rotating disk electrode (RDE) was only a GC disk coated with catalyst. The counter electrode and reference electrode are graphite rod and Ag/AgCl (3 M Cl⁻, double junction), respectively. The electrolyte used for the electrochemical measurements is 0.1 M KOH. The mass-loading of the catalysts on the GC disk was 0.6 mg cm⁻². In ORR polarization measurement, linear sweep voltammetry (LSV) using RRDE or RDE were conducted with the electrode rotated from 400 to 2500 rpm. A potential of 1.46 V was set for the Pt ring. The long term stability of the catalysts toward ORR was evaluated by accelerated durability test (ADT) with potential cycles.

The LSV for OER were performed from 0.96 to 1.96 V at 1600 rpm in N₂-saturated electrolyte. The durability of the catalysts toward OER was checked by ACT with potential cycles.

To study the catalysts/electrolyte interface, the electrochemical impedance spectroscopy (EIS) was performed in the frequency of 0.01–50000 Hz.

2.4. Zn-air battery assemble and test

In the Zn-air battery (ZAB), the air cathode was a piece of hydrophobic carbon paper coated with catalyst ink providing a mass loading of 1 mg cm⁻². Briefly, 1 mg of catalyst and 0.25 mg of carbon black were dispersed into 0.25 mL of ethyl alcohol mixed with 10 µL of Nafion solution (5 wt.%). A Zn plate worked as the anode, 6 M KOH and 0.2 M C₆H₃O₂Zn·2H₂O were the electrolyte. All the electrochemical measurements were performed with the home-made cell for discharge-charge curve on a battery test system (LAND BT 2000, WuHan, P. R. China) and on the primary cell for polarization curve with

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Electrochemical Workstation (IM6e, ZAHNER, Germany).

2.5. Computational methods

The density functional theory (DFT), implemented with DMol³ program, was used for the theoretical calculations. The generalized-gradient approximation (GGA) was used to depict the exchange-correlation potential. In an optimized structure, the convergence tolerance of energy, maximum force, and displacement are $2.0 \times 10^{-5}$ Ha, 0.004 Ha Å$^{-1}$ and 0.005 Å, respectively. An optimized hydrogen terminated N-doped graphene fragment (C_{38}H_{16}N_{4}), together with an embedded TM-N_{4} (TM = Fe, Co, Ni) moiety, was selected as the model for our study. The adsorption energy was calculated based on the following equation:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{catalyst}} - E_{\text{intermediate}}$$

where $E_{\text{ads}}$, $E_{\text{total}}$, $E_{\text{catalyst}}$, and $E_{\text{intermediate}}$ are the adsorption energy, total energies of TM-N_{4} embedded N-graphene with an adsorbed intermediate, TM-N_{4} embedded N-graphene, and isolated intermediate, respectively. The thermodynamic free energy of individual reaction step on these catalysts was obtained on the basis of a hydrogen electrode model:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$


3. Results and discussions

As illustrated in Fig. 1a, the TM/TM-N-C (TM = Fe, Co, Ni) was synthesized by the pyrolysis of the mixture of lysine monohydrochloride (C_{6}H_{15}O_{2}N_{2}Cl), transition metal chloride (FeCl_{3}.6H_{2}O, CoCl_{2}.6H_{2}O, NiCl_{2}.6H_{2}O) and NaCl. The lysine monohydrochloride is the carbon and N source, while the NaCl acts as the template. The nitrogen-doped carbon hollow cubes (N-C) are formed by pyrolyzing the C_{6}H_{15}O_{2}N_{2}Cl and NaCl [27]. Interestingly, the addition of transition metal chlorides (e.g., FeCl_{3}.6H_{2}O, CoCl_{2}.6H_{2}O, or NiCl_{2}.6H_{2}O) into the precursors can significantly affect the structure and morphology of the products. Different from the hollow cubes of N-C (Fig. 1b), the carbon nanosheets with nanoparticles wrapped in, nanosheets loaded on and nanocubes embedded in have been obtained for Fe/Fe-N-C (Fig. 1c), Co/Co-N-C (Fig. 1d) and Ni/Ni-N-C (Fig. 1e), respectively. More details of different structure and morphology for the samples can be found in Fig. S2 – 4 (Supporting Information).

The TEM (Fig. 2a) and high-resolution TEM (HRTEM) image (Fig. 2e) reveal the formation of hollow cubes with a thickness of ~6 nm and the graphitic layer of ~0.34 nm in N-C. The elemental mapping image (Fig. 2i) shows the evenly distribution of elements C, N and O in the sample. Instead of the hollow cubes presented by N-C, the Fe/Fe-N-C display nanosheets with nanoparticles wrapped in (Fig. 2b and f), and the lattice spacing of ~0.203 nm corresponds to (110) face of Fe (Fig. 2f). The Co/Co-N-C shows small nanosheets loaded on 2D nanosheets (Fig. 2c and g), and the lattice spacing of ~0.205 nm can be assigned to (111) face of Co (Fig. 2g). The distribution of Fe (Fig. 2j) and Co (Fig. 2k) in the samples is in accordance with that of N, O and C, indicating the uniform distribution of these elements. In contrast to Fe/Fe-N-C and Co/Co-N-C, the Ni/Ni-N-C demonstrates nanocubes embedded in nanosheets (Fig. 2d and h), and the lattice spacing of ~0.204 nm is corresponding to (111) face of Ni (Fig. 2h). The distribution of Ni is opposite to that of C, O and N, which manifests that Ni nanocubes are embedded in carbon nanosheets (Fig. 2i). The XRD patterns (Fig. S5, Supporting Information) further confirm the formation of Fe, Co and Ni metal in Fe/Fe-N-C, Co/Co-N-C and Ni/Ni-N-C, respectively.

The structures and morphologies of TM/TM-N-C are different from each other depending on the choice of Fe, Co or Ni, which can be ascribed to: 1) the Fe, Co, Ni exhibits different catalytic effect in the formation of different structure of carbon; 2) the reduction potentials of Fe^{2+}, Co^{2+}, Ni^{2+} to zero-valent metals are different, which follow the order of Fe (-0.447 V), Co (-0.280 V), Ni (-0.257 V).
As revealed by the N$_2$ adsorption-desorption isotherm plots for various samples, the Fe/Fe-N-C, Co/Co-N-C and Ni/Ni-N-C have BET specific surface area of 434, 238 and 332 m$^2$ g$^{-1}$, respectively, which are much larger than that of N-C (123 m$^2$ g$^{-1}$, Fig. 3a, Supporting Information). These samples are enriched with both micropores (centered at 0.60--0.71 nm) and mesopores (centered at 2.6--7.7 nm) (Fig. S6a, Supporting Information), which are beneficial for not only accommodating high density of active sites but also promoting effective mass transport in catalytic reactions.

Carbon has been intensively studied as catalyst for ORR. However, being employed as bifunctional catalyst, especially under highly oxidative conditions (ca. 1.6--1.9 V vs. RHE), has rarely been studied [3,29]. We first performed rigorous stability tests by an RDE setup from 0.06 to 1.96 V (vs. RHE) in 0.1 M KOH electrolyte to evaluate the durability of catalysts. The bifunctional ORR-OER durability was evaluated from the potential change ($\Delta E$) underwent both the ORR and OER reactions, that is the difference between the potential at 3 mA cm$^{-2}$ for ORR and the potential to achieve 10 mA cm$^{-2}$ for OER. As can be seen in Fig. 3a, the N-C showed a large decay in $\Delta E$ after 200 harsh potential cycles ($\Delta E_{200} = 1.36$ V). With the addition of TM, the catalysts exhibited better ORR-OER stability (Fig. 3b-d). Compared to Fe/Fe-N-C ($\Delta E_{200} = 1.28$ V) and Co/Co-N-C ($\Delta E_{200} = 1.08$ V), the Ni/Ni-N-C showed the smallest potential change after 200 cycles ($\Delta E_{200} = 0.94$ V), demonstrating the best OER stability among the three samples under highly oxidative conditions.

In O$_2$-saturated 0.1 M KOH, the CV of Fe/Fe-N-C presented a distinct cathodic peak at 0.8 V because of the O$_2$ reduction (Fig. S7a, Supporting Information). The more positive peak position of Fe/Fe-N-C with respect to that of Co/Co-N-C and Ni/Ni-N-C demonstrates its higher ORR activity. Furthermore, the LSV of the Fe/Fe-N-C at 1600 rpm presented a half wave potential ($E_{1/2}$) of 0.881 V, showing a positive shift of ~17 mV with respect to that of commercial Pt/C (Fig. 4a). This further proves the higher activity of Fe/Fe-N-C toward ORR. Note that the peak between 0.7 and 0.8 V in the LSVs (Fig. 4a) most likely arise from the reduction of O$_2$ trapped in the amorphous pores of catalysts [30--32,27]. With the disk and ring current (Fig. 4a and Fig. S7b, Supporting Information) over the entire potential range, the HO$_2^-$ and e$^-$ were calculated to be < 2% and > 3.8, respectively, for Fe/Fe-N-C (Fig. S7c, Supporting Information), indicating a predominant 4 e$^-$ reduction process of O$_2$. As shown in Fig. 4b, the Tafel slopes are 120, 59, 62, 63, and 61 mV dec$^{-1}$ for N-C, Fe/Fe-N-C, Co/Co-N-C, Ni/Ni-N-C and Pt/C, respectively, which are beneficial for not only accommodating high density of active sites but also promoting effective mass transport in catalytic reactions.

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The OER activities of N-C, TM/TM-N-C and the commercial IrO$_2$ were compared. Amongst all the studied catalysts, the Ni/Ni-N-C exhibits the lowest onset potential (Fig. 4d). The potential to achieve 10 mA cm$^{-2}$ is 1.536 V for Ni/Ni-N-C, lower than that of the commercial IrO$_2$ (1.583 V). Furthermore, the Tafel slope for the Ni/Ni-N-C (122 mV dec$^{-1}$) is smaller than that of N-C (198 mV dec$^{-1}$), Fe/Fe-N-C (175 mV dec$^{-1}$), Co/Co-N-C (138 mV dec$^{-1}$) and IrO$_2$ (130 mV dec$^{-1}$) (Fig. 4e), suggesting a fast OER kinetics of Ni/Ni-N-C. The long-term stability of the samples toward OER was studied with an ADT by scanning CV in 1.0--1.9 V at 1600 rpm (Fig. 4f). Compared to IrO$_2$, only a slight increase of 3 mV in the potential and almost no decreasing of current density for Ni/Ni-N-C after 200 cycles continuous operation are observed.

Table S1 summarized and compared the electrocatalytic activities of the as-fabricated samples for ORR/OER with those of state-of-the-art metal complex N-doped carbon materials reported. The ORR/OER activities of our samples are among the highest ones.

The Nyquist curves of the catalysts obtained from EIS measurement are displayed in Fig. 4g. The equivalent circuit (inset of Fig. 4g) consists of Rs, Rc, Rt, CPE$_i$, and CPE$_o$, which represent the electrolyte resistance, intrinsic resistance of catalyst, charge transfer resistance of catalyst, constant phase elements, respectively [33]. Compared with that of N-C, the substantially smaller Rs of all the TM/TM-N-C indicates higher electronic conductivity of these carbon-based catalysts modified with metal particles. Notably, the Rt of Ni/Ni-N-C (3.88 $\Omega$ cm$^{-2}$) is smaller than that of Co/Co-N-C (6.71 $\Omega$ cm$^{-2}$), Fe/Fe-N-C (27.4 $\Omega$ cm$^{-2}$).
Fig. 3. Rigorous ORR-OER durability for N-C (a), Fe/Fe-N-C (b), Co/Co-N-C (c), and Ni/Ni-N-C (d) in the potential of 0.06 - 1.96 V at 10 mV s⁻¹ in 0.1 M KOH electrolyte without IR-corrected.

Fig. 4. LSVs of ORR (a) and OER (d) on N-C, Fe/Fe-N-C, Co/Co-N-C, Ni/Ni-N-C, commercial IrO₂ and Pt/C (20 wt.%) in 0.1 M KOH (1600 rpm, 10 mV s⁻¹); Corresponding Tafel plots for ORR(b) and OER (c); c) LSVs of ORR for Fe/Fe-N-C and commercial Pt/C before and after 10,000 cycles; f) LSVs of OER for Ni/Ni-N-C and IrO₂ before and after 200 cycles; g) EIS of various catalysts during OER.
The small charge transfer resistance of Ni/Ni structure that results in facilitated transportation of O2. As shown in the cathode can be ascribed to its high ORR activity and porous nanosheets (Fig. 5b). The high performance of primary ZAB containing Fe/Fe than that of Ni/Ni (Fig. 5c, a specific discharge capacity of 741 mA h gZn⁻¹ and an energy density of 904 Wh kgZn⁻¹, a specific capacity of 733 mA h gZn⁻¹ and an energy density of 880 Wh kgZn⁻¹, have been obtained for Fe/Fe-N-C and Ni/Ni-N-C, respectively. Interestingly, the voltage plateaus of Ni/Ni-N-C got closer and closer to that of Fe/Fe-N-C as the discharge current density increased (Fig. 5d), suggesting a higher rate capability of Ni/Ni-N-C.

Inspired by the outstanding OER catalytic activity and long-term ORR-OER stability of Ni/Ni-N-C electrocatalyst, the electrochemical performance of a rechargeable ZAB using Ni/Ni-N-C as the air electrode catalyst was evaluated, and that of Fe/Fe-N-C based rechargeable ZAB is also included for comparison, as shown in Fig. 5e. The Ni/Ni-N-C produced significantly lower charging voltage than that of Fe/Fe-N-C because of its superior OER activity. It’s noticed that the ORR activity of Fe/Fe-N-C would be attenuating when exposed to positive voltage. The voltage gap of Fe/Fe-N-C between charge and discharge became larger after the first three discharge/charge cycles. In contrast, the voltage gap of Ni/Ni-N-C between charge and discharge remained almost unchanged. This interesting phenomenon is consistent with the ORR-OER stability results (Fig. 5b and d). Furthermore, Ni/Ni-N-C cathode showed significantly higher discharging voltage than that of commercial Pt/C and lower charging voltage than that of commercial IrO₂ (Fig. 5f). Notably, the rechargeable ZAB assembled with the Ni/Ni-N-C as air electrode catalyst showed remarkable cycling stability at 10 mA cm⁻² when repeatedly charged and discharged for 210 h with a period of 1 h/cycle. The Ni/Ni-N-C based ZAB produced a small voltage gap of 0.773 V in the first cycle (inset of Fig. 5f). And only a slight increase of 5 % in the voltage gap was observed for Ni/Ni-N-C after 150 cycles testing. In contrast, Pt/C and IrO₂ showed a significantly increased voltage gap, suggesting the superior long-cycling durability of Ni/Ni-N-C when used as the air electrode catalyst. As illustrated in Fig. 5g, two connected ZAB containing the Ni/Ni-N-C air electrode can turn on a light-emitting diode (LED, 2.4 V).

In order to unravel the origin of ORR/OER activity of the as-fabricated TM/TM-N-C, XPS as well as XAS was performed to investigate the surface elemental composition and electronic structure of these catalysts. Fig. 6a shows the deconvoluted N 1s spectra for the catalysts. The four peaks at 398.1, 399.0, 399.7, 401.1 and 402.9 eV are corresponding to pyridinic-N, metal-N, pyrrolic-N, graphitic-N and oxidized-N, respectively [34,35]. Note that pyridinic-N and graphitic-N are the majority species in the fitted N 1s, both of which are the highly active sites for ORR, whereby the positively charged C⁺ benefits the adsorption of reaction intermediates and the transfer of electron [36–38]. It is noticed that part of the pyrrolic-N and pyridinic-N in N-C are
transformed into energetically favorable metal-N upon coupling with the metal atoms in TM/TM-N-C (TM = Fe, Co, Ni) which is beneficial for ORR/OER activities [39]. The N-C prepared by this simple method shows high content of N (6.3 at.%), and the TM/TM-N-C still holds N-doping level of 3.8 at.% for Fe/Fe-N-C, 3.5 at.% for Co/Co-N-C and 4.0 at.% for Ni/Ni-N-C, which favors for the successful combination of TM-N bonding in samples (Fig. S15, Supporting Information).

Further detailed TM-N coordination and chemical information was provided by the XAS analysis, including the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements [40]. The N K-edge XANES spectra of the catalysts demonstrate that the increased intensity of the enhanced π* band could be attributed to the charge transfer from N to metal caused by the coordination of metal to N in TM/TM-N-C samples, and the broadened σ* peak at ca. 408.0 eV could be ascribed to the stronger C-N bonding induced by coupling of N and metal (Fig. 6c) [41,42,7]. Moreover, a new second-order photon excited TM L2 line at ~397.9 eV appears in TM/TM-N-C (TM = Fe, Co, Ni) in comparison to metal-free N-C. The Fourier transform (FT) k3-weighted EXAFS spectra of TM K-edge, including TM foil, TM phthalocyanine (TMPc) and prepared TM/TM-N-C (TM = Fe, Co, Ni), are shown in Fig. 6b. As for Fe, the EXAFS spectrum of Fe/Fe-N-C shows the obvious Fe-Fe interaction at ~2.2 Å and in-conspicuous Fe-N bond at about 1.5 Å, indicating the presence of Fe cluster and Fe-Nx configuration with carbon outer layer. Similarly, the Co/Co-N-C and Ni/Ni-N-C are comprised of Co(Ni) metal cluster and Co (Ni)-N species.

The electronic structures were analyzed with the XPS spectrum of Fe 2p, Co 2p, and Ni 2p as well as Fe L-edge, Co L-edge and Ni L-edge XANES spectrum (Fig. 6d). The XPS spectra of Fe 2p1/2/Fe 2p3/2, Co 2p1/2/Co 2p3/2, and Ni 2p1/2/Ni 2p3/2 can be deconvoluted into two distinct chemical states, i.e., Fe2+ (710.8/723.7 eV) and Fe3+ (713.6/726.1 eV), Co2+ (780.5/796.3 eV) and Co3+ (782.7/797.5 eV), Ni2+ (854.7/871.8 eV) and Ni3+ (856.5/873.6 eV). As shown in the XANES spectra, Fe3+ dominates in Fe/Fe-N-C, and Co3+ is on par with Co2+ in Co/Co-N-C. In contrast, Ni3+ dominates in Ni/Ni-N-C. According to previous studies, the electrocatalysis of ORR/OER is closely related to TM2+ /TM3+ redox transition [43-47]. In Ni/Ni-N-C, the major Ni3+-N part in Ni2+- Ni3+-N redox transition plays an important role in boosting the electrocatalytic activity of OER. The formation of stable Ni3+-N protects the carbon from oxidation.

To further elucidate the effect of the embedded TM-N4 motif on the ORR/OER activity of carbon nanosheets, DFT calculations were carried out. The constructed and optimized structure of TM-N4 embedded N-doped graphene (TM-N4-G) is shown in Fig. 7a. The weak interactions of the N-doped graphene (N4-G) with O2 and OOH* intermediates suggest that the N-doped graphene is inefficient towards catalyzing ORR (Fig. 7b), matching well with the previous reports [48,49]. This is due to the fact that very weak adsorptions of these two O-containing species result in a difficulty of O2 molecule hydrogenation [50]. In contrast, the adsorptions of oxygenated adsorbates on the TM-N4-G are relatively strong, suggesting a sufficient activation of these O-containing intermediates. The adsorption strength of ORR species is directly related to the bond distance between the metal and the nearest oxygen atom, as clearly shown in Fig. 7c. A shorter distance of metal – oxygen bond and a longer O–O bond implies stronger interaction between adsorbates and catalysts [51], and thus stronger activation. Based on the results and analysis presented above, the activation of the ORR species follows the order of Fe-N4-G, Co-N4-G, Ni-N4-G, which is well consistent with the experimental results.

As for OER, the reaction activity depends greatly on the adsorption strength of the O-containing intermediates [52,53]. Based on previous studies, the OER mechanism is considered as a reverse reaction of ORR...
[54]. As illustrated in Fig. 7e, Fe-N₄-G possesses much stronger binding strength to OOH⁺ than the other two, which leads to the difficulty for the formation of O₂ from the adsorbed OOH⁺ (needing 2.20 eV energy to proceed). The remaining three steps of OER on Fe-N₄-G are the formation of OH⁻, the formation of O²⁻, and the formation of O₂O⁻, respectively. And their corresponding Gibbs free energy are 0.36, 0.57, and 1.79 eV, respectively. It can be found that the formation of O₂ possesses the largest energy change of all steps (i.e., the potential-determining step) among the OER process on Fe-N₄-G. And overpotential (η_{OER}) is estimated as $\eta_{OER} = \Delta G_{\text{max}}/e = 1.23$, where $\Delta G_{\text{max}}$ is the change of Gibbs free energy of the potential-determining step. Therefore, the $\eta_{OER}$ is 0.97 V for Fe-N₄-G. For Co-N₄-G and Ni-N₄-G, the potential-determining step and $\eta_{OER}$ can be obtained by using the same method described above based on the data in Fig. 7e. In contrast, the largest energy change of each step (i.e., the rate-determining step) among the OER process is only 1.77 and 1.89 eV on Co-N₄-G and Ni-N₄-G, respectively. In other words, although Fe-N₄-G has relatively high activity toward ORR, its OER behavior is not competitive with the other two.

The origin of catalytic activity can be obtained by analyzing the electron transfer from the catalyst to the reaction intermediates during the reaction process, as shown in Table S3. It can be found that the reaction intermediates on the Fe-N₄-G have more negative charges than those on the Co-N₄-G and Ni-N₄-G, which leads to shortening of metal-oxygen bond and elongating of O–O bond on the Fe-N₄-G. This means that there are stronger interactions between adsorbates and the Fe-N₄-G, leading the high ORR activity and relatively low OER activity of the Fe-N₄-G. On the contrary, for the Co-N₄-G/Ni-N₄-G, the weak interaction between the catalyst and the adsorbates caused by the less electron transferred is the reason for its high OER activity.

There are additional metal atoms on the surface of TM-N₄-G based on the experimental results. According to the previous work [55], a new model (TM/TM-N₄-G) shown in Fig. 7d and Fig. S16 (Supporting Information) is selected to represent the catalyst. As is clearly seen in Fig. 7f, the additional metal atoms are ready to offer the extra electron to TM-N₄ moiety, leading to the decrease of the Hirschfeld charges on central TM atom. Moreover, for all the TM-N₄-G, their energy levels of highest occupied molecular orbital (HOMO) arise, leading to more electrons transfer to adsorbed O₂ to weaken the O–O bond [56]. Hence the adsorption energy of O₂ on TM/TM-N₄-G is slightly more negative than that on bare TM-N₄-G, which favors the adsorption of O₂ on the metal sites and therefore accelerates the ORR process. Likewise, additional metal atoms on TM-N₄-G are beneficial for the OER process.

By combing the DFT calculations and experimental results, it is found that Fe-N₄ center significantly enhances the ORR, while Co-N₄ and especially Ni-N₄ prefer to facilitate the process of OER. The synergistic effect between TM and TM-N₄-C plays an important role in enhancing both ORR and OER activities.

4. Conclusions

In summary, nitrogen and transition metal co-doped porous carbon nanosheets modified with metal (TM/TM-N-C, TM = Fe, Co, Ni) as highly active and durable electrocatalysts for ORR/OER have been developed from biomass lysine by employing a NaCl template together with a molten-salt-promoted graphitization process. The structure, catalytic activity as well as long-term stability of the resulting TM/TM-N-C are greatly dependent on the choice of the transition metal. The Fe/Fe-N-C with Fe wrapped in 3D porous carbon nanosheets shows a high ORR activity with $E_{1/2}$ of 0.881 V. While the Ni/Ni-N-C with Ni nanocubes embedded in carbon nanosheets presents an excellent OER activity, a low potential of 1.536 V to achieve 10 mA cm⁻² is obtained. More importantly, a long-term stability has been achieved for Ni/Ni-N-C over a potential of 0.1–1.9 V. Benefiting from its high OER activity and durability, the Ni/Ni-N-C endows the assembled rechargeable Zn-air battery (ZAB) a superb electrochemical performance. It produces a small voltage gap of 0.773 V for the first cycle, which is only slightly increased by 5% after 150 cycles testing. The exceptional OER activity and durability of Ni/Ni-N-C can be ascribed to: (1) highly active Ni-N₄-C configuration with high density endowed by high N content; (2) synergistic effect between Ni and Ni-N₄-C; (3) porous carbon nanosheets for efficient transport for O₂ and reactant species; and (4) formation of stable Ni²⁺-N for protecting carbon from oxidation. It is anticipated that this ecofriendly, facile and easy to scale up approach can be extended to synthesize other metal alloys on heteroatom-doped carbon and applied in other fields, such as Li-ion batteries and supercapacitors.
Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “Indiscrete Metal/Metal-N-C Synergic Active Sites for Efficient and Durable Oxygen Electrocatlalysis toward Advanced Zn-air Batteries”.  

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