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Universal Synthesis of Half-Metallic Diatomic Catalysts for Efficient Oxygen Reduction Electrocatalysis

Yuechao Yao, Tao Jiang, Sung Yul Lim, Cathrine Frandsen, Zhangjian Li, Yibo Dou, Feiyan Wu, Jibo Qin, Jizhao Zou, Eugen Stamate, and Wenjing Zhang*

Developing efficient and low-cost noble-free metal electrocatalysts is an urgent requirement. Herein, a one-step, solid-state template-assisted method for fabricating isolated half-metallic diatomic M, Zn–N–C (M=Fe, Co, and Ni) catalysts is reported. In particular, the fabricated Fe, Zn–N–C structure exhibits superior oxygen reduction reaction capabilities with a half-wave potential of 0.867 V versus RHE. The Mossbauer spectra reveal that the Fe, Zn–N–C half-metallic diatomic catalyst has a large proportion of the D2 site (ferrous iron with a medium spin state). Density functional theory (DFT) reveals that in Fe, Zn–N–C structures, the zinc sites play a unique role in accelerating the protonation process of O_2 in ORR. In assembled zinc–air batteries, a maximum power density of 138 mW cm⁻² and a capacity of 748 mAh g zn⁻¹ can be obtained. This work fabricates a series of efficient M, Zn–N–C diatomic electrocatalysts, and the developed solid-state reaction method can hopefully apply in other energy conversion and storage fields.

1. Introduction

Electrochemical oxygen reduction reaction (ORR) is critical in energy conversion devices, especially metal–air batteries and fuel cells.^[1–3] However, the sluggish reaction kinetics of ORR, involving a multistep proton-coupled electron transfer, seriously impede the development of related research.^[4] Thus far, platinum (Pt)-based materials have been recognised as one type of state-of-the-art electrocatalyst in acid and alkaline electrolyte systems.^[5-9] However, Pt-based electrocatalysts face the dual dilemma of scarce reserves and high prices. Moreover, some disadvantages of Pt, including the low methanol cross-over tolerance and carbon monoxide poisoning, also hamper its more widespread application.^[10–12] Thus, developing replaced Pt electrocatalysts for ORR, with the merits of cost-effectiveness, high activity and durability, is highly desired but suffers from the issue of tremendous barriers.

To date, a great deal of work has been done to fabricate advanced noble-free metal catalysts to replace Pt-based oxygen reduction electrocatalysts.^[2,12–14] During the ORR process, the electronic structure of catalytic

sites mainly influences electrochemical activity. Transition metals (TMs), such as Mn, Fe, Co, Ni, Cu, etc., endow unique 3d unoccupied orbitals that accommodate foreign electrons. As a result, catalytic active centres can be modulated by introducing the foreign electron in the 3d orbital, which means that the TM possesses the ability to optimise the binding strength between

Y. Yao, T. Jiang, F. Wu, J. Qin, W. Zhang Department of Environmental and Resource Engineering Technical University of Denmark Miljøvej 115, Kgs. Lyngby 2800, Denmark E-mail: wenz@dtu.dk S. Y. Lim Department of Chemistry and Research Institute for Basic Science Kyung Hee University Seoul 02447, Republic of Korea

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202304655

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C. Frandsen Department of Physics Technical University of Denmark Kongens Lyngby 2800, Denmark Z. Li, J. Zou Shenzhen Key Laboratory of Special Functional Materials & Shenzhen Engineering Laboratory for Advance Technology of Ceramics College of Materials Science and Engineering Shenzhen University Shenzhen, Guangdong 518060, P. R. China Y. Dou State Key Laboratory of Chemical Resource Engineering Beijing University of Chemical Technology Beijing 100013, P. R. China E. Stamate National Centre for Nano Fabrication and Characterization Technical University of Denmark Kgs. Lyngby 2800, Denmark



the catalytic active centres and oxygenated intermediates (OO*,

O*, and OH*), thereby ensuring ideal ORR performance.[15,16]

A TM-nitrogen-carbon (M–N–C) structure with M-Nx moiety offers the ability to improve electrocatalytic activities and has

been reported.^[17-19] Yeager et al.,^[20] in 1989, first produced a

Fe-N-C catalyst via heat treatment in a mixer, including the

polyacrylonitrile, Fe salts and active carbon. In the past 30 years,

the M-N-C fabrication method has progressed, exemplified

by hard/soft template methods.^[4,17,21-25] In 2019, Wang et al.^[26]

synthesised a Fe-N-C catalyst with a directly pyrolysed Fe-

doped ordered macro/microporous single-crystalline zeolitic im-

idazolate framework-8. Recently, Jiao et al., [18] reported a chem-

ical vapour deposition method to prepare Fe-N-C catalysts by

flowing iron chloride vapour over a metal-organic framework-

derived Zn-N-C substrate at 750 °C. The common method em-

ployed to prepare an M-N-C structure involves the carboniza-

tion of precursors comprising the transition metal, a nitrogen

source and a carbon source. However, it is well known that the

electrochemical active surface is vital for ideal electrocatalytic

performance.^[26-28] Thus, to appeal to an effective catalytic ac-

tive surface, precursor preparation should be rationally designed.

For example, metal-organic frameworks^[17] and porous carbon

materials^[29] are used as a carbon source because of their high

specific surface area. However, inevitably, these materials have

a relatively complicated fabrication process, resulting in a liquid

phase reaction and high cost. Thus, based on this consideration,

developing facile and universal strategies to synthesise oxygen re-

duction electrocatalysts with an M-N-C structure is still highly

synthesis, but there is still a lack of broad research on fabricating

atomically dispersed M-N-C catalysts, which could culminate

in a solid-state chemical reaction impeding the diffusion of metal

elements and causing metal atoms to aggregate easily instead of

forming dispersed metal atoms. Here, in turn, due to the low

probability of particles colliding with each other in solid-state re-

actions, maintaining relatively dispersed particle distribution in

the carbonised precursor could help in the preparation of atomi-

herein a facile and universal method to synthesise a series of

half-metallic diatomic M, Zn-N-C (M=Fe, Co, and Ni) catalysts

via directly carbonising unique precursors derived from a solid-

state chemical reaction process. This technique achieves the ef-

ficient dispersion of metal elements in a non-solution through

a rapid thermal expansion reaction process. During the subse-

quent high-temperature pyrolysis process, these solid-state pre-

cursors maintain their original structure, thus efficiently limit-

ing the secondary diffusion of metal elements and thereby avoid-

ing further particle agglomeration. Moreover, we further investi-

gate oxygen reduction electrocatalytic activities for all fabricated

M, Zn-N-C (M=Fe, Co, and Ni) catalysts. To understand bet-

ter the relationship between the M, Zn-N-C structure and its

properties, DFT calculations were used to reveal their ORR re-

action kinetics. Next, we assembled zinc-air batteries and evalu-

ated their performance by employing the Fe, Zn-N-C as a cat-

alyst layer in the air electrode and a zinc plate as an anode. Fi-

nally, the inactive mechanism of Fe, Zn-N-C catalysts was also

Inspired by the abovementioned consideration, we develop

cally dispersed M-N-C catalysts by solid-state methods.

Solid-state chemical reactions are a facile method in materials

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2. Results and Discussion

2.1. Materials Synthesis and Characterisation

The atomically dispersed M, Zn-N-C (M=Fe, Co, and Ni) diatomic catalyst was synthesised by direct carbonisation precursors treated via a solid-phase thermal reaction between 2-Mim and metal salts, as shown in Figure 1a. Moreover, Zn-N-C as a control sample was prepared by using the same method, with the only difference being the absence of metal salt of Fe, Co, and Ni. It is notable that during the solid-thermal reaction process, there was an almost 22-fold volume change between the reactants (including the 2-Mim, zinc salt, and other transition metal salts) and the treated precursor (Figure S1, Supporting Information). This enormous volume-expanding process can efficiently disperse the primary mixed metal salt into smaller parts, thereby offering possibilities for synthesising atomically dispersed M, Zn-N-C catalysts after carbonisation. Moreover, the evaporation of zinc with a low boil point (907 °C) can form many pores during the carbonisation process at 900 °C.^[30,31] The scanning electron microscopy (SEM) image in Figure 1b and Figure S2 (Supporting Information) reveals that the Fe, Zn-N-C, and Zn-N-C catalyst had a porous carbon nanosheet structure, which inherited the morphology of the treated precursor (Figure S3, Supporting Information) obtained from the solid-state thermal reaction. Figure 1c presents a transmission electron microscopy (TEM) image of Fe, Zn–N–C, revealing a structure consisting of thin carbon layers. Moreover, an aberration-corrected high-annular dark-field scanning TEM (HAADF-STEM) was employed to gather evidence of atomically dispersed Fe, Zn diatomic metal in carbon. Figure 1d illustrates that some small Fe clusters (highlighted by red frames) existed in the Fe, Zn-N-C catalysts. In Figure 1e, some bright spots are observed, where single and dual atoms (highlighted by red circles) are distributed on carbon carriers. Figure 1f is the EDS mapping of Fe, Zn-N-C, which further illustrates the even distribution of C, N, Fe, and Zn on the Fe, Zn-N-C catalyst. To additionally characterise the specific content of Fe and Zn in the prepared catalysts, inductively coupled plasma mass spectrometry (ICP-MS) was used, with the result showing that Fe and Zn are 2.65 wt.% and 0.62 wt.% refers to the Fe, Zn-N-C catalyst. Figure 1g is the atomic force microscope image for the Fe, Zn–N–C catalyst, indicating that it has a \approx 3 nm-ultrathin nanosheet structure.

X-ray diffraction was conducted to find more evidence of atomically dispersed Fe atom sites for the Fe, Zn-N-C catalyst. Figure S4 (Supporting Information) is the precursor of M-N-C, which mainly shows characteristic peaks of ZnO.^[32] In Figure 2a, no obvious diffraction peak is observable, which proves that the Fe and Zn elements mainly existed in the form of dispersed single atoms. This result is consistent with the previous STEM result (Figure 1d,e). As shown in Figure 2b, Raman spectroscopy further unveils Fe, Zn-N-C, and Zn-N-C structural information. Two prominent peaks located at \approx 1352 and 1587 cm⁻¹ represent the peak of disorder carbon and graphitisation carbon.^[33] The ratios of the area of disorder $(I_{\rm D})$ and graphitisation $(I_{\rm G})$ peaks were 2.56 and 2.86 for Fe, Zn-N-C, and Zn-N-C, respectively, thereby indicating that the Fe, Zn-N-C catalyst has a higher degree of graphitisation than Zn-N-C, which could be attributed to the catalytic effects of Fe elements during

investigated.

desired.



um

2 nm



Pre-anchored, isolated atoms

Figure 1. a) Scheme for synthesising atomically dispersed M, Zn–N–C electrocatalysts. b) SEM, c) TEM, d,e) Aberration-corrected HAADF-STEM image. f) EDS mapping of Fe, Zn–N–C. Scale bar: 25 nm. g) Atomic force microscope image of Fe, Zn–N–C and its corresponding thickness.

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C a b Fe, Zn-N-C D G Zn-N-C Fe,Zn-N-C Fe. Zn-N-C (d1S Zn-N-C (cc/g I_D/I_G=2.86 Intensity (a.u.) ntensity (a.u.) 400 2222222222222 2442444444 dsorb 300 /olume In/Ic=2.56 100 2000 2500 1000 1500 0.4 40 50 70 0.6 0.8 30 Raman Shift (cm⁻¹) Relative pressure (P/P₀) 2 theta (Degree) Fe²⁺ 2p_{3/2} Fe 2p Fe,Zn-N-C e d f N 1s Fe, Zn-N-C Zn 2p Fe, Zn-N-C Zn 2p3/2 Pvridinic N Satellite peak Fe²⁺ 2p_{1/2} Pyrrolic N M-Nx 20 . Fe meta ntensity (a.u.) ntensity (a.u.) Zn 2p ntensity (a.u.) Graphitic N Oxidic N 406 1045 1035 1030 1025 1020 404 402 400 398 1050 1040 735 730 725 720 715 710 Binding energy (eV) Binding energy (eV) Binding energy (eV) **h** 0.0 **G**0.0 D1 40 Fe. Zn-N-C D2 D3 30 **Absorption (%)** 7:0 D4 Absorption (%) γ-Fe Proportion (%) 0.5 293 K 30 D2 D1 D4 D2 20 K 18 D1 D4 Fe, Zn-N-C Fe, Zn-N-C V-Fe v-Fe D3 D3 Signal Signal 10 Fitsum itsum 1.5 3.0 -2 0 -2 -4 2 4 -4 0 Velocity (mm/s) Velocity (mm/s)

Figure 2. a) XRD pattern for Fe, Zn–N–C. b) Raman spectrum and c) N_2 adsorption-desorption isotherm for Zn–N–C and Fe, Zn–N–C. d–f) XPS spectra of Zn 2p, Fe 2p, and N 1s in Fe, Zn–N–C, respectively. g) Room temperature (293 K), Mossbauer spectrum of Fe, Zn–N–C. h) Low temperature (20 K), Mossbauer spectrum of Fe, Zn–N–C. i) The specific proportion of the chemical state of the Fe species in Fe, Zn–N–C, based on Figure 2g.

carbonisation.^[34] These results also ensure better conductivity in the electrochemical process. Figure 2c is the N₂ desorptionabsorption isotherm of Fe, Zn-N-C, revealing a higher specific surface area (603 m² g⁻¹, Table S1, Supporting Information) than the Zn-N-C control sample (501 m² g⁻¹, Table S1, Supporting Information). Moreover, the hysteresis loop in Figure 2c proves the existence of mesopores in the Fe, Zn–N–C catalyst, and by combining the pore distribution curves (Figure S5b, Supporting Information) we conclude that it has the merit of a hierarchically porous structure. According to the report, the micropore provides electrocatalytic active sites, mesopores act as a mass transfer channel and macropores provide proper electrolyte storage.^[26,35] To verify the universality of this method, we change the types of Fe doping metal for other metal elements, including Co and Ni. These results relating to XRD and the N2-desorptionadsorption isotherm and the Raman spectrum illustrate that the synthesised series of M, N-C (M=Fe, Co, and Ni) catalysts has merit in terms of sheet morphology, a large specific area and a high degree of graphitisation. More specific information can be found in Table S1 (Supporting Information), and Figures S2–S6 (Supporting Information).

Next, X-ray photoelectron spectroscopy (XPS) was used to identify the valence state and surrounding coordination environment of Fe, in order to provide an in-depth insight. The XPS full spectrum (Figure S7a, Supporting Information) confirmed the Fe, Zn, C, N, and O elements in the prepared Fe, Zn-N-C catalyst. Figure 2d is the high-resolution Zn 2p spectrum, which has two peaks at 1021.8 eV (2p 3/2) and 1044.9 eV (2p 1/2), classified into the oxidation state of a single Zn atom (25, 33). Moreover, by comparing the Zn spectrum of Zn-N-C in Figure S7b (Supporting Information), they are the same peak, indicating the same coordination environment for Zn atoms. As exhibited in Figure 2e, the high-resolution Fe 2p spectrum can be fitted into four groups with six peaks at 708.1, 711.3/714.6, 718.7, and 724.3/728.3 eV, belonging to Fe^0 , Fe^{2+} , and Fe^{3+} of $2p_{3/2}$, the satellite peak and Fe^{2+} and Fe^{3+} of $2p_{1/2}$, indicating that most Fe coordinates with N to form $Fe^{2+/3+}-N_{\nu}$ moieties.^[36,37] Moreover, small quantities of metallic iron, assigned to Fe⁰ in 708.1 eV,

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2.2. Electrocatalytic Activity for Oxygen Reduction

The ORR performance of Fe, Zn-N-C and Zn-N-C was inves-

can be observed. The high-resolution N 1s spectrum (Figure 2f) was deconvoluted into five peaks, including oxidic-N (402.7 eV), graphite-N (401.2 eV), pyrrolic-N (400.3 eV), metal-N (399.4 eV), and pyridinic-N (398.4 eV), while the metal-N peak further confirmed single Fe atoms coordinating with the N species.^[25] Moreover, in Figure S7c (Supporting Information), the Co, Zn, and Ni, Zn elements are detected in the full XPS spectrum of the Co, Zn–N–C, and Ni, Zn–N–C samples. The high-resolution XPS spectrum of Co 2p and Ni 2p (Figure S7d,e, Supporting Information) is deconvoluted into Co $2p_{3/2}$, $2p_{1/2}$, and Ni $2p_{3/2}$, $2p_{1/2}$, respectively.

To identify the chemical state of the Fe species, Mössbauer spectroscopy analysis was conducted. Spectra obtained from sample Fe, Zn-N-C at 293 and 18 K were fitted with five components each (a singlet and four doublets, Figures 2g,h). The singlet has an isomer shift slightly below 0 mm s⁻¹ at room temperature and a low abundance (ca. 5% of the Fe in the sample at both 293 and 18 K). The singlet is assigned to metallic iron, either in the form of paramagnetic $\gamma\text{-}\text{Fe}^{[38]}$ or superparamagnetic α -Fe particles.^[39,40] The four doublets (D1-D4) are assigned to FeN4-sites. The doublets D1-D3 are similar to those found in recent work by Kramm et al.[39,40] Following their identification,^[39,40] D1 with an isomer shift (δ) of $\approx 0.33 \text{ mm s}^{-1}$ and quadrupole splitting (ΔE_{0}) of $\approx 0.78 \text{ mm s}^{-1}$ at 293 K, can be assigned to the $Fe^{II}N_4$ -site's low-spin structure, while D2 ($\delta \approx 0.32$ mm s⁻¹, $\Delta E_Q \approx 2.45$ mm s⁻¹), and D3 ($\delta \approx 0.34$ mm/s, $\Delta E_0 \approx 1.30$ mm/s), respectively, can be attributed to the phthalocyanine- and porphyrin-like Fe^{II}N₄ sites with midspin structures.^[39,40] As also reported by Kramm et al.,^[39,40] ferrous low- and mid-spin states can have Mössbauer parameters close to those of ferric high-spin states, and we cannot distinguish between them based solely on these Mössbauer parameters. Nevertheless, it has been reported that the D2 sites with mid-spin structures endow catalytic activity in chemical reactions.^[39,40] The doublet D4 has parameters ($\delta \approx 1.32 \text{ mm s}^{-1}$, $\Delta E_{\odot} \approx 2.60 \text{ mm s}^{-1}$) that are unambiguous for FeII high-spin and can be assigned to the N-(Fe^{II}N₄) high-spin structure. Table S2 (Supporting Information) lists δ and $\Delta E_{\rm O}$ for the five components at 293 and 18 K. Data fitting at both temperatures is consistent in the sense that they show realistic temperature dependences on δ and ΔE_{0} for the different components and reveal no change in the coordination structure of Fe species between 293 and 18 K.

The quantitative analysis of the Mössbauer components (Figure 2i; Table S2, Supporting Information) reveals that the doublets D1, D2, D3, D4, and the singlet γ -Fe, respectively, account for 40 (10%), 30 (8%), 18 (5%), 6 (3%), and 6 (3%) of the iron in the sample. The result suggests that the Fe^{II} in Fe, Zn/N–C is predominantly (>90%) present as low- and mid-spin Fe^{II} (D1–D3). As the literature^[39–41] indicates that D2 sites are highly active and stable, the high proportion of D2 (\approx 30%) could play a decisive role in efficient catalytic activity in ORR. Moreover, combining the XPS and MS spectra, a small part of Fe particles are observed in both. Based on the specific area of Figure S1 (Supporting Information)(γ -Fe) in all Fe species (Table S2, Supporting Information), \approx 4–6% Fe particles exist, indicating that almost Fe exists with coordination in the Fe, Zn–N–C catalysts.

tigated in 1 M KOH electrolyte, using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements. The CV curve in Figure 3a shows a pronounced reduction peak at 0.845 V for the Fe, Zn-N-C catalyst, thus proving the existence of efficient electrocatalytic activities for ORR. LSV curves (Figure 3b) were used to evaluate the specific ORR activity for various catalysts in O_2 -saturated 0.1 M KOH with a loading mass of 0.102 mg cm⁻². It is notable that the Zn-N-C revealed poor electrocatalytic activities, including a more negative half-wave potential $(E_{1/2})$ than Fe, Zn-N-C, as well as the lowest current density of all catalysts. Moreover, the existing valley in Co, Zn-N-C reveals that during the following voltage (<0.78 V vs RHE), i.e., current density controlled by the diffusion, Co, Zn-N-C has a more limited mass transfer rate than Fe, Zn-N-C structure.[42,43] More specifically, the estimated half-wave potential and current density at 0.80 V for all catalysts (20 wt.% Pt/C was also included as a reference) are listed in Figure 3c. The Fe, Zn-N-C catalyst shows high half-wave potential ($E_{1/2} = 0.867$ V) and a significant current density of 4.75 mA cm⁻², both of which are superior to other M, N-C catalysts (M=Ni and Co), and even better than a 20 wt.% Pt/C catalyst ($E_{1/2}$ = 0.85 V, limiting current density of 4.36 mA cm⁻²). Moreover, it is concluded that for a series of M, Zn-N-C catalysts followed the electrocatalytic performance for ORR: Fe, Zn-N-C > Co, Zn-N-C > Ni, Zn-N-C > Zn-N-C. ORR kinetics were further evaluated by the Tafel plot (Figure 3d). The Tafel slope for all catalysts ranged from 51 to 73 mV dec⁻¹, indicating fast kinetics, apart from Zn-N-C (113 mV dec⁻¹). Figure 3e reveals the electrochemical double-layer capacitance of Fe, Zn-N-C, which is in proportion to the electrochemical surface area. By comparing Fe, Zn-N-C and Pt/C, the former prefers the higher electrochemical active surface. The electron transfer number is a vital parameter in evaluating the ORR. Thus, Figure 3f presents LSV curves with different rotation speeds and their corresponding Koutecky-Levich (K-L) curves. The calculated electron transfer number is 4 to 4.08, which is close to the standard four-electron transfer process. Moreover, the electron transfer number and H₂O₂ yield were further evaluated with the rotating ring-disk electron (RRDE, Figure 3g) technique, in which the four-electron transfer process was confirmed (the number was almost four and H_2O_2 yield was below 2.5%). Anti-methanol abilities were studied by injecting almost 10 mL of methanol into a 110 mL electrolyte. Meanwhile, the i-t curves were obtained, as shown in Figure 3h, indicating stable anti-methanol abilities without disturbing the current, which is in stark in contrast to the substantial current change and potential reversing of the Pt/C catalyst. Moreover, the LSV curves in Figure S8a,b (Supporting Information) further prove this point. Durability was studied by comparing LSV change after the CV cycling test (-0.164 to 1.164 V vs RHE at 50 mV s^{-1}). Figure 3i illustrates the LSV curves, and notably, the Fe, Zn-N-C catalyst has a negative shift of 30 mV after 5532 cycles. However, for the Pt/C control sample with 1700 cycles, 37 mV degradation is observed, which illustrates that Fe, Zn-N-C has better durability than Pt/C in alkaline electrolytes. In Table S3 (Supporting Information), it is noticeable that the prepared Fe, Zn-N-C catalyst endows a better

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Figure 3. a) CV curves of Fe, Zn–N–C in O₂-saturated or Ar-saturated in 0.1 μ KOH at a sweep rate of 25 mV s⁻¹. b) LSV curves of M, N–C (M=Fe, Co, and Ni) and 20 wt.% Pt/C. c) Current density (0.8 V vs RHE) and E1/2 of M, N–C and 20 wt.% Pt/C. d) Transferred Tafel slope from the LSV curves of M, N–C (M=Fe, Co, and Ni) and 20 wt.% Pt/C. e) Electrochemical double-layer capacitance (CdI) at 1.014 V versus RHE of Fe, Zn–N–C and 20 wt.% Pt/C versus RHE. f) LSV curves of Fe, Zn–N–C at various rotation speeds; the inset in Figure 3f is the transferred K-L curves. g) H₂O₂ yield and electron transfer number from the RRDE measurement of Fe, Zn–N–C. Insert figures are corresponding RRDE voltammograms recorded in O₂-saturated 0.1 μ KOH at 1600 rpm. h) Anti-methanol test for Fe, Zn–N–C and Pt/C. i) Durability test for Fe, Zn–N–C and Pt/C, which was assessed by a CV test between 0.164 and 1.164 V at 50 mV s⁻¹.

half-wave potential of 0.867 V even under the ultralow loading mass of 0.1 mg cm⁻² (Normally reported works, $E_{1/2} = 0.87$ V with a loading mass of 0.4 mg cm⁻², four times of this work), highlighting that the prepared Fe, Zn–N–C catalyst with high unit mass activity has a vast application potential.

2.3. The Zinc–Air Battery and Inactivation Mechanism of Fe, Zn–N–C

To evaluate Fe, Zn—N—C practical applications, zinc–air batteries were assembled using the Fe, Zn—N—C as a cathode and a zinc plate as an anode in 6 \bowtie KOH electrolyte (**Figure 4**a). Moreover, for comparison, a 20 wt.% Pt/C and RuO₂ at a ratio of 1:1 were also used in the zinc–air batteries. The details of assembling of zinc–air battery system can be observed in Figure S9 (Support-

ing Information). Figure 4b illustrates the open-circuit voltage (OCV) curves of Fe, Zn-N-C, and Pt/C-RuO₂ in the assembled batteries. Zinc-air batteries assembled by the Fe, Zn-N-C catalyst exhibits a higher OCV of 1.45 V than the prepared control sample (1.43 V). As a result, the two assembled batteries in series can generate an output voltage of 2.83 V. Compare the I-V curve of Pt/C-RuO₂ and Fe, Zn-N-C catalyst, the current density of Fe, Zn-N-C catalyst (100 mA cm⁻²) is higher than Pt/C- RuO_2 (83 mA cm⁻²) at 0.95 V, indicating the good performance of Fe, Zn-N-C catalyst. Moreover, in Figure 4c, the peak-power density of $\approx 138 \text{ mW cm}^{-2}$ is superior to commercial Pt/C and RuO_2 ($\approx 115 \text{ mW cm}^{-2}$). In the low voltage window(<0.6 V), there is no obvious concentration polarization of Fe, Zn-N-C catalyst, indicating a fast mass transfer process of Fe, Zn-N-C catalyst. Moreover, we investigated the influence of loading mass for Fe, Zn-N-C catalyst (Figure S10a,b, Supporting Information).

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Figure 4. a) Configuration of the zinc-air battery. b) Open-circuit voltage curves of Fe, Zn-N-C and $Pt/C-RuO_2$ as cathode-assembled zinc-air batteries. The inset picture is in a series of two units of Fe, Zn-N-C cells. c) Discharge polarisation curves and corresponding power density curves of the samples in air. d) Durability test curve of the Fe, Zn-N-C cathode. e) Discharge curves and corresponding specific capacity of zinc in Fe, Zn-N-C and the control sample. f) Cdl of Fe, Zn-N-C at 1.014 V versus RHE over various cycling times. g) Fe 2p and h) N 1s of the Fe, Zn-N-C catalyst when it serves for >220 h in zinc-air batteries.

The catalyst can still obtain 97 mW cm⁻² peak power density under the loading mass of 0.25 mg cm⁻², which reveals the high utilization rate per unit mass for prepared Fe, Zn-N-C catalyst. But, when the loading mass increased to 1 mg cm^{-2} , the peak power density dramatically dropped to 51 mW cm⁻², which could ascribe to the limitation of mass transfer (O_2) . Specifically, the prepared Fe, Zn-N-C catalyst has low density, and the overhigh loading mass catalyst will lead to an over-thick catalyst layer that hampers the O₂ transfer process, thereby indicating a poor peak power density. The results reveal that 0.5 mg cm⁻² loading mass is an optimized recipe for assembling high-performing zinc-air batteries in prepared Fe, Zn-N-C catalyst. Next, Fe, Zn-N-C catalyst stability is illustrated via a 220 h cycling test at 5.0 mA cm^{-2} (Figure 4d), whereby the discharge voltage changes slightly (from 1.07 to 1.03 V). Figure 4e provides the specific capacity for the zinc anode, whereby Fe-N-C has a specific capacity of 748 mAh g zn-1 at a discharge current density of 5 mA cm⁻², which is close to the commercial Pt/C and RuO₂ (772 mAh g zn⁻¹). Thus, zinc–air batteries assembled by the Fe, Zn–N–C catalyst have enormous application potential in electrode materials.

The inactivation mechanism for the Fe, Zn–N–C catalyst was studied further. First, the Fe, Zn–N–C catalyst morphology was investigated by TEM after a durability test (5000 CV cycles). As shown in Figure S11 (Supporting Information), the whole structure has no noticeable change. However, slightly accumulated Fe particles are observed when enlarging some part of an area. Second, electrochemical double-layer capacitance was calculated over various service times, based on the CV technique (Figure 4f). It is notable that electrochemical double-layer capacitance tends to decrease (from 18.1 to 15. 7 mF cm⁻²) when service time is continuously prolonged (from 1 to 5532 cycles). Meanwhile, the $E_{1/2}$ of Fe, Zn–N–C degrades by 30 mV (Figure 3i). These results illustrate that this decrease in the electrochemical active surface

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Figure 5. a) The reaction pathway of ORR by using the Fe, Zn–N–C as the example. Gibbs free energy diagram of M, Zn–N–C (M represents the Fe, Co, and Ni) catalysts at 1.23 V. Full oblique line corresponding values indicate the change of adsorption free energies for the catalysts. b) represents Zn sites and c) represents Fe, Co, and Ni sites. Red, pink, yellow, brown, and grey balls represent O, H, Fe, C, and N, respectively.

could be partly responsible for deactivating Fe, Zn-N-C catalysts. Moreover, we also identified the valence state of the prepared Fe, Zn-N-C catalyst via XPS analysis when cycled for >220 h in the zinc batteries. Compared to the original peak of N 1s (Figure 4g and Figure 2e), the cycled catalyst exhibited a significant loss of pyrrolic and graphitic N in N 1s. Furthermore, for the Fe 2p XPS spectrum in the cycled Fe, Zn-N-C catalyst, the prominent Fe metal characteristic peak (Figure 4h and Figure 2d) increased, thus indicating that the previous Fe, coordinated with the N atom partly reduced to Fe metal during the catalytic process. Overall, the inactivation of Fe, Zn-N-C catalysts could be ascribed to the decreased electrochemical active surface, as well as the degraded Fe, Zn-N-C structure, which is consistent with the paper reported main reasons, including carbon framework oxidation, demethylation and nitrogen protonation.^[39] In the future, stabilising the carbon structure and coordinating between

Fe and nitrogen should be considered ideal solutions for optimising these catalysts.

2.4. Atomistic Insight Into Half-Metallic Diatomic M, Zn–N–C Activity

In order to determine the highest intrinsic ORR activity for the Fe, Zn–N–C in all M, Zn–N–C configurations, density functional theory (DFT) calculations were employed to investigate the catalytic mechanisms by using MN₄ moieties. A poisoning experiment was conducted by using KSCN to block the M-Nx sites. A negative shift in the ORR peak (Figure S12a, Supporting Information) and a negative movement of $E_{1/2}$ by ≈144 mV (Figure S12b, Supporting Information) are observable, each of which is ascribed to the M-Nx moieties covered via the ADVANCED SCIENCE NEWS www.advancedsciencenews.com

adsorption of SCN⁻, thereby proving the existence of M-N_x for prepared catalysts.^[44-46] Combining with the above analyzed XPS spectrum (M-Nx in Figure 2f), MS spectrum (Figure 2g,h), reported similar literature^[47] and the poisoning experiment, all M, Zn-N-C structures (Figure S13, Supporting Information) were constructed. The obtained computational detail is added in the supporting materials (Table S4 and Figures S14 and S15, Supporting Information). First, to understand better the specific reaction process, using Fe, Zn-N₈ as a module, the reaction steps are indicated in **Figure 5**a-I–V, including the adsorption of O_2 , the dissociation of O-O bond, etc. The bond length between oxygen intermediates and the metal catalysis active sites is a valid parameter for evaluating adsorption ability.^[48] More specifically, if the interaction of M with oxygen intermediates is too weak, the adsorption process will be limited. On the other hand, if the interaction of M to oxygen intermediates is too strong, the desorption process will be impeded.^[49] As a result, neither option is good for the electrocatalytic process, as they result in poor ORR activity. In Table S5 (Supporting Information), Fe-OOH (1.873 Å), O (1.681 Å), and OH (1.883 Å), with a proper bond length and suitable binding energy, help optimise the kinetics, instead of too weak binding strength, like Ni-OOH (2.153 Å) Co-OH (1.936 Å). Figure S16 (Supporting Information) is a Gibbs free energy diagram of the M, Zn-N-C (M represents Fe, Co and Ni) catalysts at 0 V, and all M, Zn-N-C catalysts are facilereacted. To understand the catalytic performance of M, Zn-N-C catalysts under potentials, the computational hydrogen electrode model was used. Adsorption Gibbs free energies of *OOH on Zn sites of all the catalysts at 1.23 V are exothermic, while these energies are endothermic on Fe, Ni, and Co sites, revealing that Zn sites are thermodynamically favorable for the protonation of O₂ to from ^{*}OOH (Figure 5b). Among those catalysts, the Fe, Zn-N-C catalyst shows the strongest *OOH binding on Zn site, suggesting that the least energy is required to activate O₂ on the Fe, Zn-N-C surface. The existence of Zn could optimize the electronic structure of the Fe sites, and the formed Fe, Zn-N-C structure could populate spontaneous spin-polarised conduction electrons at the Fermi level, enhancing free O2 capture and bonding.^[47] Adsorption Gibbs free energies of O* on both Zn and Fe sites in Fe, Zn-N-C are negative at 1.23 V, while O* on Fe shows stronger adsorption. In Figure 5c, all the elementary steps on both Co, Zn-N-C and Ni, Zn-N-C are uphill at 1.23 V, which suggests that extra energy is necessary to perform ORR on those two surfaces. However, the Fe site in Fe, Zn-N-C has strong O^{*} binding, which is helpful for surface reaction. The results show that the Zn site in Fe, Zn–N–C could activate O₂ (protonation process),^[47] and the Fe site gives proper O^{*} and ^{*}OH binding energies for ORR, thereby improving the ORR reaction process through a synergistic effect of both. Moreover, the calculation result is consistent with the experimental observation $(E_{1/2}: Fe, Zn-N-C > Co, Zn-N-C > Ni, Zn-N-C, Figure 3b).$ Overall, Fe, Zn-N-C structure endows the best ORR activity in all prepared M, Zn-N-C catalysts.

3. Conclusion

In conclusion, we developed a facile and universal method to fabricate M, Zn–N–C typed half-metallic diatomic catalysts via directly carbonised thermal-treated precursors and a solid-state

chemical reaction process. The fabricated M, Zn-N-C exhibited the superior ability to create an oxygen reduction reaction (ORR) with higher than 0.8 V versus RHE half-wave potential $(E_{1/2})$, including Fe and Co, Zn-N-C, in which Fe, Zn-N-C with a large proportion of D2 mid-spin state Fe species shows an $E_{1/2}$ of 0.867 V versus RHE, even better than commercial Pt/C. Moreover, the DFT calculation reveals that the Fe, Zn-N-C structure has the highest intrinsic ORR activity among all M, Zn-N-C typed catalysts, which is consistent with the experimental results. When the Fe, Zn-N-C catalyst was used as a cathode material in zinc-air batteries, it exhibited a higher power density (138 mW cm⁻²) than Pt/C and long cycling stability. This work developed a series of robust atomically dispersed M, Zn-N-C (Fe, Co and Ni) oxygen reduction electrocatalysts. More importantly, the methodology (facile, environmental friendly (solventfree), and universality) devised herein offers more possibilities for designing robust atomically dispersed M, Zn-N-C materials, and it can also be extended to most metal elements on earth.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dual atoms, half-metallic diatomic catalysts, oxygen reduction reaction (ORR), zinc-air batteries

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