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# Synthesis of Nanoporous Structured Iron Carbide/ Fe-N-Carbon Composites for Efficient Oxygen Reduction Reaction in Zn-Air Batteries †

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Large-scale industrial level applications of fuel cells and metal-air batteries have called for the development of highly efficient and low-cost oxygen reduction electrodes. Here we report the effective and simple preparation of iron carbide-embedded Fe-N-doped carbon (Fe<sub>3</sub>C/Fe-N/C) composites using iron–phenanthroline (Fe–Phen) complex and dicyandiamide (DCA) as the precursors that are subsequently heat treated. The optimal catalyst pyrolyzed at 800 °C (Fe–Phen–N–800) exhibits superior oxygen reduction activity with onset and half-wave potentials of 0.99 and 0.86 V in 0.1 M KOH, respectively, which are higher to those of Pt/C (onset and half-wave potentials of 0.98 and 0.84 V) at the same catalyst loading. Moreover, the obtained Fe–Phen–N–800 displays comparable activity to Pt/C in 0.1 M HClO<sub>4</sub> solution. Notably, the well-developed Fe–Phen–N–800 catalyst shows much higher long-term stability and better methanol tolerance than Pt/C. The results suggest our catalyst is one of the most promising candidates to replace Pt catalysts toward oxygen reduction. Striking, a primary Zn-air battery using Fe–Phen–N–800 as the air cathode catalyst delivers higher voltages and gravimetric energy densities than those of Pt/C-based system at the discharge current densities of 10 and 25 mA cm<sup>-2</sup>, thus demonstrating the potential applications of our catalyst for energy conversion devices.

# 1. Introduction

The development of high-performance and low-cost oxygen reduction reaction (ORR) electrocatalysts for implementation into fuel cells (FCs), polymer electrolyte membrane (PEM) fuel cells and metal-air batteries cathode is crucial for the practical applications of these clean renewable energy conversion systems. Among metal-air batteries, Zn-air battery has attracted considerable interest due to its high energy density, low cost, safety and environmental benignity. The big challenge associated with the commercialization of Zn-air battery is still the sluggish kinetics of the ORR resulting in large overpotential. Pure or alloyed platinum noble metal materials are hitherto the most efficient class of ORR catalysts.<sup>1-3</sup> The high price, unsustainable supply, inferior durability and susceptibility to methanol crossover effect and CO poisoning of Pt-based catalysts, yet hinder widespread commercialization of renewable energy technologies. To break through this bottleneck, enormous research efforts have been devoted to explore highly active and stable nonprecious metal catalysts (NPMCs) as alternatives of Pt-based materials.<sup>4</sup> To achieve such desired NPMCs, several aspects should be optimized simultaneously, calling for: 1) high density of catalytic active sites, which is determined by chemical compositions and the strong synergistic effects between different components; 2) unique porous nanostructure with high surface area, which facilitates the fast charge transport and diffusion of ORR-relevant species, such as  $H^+$ ,  $OH^-$ ,  $e^-$ ,  $O_2$ ,  $H_2O;^5$  3) superior corrosion resistance in the oxygenriched environment. Thus, recent studies have mainly focused on the aforementioned variables for designing and fabricating various NPMCs towards ORR.

To date, among the various alternative NPMCs, transition-metalcoordinating nitrogen-doped carbon catalysts labelled as M-Nx/C (M = Fe, Co, etc.) have been regarded as particularly promising Ptfree ORR electrocatalysts, 6-10 especially, those often displaying high activity in acidic medium. In these catalysts, the M-Nx unit is chelated in a nitrogenous environment, which has proven to be an essential structural motif in catalyzing ORR.<sup>11</sup> Recently, a new family of metal carbide nanoparticles encapsulated in graphitic carbon shell (i.e.  $Fe_3C/C$ ) have been developed as an efficient ORR catalysts, in which catalytic active sites are regarded as the graphitic carbon layers activated by encapsulated nanoparticles.<sup>12-14</sup> Despite extensive efforts, the ORR performance achieved with single-site NPMCs is still inferior to that of the state-of-the-art Pt catalyst. Therefore, the construction of functional hybrid catalysts with two or more active sites might be more promising to significantly boost the ORR activity. Recently, Wei et al. prepared a hybrid of Fe<sub>3</sub>C and Fe-N-doped carbon for ORR through a iron-tannin-framework ink coating strategy.<sup>15</sup> Wu et al. fabricated Fe<sub>3</sub>C/Fe-N-doped carbon nanofibers showing high ORR activity.<sup>16</sup> However, the synthetic

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routes appear to be tedious, which makes it expensive for mass production. Apparently, the exploration of a facile, sustainable and cost-effective approach to prepare hybrid NPMCs for efficient ORR is highly desirable for the industrial applications of metal-air batteries and fuel cells.

Herein, we report a high-performance ORR electrocatalyst composed of Fe<sub>3</sub>C nanoparticles (NPs) embedded in nitrogen-doped carbon with Fe-N-enriched active sites (Fe<sub>3</sub>C/Fe-N/C), which is synthesized by a simple method using iron-phenanthroline (Fe-Phen) complex and dicyandiamide (DCA) as the precursors that are subsequently heat treated. The six-coordinated complex of Fe-Phen is formed with 1,10-phenanthroline (Phen) as bidentate ligand, producing dual active sites (Fe-Nx and Fe<sub>3</sub>C/C). DCA material is selected due to its high N content (61%), which is favorable for the enhancement of ORR activity of Fe-N/C catalysts. The advantages of our synthetic route include: 1) it is a versatile, efficient and controllable avenue since the used precursors are economical and commercially available; 2) this synthetic approach is readily costeffective and potential to achieve an industrial level production; 3) remarkably, the optimal sample pyrolyzed at 800 °C (Fe-Phen-N-800) shows a more positive onset potential, better durability and higher half-wave potential as compared to commercial Pt/C catalyst (20 wt% Pt, Johnson Matthey) with the same mass loading in alkaline medium. To the best of our knowledge, the ORR activity of our Fe-Phen-N-800 catalyst is among the best of NPMCs reported to date. Meanwhile, the Fe-Phen-N-800 sample displays excellent ORR activity in acidic medium. Furthermore, the performance of Zn-air batteries fabricated with the developed catalyst outperforms the Pt/C based system. It is anticipated that our novel Fe-based catalyst is a very promising alternative to Pt/C for practical application in metal-air batteries.

# 2. Experimental

#### 2.1 Materials

1,10-phenanthroline (Phen), ferrous chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O) and dicyandiamide (DCA) were purchased from Sinopharm Chemical Reagent Co. Ltd. These were used as received without further purification.

#### 2.2 Preparation

5 mmol (0.99 g) Phen and 1.67 mmol (0.33 g)  $FeCl_2 \cdot 4H_2O$  were dissolved in mixture solutions of deionized water and ethanol under N<sub>2</sub> flow, the solution rapidly became red color, indicating the formation of Fe-Phen complex. Then, 4.5 g DCA was added. After removal of water and ethanol by rotary evaporation under vacuum (76 Torr) below 60 °C, a red precursor was obtained and dried in vacuo at 60 °C for 24 h.

The as-obtained precursors were placed in a tube furnace and heated at 500 °C for 30 min with a ramp rate of 2 °C /min, then 800 °C for 60 min with the same ramp rate in flowing N<sub>2</sub> atmosphere. In this process, DCA was thermally transformed first to  $g-C_3N_4$  around 500 °C and then to N-doped carbon species coupled with Fe<sub>3</sub>C nanoparticles as the temperature increases. The produced black powders were leached in 6 M HCl for 24 h at 45 °C to remove inactive iron species. Finally, the leached samples were washed to

neutral with water for several times and dried in vacuum at 60 °C overnight. The productive rate of the catalyst is ~20%. Additional samples by heating at 700, 750, 850 and 900 °C were also prepared. **2.3 Catalyst characterization** 

# The X-ray powder diffraction (XRD) patterns of the samples were collected on a Rigaku/Max-3A X-ray diffractometer with Cu Ka radiation (the operation voltage and current was maintained at 40 kV and 200 mA, respectively), with a wavelength of 0.1542 nm and analyzed in the range of $10^{\circ} \le 2\vartheta \le 70^{\circ}$ . Raman spectra were taken using a LabRAM HR Evolution Raman microscope with laser excitation at 514.5 nm at room temperature. Field emission scan electron microscopic (FE-SEM) images were recorded on JEOL-JSM-6701F, field-emission scanning electron microscope and operated at an accelerating voltage of 5 kV. Transmission electron microscopic (TEM) images were obtained on a Hitachi-7650 microscope at 100 kV. Thermal gravimetric (TG) measurements were recorded on a ShimadzuTGA-50 thermal gravimetric analyzer at a constant heating rate of 5.0 K·min<sup>-1</sup> under air atmosphere with a gas flow of 25 mL·min<sup>-1</sup>. Time of Flight Secondary Ion-Mass Spectrometer (TOF-SIMS) (Bruker Germany) was employed to get idea about the coordination of the Fe-Nx-C sites in the doped material. The electrical transport property measurements were performed on pressed pellets using a Keithley 4200-SCS semiconductor characterization system and the four-point probe method. The X-Ray photoelectron spectroscopy (XPS) was done on a Perkin-Elmer RBD upgraded PHI-5000C ESCA system. The nitrogen (N<sub>2</sub>) adsorption and desorption isotherms were measured at 77 K using Micromeritics ASAP-2020.

## 2.4 Electrochemical measurements

Electrochemical measurements for the prepared catalysts were studied on CHI 660E electrochemical workstation using a threeelectrode system with a platinum counter electrode, an Ag/AgCl reference electrode and with 0.1 M KOH or 0.1 M  $HClO_4$  as the electrolyte. To prepare catalyst ink, 2.0 mg of the catalyst was dispersed in 0.99 mL ethanol, followed by the addition of 10 µL 5% Nafion solution (D520, Dupont Inc., USA) under ultrasonic irradiation. Then, 10  $\mu$ L of the catalyst ink was transferred onto a glassy carbon (GC) electrode with a diameter of 5 mm (geometric area: 0.196  $\text{cm}^2$ ), yielding a catalyst loading of 0.1 mg  $\text{cm}^{-2}$ . For comparison, commercial Pt/C catalyst (20 wt%, Johnson Matthey) was also tested with the same loading. Prior to tests, electrolyte was saturated with oxygen by bubbling  $O_2$  and a flow of  $O_2$  was maintained over the electrolyte during the measurements. Cyclic voltammetry (CV) curves of the catalyst under N<sub>2</sub>-saturated alkaline electrolyte were also measured. Linear sweep voltammetry (LSV) measurements of the catalysts were determined using a rotating disk electrode (RDE) (Pine Research Instrumentation, USA). The scan rate was 10 mV s<sup>-1</sup> and the rotating speed was varied from 400 to 1600 rpm. The number of electrons transferred (n) during ORR was calculated according to Koutecky-Levich equation, at various electrode potentials:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$
(1)

where J is the measured current density,  $J_{\kappa}$  and  $J_{L}$  are the kinetic and diffusion-limiting current densities,  $\omega$  is the angular velocity

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( $\omega\text{=}2\pi N,~N$  is the rotation speed), B is Levich slope which is calculated as below:

$$B = 0.62 n F C_0 D_0^{2/3} V^{-1/6}$$
 (2)

where n is transferred electron number, F is the Faraday constant (96485 C mol<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> ((1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), and v is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).

The specific kinetic current density can be calculated from K-L equation:

$$J_{K} = \frac{J_{L}*J}{J_{L}-J}$$
(3)

Where  $J_{K}$  is the kinetic current density; J is the measured current density;  $J_{L}$  is the diffusion-limited current density, respectively.

The measured potential against Ag/AgCl was converted *vs.* the reversible hydrogen electrode (RHE) using Nernst equation. The conversion was given as follows:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059pH + E_{\rm Ag/AgCl}^{\vartheta}$$
(4)

The standard potential of Ag/AgCl at 25  $^\circ C$  is 0.197 V, therefore in 0.1 M KOH solution:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.966 \, \rm V \tag{5}$$

while in 0.1 M HClO<sub>4</sub> solution:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.256 \, V \tag{6}$$

Rotating ring-disk electrode (RRDE) tests were measured on CHI 760E potentiostat. The electrolytes were 0.1 M KOH or 0.1 M HClO<sub>4</sub>. The disk electrode was scanned at 10 mV s<sup>-1</sup>, and the ring electrode potential was held at 1.2 V vs. RHE. The ring current collection efficiency (N) was determined to be 37%. The hydrogen peroxide yield (% H<sub>2</sub>O<sub>2</sub>) and number of electrons transferred were calculated by the followed equations:

$$\% H_2 O_2 = 200 \frac{I_R / N}{I_D + I_R / N}$$
(7)  
n = 4  $\frac{I_D / N}{I_D + I_R / N}$ (8)

where  $I_D$  and  $I_R$  are the disk and ring currents, respectively.

Primary Zn-air batteries were performed on a home-built electrochemical cell. For catalyst ink preparation, 2.0 mg of the catalyst was ultrasonically dispersed in 1.0 mL of mixture of ethanol (0.98 mL) and 5% Nafion solution (20  $\mu$ L). The homogeneous ink (0.25 mL) was loaded on carbon fibre paper (1.0 cm<sup>2</sup>), catalyst with catalyst loadings of 0.5 mg cm<sup>2</sup>, as the air cathode, and Zn foil was used as the anode in 6 M KOH solution. All data were collected from the as-fabricated cell with a CHI 660E electrochemical workstation at room temperature.

# 3. Results and discussion

The synthetic process of the Fe–Phen–N samples is illustrated in Fig. 1. Ferrous chloride (FeCl<sub>2</sub>) was added into a mixture solution of water and ethanol containing Phen molecules (Fig. 1a). The coordination complex ink of Fe–Phen was rapidly formed at room temperature due to the strong chelation between Fe (II) and Phen ligand (Fig. 1b). The structure of the obtained Fe-phen complex is displayed in Fig. 1c, in which the Fe (II) ion is confined in the center. It is noted that Fe-N sextuple bonds linking three Phen molecules

provide a high density of Fe-Nx active sites in subsequent heat treatment. DCA was added as both nitrogen and carbon source. After rotary evaporation at 60 °C, the red precursor of Fe-Phen/DCA mixture was obtained (Fig. 1d). Finally, by pyrolysis at 800 °C, followed by acid leaching, the precursor was transformed to dark solid Fe-Phen-N-800 catalyst (Fig. 1e), exhibiting a loose, crumpled and porous texture (Fig. 1f). The synthesis of this catalyst can be easily scaled up, because the precursor is commercially available and cheap (Fig. S1, ESI<sup>+</sup>).



**Fig. 1** Schematic illustration of the synthetic procedures for catalyst. (a) Preparation of Fe–Phen ink by adding FeCl<sub>2</sub> into Phen solution. (b) Addition of DCA into the ink solution. (c) Structure of the Fe–Phen. (d) Photograph of the obtained precursor of Fe–Phen/DCA through rotary evaporation at 60 °C. (e) Photograph and f) corresponding SEM image of the as-prepared Fe–Phen–N–800 catalyst.

**Fig. 2a** shows X-ray diffraction (XRD) pattern of as made Fe-Phen-N-800 sample. The diffraction peaks at 37.8, 43.7, 45.0, 48.7, and 51.9° can be indexed to the phase of  $Fe_3C$  (JCPDS No 89-



**Fig. 2** (a) XRD pattern, (b) XPS survey spectrum, high-resolution (c) N1s and (d) Fe2p XPS spectra of the obtained Fe–Phen–N–800 catalvst.

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2867).<sup>17</sup> A typical strong peak at around 26° is observed, which corresponds to the (002) planes of graphitic carbon.<sup>18</sup> No peaks attributable to metallic iron were detected, suggesting acid washing removes inactive and unstable iron species, while XRD pattern of Fe-Phen-N-800 sample prior to acid washing exhibits the existence of metallic iron (Fig. S2, ESI<sup>+</sup>). The X-ray photoelectron spectroscopy (XPS) measurement and thermal gravimetric (TG) analyse (Fig. S3, ESI<sup>+</sup>) were carried out to probe the chemical compositions and bonding configurations of N and Fe in Fe-Phen-N-800 sample. The XPS survey spectrum shown in Fig. 2b clearly demonstrates the presence of four kinds of elements, C (89.32%), N (6.25%), O (3.65%) and Fe (0.78%). The occurrence of oxygen peak presumably originates from physically adsorbed oxygen. The N 1s XPS spectrum (Fig. 2c) reveals that the peaks at 398.4, 399.6 and 401.1 eV can be assigned to pyridinic N (N1, 25.72%), pyrrolic N (N2, 30.05%) and graphitic N (N3, 44.23%),



Fig. 3 (a, b) TEM images of the Fe–Phen–N–800 catalyst with different magnifications. (c) HRTEM image of Fe<sub>3</sub>C nanoparticles in the Fe–Phen–N–800 catalyst; the down-left inset is an enlarged HRTEM image. (d) HAADF-STEM image of the Fe–Phen–N–800 catalyst and corresponding elemental mappings of the area indicated by the white dashed frame in (d).

respectively.<sup>19</sup> The N1 and N2 atoms can coordinate with Fe species due to their lone-pair electrons.<sup>20</sup> The high contents of these two types of N1 and N2 are favorable for the formation of Fe-Nx active sites. The Fe2p spectrum could be deconvoluted into four peaks (Fig. 2d). The peaks at 710.3 and 714.7 eV are attributed to the binding energies of the 2p3/2 bands of Fe<sup>2+</sup> and Fe<sup>3+</sup> species, respectively. The peaks for 2p1/2 orbitals of Fe<sup>2+</sup> and Fe<sup>3+</sup> are observed at 723.3 and 727.1 eV.<sup>21</sup>

The detailed structure and morphology of as-prepared Fe–Phen–N–800 catalyst was investigated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As shown in **Fig. 3a**, the active catalyst is composed of many solid Fe<sub>3</sub>C NPs with the size of 5-20 nm, which are randomly distributed in the carbon matrix. The enlarged TEM image reveals that the sample has a unique nanoporous structure (Fig. 3b). Some of the irregular pores might be the vacancies that formed after the removal of unstable metallic Fe species by acid treatment. Fig. 3c exhibits that Fe<sub>3</sub>C NPs are encapsulated by graphitic carbon layers. These graphite shells

can efficiently protect Fe<sub>3</sub>C NPs from gradually etching under harsh ORR conditions.<sup>22</sup> Moreover, the coated Fe<sub>3</sub>C NPs could activate the graphitic carbon layer and trigger surrounding carbon active for ORR.<sup>23</sup> These activated graphitic layers could further increase the catalytic activity when combined with Fe-N species. HRTEM image (inset in Fig. 3c) shows a lattice spacing of 0.208 nm, corresponding to the (211) plane of Fe<sub>3</sub>C crystal.<sup>24</sup> High-angle annular dark-field scanning TEM (HAADF-STEM) image further reveals Fe<sub>3</sub>C NPs decorated structure (Fig. 3d). The corresponding elemental mapping shows the homogeneous distribution of C, N and O atoms in the Fe-Phen-N-800 catalyst. The very strong Fe signal is observed in the regions of NPs, suggesting that bright dots consist of Fe<sub>3</sub>C. Simultaneously, the relative weak Fe signal is found in the N-doped carbon matrix, and the Fe and N signals highly overlap with each other, indicating that some portion of Fe species complex with doped N, which is believed to be the Fe-Nx active sites. A further investigation of Fe-Nx active sites was carried out using time-of-flight secondary ion mass spectrometry (TOF-SIMS). From TOF-SIMS spectrum (Fig. S4, ESI $\dagger$ ), a series of FeNxCy<sup> $\dagger$ </sup> species was observed, including  $\text{FeN}^+$  (m/z = 59.9),  $\text{FeNC}^+$  (m/z = 81.9),  $\text{FeN}_2^+$ (m/z = 83.9), FeN<sub>3</sub>C<sub>2</sub><sup>+</sup> (m/z = 121.9), FeN<sub>4</sub>C<sub>3</sub><sup>+</sup> (m/z = 147.9), suggesting the existence of Fe-Nx sites. The surface areas and pore structure of the Fe-Phen-N-800 sample were characterized by N<sub>2</sub> adsorption-desorption measurement. A type IV isotherm profile with a hysteresis is clearly observed at a relatively higher N<sub>2</sub> pressure ( $P/P_0 = 0.5-1.0$ ), typical of mesoporous materials (Fig. S5, ESI<sup>+</sup>). The specific surface area of Fe–Phen–N–800 is 269 m<sup>2</sup> g<sup>-1</sup> and pore size distribution centers at 5 nm. High surface area and nanoporous structure endows the Fe-Phen-N-800 as an ideal ORR catalyst, because high surface area can allow active sites better accessible, and abundant porosity is beneficial for fast mass transport of reactants to active centers,<sup>25</sup> thus enhancing the ORR activity.

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**Fig. 4** (a) CV curves of Fe–Phen–N–800 and Pt/C catalysts in N<sub>2</sub>saturated and O<sub>2</sub>-saturated 0.1 M KOH solutions. (b) RDE polarization curves of Fe–Phen–N–800 and Pt/C catalysts in O<sub>2</sub>saturated 0.1 M KOH solution (the catalyst loading is 0.1 mg cm<sup>-2</sup>). Inset: comparison of the kinetic current density normalized to electrode surface area of the catalysts measured at 0.85 V (vs. RHE). (c) RDE polarization curves for Fe–Phen–N–800 at various rotation rates. The inset is the corresponding K-L plots at different potentials. (d) Peroxide yield and the electron-transfer number (n) of Fe–Phen–N–800 and Pt/C catalysts in O<sub>2</sub>-saturated 0.1 M KOH. (e) Durability test of Fe–Phen–N–800 sample for 10000 cycles in O<sub>2</sub>saturated 0.1 M KOH solution. (f) Comparison of the chronoamperometric responses of Fe–Phen–N–800 and Pt/C catalysts upon the addition of 3 M methanol in O<sub>2</sub>-saturated 0.1 M KOH solutions at 0.6 V vs. RHE.

To evaluate the ORR activity of the catalysts, cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements were performed for the Fe-Phen-N-800 catalyst and commercial Pt/C as reference at the same mass loading. As shown in Fig. 4a, there is no cathodic peak observed for Fe-Phen-N-800 in N2-saturated 0.1 M KOH solution, only quasi-rectangular double-layer charging is recorded.  $^{\rm 26}$  In sharp contrast, under  ${\rm O_2}\mbox{-saturated}$  condition, a welldefined peak at potential of around 0.87 V vs. reversible hydrogen electrode (RHE) is clearly found for Fe-Phen-N-800 sample, which is ~10 mV larger than that of Pt/C catalyst (0.86 V vs. RHE), implying its superior ORR electrocatalytic activity. To study the mass-transfer kinetics of the ORR activity of the electrode, the RDE measurements at 1600 rpm and 10 mV s<sup>-1</sup> were conducted. As shown in Fig. 4b, the RDE polarization curve of Fe-Phen-N-800 displays a high onset ( $E_{\text{onset}}$ : 0.99 V vs. RHE) and half-wave potentials ( $E_{1/2}$ : 0.86 V vs. RHE), which is 10 mV and 20 mV higher than that of Pt/C, and also higher than of most NPMCs reported in literature (Table S1,ESI<sup>+</sup>).

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The limiting current density (j) of Fe–Phen–N–800 is 5.7 mA cm<sup>-2</sup>. These results clearly prove Fe-Phen-N-800 is a highly efficient ORR electrocatalyst in 0.1 M KOH. The kinetic current density normalized to geometrical electrode surface area  $(j_{ks})$  of the catalyst at 0.85 V vs. RHE was also examined. The inset in Fig. 4b shows that Fe-Phen-N-800 affords a  $j_{kys}$  value of 7.5 mA cm<sup>-2</sup>, which is 2.5 times higher than that of Pt/C (3 mA cm<sup>-2</sup>). This can be attributed to the unique nanoporous structure that favors the quick diffusion of oxygen species and electrolyte during the ORR process. The kinetic reaction pathway for electrocatalytic reduction of oxygen in alkaline was assessed by using the Koutecky-Levich (K-L) equation. According to previous studies, the ORR process proceeds either by two-step two-electron (2e) pathway, in which peroxide species is produced as an intermediate species, or by a more efficient direct four-electron (4e) pathway, in which O<sub>2</sub> is converted into H<sub>2</sub>O as only byproduct.<sup>27</sup> Generally, the 4e<sup>-</sup> pathway is believed to be more efficient than the 2e<sup>-</sup> pathway, additionally, the peroxide species produced via the 2e pathway may cause the degradation of the catalyst. The K-L plots, derived from the RDE curves of Fe-Phen-N-800 catalyst at various rotation speeds from 400 to 1600 rpm (Fig. 4c), display good linearity (inset in Fig. 4c), suggesting first-order reaction kinetics with respect to the dissolved  $O_2$  concentration. The average value of electron transfer number (*n*) was calculated to be 4.05 at the potential ranging from 0.40 to 0.60 V, indicating that the ORR over Fe-Phen-N-800 undergoes direct four-electron (4e) reduction process. To further validate this conclusion, rotating ring-disk electrode (RRDE) measurements were performed to determine the yield of peroxide species and 4e selectivity of Fe-Phen-N-800 catalyst. As shown in Fig. 4d, the peroxide yield (%) for Fe-Phen-N-800 catalyst is less than 5% over the whole measured potential range and even lower than that of Pt/C in the potential range from 0.6 V to 0.85 V vs. RHE. The average n is 3.97, which is in line with the results based on the K-L plots, this proves that Fe-Phen-N-800 promotes the four-electron reduction process of the oxygen reduction. The long-term stability of Fe-Phen-N-800 catalyst was evaluated in O2-saturated 0.1 M KOH by cycling potential between 1.1 V and 0.1 V vs. RHE at a scan rate of 100 mV s<sup>-1</sup>. The RDE curves recorded before and after 10000 cycles exhibit that the  $E_{1/2}$  drop for Fe–Phen–N–800 is only 13 mV (Fig. 4e), whereas Pt/C suffers a decrease of 75 mV for the  $E_{1/2}$  (Fig. S6, ESI<sup>+</sup>), indicating that its durability is superior to Pt/C. The obvious negative shift of  $E_{1/2}$  for Pt/C catalyst could result from the dissolution, migration and aggregation of Pt NPs during the potential cycling.<sup>28</sup> Unlike Pt/C, a small decay of performance for Fe-Phen-N-800 is mainly ascribed to degradation of supporting carbon and oxidation of active sites.<sup>29</sup> The less prominent performance decay of the Fe-Phen-N-800 proves the highly stable coordination of Fe-N with carbon moiety, which was already suggested by its resistance to acid leaching. Chronoamperometric (CA) test was performed to probe the possible crossover effect caused by small organic molecules (e.g. methanol). As shown in Fig. 4f, there is no noticeable current density change for Fe-Phen-N-800, while a sharp decrease in current density is observed for the Pt/C catalyst after the addition of 3 M methanol, indicating that our Fe-Phen-N-800 catalyst exhibits high selectivity for the ORR with excellent resistance to the methanol crossover.

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**Fig. 5** (a) CV curves of Fe–Phen–N–800 and Pt/C catalysts in  $O_2$ -saturated and  $N_2$ -saturated 0.1 M HClO<sub>4</sub> media. (b) RDE polarization curves of Fe–Phen–N–800 and Pt/C catalysts in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> solution (the catalyst loading is 0.1 mg cm<sup>-2</sup>), Inset: comparison of the kinetic current density normalized to electrode surface area of the catalysts measured at 0.65 V vs. RHE. (c) RDE polarization curves for Fe–Phen–N–800 at various rotation rates. The inset is the corresponding K-L plots at different potentials. (d) Peroxide yield and the electron-transfer number of Fe–Phen–N–800 and Pt/C catalyst in  $O_2$ -saturated 0.1 M HClO<sub>4</sub>. (e) Durability test of Fe–Phen–N–800 catalyst for 10000 cycles in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> solution. (f) Comparison of the CA responses of Fe–Phen–N–800 and Pt/C catalysts upon the addition of 3 M methanol in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> solutions at 0.8 V vs. RHE.

In addition, the obtained Fe-Phen-N-800 catalyst exhibits high ORR activity in acidic condition. The CV curve in Fig. 5a presents a pair of symmetric peaks at potential of about 750 mV in N2saturated 0.1 M HClO<sub>4</sub> electrolyte for Fe–Phen–N–800. These peaks are expected for a reversible redox reaction process involving Fe(II) and Fe(III). Besides, a clearly oxidation peak appears at 790 mV in O2-saturated condition for Fe-Phen-N-800, which implying iron incorporated into the carbon matrix may serve as a mediator in the electron-transfer process during the ORR.<sup>30,31</sup> The oxygen reduction peak potential for Fe-Phen-N-800 is 0.71 V vs. RHE, which is only 10 mV negative as compared to that of Pt/C catalyst (0.72 V vs. RHE) in 0.1 M HClO<sub>4</sub>, suggesting the excellent electrochemical activity of Fe-Phen-N-800 catalyst towards ORR. The RDE polarization curves shown in Fig. 5b display that the values of the  $E_{\text{onset}}$  and  $E_{1/2}$  over Fe–Phen–N–800 active material are only 38 mV and 59 mV lower than those of Pt/C catalyst in acidic medium. The value of *j* measured for Fe-Phen-N-800 significantly increases (20%) in comparison with Pt/C under the same mass loading. These

results indicate that the activity of our catalyst is higher than or comparable to recently reported catalysts (Table S2, ESI<sup>+</sup>). The value of  $j_{kvs}$  for Fe–Phen–N–800 at potential of 0.65 V is 11.8 mA  $cm^{-2}$  (inset in Fig. 5b), larger than that of Pt/C (10.6 mA  $cm^{-2}$ ). RDE polarization curves of Fe-Phen-N-800 at rotation speeds from 400 to 1600 rpm are presented in Fig. 5c. The corresponding K-L plots (inset in Fig. 5c) exhibit a good linear relationship between  $j^{-1}$  and  $\omega^{-1/2}$ . The average value of *n* is 3.98. As a result, the ORR over Fe-Phen-N-800 catalyst also follows a dominant four-electron pathway in 0.1 M HClO<sub>4</sub> solution. Fig. 5d provides a comparison of the peroxide yield and n value for the Fe-Phen-N-800 and Pt/C catalysts in acidic condition, it can be seen that the peroxide yield is less than 2% for our catalyst in the whole range of potentials. The value of n for Fe-Phen-N-800 is nearly unchanged (4.0) in the measured potential range from 0.06 V to 0.6 V, and the average n obtained from the curve is about 3.99. These results further verify the exclusive involvement of the preferred 4e transfer pathway followed by Fe-Phen-N-800 material. As shown in Fig. 5e, the durability test result reveals that the negative shift of  $E_{1/2}$  for Fe-Phen-N-800 is 19 mV after 10000 cycles under acidic condition, much less than 61 mV negative shift of  $E_{1/2}$  for Pt/C catalyst (Fig. S7, ESI<sup>†</sup>). The CA measurements exhibit that Fe-Phen-N-800 has outstanding immunity towards methanol crossover effect (Fig. 5f).

To investigate the influence of the pyrolysis temperature on the activity of Fe-Phen-N catalysts, the precursors were annealed at various temperatures (700- 900 °C), The Raman spectra (Fig. S8, ESI<sup>+</sup>) of Fe-Phen-N catalysts reveal that the ratio of integrated intensity  $(I_D/I_G)$  for the D band to G band was determined to be 1.96 (700 °C), 1.58 (750 °C), 1.45 (800 °C), 1.39 (850 °C), and 1.36 (900 °C), respectively. Since the value of  $I_{\text{D}}/I_{\text{G}}$  reflects the ratio of disordered carbon and the graphitic carbon,<sup>32</sup> the gradually decreasing values of  $I_D/I_G$  imply that the degree of graphitization is enhanced with increasing pyrolysis temperature, which is further proved by XRD patterns, as shown in Fig. S9, the peak centered at around 26° becomes sharper and narrower when the pyrolysis temperature increases from 700 to 900 °C, indicating the formation of more ordered graphitic structure domains,<sup>33</sup> which is beneficial for improving the electrical conductivity of the carbon support. The electronic conductivity for the five powder samples using four point probe method further reveals that the electrical conductivity increases with the elevating pyrolysis temperature (Fig. S10, ESI<sup>+</sup>). The elemental compositions of Fe-Phen-N catalysts based on XPS analysis are provided in Fig. S11. Both the contents of N and Fe are reduced, while the content of C increases from 75.53 to 93.58 at% with increasing pyrolysis temperature (Table S3, ESI<sup>+</sup>). Fig. S12 reveals the normalized ratios of three different types of N species, namely N1, N2 and N3, obtained from the deconvolution of highresolution N1s spectra of Fe-Phen-N samples (Fig. S13, ESI<sup>+</sup>). It is found that the content of N2 is declined, while that of N3 significantly increases with the elevated pyrolysis temperature. For the N1 species, the decrease of N1 content is also observed, but this tendency is not obvious at higher temperature. According to previous report, both N1 and N3 species play an important role in electroreduction of oxygen.<sup>34,35</sup> Besides, N1 can act as metalcoordination sites because of the lone-pair electrons. RDE polarization curves shown in Fig. S14 and S15 confirm that

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Fe-Phen-N-800 sample has the best catalytic performance towards ORR under both alkaline and acidic conditions. These results imply that the optimal pyrolysis temperature is 800 °C. At this temperature, the factors affecting the ORR activity, including the contents of N and Fe, electrical conductivity of carbon matrix and numbers of active sites, can reach a near ideal compromise. On the other hand, to check whether acid treatment has any influence on the catalytic activity of Fe-Phen-N-800. A control catalyst was prepared under the same conditions as Fe-Phen-N-800, but without the final acid etching. The RDE polarization curves shown in Fig. S16 display that this sample exhibits an inferior ORR activity as compared to Fe-Phen-N-800 sample by acid etching. Consequently, the metallic iron might not be active species for ORR. On the contrary, it might block the accessible active sites. Before acid etching, the BET surface area of Fe-Phen-N-800 catalyst before acidic etching is 153  $m^2g^{-1}$  (Fig. S17, ESI<sup>+</sup>), smaller than that of the catalyst Fe–Phen–N–800 after acid etching (269  $m^2g^{-1}$ ). The higher surface area might be a reason that the acid-treated sample exhibits a much higher activity in ORR.

Finally, the practical applicability of the Fe–Phen–N–800 catalyst was assessed by using Fe–Phen–N–800 as cathode catalyst in primary Zn-air battery, commercial 20% Pt/C was also employed for fabricating the air electrode for comparison. As shown in Fig. S18, the as-constructed Zn-air cells display an open circuit voltage (OCV)



**Fig. 6** The galvanostatic discharge curves of Zn–air batteries using Fe–Phen–N–800 and Pt/C as air cathode catalysts at a current density of (a) 10 mA cm<sup>-2</sup> and (b) 25 mA cm<sup>-2</sup>. (c) Specific capacities of primary Zn–air batteries with Fe–Phen–N–800 and Pt/C as cathode catalysts, which are normalized to the mass of completely consumed Zn. (d) Endurance test of the Zn–air battery with Fe–Phen–N–800 catalyst at a current density of 10 mA cm<sup>-2</sup>. The battery was recharged by replenishing the Zn anode and the electrolyte for 5 cycles. The arrows indicate the recharge process.

of 1.55 V by using Fe–Phen–N–800 (0.5 mg cm<sup>-2</sup>) loaded carbon paper as air cathode, which is higher than 1.52 V attained by Pt/C catalyst. The galvanostatic discharge at current densities of 10 and 25 mA cm<sup>-2</sup> reveals that the voltage delivered by the Zn-air batteries from Fe–Phen–N–800 catalyst is 1.26 V and 1.21 V, respectively (**Fig. 6a** and 6b), which is higher than the voltage of 1.24 V and 1.18 V derived from Pt/C-based Zn-air battery. The

specific capacity of 708 mAh  $g^{-1}$  at the current density of 10 mA cm<sup>-</sup>  $^{2}$ , corresponding to the gravimetric energy density of ~892 Wh kg $^{-1}$ , is achieved from Fe-Phen-N-800-based battery (Fig. 6c). When the current density is increased to 25 mA  $cm^{-2}$ , the specific capacity of the battery is 662 mAh  $g^{-1}$ , corresponding to the gravimetric energy density of  $\sim$ 801 Wh kg<sup>-1</sup>. Notably, this energy density is higher than 851 Wh  $\rm kg^{-1}$  at 10 mA  $\rm cm^{-2}$  and 752 Wh  $\rm kg^{-1}$  at 25 mA  $\rm cm^{-2}$ generated from Zn-air batteries with Pt/C catalyst. Such exceptional performance of Zn-air batteries is ascribed to the superior activity of our Fe-Phen-N-800 catalyst. With respect to the previously reported NPMCs, the Zn-air battery made by Fe-Phen-N-800-based catalyst presents significantly improved performance (see comparison in Table S4, ESI<sup>+</sup>). Most importantly, it is found that, after complete discharging, the battery could be recovered by periodically refueling Zn foil and electrolyte without obvious decay of voltage for 5 cycles at a current density of 10 mA  $cm^{-2}$  (Fig. 6d), thus confirming again the remarkable stability of the Fe-Phen-N-800 catalyst.

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# Conclusions

In summary, a cost-effective and simple way for the fabrication of Fe<sub>3</sub>C/Fe-N-carbon composites towards excellent ORR is demonstrated using iron-phenanthroline coordination compound and dicyandiamide as the precursors. It is found that the pyrolysis temperature has a significant influence on the ORR activity of the as-prepared catalysts. The optimal catalyst pyrolyzed at 800 ºC (Fe-Phen-N-800) exhibits a remarkable (superior to commercial Pt/C) performance under alkaline condition and an excellent ORR activity comparable to that of Pt/C under acidic solution. The ORR over the Fe-Phen-N-800 catalyst follows the effective fourelectron-transfer route and the peroxide yield is lower than 5% in both KOH and HClO<sub>4</sub> media. Moreover, the Fe-Phen-N-800 catalyst exhibits a better stability and tolerance to methanol crossover than Pt/C catalyst. The practical applicability of our catalyst in energy conversion devices has been demonstrated by a primary Zn-air battery with a performance outperforming Pt/C based Zn-air battery. We anticipate our catalyst could serve as a potential candidate for renewable energy conversion systems, especially for metal-air batteries and proton exchange membrane fuel cells.

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The iron carbide-embedded Fe-N-doped carbon catalyst with high-performance for oxygen reduction in Zn-air battery was prepared through a facile and effective strategy.

