Iron polyphthalocyanine-derived ternary-balanced Fe₃O₄/Fe₃N/Fe-N-C@PC as a high-performance electrocatalyst for the oxygen reduction reaction

Rui Hao^{1,2}, Jingjing Chen², Zhenyu Wang², Junjun Zhang², Qingmeng Gan², Yanfang Wang², Yingzhi Li², Wen Luo², Zhiqiang Wang², Huimin Yuan², Chunliu Yan², Wei Zheng², Yanping Huang¹, Penggao Liu¹, Jun Yan¹, Kaiyu Liu^{1*}, Chen Liu^{3*} and Zhouguang Lu^{2*}

ABSTRACT The oxygen reduction reaction (ORR) is the cornerstone reaction of the cathode in metal–air batteries; however, slow kinetics requires high-performance catalysts to promote the reaction. Polyphthalocyanine (PPC) has a typical chemical cross-linking structure and uniformly dispersed metal active sites, but its poor activity and conductivity limit its applications as an ORR catalyst. Herein, a manageable and convenient strategy is proposed to synthesize ternary ORR catalysts through the low-temperature pyrolysis of FePPc. The optimal catalyst, Fe₃O₄/Fe₃N/Fe-N-C@PC-2.5, exhibits excellent ORR activity in alkaline solution with a half-wave potential of 0.90 V, which is significantly higher than that of commercial 20% Pt/C (0.84 V). Electrochemical tests and extended X-ray absorption fine structure spectroscopy reveal that the superior ORR activity of Fe₃O₄/Fe₃N/Fe-N-C@PC-2.5 could be ascribed to the balance of its ternary components (i.e., Fe₃O₄, Fe₃N, and Fe-N₄ species). A Zn–air battery incorporating Fe₃O₄/Fe₃N/Fe-N-C@PC-2.5 as an air cathodic catalyst delivers a high open-circuit voltage and peak power density. During galvanostatic discharge, the battery demonstrates a specific capacity of 815.7 mA h g^{−1}. The facile strategy of using PPC to develop high-performance composite electrocatalysts may be expanded to develop new types of catalysts in the energy field.

Keywords: metal polyphthalocyanine, nonprecious catalyst, hierarchical porous structure, oxygen reduction reaction, Zn–air battery

INTRODUCTION

Growing demands for alternative energy sources to replace dwindling fossil fuel resources has led to the gradual development of metal–air batteries, which feature high energy density, low cost, and environmental friendliness [1–3]. The oxygen reduction reaction (ORR) is an indispensable half-reaction that occurs in metal–air batteries. However, hysteretic kinetics requires the use of catalysts that could promote the ORR rate. Although Pt-based electrocatalysts are considered the best choice for the ORR, their exorbitant price, poor durability, and limited resources restrict the large-scale application of this type of catalyst [4]. Thus, nonprecious metal catalysts, which have the advantages of low cost and excellent activity, have been proposed as ORR catalysts for metal–air batteries [5–8]. Fe-based catalysts, including Fe-N-C, Fe_xO_y, and Fe_xN, have caught the attention of scientific researchers owing to their abundant raw material resources and potential good performance [9–14].

Since they were first reported in 1964, metal macrocyclic compounds (e.g., metal porphyrins, metal phthalocyanines, and their derivatives) have played important roles in ORR studies [15–19]. Unfortunately, the available metal macrocyclic compounds are hindered by their low electronic conductivity and poor stability. Compositing with carbon materials and high-temperature pyrolysis (>800°C) have been proven to be effective methods to improve the ORR performance of metal macrocyclic

¹ Hunan Provincial Key Laboratory of Chemical Power Sources, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

² Department of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen 518055, China

³ Guangdong Research Center for Interfacial Engineering of Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

* Corresponding authors (emails: kaiyuliu309@163.com (Liu K); liuchen@szu.edu.cn (Liu C); luzg@sustech.edu.cn (Lu Z))

compounds [20–23]. As a derivative of metal macrocyclic compounds, transition-metal-containing polyphthalocyanine (TMPPc), which presents a typical chemical cross-linking structure, is beneficial for enhancing electron conductivity and reduce the aggregation of active sites during pyrolysis [24–26]. However, high pyrolysis temperatures are still required to prepare such catalysts and their ORR performance remains unsatisfactory.

In the present study, a TMPPc, i.e., Fe polyphthalocyanine (FePPc), was successfully loaded on porous carbon (PC) to prepare an ORR catalyst with high activity and low cost by low-temperature pyrolysis. The synergistic effect of a hierarchical porous structure and balanced ternary components (i.e., Fe_3O_4 , Fe_3N , and Fe-N₄ species) endows the catalyst with superior ORR activity and stability. When evaluated as a cathodic catalyst for a Zn–air

battery (ZAB), the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ delivered a specific capacity of $815.7 \text{ mA h g}^{-1}$, which is close to the theoretical capacity of Zn anodes.

RESULTS AND DISCUSSION

Structural characterization and component analysis

The preparation process of the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}x$ catalysts is schematically illustrated in Fig. 1a. FePPc was synthesized *via* a solid-phase method, and PC was obtained by sodium citrate carbonization. Scanning electron microscopy (SEM) analysis of FePPc demonstrates that the particles are formed *via* the stacking of lamellar structures (Fig. S1). Atomic force microscopy (AFM) reveals that the FePPc sample obtained after ultrasonic dispersion exhibits a 2D sheet morphology with a

Figure 1 (a) Preparation process of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}x$. (b) SEM micrograph of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}$. (c) SEM, (d) TEM, (e) high-resolution TEM (HR-TEM), (f) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and (g) elemental mapping of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$.

thickness of approximately 1.2 nm (Fig. S2). FePPc and PC were uniformly mixed and then pyrolyzed under an Ar atmosphere to obtain the desired catalysts. As shown in Fig. 1b, the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}$ sample obtained by the pyrolysis of pure FePPc mainly exists as bulk particles. The 3D structure of PC promotes sufficient contact between the electrolyte and catalyst (Fig. S3) [27]. Thus, PC was introduced as a support for the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}$ nanoparticles (NPs) (Fig. 1c). As the content of FePPc increases, more NPs are loaded onto PC, and the gradual blocking of pores occurs in the latter (Fig. S4). The even distribution of NPs on the PC matrix was analyzed by

transmission electron microscopy (TEM) (Fig. 1d). In Fig. 1e, the lattice fringes of 0.253 and 0.207 nm may be ascribed to the (311) plane of Fe_3O_4 and the (111) plane of Fe_3N , respectively, thus demonstrating the formation of Fe_3O_4 and Fe_3N following pyrolysis. Elemental mapping shows that C species is uniformly distributed throughout the composite, while Fe, N, and O species mainly exist in the NPs (Fig. 1f, g).

The X-ray diffraction (XRD) patterns of all samples were collected to confirm the existence of Fe_3O_4 and Fe_3N in the catalysts. In Fig. 2a, PC shows a typical broad peak at 22.4° , which is attributed to the (002) plane of graphitic

Figure 2 (a) XRD patterns of PC, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-x$, and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}$. (b) High-resolution Fe 2p spectrum of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-2.5$. B.E. stands for binding energy. (c) Fe K-edge XANES and (d) k^3 -weighted FT-EXAFS spectra of Fe foil, Fe_3O_4 , and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-2.5$. (e) N_2 adsorption-desorption isotherms and (f) Raman spectra of PC, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-x$, and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}$.

layers. After the pyrolysis of the FePPc and PC matrix, all of the catalysts exhibit similar diffraction profiles. The peaks at 30.1° , 35.4° , 43.0° , 56.9° , and 62.5° correspond to Fe_3O_4 (JCPDS Card No. 89-2355), while the peaks at 38.3° , 41.2° , 43.7° , and 57.5° belong to Fe_3N (JCPDS Card No. 86-0232). These results agree well with the HR-TEM image and demonstrate that Fe_3O_4 and Fe_3N co-exist in the catalysts (Fig. 1e).

X-ray photoelectron spectroscopy (XPS) was utilized to elucidate the chemical environment of the active species in the catalysts. In Fig. S5, the survey spectra of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}@F\text{-}N\text{-}C\text{-}x$ display multiple characteristic peaks, thus confirming the existence of C, N, O, and Fe elements. The N 1s spectra of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC\text{-}x$ could be deconvoluted into five peaks at 398.1, 399.4, 400.5, 401.3, and 403.7 eV (Fig. S6), indicating the presence of pyridinic-N, Fe-N, pyrrolic-N, graphitic-N, and oxidized-N, respectively [28–30]. In the Fe 2p spectrum (Fig. 2b), the two peaks at 711.2 and 724.8 eV could be assigned to $\text{Fe}^{2+} 2p_{3/2}$ and $2p_{1/2}$, respectively, while another two peaks at 713.7 and 727.6 eV could be assigned to $\text{Fe}^{3+} 2p_{3/2}$ and $2p_{1/2}$, respectively [31,32]. The satellite peaks of Fe are located at 718.2 and 732.7 eV, and the peak at 706.7 eV could be attributed to the characteristic peak of Fe_3N in the catalyst [33–35]. In the O 1s spectrum (Fig. S7), the deconvoluted peaks at 530.2, 530.7, 532.0, and 533.1 eV respectively correspond to the Fe–O bond in Fe_3O_4 , adsorbed oxygen, carboxyl groups, and hydroxyl groups [36]. Thus, the composition analysis confirms the co-existence of Fe_3N and Fe_3O_4 .

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy were implemented to identify the surrounding environment of atomic Fe. In Fig. 2c, the absorption energy of Fe in $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC\text{-}2.5$ is slightly lower than that of Fe_3O_4 , thus confirming that the average valence state of this element in $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC\text{-}2.5$ is between those in Fe foil and Fe_3O_4 . Following the Fourier transform of the k^3 -weighted EXAFS spectra (Fig. 2d), the peak of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC\text{-}2.5$ at 1.47 Å is assigned to Fe–N(O), while the peak between 2 and 3.5 Å is mainly related to the nearest Fe_A and Fe_B neighbors in Fe_3O_4 [37]. The fitting results suggest that the bond length of Fe–N(O) in the sample is slightly larger than that of Fe–O in Fe_3O_4 , thus proving the existence of the Fe–N bond (Fig. S8 and Table S1). However, attributing the Fe–N bond to Fe-N_x is difficult at this point because of the existence of Fe_3N . The origin of the Fe–N bond is discussed later in this paper.

The N_2 adsorption–desorption isotherms were mea-

sured to show the specific surface areas (SSAs) and pore size distribution of the catalysts (Fig. 2e). PC mainly exhibits type-II isotherms, thus revealing its macroporous structure. An obvious increase in the range of $0 < P/P_0 < 0.1$ and a hysteresis loop at $0.8 < P/P_0 < 0.95$, which are usually ascribed to the simultaneous existence of micropores and mesopores, are also observed. This finding shows that PC has a hierarchical pore structure. The macroporous structure of PC promotes kinetic accessibility to active sites, which is beneficial to the ORR performance of the catalyst [38]. Interconnected micropores and mesopores can also facilitate electrolyte diffusion. Unlike that in the pure PC matrix, no obvious increase in $P/P_0 < 0.1$ could be observed in the adsorption–desorption isotherms of the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC\text{-}x$ catalysts containing NPs, thus suggesting that the microporous structure of the catalysts disappeared. This phenomenon may be attributed to the NPs generated during the pyrolysis of the FePPc and PC mixture, which block the micropores and decrease the SSA of the catalyst (Table S2). Because $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}@F\text{-}N\text{-}C$ is composed of bulk particles without the PC support, its SSA is the lowest among the samples analyzed. The pore size distribution plots confirm that the hierarchical pores of the catalysts are blocked (Fig. S9). As the FePPc content increases, the microporous structure of the catalysts disappears and their mesopore/macropore content decreases.

Raman spectroscopy reveals two characteristic peaks near 1358 and 1596 cm^{-1} , which reflects the structural defects (D band) and graphitization degree (G band) of all samples (Fig. 2f). Among the samples analyzed, PC clearly has the highest I_D/I_G ratio on account of its porous structure; more defects could promote the ORR [39]. Increases in FePPc lead to a decrease in the I_D/I_G ratio of the catalysts, thus indicating a decrease in their surface defects.

Electrochemical tests and catalytic activity analyses

Various electrocatalytic tests were performed to evaluate the new catalysts. Cyclic voltammetry (CV) curves obtained in O_2 -saturated solution demonstrate a reduction peak at 0.9 V, which disappears after the O_2 is switched to Ar. This finding confirms that the electrochemical reaction occurring in alkaline solution is the ORR (Fig. S10). Linear sweep voltammetry (LSV) with a rotating disk electrode was performed. The low half-wave potential ($E_{1/2}$) obtained reveals that $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}@F\text{-}N\text{-}C$ and PC have poor ORR performance (Fig. 3a). However, the catalysts obtained by pyrolyzing a mixture of PC and

Figure 3 (a) LSV curves of 20% Pt/C, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}x$, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}$, and PC. (b) Tafel slopes of 20% Pt/C and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$. (c) n and H_2O_2 yield of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$. (d) K–L plot of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$. (e) LSV curves of 20% Pt/C and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ before and after 5000 cycles of CV. (f) CA responses of 20% Pt/C and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ at 0.45 V versus reversible hydrogen electrode with a rotating speed of 1600 rpm in the presence of 3 mol L^{-1} methanol.

FePPc show enhanced ORR performance. Among the catalysts tested, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ presents the best ORR activity ($E_{1/2} = 0.90 \text{ V}$), far exceeding the activity of 20% Pt/C ($E_{1/2} = 0.84 \text{ V}$). The excellent ORR activity of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ is comparable to those of a number of Fe-based electrocatalysts (Table S3) [26,32,40–45]. In Fig. 3b, the Tafel slope of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ is 59 mV dec^{-1} , which is slightly lower than that of Pt/C. This finding demonstrates the excellent ORR kinetics of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$. The ideal ORR is usually a four-electron process, and H_2O_2 is a by-

product of the two-electron process. A rotating ring-disk electrode (RRDE) experiment was conducted to obtain the electron transfer number (n) and H_2O_2 yield of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$. The n is close to 4, and the H_2O_2 yield of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ is less than 5% in the range of 0.4–0.95 V, which indicates that the ORR is a four-electron reaction (Fig. 3c). The Koutecky–Levich (K–L) plots show that the n of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ calculated by the K–L equation is also approximately 4, corresponding to the results of the RRDE test. These findings reflect the high selectivity of the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-}2.5$ catalyst.

N-C@PC-2.5 catalyst (Fig. 3d). A durability test was conducted to demonstrate the superior performance of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$. The $E_{1/2}$ of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ exhibits a negative shift of 3 mV after 5000 CV cycles; under the same conditions, the decrease in $E_{1/2}$ of 20% Pt/C is approximately 15 mV. This result suggests the outstanding stability of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ (Fig. 3e). The methanol resistance of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ and Pt/C was tested by chronoamperometry (CA). After injection with 3 mol L^{-1} methanol, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ retains 85% of its initial current, whereas Pt/C retains only 63% of its initial current. This

finding indicates the excellent methanol tolerance of the developed catalysts (Fig. 3f).

The activity of ORR catalysts is affected by the type and content of active species. The Fe_3O_4 and Fe_3N species in $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ were removed by acid-etching to investigate the contribution of each of the chemical components of the catalyst to its ORR activity. The TEM micrograph shown in Fig. S11 illustrates that the catalyst maintains its main structure after acid-etching. The aberration-corrected HAADF-STEM (AC-HAADF-STEM) image in Fig. 4a shows that single Fe atoms distribute at the edges of the structure. The XRD

Figure 4 (a) AC-HAADF-STEM of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$. (b) XRD patterns of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ and $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$. (c) Fe 2p spectrum of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$. (d) k^3 -weighted FT-EXAFS spectra of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$, and FePc. (e) LSV curves of 20% Pt/C, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$, $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$, and PC. (f) $E_{1/2}$ curve and Brunauer-Emmett-Teller (BET) surface area plot obtained with increasing Fe content.

spectrum of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$ does not reveal any diffraction peak belonging to Fe_3O_4 or Fe_3N (Fig. 4b). In the Fe 2p spectrum of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$ (Fig. 4c), the disappearance of the Fe_3N peak suggests that Fe_3N is completely removed from the catalysts. The detection of the Fe–N peak in the N 1s spectrum indicates the presence of some Fe species in the form of Fe–N_x in the catalysts (Fig. S12). EXAFS was performed to prove the form of Fe–N_x in the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$. In the spectrum of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$, the peak at 1.50 Å is nearly identical to that of Fe phthalocyanine (FePc), which indicates the existence of Fe in Fe–N₄ active sites (Fig. 4d) [46–48]. The fitting results show that the coordination number of a single Fe atom is less than 5 with an average bond length of 2.03 Å (Fig. S13 and Table S1). Considering that the sample was sealed by tape to isolate the O₂ in the air during the test and that the coordination number of Fe–O is less than 1, Fe–N_x must exist in the catalyst in the form of Fe–N₄ [49].

The removal of Fe_3O_4 and Fe_3N leads to a slight negative shift in the LSV curve of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$, thereby indicating that the presence of Fe_3O_4 and Fe_3N promotes the ORR activity of this catalyst (Fig. 4e). Compared with that of PC, the high $E_{1/2}$ (0.88 V) of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5-acid}$ indicates that its ORR activity mainly originates from Fe–N₄ [50,51]. Therefore, the superior ORR activity of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ may be attributed to the ternary balance of Fe_3O_4 , Fe_3N , and Fe–N₄ species.

Because the contents of active species (Fe and pyridinic-/Fe–N) are positively and linearly correlated, increases in FePPc during the preparation process may be expected to lead to a continuous increase in reaction active sites, which means catalysts with high contents of active species may possess better ORR activity than those with low contents (Tables S4, S5 and Fig. S14). The ORR activity of the catalysts peaks when the mass ratio of FePPc/PC is 2.5. Further increases in the contents of active species do not bring about improvements in performance and lead to a decline in ORR performance instead (Fig. 4f). This phenomenon may be attributed to reductions in the SSAs of the catalyst with increasing contents of active species. At FePPc/PC ratios less than 2.5, the pores of PC provide channels for ion diffusion and gas adsorption. Although NPs could block the catalyst micropores, the remaining mesoporous and macroporous structures are still able to support electrolyte diffusion and material transport. Therefore, a positive relationship may be observed between $E_{1/2}$ and Fe con-

tent. These observations indicate that the ORR activity of the catalysts is mostly controlled by the content of active species. As the content of active species continuously increases, blockage of the hierarchical pores could reduce the SSA of the catalyst after its activity peak, thereby inhibiting contact between the electrolyte and active species. Although $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ does not have the highest active species content or the largest SSA, the synergistic effect of these two factors endows it with the best ORR performance among the catalysts tested.

Zn–air battery performance

A ZAB was assembled to assess the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ as a cathodic catalyst for practical applications (Fig. S15). During the standing process, the open-circuit voltage of $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ is maintained at 1.57 V, which is higher than the open-circuit voltage of 20% Pt/C (i.e., 1.49 V) (Fig. 5a). In the LSV test, the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ -based ZAB displays a peak power density of 103.8 mW cm^{−2}; by comparison, the peak power density of 20% Pt/C is only 87.6 mW cm^{−2} (Fig. 5b). In Fig. S16, the results of a rate capability test show that the ZAB can recover its original high discharge voltage when the current density is reduced from 20 to 1 mA cm^{−2}. During the galvanostatic discharge process, all batteries equipped with $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ as the ORR catalyst are able to maintain their voltage during continuous discharging (Fig. 5c). After normalization of the mass of consumed Zn, the specific capacity of the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ -based ZAB reaches 815.7 mA h g^{−1} at 5 mA cm^{−2}. The galvanostatic discharge voltage and specific capacity of the $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ -based ZAB consistently remain higher than those of 20% Pt/C even at 20 mA cm^{−2} (Fig. 5d). The above tests confirm that $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ is a promising cathode catalyst for ZABs.

CONCLUSIONS

In this work, we adopted a simple and efficient strategy to develop high-performance ORR catalysts *via* the pyrolysis of FePPc at low temperatures. The activity species of the obtained catalysts may be mainly attributed to the ternary balance of Fe_3O_4 , Fe_3N , and Fe–N₄ species. The synergistic effect of abundant active species and a hierarchical porous structure endows $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ with superior catalytic activity. $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ exhibits high specific capacity and stability as an air cathodic catalyst for ZABs; thus, the material may be a suitable replacement for expensive Pt/C catalysts. The strategy described in this work provides a feasible ap-

Figure 5 (a) Open-circuit voltages; (b) polarization and power density curves of ZABs using $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ and 20% Pt/C as ORR catalysts. (c) Galvanostatic discharge curves of ZABs using $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ as an ORR catalyst under different current densities. (d) Galvanostatic discharge curves of ZABs using $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C@PC-2.5}$ or 20% Pt/C as an ORR catalyst at 20 mA cm^{-2} .

proach to prepare ternary-balanced electrocatalysts with superior ORR activity and may be extended to new types of catalysts.

Received 21 March 2021; accepted 30 April 2021;
published online 16 June 2021

- Kulkarni A, Siahrostami S, Patel A, *et al.* Understanding catalytic activity trends in the oxygen reduction reaction. *Chem Rev*, 2018, 118: 2302–2312
- Cano ZP, Banham D, Ye S, *et al.* Batteries and fuel cells for emerging electric vehicle markets. *Nat Energy*, 2018, 3: 279–289
- Steele BCH, Heinzel A. Materials for fuel-cell technologies. *Nature*, 2001, 414: 345–352
- Tian X, Zhao X, Su YQ, *et al.* Engineering bunched Pt-Ni alloy nanocages for efficient oxygen reduction in practical fuel cells. *Science*, 2019, 366: 850–856
- Wang X, Li Z, Qu Y, *et al.* Review of metal catalysts for oxygen reduction reaction: From nanoscale engineering to atomic design. *Chem*, 2019, 5: 1486–1511
- Tian X, Lu XF, Xia BY, *et al.* Advanced electrocatalysts for the oxygen reduction reaction in energy conversion technologies. *Joule*, 2020, 4: 45–68
- Gewirth AA, Varnell JA, DiAscro AM. Nonprecious metal catalysts for oxygen reduction in heterogeneous aqueous systems. *Chem Rev*, 2018, 118: 2313–2339
- Wu S, Zhu Y, Huo Y, *et al.* Bimetallic organic frameworks derived CuNi/carbon nanocomposites as efficient electrocatalysts for oxygen reduction reaction. *Sci China Mater*, 2017, 60: 654–663
- Niu W, Li L, Liu X, *et al.* Mesoporous N-doped carbons prepared with thermally removable nanoparticle templates: An efficient electrocatalyst for oxygen reduction reaction. *J Am Chem Soc*, 2015, 137: 5555–5562
- Han S, Hu X, Wang J, *et al.* Novel route to Fe-based cathode as an efficient bifunctional catalysts for rechargeable Zn-air battery. *Adv Energy Mater*, 2018, 8: 1800955
- Xu X, Shi C, Li Q, *et al.* Fe-N-doped carbon foam nanosheets with embedded Fe_2O_3 nanoparticles for highly efficient oxygen reduction in both alkaline and acidic media. *RSC Adv*, 2017, 7: 14382–14388
- Li Y, Huang H, Chen S, *et al.* 2D nanoplate assembled nitrogen doped hollow carbon sphere decorated with Fe_3O_4 as an efficient electrocatalyst for oxygen reduction reaction and Zn-air batteries. *Nano Res*, 2019, 12: 2774–2780
- Su H, Zhou S, Zhang X, *et al.* Metal-organic frameworks-derived core-shell $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N@graphite}$ carbon nanocomposites as excellent non-precious metal electrocatalyst for oxygen reduction. *Dalton Trans*, 2018, 47: 16567–16577
- Chen Y, Li Z, Zhu Y, *et al.* Atomic Fe dispersed on N-doped carbon hollow nanospheres for high-efficiency electrocatalytic oxygen reduction. *Adv Mater*, 2019, 31: 1806312
- Jasinski R. A new fuel cell cathode catalyst. *Nature*, 1964, 201: 1212–1213
- Lin L, Li M, Jiang L, *et al.* A novel iron (II) polyphthalocyanine catalyst assembled on graphene with significantly enhanced performance for oxygen reduction reaction in alkaline medium. *J Power Sources*, 2014, 268: 269–278
- Cui L, Cui L, Li Z, *et al.* A copper single-atom catalyst towards efficient and durable oxygen reduction for fuel cells. *J Mater Chem*

- A, 2019, 7: 16690–16695
- 18 Zhao L, Xu Q, Shao Z, *et al.* Enhanced oxygen reduction reaction performance using intermolecular forces coupled with more exposed molecular orbitals of triphenylamine in Co-porphyrin electrocatalysts. *ACS Appl Mater Interfaces*, 2020, 12: 45976–45986
- 19 Yu X, Lai S, Xin S, *et al.* Coupling of iron phthalocyanine at carbon defect site *via* π - π stacking for enhanced oxygen reduction reaction. *Appl Catal B-Environ*, 2021, 280: 119437
- 20 Li M, Bo X, Zhang Y, *et al.* Comparative study on the oxygen reduction reaction electrocatalytic activities of iron phthalocyanines supported on reduced graphene oxide, mesoporous carbon vesicle, and ordered mesoporous carbon. *J Power Sources*, 2014, 264: 114–122
- 21 Jiang Y, Lu Y, Lv X, *et al.* Enhanced catalytic performance of Pt-free iron phthalocyanine by graphene support for efficient oxygen reduction reaction. *ACS Catal*, 2013, 3: 1263–1271
- 22 Harnisch F, Savastenko NA, Zhao F, *et al.* Comparative study on the performance of pyrolyzed and plasma-treated iron(II) phthalocyanine-based catalysts for oxygen reduction in pH neutral electrolyte solutions. *J Power Sources*, 2009, 193: 86–92
- 23 Oberst JL, Thorum MS, Gewirth AA. Effect of pH and azide on the oxygen reduction reaction with a pyrolyzed Fe phthalocyanine catalyst. *J Phys Chem C*, 2012, 116: 25257–25261
- 24 Yang S, Yu Y, Dou M, *et al.* Two-dimensional conjugated aromatic networks as high-site-density and single-atom electrocatalysts for the oxygen reduction reaction. *Angew Chem Int Ed*, 2019, 58: 14724–14730
- 25 Zhang Z, Yang S, Dou M, *et al.* One-step preparation of N-doped graphitic layer-encased cobalt/iron carbide nanoparticles derived from cross-linked polyphthalocyanines as highly active electrocatalysts towards the oxygen reduction reaction. *Catal Sci Technol*, 2017, 7: 1529–1536
- 26 Pan Y, Liu S, Sun K, *et al.* A bimetallic Zn/Fe polyphthalocyanine-derived single-atom Fe-N₄ catalytic site: A superior trifunctional catalyst for overall water splitting and Zn-air batteries. *Angew Chem Int Ed*, 2018, 57: 8614–8618
- 27 He Y, Zhuang X, Lei C, *et al.* Porous carbon nanosheets: Synthetic strategies and electrochemical energy related applications. *Nano Today*, 2019, 24: 103–119
- 28 Lin Q, Bu X, Kong A, *et al.* New heterometallic zirconium metalloporphyrin frameworks and their heteroatom-activated high-surface-area carbon derivatives. *J Am Chem Soc*, 2015, 137: 2235–2238
- 29 Ma X, Lei Z, Feng W, *et al.* Living Fe mineral@bacteria encrustation-derived and self-templated preparation of a mesoporous Fe-N-C electrocatalyst with high activity for oxygen reduction. *Carbon*, 2017, 123: 481–491
- 30 Xue N, Liu J, Wang P, *et al.* Scalable synthesis of Fe₃N nanoparticles within N-doped carbon frameworks as efficient electrocatalysts for oxygen reduction reaction. *J Colloid Interface Sci*, 2020, 580: 460–469
- 31 Huang Y, Liu P, Hao R, *et al.* Engineering porous quasi-spherical Fe-N-C nanocatalysts with robust oxygen reduction performance for Zn-air battery application. *ChemNanoMat*, 2020, 6: 1782–1788
- 32 Li T, Li M, Zhang M, *et al.* Immobilization of Fe₃N nanoparticles within N-doped carbon nanosheet frameworks as a high-efficiency electrocatalyst for oxygen reduction reaction in Zn-air batteries. *Carbon*, 2019, 153: 364–371
- 33 Zhang Y, Wang N, Jia N, *et al.* A low-cost and facile method for the preparation of Fe-N/C-based hybrids with superior catalytic performance toward oxygen reduction reaction. *Adv Mater Interfaces*, 2019, 6: 1900273
- 34 Ma X, Xiong X, Zeng J, *et al.* Melamine-assisted synthesis of Fe₃N featuring highly reversible crystalline-phase transformation for ultrastable sodium ion storage. *J Mater Chem A*, 2020, 8: 6768–6775
- 35 Huang H, Gao S, Wu AM, *et al.* Fe₃N constrained inside C nanocages as an anode for Li-ion batteries through post-synthesis nitridation. *Nano Energy*, 2017, 31: 74–83
- 36 Su Y, Jiang H, Zhu Y, *et al.* Enriched graphitic N-doped carbon-supported Fe₃O₄ nanoparticles as efficient electrocatalysts for oxygen reduction reaction. *J Mater Chem A*, 2014, 2: 7281–7287
- 37 Subías G, García J, Blasco J. EXAFS spectroscopic analysis of the Verwey transition in Fe₃O₄. *Phys Rev B*, 2005, 71: 155103
- 38 Lee SH, Kim J, Chung DY, *et al.* Design principle of Fe-N-C electrocatalysts: How to optimize multimodal porous structures? *J Am Chem Soc*, 2019, 141: 2035–2045
- 39 Zhu A, Qiao L, Tan P, *et al.* Iron-nitrogen-carbon species for oxygen electro-reduction and Zn-air battery: Surface engineering and experimental probe into active sites. *Appl Catal B-Environ*, 2019, 254: 601–611
- 40 Zhou Y, Yu Y, Ma D, *et al.* Atomic Fe dispersed hierarchical mesoporous Fe-N-C nanostructures for an efficient oxygen reduction reaction. *ACS Catal*, 2021, 11: 74–81
- 41 Cui X, Gao L, Lei S, *et al.* Simultaneously crafting single-atomic Fe sites and graphitic layer-wrapped Fe₃C nanoparticles encapsulated within mesoporous carbon tubes for oxygen reduction. *Adv Funct Mater*, 2020, 31: 2009197
- 42 Gong X, Zhu J, Li J, *et al.* Self-templated hierarchically porous carbon nanorods embedded with atomic Fe-N₄ active sites as efficient oxygen reduction electrocatalysts in Zn-air batteries. *Adv Funct Mater*, 2021, 31: 2008085
- 43 Hu S, Ni W, Yang D, *et al.* Fe₃O₄ nanoparticles encapsulated in single-atom Fe-N-C towards efficient oxygen reduction reaction: Effect of the micro and macro pores. *Carbon*, 2020, 162: 245–255
- 44 Zhao L, Zhang Y, Huang LB, *et al.* Cascade anchoring strategy for general mass production of high-loading single-atomic metal-nitrogen catalysts. *Nat Commun*, 2019, 10: 1278
- 45 Zhang X, Zhang S, Yang Y, *et al.* A general method for transition metal single atoms anchored on honeycomb-like nitrogen-doped carbon nanosheets. *Adv Mater*, 2020, 32: 1906905
- 46 Wu Y, Wu X, Tu T, *et al.* Controlled synthesis of FeN_x-CoN_x dual active sites interfaced with metallic Co nanoparticles as bifunctional oxygen electrocatalysts for rechargeable Zn-air batteries. *Appl Catal B-Environ*, 2020, 278: 119259
- 47 Chen Y, Ji S, Wang Y, *et al.* Isolated single iron atoms anchored on N-doped porous carbon as an efficient electrocatalyst for the oxygen reduction reaction. *Angew Chem Int Ed*, 2017, 56: 6937–6941
- 48 Zhang H, Hwang S, Wang M, *et al.* Single atomic iron catalysts for oxygen reduction in acidic media: Particle size control and thermal activation. *J Am Chem Soc*, 2017, 139: 14143–14149
- 49 Miao Z, Wang X, Tsai M-, *et al.* Atomically dispersed Fe-N_x/C electrocatalyst boosts oxygen catalysis via a new metal-organic polymer supramolecule strategy. *Adv Energy Mater*, 2018, 8: 1801226
- 50 Zitolo A, Goellner V, Armel V, *et al.* Identification of catalytic sites for oxygen reduction in iron- and nitrogen-doped graphene materials. *Nat Mater*, 2015, 14: 937–942
- 51 Chung HT, Cullen DA, Higgins D, *et al.* Direct atomic-level insight

into the active sites of a high-performance PGM-free ORR catalyst. *Science*, 2017, 357: 479–484

Acknowledgements This work was financially supported by the Basic Research Project of the Science and Technology Innovation Commission of Shenzhen (JCYJ20200109141640095 and JCYJ20190809115413414), the National Natural Science Foundation of China (21671096 and 21905180), the Natural Science Foundation of Guangdong Province (2018A030310225), and Guangdong Provincial Key Laboratory of Energy Materials for Electric Power (2018B030322001). The authors gratefully acknowledge the support from the Center for Computational Science and Engineering and Core Research Facilities of SUSTech.

Author contributions Hao R synthesized the materials, performed the tests, and wrote the manuscript. Chen J, Zhang J, and Huang Y provided suggestions for the manuscript. Wang ZY performed the HAADF-STEM analysis. Gan Q conducted the TEM analysis. Wang Y and Li Y collected the XANES data. Luo W performed the AFM analysis. Wang ZQ provided advice on the TOC image. Liu K, Liu C, and Lu Z reviewed and revised the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors have no conflict of interest to declare.

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

Rui Hao is a PhD candidate at the College of Chemistry and Chemical Engineering, Central South University. His research interests include the design and synthesis of high-performance electrocatalysts for metal–air batteries.

Kaiyu Liu earned his PhD from the College of Chemistry and Chemical Engineering, Central South University, in 2003. He is now a professor at the same college and university. His research focuses on new energy-storage devices and the related materials, such as electrode materials for lithium/sodium/zinc-ion batteries and metal–air battery catalysts.

Chen Liu is an assistant professor at the College of Materials Science and Engineering, Shenzhen University. She received her PhD from the Department of Physics and Materials Science, City University of Hong Kong, in 2017. Her research interests include polymer composites/nanomaterials for electrochemical and energy applications, especially the design of solid composite electrolytes for lithium/sodium solid-state batteries.

Zhouguang Lu obtained his PhD from the City University of Hong Kong in 2009. He is now a professor at the Department of Materials Science and Engineering, Southern University of Science and Technology. His research interests include the design and synthesis of nanostructures and their applications in energy storage and conversion.

聚酞菁铁驱动的三元平衡 $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC$ 作为氧还原反应高效催化剂

郝睿^{1,2}, 陈晶晶², 王振宇², 张钧君², 甘庆孟², 王彦方², 李英芝², 罗文², 王志强², 袁惠敏², 闫春柳², 郑薇², 黄燕平¹, 刘鹏高¹, 颜军¹, 刘开宇^{1*}, 刘琛^{3*}, 卢周广^{2*}

摘要 聚酞菁具有典型的化学交联结构和均匀分散的金属活性位点, 但是较差的活性和导电性限制了其作为氧还原催化剂的应用. 本文通过热解聚酞菁铁与多孔碳的混合物制备了三元氧还原催化剂, 产物 $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-2.5$ 在碱性溶液中的半波电势为 0.90 V, 远高于市售 20% Pt/C 的半波电势. 电化学测试和 X 射线吸收精细结构相结合, 将 $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-2.5$ 的优异氧还原活性归因于 Fe_3O_4 , Fe_3N 和 Fe-N_4 三种组分的共存. 以 $\text{Fe}_3\text{O}_4/\text{Fe}_3\text{N}/\text{Fe-N-C}@PC-2.5$ 作为空气阴极催化剂的锌空气电池具有较高的开路电压和峰值功率密度. 在恒电流放电过程中, 该电池的比容量可达到 $815.7 \text{ mA h g}^{-1}$.