Fe-doped Co-N/C as effective electrocatalyst for oxygen reaction

Qin Lin, Chaoqun Shang, Zhihong Chen, Eser Metin Akinoglu, Xin Wang and Guofu Zhou

1. Introduction

Metal-air batteries have the advantages of high-energy density, low cost, and environmental friendliness, so they are extensively attracted researchers' attention [1–3]. The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are two important extremely reactions in a rechargeable metal-air battery [4]. However, the intrinsic sluggish kinetics and different catalytic sites of oxygen reaction hinder the effective ORR and OER [5, 6]. At present, the most active electrocatalysts for ORR are Pt-based materials, while the effective OER electrocatalysts are Ru- or Ir-based materials [7–9]. The noble metal based catalysts are suffered from high price, exiguity and mono-functionality [10–12]. Developing inexpensive and efficient bifunctional oxygen catalysts is of great urgent.

Among numerous nonprecious metal bifunctional electrocatalysts such as metal–free heteroatom-doped carbon [13], metal-nitrogen–doped carbons (M–N–C) [14] and transition-metal-based catalysts [15], Co-based catalysts become a potential candidate, which is attributed to their earth-abundance and environmental friendliness, especially the bifunctional catalytic effects. Ning et al synthesized porous N-doped carbon-encapsulated CoNi alloy nanoparticles by using ZIF-67 as precursor for oxygen electrocatalysis [16]. Kuang et al show that a bimetal (Cu and Co) embedded N-doped carbon framework was an efficient electrocatalyst for oxygen evolution reaction [17]. The introduction of transition metal could modify the electronic structure, thus enhancing electrocatalytic performance. Fe-doping becomes the focus of researchers due to its low price and abundant resources. Furthermore, the introduction of Fe into Co-based electrocatalyst could enrich the catalytic sites guaranteed by the synergistic Fe–Co interactions [18]. For instance, Xu and co-workers have prepared Fe–Co nanoparticles embedded in a nitrogen-doped 3D carbon matrix, which presents suitable ORR/OER activity [19]. Guan and co-workers have reported porous Fe–Co alloy/N-doped carbon cages, which exhibits excellent electrocatalytic performance due to the structural and compositional advantages [20].

Abstract

The development of cost-effective bifunctional electrocatalysts for metal-air batteries with high electrocatalytic activity and stability is crucial for the conversion of clean and renewable energy. In this work, Fe doped nitrogen–enriched porous carbon derived from ZIF-67 was synthesized via a simple ligand exchange reaction with subsequent calcination and acid leaching treatment. The catalysts pyrolysis at 700 °C (CoFe@NC-700) exhibited high electrocatalytic activity and superior stability toward oxygen reaction. Larger surface area and abundant mesopores structure are advantageous for charge transportation and exposure of active sites. More importantly, the synergistic effect of Co–N and Fe–N active sites and the increased number of active sites by modulating the local electronic structure further enhance the electrocatalytic performance of the as-prepared CoFe@NC-700.
Herein, Fe doped Co encapsulated nitrogen-enriched porous carbon were prepared by effective temperature adjustment. The electrocatalyst pyrolysis at 700 °C (CoFe@NC-700) exhibits excellent catalytic activity toward both ORR and OER, which could be benefited from the following advantages: (i) increased surface area and pore volume greatly accelerated mass transport and exposure of active sites; (ii) proper treatment temperature realize good electrical conductivity ensuring fast electron transport pathway; (iii) the synergistic effect of Co–N and Fe–N catalytic sites provide effective catalytic activity; (iv) the Fe-doping tunes electronic structure of Co@NC by activated Co center through a charge transfer process.

2. Results and discussion

CoFe@NC samples were synthesized by the pyrolysis of the bimetallic CoFe@ZIF in Ar/H₂ atmosphere and acid leaching (figure S1 is available online at stacks.iop.org/MRX/7/085002/mmedia). As displayed in figure 1(a), the as-prepared CoFe@ZIF shows octahedral structure with smooth surface, which is similar to that of Co@ZIF in the absence of Fe ions (figure S2). Besides, CoFe@ZIF possesses similar XRD pattern to that of Co@ZIF (figure S3), indicating successful dopant of Fe in Co@ZIF without change the crystallinity of Co@ZIF. After pyrolysis at 700 °C, the CoFe@NC-700 maintains the octahedral structure with shrinkage in some extent owing to the pyrolysis of organic species and carbonization. The pyrolysis temperature plays an important role in the electrocatalytic performance that the low temperature treatment leads to the incompletely carbonization with
poor electrical conductivity while high temperature calcination resulting the collapse of nanostructure and the loss of active sites [16]. Therefore, the CoFe@ZIF was annealed at 600 °C and 800 °C as a fair comparison. The as-prepared CoFe@NC-600 (figure S4(a)) and CoFe@NC-800 (figure S4(b)) show the similar morphology to that of CoFe@NC-700 with octahedral nanostructure as well as the annealed Co@ZIF at 700 °C (figure S5). Figure 1(d) confirms the hollow carton structure of CoFe@NC-700, which provides sufficient active sites for electrolyte penetration. As illustrated in HETEM of figure 1(e), the lattice fringe of 0.203 nm and 0.363 nm of CoFe@NC-700 is corresponding to the (111) facet of Co and (002) facet of graphite carbon, respectively [21]. Compared to graphite carbon (0.335 nm), the obvious interlayer expansion might be caused by the doping of Fe and N atoms in the graphite carbon layer [22]. Elemental mappings (figure 1(f)) clearly demonstrated that the C, N, Co and Fe elements are dispersed homogeneously among the whole octahedral structure. Those all above demonstrated that Fe and nitrogen successfully doped in the octahedral structure.

According to the XRD analysis (figure 2(a)), there is a relatively broad peak at 2θ = 26.4° in all the samples, which is corresponding to the (002) plane of carbon, indicating the formation of graphitic carbon [23]. Obviously, a low temperature treatment leads to incomplete reduction of CoFe@ZIF that Co3O4 can be observed in CoFe@NC-600. A high calcination temperature causes severe agglomeration that large amount of metal particles are removed by acid leaching [17]. It was noted that the Co peaks at 700 °C is strongest. This result indicated that moderate temperature was beneficial to increase crystallinity [24]. It is worth mentioning that there is no peak of Fe species because of the relatively lower content of Fe. To distinguish the carbonization, Raman spectra of the samples were displayed in figure 2(b), where the peaks at 1569 and 1332 cm⁻¹ present the G- and D- band, respectively [16, 25]. The higher I_D/I_G ratio means more defects and less graphitization [26]. The I_D/I_G of CoFe@NC-700 (1.05) is slight higher than those of CoFe@NC-600 (1.03), CoFe@NC-800 (1.02), and Co@NC-700 (1.02), indicating more defects of CoFe@NC-700 with more catalytic active sites. The typical type-IV isotherms could be verified by the N₂ adsorption/desorption isotherms in figure 2(c), indicating the presence of mesopores. The pore size distribution with average sized pores of 3.5–4.3 nm is shown in figure 2(d).

The specific surface areas (SSA) of all samples are listed in table S1. As for CoFe@NC, the SSA and pore volume increased with the calcination temperature increased, which could be attributed to the enhanced carbonization degree and removal of unstable species after acid leaching. Compared to Co@NC-700 with SSA of 400.88 m² g⁻¹, CoFe@NC-700 shows a higher SSA of 485.55 m² g⁻¹, further demonstrating the important role of Fe introduction [27]. CoFe@NC-700 with mesoporous nanostructure and high SSA could facilitate the electrolyte penetration.

Figure 2. (a) XRD patterns, (b) Raman spectra, (c) N₂ sorption isotherms, and (d) the pore size distribution of the as-synthesized CoFe@NC electrocatalysts and Co@NC-700.
penetration and large contact area between oxygen species and active sites, further improving the electrochemical performance.

To clarify the chemical of as-prepared samples, the X-ray photoelectron spectroscopy (XPS) is conducted. The Co 2p spectrum shown in the figure 3(a) could be divided into five components: Co0, Co2+, Co–N, Co3+ and the satellite peaks [28]. The Co0 peaks at 778.33 eV of CoFe@NC transfer to lower binding energy about 0.1 eV than that of Co@NC-700, indicating the introduce of Fe results in electron transfer from Fe to Co due to electronegativity difference (Fe : 1.83, Co : 1.88), which enriches CoFe@NC OER catalytic activity [18]. The deconvoluted Fe 2p spectrum (figure 3(b)) revealed five different contents coexisting on the surface: Fe0, Fe2+, Fe–N, Fe3+, satellite peaks, respectively. These results reflect the strong electron interactions between the Co and Fe after doping [16]. The C1s spectra of the synthesized samples can be deconvoluted into three peaks and attributed to C–C (284.60 eV), C–N (285.90 eV) and C–O (289.70 eV). The existence of C–N clearly demonstrates that nitrogen element is embedded in the carbon matrix [29]. As displayed in figure 3(d) of N 1s spectrum, the peaks located at 398.70, 399.40, 400.50, 401.40 and 403.80 eV were related to pyridinic N, metallic N, pyrrolic N, graphite N, oxidized N, respectively [30]. The contents of N-doping amount decrease with the increasing pyrolysis temperature (table S2), which is related to the unstable state of N atoms at high temperature [31]. N-doping could modify the electronic interaction with close metal/carbon to offer catalytic sites and generate defects in N-doped-carbon materials [32]. The O 1s spectra was shown in figure S6, Four peaks at 531.95, 532.90, 533.80, 534.30 eV can be assigned to metal O, surface-adsorbed O, structural water and oxygen vacancies, respectively [33].

To determine the optimal amount of Fe, the ORR and OER performance of three samples (the molar ratios of n(Co)/n(Fe) are 9.5:0.5, 9:1, 8.5:1.5, respectively) were measured in figure S7. The CoFe@NC (9:1) exhibited the highest electrocatalytic performances. Excess of introduction of Fe would lead to the deterioration of the OER performance due to a relatively lower conductivity and poor stability of Fe [16]. Furthermore, the calcination times were studied. As shown in figure S8, the optimal calcination time is 3 h. The short-time calcination would lead to the incomplete carbonization while long-time calcination would cause structural collapse. Therefore, favorable metal ratios and calcination times play important roles in improved electrocatalytic performance. The electrocatalytic performances of the as-prepared catalysts for ORR were carried out by linear sweep voltammetry (LSV) in alkaline solution (O2-saturated 0.1 M KOH) at a scan rate of 10
mV s⁻¹. The onset potentials (E_onset) and half-wave potentials (E₁/₂) of all the samples were summarized in table S3. As shown in figure 4(a), CoFe@NC-700 exhibited higher E_onset and E₁/₂ (E_onset = 1.01 V, E₁/₂ = 0.89 V) than those of CoFe@NC-600 (E_onset = 0.94 V, E₁/₂ = 0.87 V) and CoFe@NC-800 (E_onset = 0.94 V, E₁/₂ = 0.88 V), which was comparable to that of commercial Pt/C (E_onset = 1.08 V, E₁/₂ = 0.90 V), indicating the promising oxygen reduced performance of CoFe@NC-700. Compared to Co@NC-700 (E_onset = 0.93 V, E₁/₂ = 0.87 V), Fe doping could effectively enhance ORR performance, which is possibly due to the synergistic effect of Fe–N–C and Co–N–C active sites [19, 25]. Furthermore, Tafel plots (figure S9) show the lower slope of CoFe@NC materials than that of Pt/C, suggesting that CoFe@NC possess comparable ORR kinetics to commercial Pt/C [34]. The current density increase with the change of rotation speed from 400 to 2500 rpm, which could be ascribed to the enhanced diffusion of electrolyte [35]. The LSV curves and the corresponding Koutecky–Levich (K–L) plots were displayed in figures 5(b) and S10–S13, where the good linear relationship reflected the first-order reaction kinetics [36]. In order to understand the reaction pathway, rotating ring-disk electrode (RRDE) measurements were used to detect the formed peroxide (HO₂⁻) and electron transfer number during the ORR process (figures 5(c) and S14). In particular, CoFe@NC-700 shows the lowest peroxide yield (4%) and higher electron transfer number above 3.90 than Co@NC-700, indicating the existence of Fe improve selectivity of electrocatalysts at some extent. The long-term stability of CoFe@NC-700 and Pt/C were investigated by comparing the LSV curves under a rotating speed at 1600 rpm before and after 1000 CV cycles (figures 5(d), S15). Strikingly, the E₁/₂ of CoFe@NC-700 decreased for only 4 mV, which was much lower than 62.9 mV of Pt/C, indicating the good long-term stability of CoFe@NC-700.

Apart from the promising ORR activity, the OER polarization curve of CoFe@NC-700 was shown in figure 5(a), which exhibits an overpotential of 0.47 V compared to IrO₂ (an overpotential of 0.39 V) at a current density of 10 mA cm⁻². In addition, the Tafel slope of all catalysts were evaluated by LSV curves (figure 5(b)), the value of CoFe@NC-600 (69.53 mV dec⁻¹), CoFe@NC-700 (135.70 mV dec⁻¹) and CoFe@NC-800 (126.85 mV dec⁻¹) is lower than the value of Co@NC-700 (165.65 mV dec⁻¹), which further suggest that Fe-doping is contributed to elevate OER performance [37]. A highly charged Fe site surrounded by nearest Co exhibit decreased affinity for OER intermediates, resulting in the formation of optimal adsorption energies at Fe sites, thereby enhance the OER performance [38]. TOF was used to evaluate the intrinsic activity. The corresponding TOF values of CoFe@NC, Pt/C, IrO₂ and other catalysts were shown in table S4. After the introduction of Fe, the
TOF values of CoFe@NC have been significantly improved, which indicating that Fe-doping greatly enhances the intrinsic activity. After 1000 CV cycles, CoFe@NC-700 shows no obvious change of overpotential at the current density of 10 mA cm$^{-2}$, but IrO$_2$ exhibited sharply decreased (figures 5(c) and S16), indicating the good stability of CoFe@NC-700.

As summarized in figure 5(d) and table S3, CoFe@NC-700 exhibits promising bifunctional catalytic activity toward oxygen reaction and presents the smallest potential gap ($\Delta E$) of 0.81 V. Moreover, the $\Delta E$ values for CoFe@NC-700 outperform Co@NC-700 (0.89 V), which is most likely attributed to the synergetic Fe–Co interaction. To get an insight into the possible origin for the high catalytic performance of CoFe@NC-700, the electrochemical surface area (ECSA) was evaluated. As illustrated in figure S17, the corresponding calculated double-layer capacitance ($C_{dl}$) is shown in figure S18 which is generally regard as the indicative of ECSA [39]. CoFe@NC-700 has smaller $C_{dl}$ value (21.74 mF cm$^{-2}$) than that of CoFe@NC-600 (26.33 mF cm$^{-2}$), which is attribute to the higher intrinsic activity of CoFe@NC-700 [40]. By contrast, CoFe@NC-700 (21.74 mF cm$^{-2}$) has much larger $C_{dl}$ value than that of Co@NC-700 (12.38 mF cm$^{-2}$), further suggesting the introduction of Fe could efficiently increase the ESCA and make active sites expose more easily. In order to demonstrate the existence of Fe/Co–N active sites, the principle was used that the thiocyanate ion (SCN$^-$) could complex with metal ions of M–N active sites, leading to block the M–N active sites and reduce the ORR activity. In figure S19, after adding 0.01 M KSCN solution, the onset potential, half-wave potential and limiting current density of CoFe@NC-700 was found to decrease significantly, which suggested the existence of Fe–N–C and Co–N–C catalytic sites and confirmed the importance of Fe/Co–N active sites for the excellent ORR activity of CoFe@NC-700 [22]. The introduction of Fe could greatly increase the charge carrier density of CoFe@NC. The electron transfer from Fe to Co due to the electronegative difference, which is favorable to increase the concentration of OH$^-$ at oxygen evolution reaction and enhance OER activity [18]. The deprotonation of HO$^+$ to O$^-$ on Co sites was regard as the potential limiting step of both Co@NC and CoFe@NC. The incorporation of Fe could greatly lower the free energy value of potential limiting step, which suggest that energy barrier of formation of O$^-$ was lowered significantly [41].

Figure 5. (a) LSV, and (b) Tafel curves of CoFe@NC-700 and the compared samples in 1 M KOH with a scan rate of 2 mV s$^{-1}$ at room temperature. (c) LSV curves of CoFe@NC-700 catalyst before and after 10 h in the stability test over in 1 M KOH under a rotating speed of 1600 rpm. (d) overpotentials between the $E_{1/2}$ of ORR and $E_{10}$ of OER for all samples.
3. Conclusions

In summary, we synthesized Fe-doped Co-N/C through a facile ligand exchange reaction by a calcination and acid leaching treatment. According to the annealing temperature adjustment, CoFe@NC-700 exhibit the promising catalytic performance toward ORR ($E_{1/2} = 0.89 \text{ V}$) and OER ($E_{10} = 0.47 \text{ V}$) and long-term stability. The favorable catalytic performance should be attributed to the porous structure facilitating mass transport, higher surface area increasing the exposure of active sites and the synergic effect of Fe/Co–N guaranteeing bifunctional catalytic activity.

Acknowledgments

This research was funded by the National Natural Science Foundation of China Program (No. 51602111); the Natural Science Foundation of Guangdong Province (2018A030313739); Cultivation project of National Engineering Technology Center (2017B090903008); Xijiang R&D Team (X W), Guangdong Provincial Grant (2017A050506009); Special Fund Project of Science and Technology Application in Guangdong (2017B020240002) and 111 project, Guangdong Innovative and Entrepreneurial Team Program (No.2016YT06C517).

Conflicts of interest

The authors declare no conflict of interest.

ORCID iDs

Chaoqun Shang https://orcid.org/0000-0003-4653-3788
Xin Wang https://orcid.org/0000-0002-4771-8453

References

[1] Hang C, Zhang J, Zhu J, Li W, Kou Z and Huang Y 2018 Adv. Energy Mater. 8 1703539
[2] Zhang S L, Guan B Y and Lou X W D 2019 Small 15 1805324
[3] Li C, Liu H and Yu Z 2019 Appl. Catal. B: Environ. 241 95–103
[4] Fu G, Jiang X, Chen Y, Xu L, Sun D, Lee J-M and Tang Y 2018 NPG Asia Mater. 10 618–29
[5] He X, Yi X, Yin F, Chen B, Li G and Yin H 2019 J. Mater. Chem. A 7 6753–65
[6] Meng F, Zhong H, Bao D, Yan J and Zhang X 2016 J. Am. Chem. Soc. 138 10226–31
[7] Xu N, Zhang Y, Wang M, Fan K, Zhang T, Peng L, Zhou X-D and Qiao J 2019 Nano Energy 65 104021
[8] Zhang L, He D, Su H, Chen X, Pan M and Mu S 2014 J. Mater. Chem. A 2 1242–6
[9] Wang R, Cao J, Cai S, Yan X, Li J, Yourey W M, Tong W and Tang H 2018 ACS Appl. Energy Mater. 1 1060–8
[10] Lin Y, Yang L, Zhang Y, Jiang H, Xiao Z, Wu C, Zhang G, Jiang J and Song I 2018 Adv. Energy Mater. 8 1703623
[11] Ji D, Fan L, Tao L, Sun Y, Li M, Yang G, Tran T Q, Ramakrishna S and Guo S 2019 Angew. Chem. Int. Ed. 58 13840–4
[12] Tan H, Tang J, Kim J, Kaneti Y V, Kang Y-M, Sugahara Y and Yamauchi Y 2019 J. Mater. Chem. A 7 1380–93
[13] Wang Y et al 2013 Angew. Chem. Int. Ed. 54 9997–1003
[14] Palaniselvam T, Kashyap V, Bhanage S N, Baek J-B and Kurungot S 2016 Adv. Funct. Mater. 26 2130–62
[15] Guo Y et al 2018 ACS Nano 12 1894–901
[16] Ning H, Li G, Chen Y, Zhang K, Gong G, Nie R, Hu W and Xia Q 2019 ACS Appl. Mater. Interfaces 11 1957–68
[17] Kuang M, Wang Q, Han P and Zheng G 2017 Adv. Energy Mater. 7 1700193
[18] Liu T, Yang F, Cheng G and Luo W 2018 Small 14 1703748
[19] Liu X, Wang L, Yu P, Tian C, Sun F, Ma J and Fu H 2018 Angew. Chem. Int. Ed. 57 16166–70
[20] Guan B Y, Liu Y, Wang Y, Wu M and Lou X W D 2018 Adv. Mater. 28 1707638
[21] Zhang W, Yao X, Zhou S, Li X, Li L, Yu Z and Gu I 2018 Small 14 1800423
[22] Zhou T, Ma R, Zhang T, Li Z, Yang M, Liu Q, Zhu Y and Wang J 2019 J. Colloid Interface Sci. 536 46–52
[23] Xia W, Tang J, Li J, Zhang S, Wu K C, He J and Yamauchi Y 2019 Angew. Chem. Int. Ed. 58 13354–9
[24] Yang L, Peng S, Xu Y, Gai B and Zhang I 2019 ACS Sustainable Chem. Eng. 7 3462–75
[25] Li S, Chen W, Pan H, Cao Y, Jiang Z, Tian X, Hao X, Maiyalagan T and Jiang Z 2019 ACS Sustainable Chem. Eng. 7 8350–41
[26] Fu Y, Yu H-Y, Jiang C, Zhang T-H, Zhan R, Li X, Li J-F, Tian J-H and Yang R 2018 Adv. Funct. Mater. 28 1705094
[27] Yu P, Wang L, Sun F, Xie Y, Liu X, Ma J, Wang X, Tian C, Li J and Fu H 2019 Adv. Mater. 31 1901666
[28] Meng Z, Cai S, Wang R, Tang H, Song S and Tsai karas P 2019 Appl. Catal. B: Environ. 244 120–7
[29] Chen Z, Ha Y, Liu Y, Wang H, Yang H, Xu H, Li Y and Wu R 2018 ACS Appl. Mater. Interfaces 10 7134–44
[30] Gao J, Wang J, Zhou L, Cai X, Zhan D, Hou M and Lai I 2019 ACS Appl. Mater. Interfaces 11 10364–72
[31] Chung H T, Won J H and Zelenay P 2013 Nat. Commun. 4 1922
[32] Jiang Z, Zhao X, Tian X, Luo L, Fang J, Gao H and Jiang Z 2015 ACS Appl. Mater. Interfaces 7 19398–407
[33] Xu L, Jiang Q, Xiao Z, Li X, Hua J, Wang S and Dai L 2016 Angew. Chem. Int. Ed. 55 5277–81
[34] Wang X T, Ouyang T, Wang L, Zhong J H, Ma T and Liu Z Q 2019 Angew. Chem. Int. Ed. 58 13291–6
[35] Ai W, Luo Z, Jiang J, Zhu J, Du Z, Fan Z, Xie L, Zhang H, Huang W and Yu T 2014 Adv. Mater. 26 6186–92
[36] Yoon K R, Choi J, Cho S-H, Jung J-W, Kim C, Cheong J Y and Kim I-D 2018 J. Power Sources 380 174–84
[37] Zhou Y, Luo M, Zhang Z, Li W, Shen X, Xia W, Zhou M and Zeng X 2018 Appl. Surf. Sci. 448 9–15
[38] Wu Z, Zou Z, Huang J and Gao F 2018 J. Catal. 358 243–52
[39] Liu Y, Hu Y, Ma P, Li F, Yuan F, Wang S, Luo Y and Ma J 2019 Chem. Sus. Chem. 12 2679–88
[40] Wang P, Li F-L, Huang X, Young D J, Wang H-F, Braunstein P and Lang J-P 2019 Angew. Chem. Int. Ed. 131 7125–30
[41] Zou Z, Wang T, Zhao X, Jiang W-I, Pan H, Gao D and Xu C 2019 ACS Catal. 9 7356–64