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Synthesis of a Zn/Fe–N–C electrocatalyst towards efficient oxygen reduction reaction via a facile one-pot method

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Abstract

The high price and unsatisfactory stability of Pt-based catalysts for the sluggish oxygen reduction reaction (ORR) severely limit the development of fuel cells and metal-air batteries. Therefore, developing Pt-free electrocatalysts with excellent activities and stabilities is significant. Herein, an efficient Zn/Fe–N–C electrocatalyst is synthesized via a facile one-pot method. Owing to its curved nanosheet structure, appropriate microporous and mesoporous specific surface areas, abundant defects and high Fe–Nx content, Zn/Fe–N–C exhibits remarkable ORR activity and stability in alkaline electrolyte. Its half-wave potential is 0.843 V, which is 10 mV higher than that of Pt/C. Moreover, Zn/Fe–N–C also manifests satisfactory performance in a practical Zn-air battery. Its maximum output power density is 108.5 mW cm−2, which is equivalent to that of Pt/C. In this work, a simple synthesis method for highly active ORR electrocatalyst is provided, which can be implemented for the future design and synthesis of electrocatalysts used in fuel cells and metal-air batteries.

1. Introduction

The development of environmentally friendly and renewable energy is of great importance for promoting energy transition and global sustainable development. Fuel cells and metal-air batteries are potential power sources due to their advantages of high energy conversion efficiency, cleanliness and low cost [1–4]. However, the slow kinetics process of oxygen reduction reaction (ORR), a key reaction in their application, severely hinders their commercialization [5, 6]. One of the main reasons is that the current commercial electrocatalysts used for ORR are Pt-based catalysts [7, 8]. However, the shortcomings of Pt-based catalysts, such as low abundance, high price and poor stability, limit their extensive applications [9–11]. Therefore, the exploration of non-precious metal electrocatalysts with high activity and stability is essential for the commercialization of fuel cells and metal-air batteries.

In recent decades, a lot of research has been conducted on non-precious metal-based catalysts and great progress has been made [12, 13]. Carbon-based materials are gradually applied in ORR process due to their low price, large specific surface area (SSA), rich hierarchical pores, and good conductivity [14–16]. Moreover, the doping of non-metallic heteroatoms such as N, S and P into carbon materials can arouse the charge rearrangement of the carbon atoms near heteroatoms and generate a series of carbon active sites, which are beneficial to accelerate the adsorption of oxygen and the breaking of O=O bonds, thereby improving the ORR activity of carbon materials [17–20]. Furthermore, the introduction of metals into carbon materials can significantly enhance the ORR performance due to the possible formation of metal oxides, carbides, sulfides, M–Nx and other active components [20–25]. Therefore, carbon materials co-doped with metal and heteroatom are promising alternatives. Among them, metal and nitrogen co-doped carbon materials (M–N–C) are currently one of the most popular and promising ORR electrocatalysts [26, 27].
Besides the doping of metal and nitrogen, the pore structure of electrocatalyst also plays a crucial role in the catalytic performance [28]. The microporous structure can disperse and expose active sites, and the mesoporous structure can facilitate mass transfer, so both microporous and mesoporous structures are highly desired [29–31]. Currently, the hard template method is widely used to prepare catalysts with large SSA and regular structure, but the complicated template synthesis and further removal limit its large-scale preparation [32–34]. Metal-organic frameworks (MOFs) have the advantages of uniform distribution of metal particles, large SSA and abundant pore structures, and are good precursors for the synthesis of M–N–C catalysts [35–38]. However, the commonly used MOFs are mainly ZIF-8, ZIF-67, and MIL-101, which limits the diversity of material development to some extent [39–41]. In addition, the preparation and modification of these MOFs are complicated and usually involve the use of large amounts of organic solvents. Although their derived catalysts exhibit excellent ORR performance, they may also be unsuitable for large-scale preparation [42]. Therefore, a simple strategy to synthesize efficient ORR electrocatalysts in non-toxic solvents and suitable for mass production is highly desired.

Herein, a facile one-pot method was proposed to synthesize ZnFe–FA precursor in aqueous solution using FeCl$_3$·6H$_2$O, Zn(OAc)$_2$·2H$_2$O and folic acid (FA). FA was used as an organic ligand to coordinate with metal ions through its abundant amino and carboxyl functional groups. Zn(OAc)$_2$·2H$_2$O was chosen as a polymerization inhibitor and pore former. On the one hand, Zn ions can compete with Fe ions to coordinate with FA, thereby inhibiting Fe aggregation. On the other hand, the coordinated Zn ions can be easily removed in the subsequent high-temperature pyrolysis, forming a hierarchical pore structure [43, 44]. After the pyrolysis of ZnFe–FA precursor and the subsequent pickling process, a large amount of Zn/Fe–N–C catalyst was obtained. Zn/Fe–N–C not only manifests outstanding ORR activity and stability in a traditional three-electrode cell, but also exhibits satisfactory maximum output power density in homemade Zn-air battery. This method is simple and has certain applicability, and can provide inspiration for the subsequent exploration of single-metal or multi-metal doped electrocatalysts for different energy conversion and storage devices.

2. Experimental

2.1. Synthesis of catalysts

The electrocatalysts were synthesized through a simple one-pot method. In detail, 1 mmol of folic acid was firstly dispersed in 30 ml of ultrapure water under continuous stirring and heated to 60 °C. Next, 2 mmol of Zn(OAc)$_2$·2H$_2$O was dissolved in 10 ml of ultrapure water and then added into the above solution dropwise. After stirring for 30 min, another 10 ml of ultrapure water containing 0.2 mmol of FeCl$_3$·6H$_2$O was added dropwise and reacted for 24 h. After centrifugation, washed with ultrapure water, and lyophilization, the precursor ZnFe–FA was obtained. Finally, the ZnFe–FA precursor was carbonized under Ar flow with a heating rate of 2 °C min$^{-1}$ at 900 °C for 2 h. After pickling in 2 M HCl for 6 h at 80 °C, the final product denoted as Zn/Fe–N–C was obtained. Similar to Zn/Fe–N–C, Zn–N–C and Fe–N–C were also synthesized in the absence of FeCl$_3$·6H$_2$O and Zn(OAc)$_2$·2H$_2$O, respectively.

3. Results and discussion

Zn/Fe–N–C was synthesized according to the synthetic route illustrated in figure 1. Based on the coordination of Zn(OAc)$_2$·2H$_2$O and FeCl$_3$·6H$_2$O with FA, the ZnFe–FA precursor was first obtained by a one-pot method. The precursor was then carbonized to remove Zn species, thereby a hierarchical porous carbon structure was formed. After pickling process, the final Zn/Fe–N–C catalyst was synthesized. For comparison, Fe–N–C and Zn–N–C were also obtained.
FESEM and TEM were performed to characterize their morphology and microstructure. As displayed in figures 2(a) and (d), Zn/Fe–N–C exhibits a curved nanosheet structure with dispersed Fe-containing nanoparticles. The inset in figure 2(d) is a high-resolution TEM image of Zn/Fe–N–C. The interplanar spacing of 0.340 nm is ascribed to the typical (002) plane of graphitic carbon, and the interplanar spacing of 0.193 nm is attributed to the (−1−11) plane of Fe3N, suggesting the observed Fe-containing nanoparticles in Zn/Fe–N–C are Fe–Nx structure. Although during the synthesis process, FA can chelate metal ions and self-assemble into supramolecular nanosheets through complementary hydrogen bonding interaction at pteridine groups \[45\]. However, without the introduction of Zn(OAc)2·2H2O, the obtained Fe–N–C presents a bulk carbon structure (figure 2(b)). This indicates that the evaporation of Zn during carbonization is very important for the final porous nanosheet structure. Compared with the bulk carbon structure, the curved nanosheet structure can expose the active sites more easily and thus is more suitable for ORR. The rough surface of Fe–N–C shown in figure 2(e) may be caused by the removal of unstable Fe species during the pickling process. Without the addition of FeCl3·6H2O, Zn–N–C exhibits a stacked thin nanosheet structure in figures 2(c) and (f). The difference in the structures of Zn/Fe–N–C and Zn–N–C indicates that Fe nanoparticles generated during pyrolysis process can serve as catalysts to accelerate the graphitization and wrinkling of ZnFe–FA precursor, thereby forming a curved 3D nanosheet structure \[46\]. As seen in figure 2(g), Zn/Fe–N–C is mainly composed of C, N, O and Fe elements, and N, O and Fe elements are uniformly dispersed in the catalyst. To note, most of Zn atoms evaporate during pyrolysis process, and the remaining Zn content is too low to be detected by EDS.

The crystal structure of the samples was analyzed by XRD. The XRD patterns of the samples before and after pickling process are illustrated in figures 3(a) and (b), respectively. The peaks at about 26° in both patterns are the typical graphitic carbon (002) crystal plane. However, the graphitic carbon peaks in Zn–N–C are sharper, while those in Zn/Fe–N–C and Fe–N–C are broader, suggesting that Zn/Fe–N–C and Fe–N–C may have higher degree of graphitization. This indicates that Fe is beneficial to promote the graphitization of materials \[47, 48\]. In addition, both Zn/Fe–N–C and Fe–N–C exhibit strong Fe3O4 phase before pickling, which could not be detected after pickling, implying that the pickling process is necessary because it can effectively remove unstable iron oxides. The new crystal phase located at about 43.5° after pickling could be ascribed to the (−1−11) plane of...
Fe₃N (JCPDS No. 73-2102), which is consistent with the lattice fringe in figure 2(d), further confirming the existence of Fe–Nx structure.

Raman test was performed to investigate the defects degree of the samples. As shown in figure 3(c), each sample has two characteristic peaks located at about 1344 cm⁻¹ and 1585 cm⁻¹, which belong to the D and G bands, respectively [49]. Generally, the D band refers to disordered and defective carbon, while the G band stands for graphitic carbon [50, 51]. The narrowness of the two peaks and their intensity ratio (I_D/I_G) can be used to evaluate the degree of disorder and defects in the materials [52–54]. Among these catalysts, Fe–N–C presents the sharpest D and G bands and the lowest I_D/I_G value (0.77), suggesting its lowest defects degree. However, after adding Zn(OAc)₂·2H₂O, the D and G bands of Zn/Fe–N–C and Zn–N–C become wider, and their I_D/I_G values rise to 1.03 and 1.07, respectively. The significantly increased defect structures caused by the evaporation of Zn may be the potential active sites. Therefore, Zn/Fe–N–C may exhibit better ORR performance than Zn–N–C and Fe–N–C due to the existence of Fe–Nx structure and abundant defect sites.

The porous structure of all the samples were studied by N₂ adsorption and desorption tests. As displayed in figure 3(d), all the samples exhibit sharp increase in the adsorption volume at very low relative pressures and show obvious type-IV isotherms, suggesting that both micropores and mesopores are present in all the samples. The corresponding PSD curves further confirm their hierarchical porous structure. The collected SSA and pore volume are listed in table S1. Zn–N–C has the highest total SSA (728.5 m² g⁻¹), but most of the pores are micropores with a SSA of 569.0 m² g⁻¹. On the contrary, the total SSA of Fe–N–C is 453.8 m² g⁻¹, while the mesoporous SSA is 342.7 m² g⁻¹, suggesting its mesoporous dominated structure. However, both microporous and mesoporous structures are important for catalytic performance. Therefore, the abundant mesoporous structure (312.0 m² g⁻¹) and microporous structure (298.4 m² g⁻¹) as well as the highest pore volume (1.53 cm³ g⁻¹) may endow Zn/Fe–N–C with excellent ORR activity.

XPS characterization was also carried out to further analyze the surface element composition and structure of all the samples. According to figure S2 (available online at stacks.iop.org/MRX/9/025604/mmedia) and table S2, Zn/Fe–N–C contains only C (86.56 at%), N (6.30 at%), O (6.78 at%) and Fe (0.36 at%) elements. The high resolution Zn 2p spectrum fluctuates too much to be analyzed, and the Zn content in Zn/Fe–N–C detected by ICP–AES is only 0.13 wt% (table S3), further indicating that most of the Zn species in Zn/Fe–N–C are evaporated during the pyrolysis process. However, the high resolution Zn 2p spectrum of Zn–N–C in figure S3
exhibits distinct characteristic peaks, and the Zn residual amount in Zn–N–C is about 2.0 wt%, which is much higher than that of Zn/Fe–N–C. Combing the TEM and XRD results, it can be inferred that the higher Zn content in Zn–N–C may be due to the formation of more stable and highly dispersed Zn–Nx structures. Combining the TEM and XRD results, it can be inferred that the higher Zn content in Zn–N–C may be due to the formation of more stable and highly dispersed Zn–Nx structures.

Figure S4 displays the XPS spectra of Fe–N–C. Its Fe 2p spectrum is also indistinguishable because of its low Fe content. The Fe content of Fe–N–C detected by ICP-AES is 0.48 wt%, which is much lower than 1.40 wt% of Zn/Fe–N–C. This suggests that without the evaporation of Zn species during pyrolysis, the Fe species in Fe–N–C are more likely to form iron oxides, which could be removed by the subsequent pickling process, resulting in its lower Fe content. In addition to metal doping, nitrogen doping, especially effective nitrogen doping, is also important for improving ORR performance. As depicted in figure 4, the high-resolution N 1s spectrum of each sample could be deconvoluted into five N-containing structures. The structures with binding energies of 398.3, 400.3, 401.3 and 403.9 eV correspond to pyridinic-N, pyrrolic-N, graphitic-N and oxidized-N, and the structure with binding energy of 399.4 eV is Fe–N–x [56, 57]. Fe–Nx, as the efficient ORR active sites, can significantly enhance ORR activity even at a low content [58–60]. According to figure 4(d) and table S4, Zn/Fe–N–C contains the most Fe–Nx sites (about 0.84 at%) among the three catalysts, and thus is assumed to possess the best ORR activity.

The ORR performance of all the samples and Pt/C was evaluated in 0.1 M KOH electrolyte. As clearly displayed in figure S5, compared with the CV curves in N2-saturated electrolyte, all the CV curves in O2-saturated electrolyte exhibit apparent oxygen reduction peaks at 0.5–0.9 V, indicating that all the catalysts have certain ORR activity. Then, LSV tests of all the catalysts were performed and the corresponding LSV curves on RDE at 1600 rpm were displayed in figure 5(a). Though Zn–N–C possesses larger SSA and higher M–Nx sites content, its ORR activity is much lower than that of Zn/Fe–N–C and Fe–N–C, suggesting that Fe–Nx structures rather than Zn–Nx structures are the main active sites. However, the introduction of Zn into the precursor is also effective. Compared with Fe–N–C, the ORR activity of Zn/Fe–N–C is significantly enhanced. The increase in ORR activity can be ascribed to the curved nanosheet structure, higher degree of defects, microporous SSA and Fe–Nx content, all of which are caused by the evaporation of Zn during pyrolysis according to physical characterizations. As listed in table S5, Zn/Fe–N–C manifests satisfactory ORR activity in terms of half-wave potential (E1/2) and limiting current density (JL). Its E1/2 and JL are 0.843 V and 5.56 mA cm−2, surpassing Pt/C (0.833 V and 5.26 mA cm−2) and some recently reported electrocatalysts (table S6). The double-layer
capacitance ($C_{dl}$) obtained based on the CV curves at different scan rates was used to evaluate the electrochemical surface area (ECSA) of all the samples. As depicted in figure S6, the $C_{dl}$ of Zn/Fe–N–C is 17.6 mF cm$^{-2}$, which is higher than 8.5 mF cm$^{-2}$ of Fe–N–C and 16.8 mF cm$^{-2}$ of Zn–N–C. The larger ECSA of Zn/Fe–N–C could expose more valid active sites, further confirming its superior ORR activity. Figure S6(b) shows the Tafel plots of the catalysts. The lower Tafel slope of Zn/Fe–N–C (64 mV dec$^{-1}$) indicates its faster ORR kinetics process. The reaction pathway of all the catalysts were also investigated by collecting their LSV curves on RDE at different rotation speeds. According to the collected LSV curves, the corresponding K-L plots and electron transfer numbers ($n$) can be obtained (figures 5(c), (d) and S7–9). The K-L plots of Zn/Fe–N–C show clear linearity, suggesting a first-order kinetics [61, 62]. The calculated $n$ of Zn/Fe–N–C is 4.09, which indicates its favorable 4e$^{-}$ ORR pathway. Besides, the LSV curves on RRDEing n ranges from 3.78 to 3.96, which is consistent well with the RDE analysis.

The influence of pyrolysis temperature and the dosage of different metal salts was also investigated. As shown in figure S10a, the catalyst carbonized at 900 °C manifests the best ORR activity in terms of $E_{1/2}$, which is more positive than those carbonized at 700, 800 and 1000 °C, suggesting that 900 °C is the optimal pyrolysis temperature. At 700 °C, only a small amount of Zn species can evaporate, so the activity is poor. As the pyrolysis temperature increases, more Zn species starts to evaporate. When the temperature rises to 900 °C, most of Zn species evaporates and only 0.13 wt% of Zn remains, so the activity is significantly enhanced. However, when the

Figure 5. (a) LSV curves on RDE and (b) Tafel plots. (c) LSV curves of Zn/Fe–N–C and (d) K-L plots. (e) LSV curves on RRDE and (f) HO$_2^-$ yield and electron transfer number.
temperature is further increased to 1000 °C, the agglomeration of the metal is intensified and the activity decreases slightly. Figures S10(b) and S10(c) display the LSV curves of catalysts with different amount of FeCl₃·6H₂O and Zn(OAc)₂·2H₂O, respectively. As can be seen, all the catalysts exhibit similar ORR activities, indicating that the dosage of different metal salts only has little influence on the activity. When the dosage of FeCl₃·6H₂O is 0.2 mmol and the dosage of Zn(OAc)₂·2H₂O is 2 mmol, the corresponding catalyst exhibits the best ORR activity. Therefore, 0.2 and 2 mmol are the optimal dosages of FeCl₃·6H₂O and Zn(OAc)₂·2H₂O, respectively.

Similar to activity, the stability and methanol resistance are also important indicators for evaluating the performance of electrocatalyst. Therefore, corresponding tests were also performed. As illustrated in figure 6(a), Zn/Fe–N–C shows only 8 mV loss of activity in terms of E₁/₂ after performing 5000 cycles of CV, suggesting its outstanding stability. In contrast, the activity loss of Pt/C is about 30 mV. Besides, after continuous conduction at 0.51 V for 40 000 s (figure 6(b)), Zn/Fe–N–C exhibits a lower current drop than Pt/C, further revealing its satisfactory long-term durability. The methanol resistance was tested by chronoamperometric response. As displayed in figure 6(c), after pouring 3 M methanol into the electrolyte, the current in Pt/C drops significantly. In contrast, the current change of Zn/Fe–N–C is slight. This indicate that Zn/Fe–N–C also has excellent methanol tolerance. Due to the satisfactory ORR activity and stability of Zn/Fe–N–C, its performance in homemade Zn-air battery was further evaluated. As illustrated in figure 6(d), when the current density is 137 mA cm⁻², Zn/Fe–N–C manifests the maximum output power density (108.5 mW cm⁻²). Such value is very close to the 108.9 mW cm⁻² of Pt/C, suggesting that Zn/Fe–N–C possesses excellent ORR performance and has the potential to be used in Zn-air battery.

4. Conclusion

In summary, an efficient Zn/Fe–N–C catalyst towards ORR was successful synthesized via a facile one-pot method. The simple synthesis process is suitable for large-scale preparation. Physical characterizations suggest that the introduction of both Fe and Zn play vital roles in the formation of curved nanosheet structure, proper microporous and mesoporous SSA, abundant defect structure and high Fe–Nx content. Due to these features, Zn/Fe–N–C manifests outstanding ORR activity and stability in alkaline electrolyte. In addition, the maximum output power density of Zn/Fe–N–C in homemade Zn-air battery is equivalent to that of Pt/C. The satisfactory...
ORR performance of Zn/Fe–N–C makes it a promising electrocatalyst. Moreover, this simple synthesis strategy is scalable and applicable, and therefore showing huge potential in the design and synthesis of various M–N–C electrocatalysts.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

The authors declare no conflict of interest.

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