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Article

Iron-incorporated nitrogen-doped carbon materials as oxygen reduction electrocatalysts for zinc-air batteries

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ABSTRACT

The application of electrocatalysts for the oxygen reduction reaction (ORR) is vital in a variety of energy conversion technologies. Exploring low-cost ORR catalysts with high activity and long-term stability is highly desirable, although it still remains challenging. Herein, we report a facile and reliable route to convert ZIF-8 modified by Fe-phenanthroline into Fe-incorporated and N-doped carbon dodecahedron nanoarchitecture (Fe-NCDNA), in which carbon nanosheets are formed *in situ* as the building blocks with uniform Fe-N-C species decoration. Systematic electrochemical studies demonstrate that the as-synthesized Fe-NCDNA electrocatalyst possesses highly attractive catalytic features toward the ORR in terms of activity and durability in both alkaline and neutral media. The Zn-air battery with the optimal Fe-NCDNA catalyst as the cathode performs impressively, delivering a power density of 184 mW cm⁻² and a specific capacity of 801 mAh g⁻¹; thus, it exhibits great competitive advantages over those of the Zn-air devices employing a Pt-based cathode electrocatalyst.

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1. Introduction

The pressing crises of environmental pollution and fossil fuel energy depletion have propelled humans to explore feasible, reliable, and renewable energy technology solutions [1]. Various fuel cells including the Zn-air battery and H₂-O₂ fuel cells are capable of directly converting chemical energy into electrical energy, and with the absence of heat engine processes and the Carnot cycle, these fuel cells show high energy conversion efficiencies [2,3]. Recently, the demand for environmentally friendly batteries with high specific energy and excel-

lent reliability has stimulated the investigation of Zn-air batteries, of which the Zn anode is highly recognized for its high capacity, high safety, and low cost. Nonetheless, many conundrums remain unsolved, e.g., sluggish oxygen reduction reactions (ORRs) on the cathode side [4,5]. The ORR, as the most important cathode reaction in the Zn-air battery, is generally recognized to have a significant impact on the performance of associated devices [6–8]. Although Pt-based catalysts have been regarded as the most efficient cathode catalysts, their prohibitive cost greatly limits their widespread commercial application. Therefore, it is of great importance to develop

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high-performance non-precious metal ORR electrocatalysts [9,10].

In recent years, transition metal carbon nitrides (M-N-C, M = Co, Fe, *et al.*) have emerged as one of the most promising alternative electrocatalysts to Pt-based materials toward the ORR. In these alternative electrocatalysts, the M-N_x moiety normally functions as the major active site [11,12], and its activity is dependent on the density of the active sites, surface area, and porous structure [13,14]. Such M-N-C catalysts can be directly synthesized by the pyrolysis of precursors containing transition metal, N, and C species; metal atoms tend to aggregate into large particles due to their high surface energy, and their porous structures cannot be effectively controlled [15–17], which leads to relatively poor catalytic activity. Currently, MOF-derived catalysts have attracted significant research interest due to their potential applications in various fields of energy conversion and storage [18–22]. This has motivated us to explore an efficient method to prepare ideal electrocatalysts with favorable properties, including abundant N species, high surface areas, and adjustable pore sizes for the ORR [5, 23].

Herein, we report a facile and reliable route for the controllable synthesis of Fe-incorporated and N-doped carbon dodecahedron nanoarchitectures (Fe-NCDNA), which were exploited as electrocatalysts for the ORR and were applied as cathode electrocatalysts in a Zn-air battery. Both results consistently confirmed the highly attractive catalytic properties of Fe-NCDNA with activity comparable to those of Pt-based materials as well as excellent durability.

2. Experimental

2.1. Chemicals and materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), absolute methanol (CH_3OH), and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion solution (5%) and 1,10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. All the reagents were used directly without further purification.

2.2. Synthesis of the catalysts

2.2.1. Synthesis of ZIF-8 [24,25]

Typically, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.000 g) and 2-methylimidazole (1.813 g) were dissolved in 45 and 30 mL of methanol, respectively. Subsequently, a 2-methylimidazole solution was injected in a $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution under vigorously stirring for 16 h at room temperature. The precipitates were centrifuged and washed with methanol and deionized water several times, followed by drying in a vacuum oven at 60 °C overnight.

2.2.2. Synthesis of Fe-NCDNA-X (X = 0, 1, 2, 3) and NC

The powders of ZIF-8 (0.300 g) and 1,10-phenanthroline (0.136 g) were added to 20 mL of methanol and sonicated for 30 min at room temperature. Thereafter, 20-mL aliquots of

methanol solutions containing 0.012, 0.015, and 0.200 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were separately injected. After vigorously stirring for 2 h at room temperature, the mixture was evaporated to dryness at 80 °C. Finally, the Fe-NCDNA-X (X = 1, 2, 3) samples were obtained by calcination at 900 °C for 2 h at a heating rate of 5 °C min⁻¹ under Ar atmosphere. Under the same conditions, Fe-NCDNA-0 was synthesized without adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. NC was prepared by the pyrolysis of ZIF-8 under the same annealing condition.

2.3. Physical characterizations

X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Miniflex6000, Rigaku) at 40 kV and 15 mA using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The specific surface area and pore size distributions of the samples were analyzed by the Brunauer–Emmett–Teller (BET) method using N₂ adsorption–desorption isotherms on a Micromeritics Instrument Corporation sorption analyzer (Micromeritics TriStar II 3020). The Raman spectra of the catalysts were recorded on a LabRAM HR over a range of 300–3000 cm⁻¹. The Fe concentrations of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-MS). The morphologies of the catalysts were determined using Hitachi SU8010 at a high vacuum pressure and an accelerating voltage of 5 kV. A scanning electron microscope (SEM, KYKY-EM3900M) and a transmission electron microscope (TEM, JEM-2010F) were used to observe the morphology and nanostructure of the materials. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi XPS system using a monochromatic Al K α source and a charge neutralizer.

2.4. Electrochemical characterization

2.4.1. Electrochemical measurements

The electrochemical measurements were conducted in a three-electrode system on a CHI760 electrochemical station (CH instrument Co.) at room temperature (25 °C). A carbon electrode served as the counter electrode. Meanwhile, a Hg/HgO in 1 M KOH solution served as the reference electrode in alkaline medium, and an Ag/AgCl electrode in saturated KCl served as the reference electrode in neutral and acidic media. A rotating disk electrode (RDE) with a glassy carbon (GC) disk of 3 mm in diameter and a rotating ring-disk electrode (RRDE) with a GC disk (4.0 mm diameter) and a Pt ring (5.0 mm inner diameter and 7.0 mm outer diameter) served as the substrate for the working electrode. Experimentally, 5.0 mg of the sample (containing 20 wt% Pt/C) was ultrasonically dispersed in 1 mL of the solution containing 50 μL of Nafion solution, 200 μL of ethanol, and 750 μL of water for 30 min to form homogeneous catalyst ink. The volumes of the catalyst ink were 6 μL and 10 μL for the RDE and RRDE tests, respectively. The O₂-saturated 0.1 M KOH, 0.1 M phosphate buffer solution (PBS, pH = 7), and 0.5 M H₂SO₄ were used as alkaline, neutral, and acidic media, respectively. For the CV measurements, the scan rate was 50 mV s⁻¹, while for the RDE/RRDE test, it was 5 mV s⁻¹.

2.4.2. Data analysis

All the potentials in this work were converted to the reversible hydrogen electrode (RHE) potential, and the potential conversion formula is as follows: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \text{ V} \times \text{pH}$ (alkaline medium) and $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ V} \times \text{pH}$ (neutral/acidic medium).

The electron transfer number (n) was obtained by the Koutecky-Levich (K-L) Eq. (1):

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{Bw^{1/2}} + \frac{1}{j_K} \quad (1)$$

where j is the measured current density; j_K and j_L are the kinetic and limiting current densities, respectively; w is the linear rotation speed (rpm s^{-1}) of the disk.

For the RRDE measurements, the polarization curves were recorded at a disk rotation rate of 1600 rpm. The potential of the ring was set at 1.4 V (vs. RHE). The H_2O_2 yield and the electron transfer number (n) were calculated by Eqs. (2) and (3), respectively, as follows:

$$\text{H}_2\text{O}_2\% = 200 \times \frac{I_r/N}{I_d + I_r/N} \quad (2)$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad (3)$$

where I_d is the disk current, I_r is the ring current, and N (0.442) is the ring collection efficiency.

2.5. Configuration and measurement of Zn-air battery

Ten milligrams of the sample was ultrasonically dispersed in 1 mL of the solution containing 100 μL of Nafion solution, 450 μL of ethanol, and 450 μL of water for 30 min to form homogeneous catalyst ink. The volume of catalyst ink coated onto carbon paper (1 cm^2) was 100 μL , after which the coated carbon paper was dried with a lamp. A Zn plate served as the anode electrode and a 6 M KOH solution was adopted as the electrolyte. The open-circuit voltage (VOC) and galvanostatic discharge data were collected in the LAND testing system. The specific capacitor of the assembled battery was calculated from Eq. (4):

$$C_{\text{sp}} = \frac{i \times t}{\Delta m} \quad (4)$$

where i , t , and Δm represent the discharge current, discharge time, and the weight of consumed Zn, respectively.

Fig. 1. Schematic illustration of the catalyst synthesis process.

3. Results and discussion

It is a classic reaction, 1,10-phenanthroline and Fe^{2+} form a red-brown Fe-phenanthroline (Fe-phen) product [26,27]. And N-rich carbon can be obtained by the direct pyrolysis of ZIF-8. Therefore, the catalysts containing Fe and N were prepared through the carbonization of ZIF-8 with absorbed Fe-phen. During the carbonization process, the N group combined with the Fe species to form FeN_x structure units, which were confined to the porous carbon structure derived from ZIF-8. Fig. 1 schematically illustrates the synthetic process for preparing Fe-NCDNA. The entire synthesis process was implemented by the initial *in situ* growth of Fe-phen complexes on the surface of ZIF-8 through a reaction between Fe^{2+} and 1,10-phenanthroline, noting that 1,10-phenanthroline can be favorably adsorbed on ZIF-8 through π - π interactions [28,29], which leads to a uniform coating of Fe-phen complexes on ZIF-8. A set of Fe-NCDNA catalysts can be obtained by pyrolyzing the composites of Fe-phen-coated ZIF-8 (ZIF-8@Fe-phen).

According to the XRD pattern (Fig. S1(a)), the as-prepared ZIF-8 catalyst shows diffraction peaks in accordance with the previous result [25], indicating the successful synthesis of ZIF-8. Simultaneously, the prepared ZIF-8 and ZIF-8@Fe-phen are determined by SEM observation to be regular dodecahedrons (Fig. S2). After a high-temperature pyrolysis reaction, ZIF-8 and ZIF-8@Fe-phen were converted to N-rich carbon and Fe, and N co-doped carbon, respectively. The XRD patterns (Fig. 2(a)) of NC and Fe-NCDNA-0 display two broad peaks near 26° and 44° , which are assigned to the (002) and (101) crystal planes of graphitic carbon [30,31]. Although the peaks of Fe,

Fig. 2. XRD patterns (a) and Raman spectra (b) of NC, Fe-NCDNA-0, Fe-NCDNA-1, Fe-NCDNA-2, and Fe-NCDNA-3.

FeC_x , and FeN_x , located around 44° , are observed for the Fe-NCDNA-3, Fe-NCDNA-2, and Fe-NCDNA-1 materials, respectively, these peaks are not sharp. This may be due to the low loading and the presence of amorphous Fe [32]. ICP-MS results confirm that the final Fe contents are 2.61 wt%, 3.30 wt%, and 4.34 wt% for Fe-NCDNA-1, Fe-NCDNA-2, and Fe-NCDNA-3 catalysts, respectively.

To further unveil the texture of carbon, the Raman spectra of the catalysts were recorded. Fig. 2(b) presents two distinct peaks in the range of $1250\text{--}1750\text{ cm}^{-1}$ corresponding to the D (around 1320 cm^{-1}) and G bands (around 1610 cm^{-1}). Mostly, the D-band is attributed to the defect sites or grain boundaries, while the G-band corresponds to the band stretching of sp^2 bonded pairs [33,34], such as $\text{C}=\text{C}$, $\text{C}=\text{O}$, and $\text{N}=\text{C}$. After normalization, the area ratio of the D-band and G-band (I_D/I_G) can indicate the defect induced by N-doping. Evidently, the I_D/I_G values for NC and Fe-NCDNA-0 are 1.20 and 1.34, respectively, which illustrates that the introduced phenanthroline induced the formation of defects during the pyrolysis process. Conversely, the I_D/I_G value decreases gradually as the Fe content increases, and the value drops from 1.34 to 1.19; this suggests a decrease in the number of defects and an improved degree of graphitization. Since Fe is an excellent catalyst to induce graphitization [33], the inductive effect increases with the Fe content; thus, the I_D/I_G value decreases.

The N_2 adsorption-desorption test was conducted to evaluate the porosity and structural features. Fig. S1(b) depicts the corresponding N_2 adsorption-desorption isotherm of ZIF-8, which is a type-I curve. Similarly, it addresses the microporous characteristics (inset in Fig. S1(b)) and typical reversible adsorption. Contrarily, all the catalysts deliver a large specific surface area. As shown in Fig. S3(a), there is a distinct hysteresis loop at P/P_0 of $0.4\text{--}1.0$, which is a distinctive feature of mesoporous materials. Nevertheless, at a low relative pressure ($P/P_0 < 0.40$), the adsorption quantity declines sharply, indicating the existence of micropores in all the materials. Meanwhile, we calculate the BET surface area of the samples. The BET surface area of Fe-NCDNA-0 is calculated to be $1240\text{ m}^2\text{ g}^{-1}$, which is higher than those of NC ($1124\text{ m}^2\text{ g}^{-1}$), Fe-NCDNA-1 ($809\text{ m}^2\text{ g}^{-1}$), Fe-NCDNA-2 ($897\text{ m}^2\text{ g}^{-1}$), and Fe-NCDNA-3 ($649\text{ m}^2\text{ g}^{-1}$). A downtrend is observed with the specific surface area when Fe doping is included, and it could be the result of Fe occupying the microporous structure [4,23]. In addition, Fe-NCDNA-2 has the highest specific surface area among the Fe-doped samples and retains the most abundant pore size distribution compared to those of all the other catalysts (Fig. S3(b)). Combined with the results of the electrochemical test, such a hierarchical pore structure could supply more sites and enhance the accessibility of oxygen and electrolyte [35].

SEM was employed to investigate the morphology of the samples. Fig. S2 shows that the synthetic ZIF-8 is a regular dodecahedron, which is in agreement with previous reports. From the SEM images in Fig. 3, it is clear that all the catalysts retain the similar morphology derived from ZIF-8. Meanwhile, the morphologies of the catalysts changed in varying degrees due to the adjustment of the Fe content. Among them,

Fig. 3. SEM images of NC (a), Fe-NCDNA-0 (b), Fe-NCDNA-1 (c), Fe-NCDNA-2 (d,e), and Fe-NCDNA-3 (f).

Fe-NCDNA-2 revealed remarkable distortion and a rough surface. Therefore, according to the N_2 adsorption-desorption test and SEM images, the amount of Fe not only affect the surface area and pore size distribution but also the morphology.

Furthermore, TEM was adopted to gain insight into the construction of the as-prepared Fe-NCDNA-2 catalyst. Figs. 4(a), 4(b), and Figs. S4(a), S4(b) show that Fe-NCDNA-2 has a carbon nanocage structure with *in situ*-formed carbon nanosheets. However, the nanoparticles commonly found in Fe, N co-doped carbon materials were not be observed. Meanwhile, the high-resolution TEM (HRTEM) image did not manifest lattice fringes and diffraction rings due to the low content of Fe and the existence of amorphous carbon (Fig. 4(c)) [32,36,37]. As displayed in the high-annular dark-field scanning TEM (HAADF-STEM) images (Fig. 4(d)) and corresponding elemental mapping images of the resultant Fe-NCDNA-2 catalyst, a uniform distribution of trace Fe (yellow), N (green), and carbon elements (red) exists in the carbon frameworks.

XPS analysis was performed to identify the elemental composition and surface chemical binding states of the samples. The results clearly reveal that the doping of Fe and N atoms in

Fig. 4. (a,b) TEM images of Fe-NCDNA-2. (c,d) HRTEM image, HAADF-STEM image, and corresponding mapping images of Fe-NCDNA-2.

Fig. 5. (a) XPS survey of Fe-NCDNA-2. Corresponding high-resolution XPS spectra of Fe 2p (b), N 1s (c), and C 1s (d).

the carbon matrix was successful (Fig. 5(a)). The C 1s high-resolution spectra (Fig. 5(d)) show that there are two distinct peaks (located at 284.8 and 285.7 eV) and a broad shoulder peak (288.3 eV), which are assigned to C=C, C=N, and C-N, respectively [23]. Furthermore, C=C accounts for more than half of the content; C=N comes second, and C-N has the least content (Fig. S5(b), Table S1). The N 1s high-resolution spectra (Fig. 5(c)) can be subdivided into four different groups: pyridinic N (398.5 eV, 34.77%), pyrrolic N or Fe-N (399.8 eV, 22.54%) [38–41], graphitic N (400.8 eV, 35.50%), and oxygenated N (402.3 eV, 7.19%) [42–44]. According to previous literatures [45,46], pyridinic N is the main catalytic active site for the ORR in N-doped carbon, and the graphitic N improves the limiting current density. In addition, the content of pyridine N is much higher than that of pyrrolic N (or Fe-N), and the content of graphitic N increases gradually when additional N and Fe are introduced (Fig. S5(a), Table S1). Fig. 3(b) manifests the Fe (Fe 2p) survey spectrum. Based on the reports [47–49], the two distinct peaks at 710.2 and 713.8 eV are attributed to the binding energies of the $2p_{3/2}$ orbitals of the Fe^{2+} and Fe^{3+} species, respectively. For the $2p_{1/2}$ orbitals, the peak at 723.3 eV is assigned to the binding energy of Fe^{2+} . This suggests the existence of FeN_x and FeC_x species in Fe-NCDNA-2 [25,50,51]. Moreover, a satellite peak is observed at 719.5 eV.

The ORR activity of the electrocatalysts was firstly assessed by cyclic voltammetry (CV) in an Ar or O_2 saturated 0.1 M KOH solution at a scan rate of 50 mV s^{-1} . As shown in Figs. S6a and S6b, Fe-NCDNA-2 displays a noticeable oxygen reduction peak at 0.857 V vs. RHE, which is superior to those of Fe-NCDNA-1 (0.853 V), Fe-NCDNA-3 (0.835 V), Fe-NCDNA-0 (0.821 V), as well as 20 wt% Pt/C (0.817 V). As a reference, the NC catalyst exhibits a poor oxygen reduction peak of 0.796 V, indicating the vital role of Fe and N atoms in improving the ORR performance.

To further evaluate the ORR performance, a linear sweep voltammetry (LSV) test with RDE was executed, and the results were compared to those of the commercial 20 wt% Pt/C catalyst (Fig. 6(a)). According to the plots, Fe-NCDNA-2 delivers the best ORR activity as it has the most positive half-wave potential ($E_{1/2} = 0.863 \text{ V}$) compared to those of Fe-NCDNA-1 (0.846 V), Fe-NCDNA-3 (0.840 V), Fe-NCDNA-0 (0.860 V), NC (0.807 V), and Pt/C (0.841 V). By comprehensive characterization and electrochemical results, it is apparent that N doping can improve the ORR activity. Moreover, the high-efficiency catalytic unit was formed to further enhance the catalytic activity due to the incorporation of Fe. Meanwhile, we noticed that the Fe content affected the structure of the sample, and Fe-NCDNA-2 could reveal more active sites [52], making its ORR performance the most outstanding. Subsequently, the Tafel slopes of the samples were obtained by analyzing the corresponding RDE polarization curves (Fig. S6(c)). Among them, Fe-NCDNA-2 presented the smallest slope of 80 mV dec^{-1} compared to those of Fe-NCDNA-1, Fe-NCDNA-3, Fe-NCDNA-0, NC, and commercial Pt/C. This demonstrates that Fe-NCDNA-2 has a relatively high catalytic current and further corroborates its outstanding ORR activity [53]. For a better understanding of the electrochemical processes, RDE measurements were employed at different rotating rates, and the corresponding kinetic parameters of Fe-NCDNA-2 were calculated using the K–L equation (Figs. 6(b), 6(c)). The computed value is 3.87, which is close to the theoretical value of 4.0 for the ORR. This indicates the efficient reduction of oxygen over the electrocatalyst via a four-electron reduction pathway. Based on the RRDE data, the yield of peroxide species (HO_2^-) and the transferred number of electrons can be determined (Fig. S6(d)). Similarly, the transferred number of electrons is consistent with the calculated value from the K–L plots. Moreover, the HO_2^- yield over

Fig. 6. ORR electrocatalytic performances in O₂-saturated 0.1 M KOH. (a) LSV curves at a scan rate of 5 mV s⁻¹ at 1600 rpm; (b) Polarization curves of Fe-NCDNA-2 at different rotating rates; (c) K–L plots of Fe-NCDNA-2 at different potentials; (d) Chronoamperometric curves of Fe-NCDNA-2 and Pt/C for a 30000 s run.

Fe-NCDNA-2 is less than 6% compared to 29.6% over the commercial Pt/C in the range of 0.2–0.9 V. This implies that the material has a relatively high four-electron pathway selectivity and avoids the two-electron pathway to peroxide. Chronoamperometric tests (Fig. 6(d)) show that Fe-NCDNA-2 exhibits better long-term stability (80%) than Pt/C (64%), i.e., retention of the initial current, after a 30000 s run in a 0.1 M KOH solution. Methanol tolerance test was employed to assess the poison tolerance of the catalyst. Fig. S7(a) shows that the curves almost coincide, while there is significant oxidation peak in Fig. S7(b), revealing that the Fe-NCDNA-2 catalyst exhibits excellent poison tolerance compared to that of Pt/C.

When in a neutral medium, a set of Fe-NCDNA catalysts also exhibits catalytic properties toward the ORR. For the CV tests (Figs. S8(a), S8(b)), Fe-NCDNA-2 displays an oxygen reduction peak at 0.689 V, which is more positive than that of Pt/C. Similar to the case in alkaline medium, the $E_{1/2}$ value of Fe-NCDNA-2 is 0.715 V, suggesting a positive potential compared to those of Fe-NCDNA-1 (0.692 V), Fe-NCDNA-3 (0.628 V), Fe-NCDNA-0 (0.631 V), NC (0.497 V), and Pt/C (0.673 V) (Fig. 7(a)). In addition, the Tafel slopes of the catalysts were obtained from analyzing the corresponding LSV data in RDE at 1600 rpm. Fig. S8(c) demonstrates that Fe-NCDNA-2 has the

lowest slope of 105 mV dec⁻¹. RDE measurements at different rotating rates (Fig. 7(b)) and RRDE measurement at 1600 rpm (Fig. S8(d)) were also conducted to evaluate the electrochemical behavior. From the results, the H₂O^{•-} yield over Fe-NCDNA-2 is less than 8% over the range of 0.1–0.8 V, revealing that the evolution of H₂O^{•-} is dramatically suppressed on the Fe-NCDNA-2 electrocatalyst. Further, the transferred number of electrons determined from the K–L plots (Fig. 7(c)) matches the calculated value obtained by RRDE measurement (close theoretical value of 4.0). This illustrates that the ORR processes over the Fe-NCDNA-2 catalyst occur preferably via a four-electron reduction pathway. As depicted in Fig. 7(d), Fe-NCDNA-2 and Pt/C have similar long-term stabilities with 77% and 76% retention of the initial current, respectively, after catalyzing for 30000 s in 0.1 M PBS solutions. Table 1 lists the electrocatalytic ORR performance parameters of the prepared materials and depicts the great competitiveness over the Pt/C and some Pt-free catalysts in both alkaline and neutral media. [41,54–58] In addition, Fe-NCDNA-2 has an $E_{1/2}$ value of 0.745 V in the O₂-saturated 0.5 M H₂SO₄ solution, which is negative compared with 0.783 V for Pt/C (Fig. S9(a)). Systematic electrochemical studies demonstrate that Fe-NCDNA-2 follows a four-electron reduction pathway and has a high long-term sta-

Fig. 7. ORR electrocatalytic performances in O_2 -saturated 0.1 M PBS. (a) LSV curves at a scan rate of 5 mV s^{-1} at 1600 rpm; (b) Polarization curves of Fe-NCDNA-2 at different rotating rates; (c) K-L plots of Fe-NCDNA-2 at different potentials; (d) Chronoamperometric curves of Fe-NCDNA-2 and Pt/C for the 30000 s run.

bility (Figs. S9(b)–9(d) and Fig. S10).

A home-made Zn-air battery was constructed to further demonstrate the practical application of Fe-NCDNA-2 as an ORR electrocatalyst. The Zn-air battery was constructed using the Fe-NCDNA-2 catalyst loaded on carbon paper as the air-cathode and Zn plate as the anode in a 6 M KOH electrolyte (Fig. 8(a)). For comparison, the 20 wt% Pt/C catalyst loaded on carbon paper was used as the air-cathode and was also measured under the same condition. The V_{oc} of the batteries were recorded for 12 h to verify that their voltages are close and that the assembled Zn-air batteries have low self-discharge (Fig. 8(b)). The battery employing the Fe-NCDNA-2 catalyst exhibited a V_{oc} of 1.46 V; this value is slightly higher than that of Pt/C (1.43 V). The power density is not only one of the important indicators for evaluating battery performance, but also reflects the catalytic activity of the material. It is worth noting that the maximum power density for the Zn-air battery employing the

Fe-NCDNA-2 catalyst as the cathode is calculated to be 184 mW cm^{-2} , which is higher than that of the commercial Pt/C (173 mW cm^{-2} , Fig. 8(c)). Moreover, from the inset in Fig. 8(c), it is evident that a red LED light ($\sim 2.0 \text{ V}$) is lit by two Zn-air batteries connected in series. During the discharge process at a current density 10 mA cm^{-2} , the batteries with the Fe-NCDNA-2 catalyst presented better performance than that of the commercial Pt/C, and their voltage plateaued at 1.28 V with a specific capacity of 801 mAh g^{-1} when normalized to the weight of the consumed Zn. This value is slightly more positive than that of Pt/C (799 mAh g^{-1} , Fig. 8(d)). The above results are superior to many reported results [52,53,58–62] and further confirm a comparable performance and application of Fe-NCDNA-2 toward the ORR. To acquire the rate discharge performance curves, the batteries employing the optimal Fe-NCDNA and Pt/C catalysts as the air cathode were employed for a discharge operation at current densities of 2, 4, 6, 8, 10, and 2 mA cm^{-2}

Table 1

Summary of the ORR properties in alkaline and neutral solutions.

Sample	0.1 M KOH			0.1 M PBS		
	$E_{onset}/\text{V vs.RHE}$	$E_{1/2}/\text{V vs.RHE}$	$j_L@0.5 \text{ V}/\text{mA cm}^{-2}$	$E_{onset}/\text{V vs.RHE}$	$E_{1/2}/\text{V vs.RHE}$	$j_L@0.2 \text{ V}/\text{mA cm}^{-2}$
NC	0.93	0.807	−4.52	0.87	0.497	−5.64
Fe-NCDNA-0	0.97	0.860	−4.35	0.91	0.631	−4.5
Fe-NCDNA-1	0.95	0.846	−5.26	0.93	0.692	−6.2
Fe-NCDNA-2	0.99	0.863	−5.55	0.94	0.715	−5.23
Fe-NCDNA-3	0.94	0.840	−5.55	0.90	0.628	−5.92
Pt/C	1.00	0.841	−6.09	0.96	0.673	−5.6

Fig. 8. (a) Schematic of the home-made Zn-air battery employing Fe-NCDNA-2 as the ORR catalyst; (b) Open-circuit voltage curve; (c) Discharge polarization curves and power density. The inset shows the digital graph of a red LED being powered by the constructed Zn-air battery; (d) Galvanostatic discharge curves of the Zn-air batteries with the Fe-NCDNA-2 and Pt/C as catalysts at the current density of 10 mA cm⁻². (Inset shows the specific capacities of the Zn-air batteries employing Fe-NCDNA-2 and Pt/C, normalized to the weight of the consumed Zn); (e) Galvanostatic discharge of the Zn-air batteries at different current densities; (f) Galvanostatic discharge-charge cycling curves at 10 mA cm⁻² per cycle for 10 min.

(Fig. 8(e)). The voltage decreased steadily as the discharge current density increased. Furthermore, there was no noticeable voltage drop during 30 h of operation. As described in Fig. 8(f), the Zn-air battery employing the Fe-NCDNA-2 catalyst exhibits a high cycling stability when repeatedly subjected to discharge and charge processes at 10 mA cm⁻² for 600 cycles without any distinct augment in the voltage gap of the charge and discharge processes. In addition, the battery with Fe-NCDNA-2 has a smaller voltage polarization, especially after a long cycle, compared to that of the device with Pt/C.

4. Conclusions

In summary, we reported a facile route for the controllable synthesis of a catalyst with a carbon dodecahedron nanoarchitecture and formed *in situ* carbon nanosheets loaded uniformly with Fe-N-C species. Systematic electrochemical tests demonstrated that the Fe-NCDNA-2 electrocatalysts exhibited a more positive half-wave potential, a lower Tafel slope, and better long-term stability than the commercial Pt/C in both alkaline and neutral media. The home-made Zn-air batteries employing the optimal Fe-NCDNA catalyst also verified the feasibility of its practical applications as an ORR electrocatalyst. The present work can inspire researchers to explore similar N-doped transition metal porous carbon catalysts for a variety of applications.

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Graphical Abstract

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Iron-incorporated nitrogen-doped carbon materials as oxygen reduction electrocatalysts for zinc-air batteries

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The modified ZIF-8 catalyst is converted to Fe-incorporated N-doped carbon catalyst, showing highly attractive catalytic features toward the ORR in alkaline and neutral media. Meanwhile, the Zn-air battery employing Fe-NCDNA-2 as the cathode displays competitive advantages over the device using a Pt-based electrocatalyst.

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基于氮掺杂碳载铁复合物的锌空电池氧阴极催化剂

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摘要: 迫在眉睫的环境和能源问题推动人类探索可行、可靠和可再生的能源技术。锌-空气电池和氢氧燃料电池等器件显示出高能量转换效率, 但是仍有许多难题有待克服, 例如阴极侧上缓慢的氧还原反应(ORR), 以及高昂的成本极大地限制了铂基催化剂在商业上的广泛应用。因此, 开发高性能的廉价ORR催化剂具有重要意义。过渡金属碳氮化合物(M-N-C, M = Co, Fe等)成为最有希望替代铂基催化剂的一类材料, M-N-C催化剂可以通过直接热解含有过渡金属、氮和碳物种的前驱体合成。然而热解时金属原子易团聚, 多孔结构不能被有效地控制, 导致相对较差的催化活性。目前, MOF衍生的催化剂在能源转化和储存技术中得到了广泛的关注, 其具有丰富的氮含量、高比表面积和可调的孔道结构等特点。本文报道了一种简便可靠可控的合成铁氮共掺杂碳十二面体纳米结构催化剂的方法, 并作为阴极电催化剂用于锌空气电池中, 测试结果证实, 合成的铁氮共掺杂的纳米碳具有与铂基材料相当的活性和更加优异的稳定性。

表面吸附了的邻菲罗啉铁的ZIF-8在碳化过程中, 氮基团能够结合铁形成FeN_x结构单元, 因此可得到铁氮共掺杂的电催化剂。粉末X射线衍射, 扫描电镜证实ZIF-8的成功合成。经过热解得到的催化剂中FeN_x或FeC_x衍射峰较弱, 表明样品中铁含量较低, 存在部分无定型铁。通过拉曼光谱分析发现, 引入的邻菲罗啉在热解过程中诱导了缺陷的形成, 所以Fe-NCDNA-0的I_D/I_G比值明显高于NC。同时I_D/I_G随着铁含量的增加而减少, 这是因为铁可以诱导石墨化, 诱导效应随着铁含量的增加而增加。分析氮气吸附-脱附等温线得出, 引入邻菲罗啉之后, 比表面积增加; 而铁的引入因其占据了微孔结构, 导致比表面积下降。同时电镜证实Fe-NCDNA-2具有较大的形貌扭曲, 使得该材料具有较大的比表面积。

系统的电化学研究表明, 氮掺杂有利于增强ORR活性, 在引入铁之后形成高效的活性中心会进一步提高催化性能。因此, Fe-NCDNA-2在碱性条件下表现出优异的ORR性能。线性扫描伏安法曲线表明, 铁氮共掺杂的材料表现出与Pt/C相似的性能, 其中Fe-NCDNA-2的半波电位($E_{1/2}$)为0.863 V, 比商业Pt/C的电位更正($E_{1/2}$ = 0.841 V)。同时, Fe-NCDNA-2具有更加优异的稳定性, 测试30000 s后的电流保持率为80%(Pt/C: 64%)。在中性介质中, 合成的材料也展示了较高的ORR活性。Fe-NCDNA-2的 $E_{1/2}$ = 0.715 V, 催化30000 s后电流保持率77%, 均优于商业Pt/C催化剂。组装的锌空气电池进一步验证其作为氧还原催化剂实际应用的可行性。相比于以Pt/C为催化剂做空气阴极的电池, 以Fe-NCDNA-2组装的电池表现出更高的开路电压, 更高的功率密度(184 mW cm⁻²), 以及更加优异的充放电循环稳定性。该工作也有利于启发研究人员探索类似的氮掺杂过渡金属碳材料在各种催化上的应用。

关键词: 氧还原反应; 电催化剂; Fe-N-C活性位点; 碱性/中性介质; 锌空气电池

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