Electrocatalytic Oxygen Reduction Reaction by the Pd/Fe-N-C Catalyst and Application in a Zn–Air Battery

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Abstract: Developing a non-platinum catalyst that effectively catalyzes the oxygen reduction reaction (ORR) is highly significant for metal–air batteries. Metal and nitrogen co-doped carbons (M-N-Cs) have emerged as alternative candidates to platinum. In this work, dual-metal Pd/Fe-N-C electrocatalysts were synthesized by the one-step pyrolysis of phytic acid, melamine, and Pd/Fe-based salts. The Pd/Fe-N-C catalyst exhibited a good catalytic ability during the ORR process and outperformed the commercial Pt/C catalyst as regards mass activity, catalytic stability, and methanol tolerance. It was found that Pd-N\textsubscript{x} is the active center, and the synergistic effect from the Fe component introduction endowed the Pd/Fe-N-C with an excellent catalytic performance towards the ORR. When assembled into a Zn–air battery, its specific capacity was ~775 mAh g\textsubscript{Zn}\textsuperscript{-1}. Meanwhile, the peak power density could reach 3.85 W mg\textsubscript{Pd}\textsuperscript{-1}, i.e., 3.4 times that of the commercial Pt/C catalyst (1.13 W mg\textsubscript{Pt}\textsuperscript{-1}). This implies that the Pd/Fe-N-C catalyst has potential applications in metal–air batteries.

Keywords: oxygen reduction reaction; M-N-C catalysts; Zn–air battery

1. Introduction

Nowadays, the energy crisis and environment degradation promote extensive research on green and renewable energy. Metal–air batteries (e.g., the Zn–air battery) as well as fuel cells are promising electrochemical devices, which can realize energy conversion with high energy and power density. Unfortunately, the slow kinetic characteristics of the oxygen reduction reaction (ORR), which occurs at the cathode, seriously limits their efficiency; therefore, it is necessary to further boost the ORR activity of catalysts [1]. Platinum-based catalysts, represented by the commercial Pt/C catalyst, exhibit a good ORR activity, but their wide application is highly hindered by the low reserve and high cost of the Pt sources [2–8]. Palladium (Pd) has very similar atomic size, crystal structure, and electronic structure to those of platinum, indicating its potential application for the ORR. Moreover, its reserve is more abundant, and its price is lower; so, it is a good substitute for platinum catalysts [4,9–14].

Since it is reported that cobalt–phthalocyanine has catalytic activity towards the ORR, metal (M) and nitrogen (N) co-doped carbons (M-N-Cs) have also attracted growing attention for their comparable activity to platinum catalysts [15–18]. In the reported M-N-Cs, M is generally a kind of third transition metal, and Fe is the most active metal species, followed by Co and Mn [19–22]. It is well known that M-N\textsubscript{x} (e.g., M-N\textsubscript{4}) are ORR active sites [23], on which the adsorption/desorption process for intermediates can be effectively promoted, resulting in a reduced reaction barrier [24–26]. Recently, it was found that dual-atoms can provide two anchoring sites for O\textsubscript{2} molecules, which results in a weakened O=O bond and favors an efficient four-electron pathway [19]. Therefore, dual-metal M-N-Cs in particular Fe/Co-N-C [27–30], Fe/Mn-N-C [25], and Fe/Cu-N-C [31,32], have become the focus of attention for their improved ORR catalytic performance. For instance,
it was reported that dual-metal Fe/Co-N-C exhibited a much higher catalytic ability than single-metal Fe-N-C and Co-N-C during the ORR process [33].

The universal approach to produce M-N-Cs, consists in the pyrolysis of appropriate carbon-based precursors and transition metal salts in high-temperature conditions [34]. To date, all kinds of precursors have been tried and explored. They can be divided into three categories: (i) carbon materials including carbon black and graphene, which are widely used as precursors; however, additional nitrogen sources such as NH₃ should be introduced to construct the M-N-C structure [35,36]; (ii) Polymers that usually contain lots of heteroatoms (e.g., nitrogen), which can work as coordinating sites to anchor metal ions. Under high-temperature conditions, the metal-containing polymers can translate into M-N-C catalysts [37,38]; (iii) Metal–organic frameworks, especially for zeolitic imidazolate frameworks, which have large specific surface area and a high nitrogen percentage, and allow a facile metal atom replacement, which makes them the first choice to synthesize M-N-C catalysts [39].

Although M-N-Cs with transition metal centers have been systematically studied, little attention has concentrated on noble metals. Up to now, there are highly limited studies reported in the ORR catalysis field for noble-metal M-N-C (M = Pt, Pd, and Ru) [40–42]. Herein, we report a facile synthesis of the Pd/Fe-N-C catalyst by a one-step pyrolysis approach and investigate the electrocatalytic performance of this catalyst towards the ORR. The obtained Pd/Fe-N-C catalyst outperformed the commercial Pt/C catalyst as regards mass activity, catalytic stability, and methanol resistance. It was found that Pd-Nx is the active center, and the synergistic effect from the Fe component endowed the Pd/Fe-N-C catalyst with an excellent catalytic performance towards the ORR. The Pd/Fe-N-C catalyst also showed a much higher power density than the commercial Pt/C catalyst when it was applied as the cathode catalyst in a Zn–air battery.

2. Results and Discussion

2.1. Catalyst Characterization

Figure 1a illustrates the synthesis procedure for the Pd/Fe-N-C catalyst, which involved the pyrolysis of a solution containing phytic acid, melamine, and Pd/Fe–based salts under an inert atmosphere. Figure 1b shows the XRD diagrams of four catalysts. All XRD patterns presented diffraction peaks at 2θ = 24.5° and 43.7°. By reference to the standard card (JCPDS # 41-1487), the diffraction peaks were attributed to the (002) and (101) crystal planes of graphitic carbons, respectively [12]. The broadness of the peaks implied a poor graphitization degree. No diffraction peaks from Pd- or Fe-related phases (e.g., Pd, Fe, and the PdFe alloy) were observed, apart from the peaks from graphite. The Raman technique was applied to further characterize the carbon component. There were two characteristic peaks located at ~1337 cm⁻¹ and ~1580 cm⁻¹ in the Raman spectra (Figure 1c). The former peak, named D-band, was attributed to the disordered or defected structure of the carbon material, while the latter was due to the sp² hybridization in graphite, that is, the ordered structure of the carbon material and the in-plane stretching vibration [43,44]. The relative intensity of the two peaks (defined as I_D/I_G) can reflect the graphitization degree of carbon-based materials. It was found that the calculated values for all catalysts were ~0.95 ± 0.02, indicating a low graphitization degree; these findings were consistent with the XRD results. Although neither a Pd- or a Fe-related phase was observed in the XRD pattern, the EDS characterization confirmed the existence of both Pd and Fe (Figure 1d). Figure 1e,f are high-resolution TEM images of Pd/Fe-N-C, which show an amorphous carbon structure with abundant mesopores. No Pd/Fe-based particles with high contrast were observed in TEM mode. However, further characterization of HAADF-STEM (Figure 1g) along with EDS element mapping confirmed the presence of both Pd and Fe elements, and their distributions well overlapped with those of C, N and P elements (Figure 1h–l). It was concluded that both Pd and Fe were uniformly co-doped into the nitrogen-containing carbon substrates.
The XPS technique can characterize the elemental composition as well as the valence. Figure 2a displays the XPS survey spectrum of Pd/Fe-N-C, revealing the presence of C, N, P, Pd, and Fe elements. The C 1s (Figure 2b) consists of four peaks located at 284.7, 285.6, 287.8, and 291.0 eV, which are related to the C=C/C–C, C=N, C–O, and π-π* bonds, respectively [44,45]. The deconvolution of N 1s (Figure 2c) implied four kinds of N-containing species: M–N, pyrrole-, graphite-, and oxidation-type N, whose peaks are located at 399.3, 400.0, 401.1, and 403.0 eV, respectively [44,46]. The binding energy signals at 132.5 and 133.6 eV belong to P–C and P–O, respectively [47]. Due to the spin–orbital coupling effect, the Pd 3d exhibited double peaks (Figure 2e). Compared with metallic Pd(0), the Pd component in Pd/Fe-N-C has a higher binding energy, which implies that the chemical state of the Pd element is +2. The peak fitting revealed the presence of both Pd(II)–N (337.5 and 342.7 eV) and Pd(II)–Cl (338.7 and 345.1 eV) species [44,48]. The small amount of Cl element derived from K₂PdCl₄ present in the raw material. Figure 2f shows the peaks of Fe 2p at 723.2, 725.4, 711.1, 714.4, and 718.8 eV, which are related to Fe(II) 2p₁/₂, Fe(III) 2p₁/₂, Fe(II) 2p₃/₂, Fe(III) 2p₃/₂, as well as a satellite peak, respectively. Notably, the peak at 711.1 eV corresponds to the coordination of Fe-N species [49]. The low content of Fe element complicated the evaluation of the peaks’ positions and the observation of satellite peaks [50]. A similar peak-fitting for other species was also conducted, as shown in Figures S1–S3 in Supplementary Materials (SM). According to the XPS analysis, the Pd weight content in Pd/Fe-N-C and Pd-N-C was 2.5 and 3.0 wt. %, respectively.
implied the occurrence of the oxygen reduction reaction, and the peaks’ positions reflect the electrocatalytic ability of the catalysts towards the ORR. For Pd/Fe-N-C, the peak was located at 0.764 V, a value more positive than the values obtained for N-C (0.730 V), Fe-N-C (0.744 V), and Pd-N-C (0.751 V), implying that Pd/Fe-N-C had the highest ORR activity [48]. Linear sweep voltammetry (LSV) was also applied to deeply investigate the ORR performance. Figure 3b shows the LSV curves of Pd/Fe-N-C at different rotations (400–1600 rpm). The reduction currents regularly increased following the rise of the rotating speeds, which implied that O₂ molecules could effectively diffuse to the catalyst surface. As an important evaluation index, the electron transfer number (n) was obtained from the Koutecky–Levich (K–L) equation (Equations (S1)–(S3)). The calculated n for Pd/Fe-N-C was 4.0 (Figure 3c), suggesting an efficient four-electron transfer path in the ORR process. Figure 3d displays the LSV curves recorded at 1600 rpm for the four catalysts. Compared with N-C, Fe-N-C exhibited a similar activity; however, Pd-N-C exhibited an obvious improvement. This implies that Pd-Nx is the active center responsible for the ORR activity [51]. It should be noted that the introduction of the Fe component could further improve the ORR activity of Pd-N-C. As exhibited in Figures 3e and S4, Pd/Fe-N-C outperformed the other catalysts as regards both the half-wave potential (E_{1/2}) and the electron transfer number (n), which appeared close to those of the commercial Pt/C (E_{1/2} = 0.86 V, n = 3.8) (Figure S5). This confirmed that the synergistic effect of Fe introduction was vital for the improvement of the ORR performance of Pd/Fe-N-C [33]. As Pd/Fe-N-C has a low content of Pd, its mass activity can reach 372 mA/mgPd at 0.85 V, which is approximately 2.1 times that of the commercial Pt/C (180 mA/mgPt), showing an application prospect.

Figure 2. (a) XPS survey spectrum of Pd/Fe-N-C. Peak-fitting of the XPS spectra of (b) C 1s, (c) N 1s, (d) P 2p, (e) Pd 3d, and (f) Fe 2p.

2.2. Evaluation of the ORR Catalytic Performance

To assess the ORR activity, cyclic voltammetry (CV) was recorded in an oxygen-saturated potassium hydroxide solution. The appearance of cathode peaks in Figure 3a implied the occurrence of the oxygen reduction reaction, and the peaks’ positions reflect the electrocatalytic ability of the catalysts towards the ORR. As Pd/Fe-N-C has a low content of Pd, its mass activity can reach 372 mA/mgPd at 0.85 V, which is approximately 2.1 times that of the commercial Pt/C (180 mA/mgPt), showing an application prospect.
Catalytic stability is also an important indicator of the ORR performance and was investigated by the accelerated durability test (ADT) with cyclic voltammetry. As illustrated in Figure 4a,b, the $E_{1/2}$ of Pd/Fe-N-C negatively shifted by 7 mV after 5000 CV cycles was smaller than that of the commercial Pt/C (25 mV). It means that Pd/Fe-N-C has a much higher catalytic stability. Methanol tolerance is also an important factor that influences a catalyst’s stability. Figure 4c shows the LSV curves of Pd/Fe-N-C before and after adding 1.0 M methanol. Almost no change was observed in the high-potential region. However, an obvious methanol oxidation rather than the ORR took place on the commercial Pt/C catalyst after introducing 1.0 M methanol (Figure 4d). This suggests that the Pd/Fe-N-C catalyst has a better anti-interference performance than the commercial Pt/C. To well evaluate the ORR catalytic process, the kinetic mechanism was studied by the rotating ring-disk electrode (RRDE) test. Figure 4e shows the test results. Compared with the disc current, the ring current for Pd/Fe-N-C was negligible, implying a low yield of the $\text{H}_2\text{O}_2$ product. On the basis of Equations (S4) and (S5), the yield of $\text{H}_2\text{O}_2$ at a high potential (0.60~0.90 V) was less than 5 %, and n was determined to be ~3.9, close to that of the commercial Pt/C (Figure S6). This further confirmed that the ORR on Pd/Fe-N-C proceeded through a high-efficiency four-electron transfer path.
2.3. Zn–Air Battery

In metal–air batteries, the ORR is an important cathode reaction, which highly determines the energy transformation efficiency. Given its high ORR activity, Pd/Fe-N-C was applied as the cathode catalyst in a Zn–air battery. Figure 5a exhibits the schematic diagram of the Zn–air battery, in which a Pd/Fe-N-C-loaded carbon paper and zinc flakes served as the cathode and anode, respectively, and a 6.0 M potassium hydroxide solution was used as the electrolyte. The effective contact area between the electrolyte and the cathode was 1.0 cm². As shown in Figure 5b, we found that the open circuit voltage (OCV) of Pd/Fe-N-C can reached 1.42 V, close to the reported value (1.43 V) for the commercial Pt/C [52]. Two Pd/Fe-N-C-based Zn–air batteries connected in series could light up an LED board labeled with the LCU logo (Figure 5c). Figure 5d shows the discharge curves at 10 mA cm⁻². The output voltage of Pd/Fe-N-C was lower than that of Pt/C in the first stage; however, it surpassed that of Pt/C in a later stage. Both Pd/Fe-N-C- and Pt/C-based Zn–air batteries showed almost the same specific capacity of ~775 mAh g⁻¹. Moreover, a similar phenomenon was also observed in a variable-current discharge process. As displayed in Figure 5e, the output voltage of Pd/Fe-N-C remained stable at each current density; however, the voltage platform for the commercial Pt/C showed a declining trend. This further confirmed that the catalytic stability of Pd/Fe-N-C is higher than that of the commercial Pt/C. Figure 5f shows the discharge polarization curve and the corresponding power density of Zn–air batteries driven by Pd/Fe-N-C and Pt/C. The peak power density of Pd/Fe-N-C was 3.85 W mg⁻¹ at 316 mA cm⁻², i.e., 3.4 times that of the commercial Pt/C (1.13 W mg⁻¹ at 307 mA cm⁻²). It implies a high utilization of metal Pd in Pd/Fe-N-C during the ORR catalytic process.
3. Experimental Section

3.1. Chemicals

Potassium tetrachloropalladate (K₂PdCl₄), iron chloride hexahydrate (FeCl₃·6H₂O), phytic acid solution (C₃₆H₆₆O₃₄P₆), and melamine (C₃H₆N₆) were purchased from Zhengzhou Alpha Chemical Co., Ltd., Zhengzhou, China. No further purification was carried out for all chemicals.

3.2. Synthesis of Pd/Fe-N-C

Firstly, 100 mg of melamine, 15 mg of K₂PdCl₄, and 37.2 mg of FeCl₃·6H₂O were well dispersed in 2 mL of phytic acid (70 wt. % in H₂O) by a sonication treatment, and then the solution was carbonized at 950 °C in a N₂ atmosphere for 2 h (heating rate: 3 °C min⁻¹). After careful grinding, the obtained powder was fully soaked in 2.0 M hydrochloric acid to remove some impurities. The final product was collected by centrifugation. For convenience, the obtained product was named Pd/Fe-N-C. In addition, Fe-N-C and Pd-N-C were obtained through a similar synthesis process based on the with above procedure. They were prepared in the absence of K₂PdCl₄ and FeCl₃·6H₂O, respectively. The N-C counterpart was also synthesized without K₂PdCl₄ or FeCl₃·6H₂O.

3.3. Electrochemical Test

The ORR evaluations were performed with a CHI820C potentiostat (Shanghai Chen Hua Co., Shanghai, China) in a 0.1 M KOH solution. An Ag/AgCl (3.0 M NaCl) electrode worked as the reference electrode. The counter electrode was a coiled Pt wire with a length of 23 cm. The working electrodes were fabricated on a rotating disk electrode (RDE) according to the following process: the catalyst powder (2 mg) was dispersed into a solution consisting of 800 µL of H₂O, 200 µL of isopropanol, and 10 µL of Nafion (5 wt. %); then, 15 µL of catalyst ink was drop-casted onto the electrode surface.
4. Conclusions

In summary, dual-metal Pd/Fe-N-C was prepared by the one-step pyrolysis of phytic acid, melamine, and Pd/Fe-based salts. The synergistic effect of Fe endowed Pd/Fe-N-C with an excellent ORR performance. In comparison with the commercial Pt/C, Pd/Fe-N-C displayed higher mass activity and catalytic stability as well as a better methanol tolerance. When applied as the cathode catalyst in a Zn-air battery, it also showed a much higher peak power density than the Pt/C catalyst. Given its excellent ORR performance, Pd/Fe-N-C, as a non-platinum catalyst, has promising applications in the metal–air battery field.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12121640/s1. Characterization techniques for the catalysts; Electrochemical formulas for ORR evaluation; Figure S1: (a) XPS survey spectrum of N-C. Peak-fitting of the XPS spectra of (b) C 1s, (c) N 1s, and (d) P 2p for N-C; Figure S2: Peak-fitting of the XPS spectra of (a) C 1s, (b) N 1s, (c) P 2p, and (d) Fe 2p for Fe-N-C; Figure S3: Peak-fitting of the XPS spectra of (a) C 1s, (b) N 1s, (c) P 2p, and (d) Pd 3d for Pd-N-C; Figure S4: LSV curves of (a) N-C, (b) Fe-N-C, and (c) Pd-N-C in O$_2$-saturated 0.1 M KOH at different rotation rates. Koutecky–Levich plots of (d) N-C, (e) Fe-N-C, and (f) Pd-N-C at different potentials; Figure S5: (a) LSV curves of commercial Pt/C in O$_2$-saturated 0.1 M KOH at different rotation rates. (b) Koutecky–Levich plots of commercial Pt/C at different potentials; Figure S6: (a) Polarization curves of Pt/C recorded on the RRDE in an O$_2$-saturated 0.10 M KOH solution at a rotation rate of 1600 rpm. (b) Calculated H$_2$O$_2$ yield and electron transfer numbers (n) for Pt/C.

Author Contributions: J.C. carried out the main experiments and finished the draft. Z.W., C.Y., G.Z., S.L. and Z.S. performed some electrochemistry experiments. L.W., R.L., K.Q. and W.K. revised the draft. H.L. supervised the work and finalized the manuscript. All authors have read and agreed to the published version of the manuscript.

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