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Biomass Wood-Derived Efficient Fe-N-C Catalysts for Oxygen

Reduction Reaction

Dingding Li,^a Zheng Han,^a Kunyue Leng,^a Shenghua Ma,^a Yi Wang,^{*a} and Jinbo Bai^{*b}

^a State Key Laboratory of Photoelectric Technology and Functional Materials, International Collaborative Center on Photoelectric Technology and Nano Functional Materials, Institute of Photonics & Photon-Technology, Northwest University, Xi'an, 710069, PR China.

^b Université Paris-Saclay, CentraleSupélec, CNRS UMR8579, Laboratoire de Mécanique des Sols, Structures et Matériaux, 91190, Gif-sur-Yvette, France.

*Corresponding author

E-mail address: yi.wang@nwu.edu.cn jinbo.bai@centralesupelec.fr

Abstract

Efficient and low cost electrocatalysts for oxygen reduction reaction (ORR) was the key for scalable application of metal-air batteries and fuel cells. Herein, iron-based nitrogen doped carbon catalysts (Fe-N-C_{wood}) was prepared, using hydrothermal-pyrolysis treated wood-derived nitrogen doped carbon as the support. This support possessed large specific surface area and macro-meso-micro hierarchical porous networks, ensuring fluent mass transfer of electrolyte and oxygen species. In the ORR electrochemical test, Fe-N-C_{wood} catalyst showed an excellent activity, with a half-wave potential of 0.90 V in 0.1 M KOH, and a half-wave potential of 0.70 V in 0.1 M HClO₄. Moreover, durability tests illustrated that Fe-N-C_{wood} possessed high stability and methanol tolerance. The Fe-N-C_{wood} based Zn-air battery delivered a peak power density of 231 mW cm⁻², suggesting its potential applications in sustainable energy conversion systems.

Introduction

Fuel cells and metal-air batteries were considered as one of the most promising sustainable energy conversion systems that required highly efficient catalysts for oxygen reduction reaction (ORR) at the cathode.[1-5] Hitherto, platinum-based materials were the most widely used cathode catalysts for ORR.[6] Unfortunately, the scarcity, high cost and poor methanol tolerance of platinum severely hindered its widespread commercial applications.[7-10] To overcome the challenge, increasing attention had been attracted to search high-performance platinum-free ORR catalysts. Among the multifarious candidates, transition metal-based nitrogen doped porous carbon (M-N-C) materials were regarded as one promising alternative.[11-14]

In general, the porous structure of M-N-C catalysts significantly influenced its mass transfer ability, which was another key determined the ORR activity, in addition to the active sites. [7,15,16] Many studies have been made on this topic, which demonstrated that the ORR activity of M-N-C were significantly influenced by the specific surface area, [17-19] as well as the ratio of micropore, mesopore, and even macropore in catalyst.[20,21] These current achievements inspired the efforts of tuning the porous structure of M-N-C to gain desired ORR performance. However, it was still a challenge to design and construct efficient mass transfer hierarchical structure, because the rational hierarchical structure was also related to

pore morphology, pore branching and precise diameter ratios for connecting multi-scale pores from macro to micro levels.[15,22]

Recently, biomass-derived carbon materials have been extensively explored in electrocatalysts and supercapacitors, mainly due to the renewable and sustainable property. [23-26] In the view of hierarchical structure, biomass exhibited rational hierarchical structure designed and optimized by the nature, ensuring fluent mass transfer throughout the network. [22] Nevertheless, the nature hierarchical structure of biomass would be partially destroyed during pyrolysis and metal impregnation. The advanced ORR catalysts usually derived from special biomass resources such as pollen [27] and peanut hull [28], which reduced its application potentials. As one of the most abundant biomass resources, wood was held great potential to overcome this challenge. [25,29,30] However, the ORR catalysts based on wood-derived carbons were generally moderate in performance. Herein, we adopt a hydrothermal-pyrolysis method to prepare N-doped carbon support, using the trunk of koelreuteria paniculate as the carbon source. In the electrochemical tests, the obtained catalyst exhibited excellent activity, with a half-wave potential of 0.90 V in 0.1 M KOH, and a half-wave potential of 0.70 V in 0.1 M HClO₄.

Results and discussion

Figure 1 showed the morphology of wood derived carbon material (Fe-N-

C_{wood}). Scanning electron microscopy (SEM) images revealed that Fe-N-C_{wood} exhibited similar morphology compared with the wood-derived carbon support (N-C_{wood}, Figure 1a-b). Transmission electron microscopy (TEM, Figure 1c) and the corresponding electron energy loss spectroscopy (EELS, Figure 1d) revealed that iron nanoparticles were homogeneously dispersed over Fe-N-C_{wood}. The lattice distance of iron nanoparticles in Fe-N-C_{wood} was measured at 0.204 nm, corresponding to Fe₃C (220) planes or Fe (110) planes.[31] Figure 1e and Figure 1f showed the morphology information of Fe-N-C_{XC-72} prepared by the same method using the commercial carbon support XC-72 (Figure S3).

Figure 2 showed the X-ray diffraction (XRD) patterns of XC-72, Fe-N-C_{XC-72}, N-C_{wood} and Fe-N-C_{wood}. The peak at 26.1° in XC-72, Fe-N-C_{XC-72}, N-C_{wood} and Fe-N-C_{wood} could be attributed to graphitic carbon (002) plane, and the peaks situated at 43.7° and 44.7° in Fe-N-C_{XC-72} and Fe-N-C_{wood} were corresponding to Fe₃C (102) plane (35-0772) and Fe (110) plane (06-0696). The high-resolution Fe 2p, N 1s and C 1s X-ray photoelectron spectroscopy of Fe-N-C_{wood} were shown in Figure 2b, Figure 2c and Figure 2d, respectively. In the Fe 2p XPS spectrum (Figure 2b), the signals of 707.1 and 720.1 eV could be assigned to Fe 2p_{3/2} and Fe 2p_{1/2} from zero-valent Fe.[32] The signals at 710.5 and 722.7 eV could be assigned to Fe 2p_{3/2} and Fe 2p_{1/2} from Fe(II) species.[33] The signals at 714.2 and 726.4 eV could be assigned to Fe 2p_{3/2} and Fe 2p_{1/2} from Fe(III) species.[33] In

the N 1s XPS spectrum (Figure 2c), four peaks were observed at 398.3, 399.8, 401.0 and 402.5 eV, which could be attributed to pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen and oxide nitrogen, respectively.[3,26] In the C 1s XPS spectrum (Figure 2d), three peaks of 284.6, 285.3 and 288.6 eV were observed, which could be attributed to the C-C, C-N and C=O groups, respectively (Figure 2d).[3] The survey scan XPS spectra as well as the C 1s and N 1s XPS spectrum for N-C_{wood} were shown in Figure S4-S7, respectively. The proportion of Fe was similar for Fe-N-C_{wood} and Fe-N-C_{XC-72}, in line with ICP-OES results (Table S1). Figure 2f and Figure 2e showed the N₂ isotherms of XC-72, Fe-N-C_{XC-72}, N-C_{wood} and Fe-N-C_{wood}, and the detailed data were presented in Table S1. N-C_{wood} showed the specific surface area of 2004.8 m²/g ($S_{\text{micro}} = 301.9 \text{ m}^2/\text{g}$ and $S_{\text{extern}} = 1702.9 \text{ m}^2/\text{g}$, Table S1), which was decreased to 840.9 m²/g ($S_{\text{micro}} = 378.4 \text{ m}^2/\text{g}$ and $S_{\text{extern}} = 462.5 \text{ m}^2/\text{g}$) for Fe-N-C_{wood}. This decreased surface area in Fe-N-C_{wood} was attributed to the loss of external surface area, suggesting that iron was mainly deposited on the external surface. Further, the pore size distributions and mercury intrusion porosimetry indicated that Fe-N-C_{wood} possessed mesopores centered at about 4 nm (Figure S8) and macropores centered at about 1.3 μm (Figure S9). In comparison, the specific surface area of XC-72 and Fe-N-C_{XC-72} were 240.5 m²/g and 131.5 m²/g, respectively.

The catalytic evaluation of Fe-N-C_{wood} was firstly tested in 0.1 M KOH at

O₂ saturated condition. The cyclic voltammetry (CV) curve (Figure S10) showed that, Fe-N-C_{wood} exhibits obvious characteristics peak at 0.84 V in the O₂ saturated condition, which was not found in the N₂ saturated condition. Linear scanning of the voltammogram (LSV) curve in the O₂-saturated condition (Figure 3a) showed that Fe-N-C_{wood} had excellent ORR activity, its half-wave potential ($E_{1/2}$) reached 0.90 V and the onset potential (E_{onset}) was 0.98 V. In comparison, the half-wave potentials for Pt/C, Fe-N-C_{XC-72}, XC-72 and N-C_{wood} were 0.83, 0.80, 0.67 and 0.78 V (Figure S11), respectively, and the onset potentials for Pt/C, Fe-N-C_{XC-72}, XC-72 and N-C_{wood} were 0.96, 0.90, 0.78 and 0.88 V, respectively. The kinetic current density (j_k) of Fe-N-C_{wood} at 0.9 V was calculated at 2.43 mA cm⁻² (Figure S12), which was significantly higher than Pt/C (0.81 mA cm⁻²) and Fe-N-C_{XC-72} (0.27 mA cm⁻²). Moreover, the Tafel slope of Fe-N-C_{wood} was calculated at 80 mV dec⁻¹, which was significantly lower than that of Pt/C (90 mV dec⁻¹) and Fe-N-C_{XC-72} (102 mV dec⁻¹) (Figure 3b and Figure S13), suggesting again the higher activity of the wood-derived catalyst. Importantly, the activity of Fe-N-C_{wood} in alkaline media outperformed most of biomass-derived catalysts, as shown in Table 1.

Figure 3c showed the LSV curve measured at different rotation rates, and the corresponding Koutecky-Levich (KL) diagram was shown in Figure S14. The yields of peroxide (%) for Fe-N-C_{wood} were monitored by RRDE measurements on the Pt ring (Figure 3d). As a result, the peroxide yield for

Fe-N-C_{wood} was less than 3.8%, and the electron transfer number was between 3.9 and 4.0. Moreover, the stability of Fe-N-C_{wood} was tested by chronoamperometry and electrochemical accelerated durability test (EADT). In the EADT, the activity of Fe-N-C_{wood} was not significantly decreased after 5,000 cycles (Figure 3e). On contrary, a significant negative shift was observed in Pt/C catalyst (Figure S15). In the chronoamperometry test (Figure 3f), Fe-N-C_{wood} lost 2% of current after 10 000 s, while Pt/C lost around 30% of the original current. Furthermore, Figure S16 showed the methanol tolerance of Fe-N-C_{wood} was measured by the chronoamperometric response with the presence of methanol. The current of Pt/C decreased during the addition of methanol, but the current of Fe-N-C_{wood} was not lost. These results illustrated the high stability of wood-derived catalyst in ORR applications with alkaline media.

In Figure S17, Fe-N-C_{wood} shows an oxygen reduction peak in 0.1 M HClO₄ at O₂ saturated condition, indicating that Fe-N-C_{wood} possessed ORR activity in acidic electrolytes. At 1600 rpm, Fe-N-C_{wood} exhibited a E_{1/2} of 0.70 V and E_{onset} of 0.81 V, which was worse than Pt/C but much better than Fe-N-C_{XC-72}, XC-72 and N-C_{wood} (Figure 4a and Figure S18). The Tafel slope as well as the LSV curves of wood-derived catalyst at different rotation rates were shown in Figure 4b and Figure 4c. Its electron transfer number in the acidic media was between 3.92 and 4 (Figure 4d). Table 2 compared the ORR activity of this catalyst with some other noble metal

free catalysts. Moreover, Fe-N-C_{wood} exhibited good stability in the EADT and chronoamperometry tests (Figure 4e, 4f and Figure S19).

Zn-air battery test was carried out using Fe-N-C_{wood} coated carbon paper cathode and zinc foil anode. Zn-air battery with Fe-N-C_{wood} catalyst exhibited a peak power density of 231 mW cm⁻² (Figure 5a), which was higher than that with Pt/C catalyst (204 mW cm⁻²) and most of other catalysts (Table 3). The specific discharge capacity of Zn-air battery with Fe-N-C_{wood} catalyst at 50 mA cm⁻² was 726.9 mAhg⁻¹ (Figure 5b), larger than that with Pt/C catalyst (626.8 mAhg⁻¹). The Fe-N-C_{wood} cathode in liquid zinc-air battery provided an open circuit potential of 1.434 V (Figure 5c). Two batteries in series can effectively make the LED lamp (8 mm, 3.2 V) work (Figure 5d). The good performance of Fe-N-C_{wood} in Zn-air battery again confirmed the excellent activity of Fe-N-C_{wood} in ORR.

As known, active site was the key that influenced the activity of catalysts,[7] and the iron phthalocyanine was a conventional iron precursor for high performance Fe-N-C catalyst.[34] It could be observed that the impregnation of Fe greatly decreased the external surface area of resultant catalyst. Through the optimization of N-C_{wood} by adding Na₂CO₃ during pyrolyzing process, its external surface area was greatly increased (the function of Na₂CO₃ was shown in Figure S21), which compensated the loss of external surface after Fe impregnation. The combination of highly efficient active sites and hierarchical structure resulted in the high activity

of Fe-N-C_{wood}. The developed synthetic approach paved a low-cost, readily scalable route for the preparation of high-performance ORR catalyst.

Conclusions

In summary, a wood-derived carbon embedded with iron nanoparticles catalyst exhibited high catalytic reactivity in ORR reaction. The obtained Fe-N-C_{wood} catalyst showed a half wave potential of 0.90 V in 0.1M KOH and a half wave potential at 0.70 V in 0.1M HClO₄. Meanwhile, this catalyst possessed impressive stability and methanol tolerance. The resultant Zn-air battery with Fe-N-C_{wood} catalyst showed an outstanding peak power density of 231 mW cm⁻². The superior catalytic performances of Fe-N-C_{wood} could be attributed to the highly efficient Fe active sites and its rational hierarchical porous structure with micropores ($S_{\text{micro}} = 378.4 \text{ m}^2/\text{g}$), mesopores ($S_{\text{extern}} = 462.5 \text{ m}^2/\text{g}$, centered at about 4 nm) and macropores (centered at about 1.3 μm).

Experimental

N-C_{wood} was prepared by fresh wood powder (koelreuteria paniculate). CH₃COOH, H₂O₂ and H₂O were mixed for hydrothermal reaction, and the resulting product was pyrolyzed with Na₂CO₃ and urea under a high-purity Ar flow (800°C, 3 hours) to obtain N-C_{wood}.

Fe-N-C_{wood} was prepared by the following method. FePc and N-C_{wood} were added to acetone, stirred and evaporated to dryness, and then pyrolyzed

under a high-purity Ar flow (900°C, 1 hours). The resulting sample was labeled as Fe-N-C_{wood}.

Fe-N-C_{XC-72} was obtained through the preparation process of Fe-N-C_{wood} by replacing N-C_{wood} with XC-72.

Details of preparation, characterizations and electrochemical tests were presented in the Supporting Information.

Conflicts of interest

The authors declare no competing financial interest.

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Figure 1. Characterization of Fe-N-C_{wood}. SEM images of N-C_{wood} (a) and Fe-N-C_{wood} (b); TEM images of Fe-N-C_{wood}, the inset shows the crystalline lattice of the marked particle (c); HAADF-TEM image of particles in Fe-N-C_{wood} coupled with electron energy loss spectroscopy (d). SEM images (e) and TEM images (f) of Fe-N-C_{XC-72}.

Figure 2. Chemical state and textural property of Fe-N-C_{wood}. XRD patterns of N-C_{wood}, Fe-N-C_{wood}, XC-72 and Fe-N-C_{XC-72} (a); high-resolution Fe 2p, N 1s and C 1s XPS spectra of Fe-N-C_{wood} (b-d); N₂ sorption isotherm of N-C_{wood}, Fe-N-C_{wood}, XC-72 and Fe-N-C_{XC-72} (e,f).

Figure 3. Electrochemical evaluation of Fe-N-C_{wood} in 0.1 M KOH. Polarization curves of Fe-N-C_{XC-72}, Fe-N-C_{wood} and Pt/C (a); Corresponding Tafel plots (b); LSV curves of Fe-N-C_{wood} at different rotating rates (c); Electron transfer number (n, bottom) and H₂O₂ yield (top) versus potential (d); LSV curves of Fe-N-C_{wood} in O₂-saturated 0.1 M KOH before and after 5,000 cycles (e); Chronoamperometric response of Fe-N-C_{wood} and Pt/C (f).

Figure 4. Electrochemical evaluation of Fe-N-C_{wood} in 0.1 M HClO₄. Polarization curves of Fe-N-C_{XC-72}, Fe-N-C_{wood} and Pt/C (a); Corresponding Tafel plots (b); LSV curves of Fe-N-C_{wood} at different rotating rates (c); Electron transfer number (n, bottom) and H₂O₂ yield (top) versus potential (d); LSV curves of Fe-N-C_{wood} in O₂-saturated 0.1 M HClO₄ before and after 5,000 cycles (e); Chronoamperometric response of Fe-N-C_{wood} and Pt/C (f).

Figure 5. Zn-air battery performance of Fe-N-C_{wood}. Discharge polarization and corresponding power density plots of Fe-N-C_{wood} and Pt/C based Zn-air battery (a). Specific capacities of Fe-N-C_{wood} and Pt/C-based Zn-air battery (b). Fe-N-C_{wood} based liquid Zn-air battery (c). LED powered by two liquid Zn-air batteries with the Fe-N-C_{wood} heterostructures electrocatalyst (d).

Table 1. Comparison of the ORR activity between Fe-N-C_{wood} and other biomass-based catalysts under alkaline condition (0.1 M KOH) in literature.

Sample	Electrolyte	E _{onset} (V)	E _{1/2} (V)	Reference
Fe-N-C _{wood}	0.1 M KOH	0.98	0.90	This work
TARC-N	0.1 M KOH	0.98	0.86	[35]
N/E-HPC-900	0.1 M KOH	0.99	0.85	[29]
Co@NCBC	0.1 M KOH	0.98	0.86	[30]
AWC-1	0.1 M KOH	0.92	0.85	[36]
NiFe@N-CFs	0.1 M KOH	0.94	0.82	[26]
Fe-N-C/rGO)	0.1 M KOH	0.94	0.81	[33]
BC-Ce-2	0.1 M KOH	0.90	0.84	[37]
Co-Fe-S@NSRPC	0.1 M KOH	-	0.80	[27]
SA-Fe/NHPC	0.1 M KOH	-	0.87	[38]
Co/Co ₃ O ₄ @HPCNF-50	0.1 M KOH	0.92	0.82	[39]
FeNC-D0.5	0.1 M KOH	-	0.87	[40]
AC/TBC(O)	0.1 M KOH	0.85	0.74	[41]
Fe-Zn-SA/NC	0.1 M KOH	-	0.85	[42]
CoOP@bio-C	0.1 M KOH	0.91	0.81	[43]
CoTBrPP@bio-C	0.1 M KOH	0.93	0.85	[44]
HI-RGO/CDs	0.1 M KOH	0.93	0.77	[45]

Table 2. Comparison of the ORR activity between Fe-N-C_{wood} and other noble metal free catalysts under alkaline condition (0.1 M HClO₄) in literature.

Sample	Electrolyte	E _{onset} (V)	E _{1/2} (V)	Reference
Fe-N-C _{wood}	0.1 M HClO ₄	0.81	0.70	This work
Fe-Pani-RGO 2 py	0.1 M HClO ₄	0.82	0.74	[46]
Fe/N/S-PCNTs	0.5 M H ₂ SO ₄	0.80	0.62	[47]
bNGr	0.1 M HClO ₄	0.88	0.70	[48]
Fe-N-DSC	0.5 M H ₂ SO ₄	0.81	0.65	[49]
Fe-N-CNT	0.1 M HClO ₄	0.77	0.46	[50]
CNx	0.1 M HClO ₄	0.80	0.67	[51]
Fe-N-C-950	0.1 M HClO ₄	0.92	0.78	[52]
Fe-N-C	0.1 M HClO ₄	0.80	0.60	[53]
S-Fe/N/C	0.1 M HClO ₄	0.83	0.66	[54]

Table 3. Comparison of the peak power density of Fe-N-C_{wood} based Zn-air battery and other reported Zn-air batteries in literature.

Sample	Loading (mg cm ⁻²)	Peak power density (mW cm ⁻²)	Reference
Fe-N-C _{wood}	1	231	This work
Cu ISAS/NC	1	280	[55]
Cu SAs/NC-900	1	242	[3]
W ₂ N/WC	0.6	172	[56]
Fe-Zn-SA/NC	2	167.2	[42]
Cu SAC	2	196	[57]
Co/Co ₃ O ₄ @HPCNF-50	1	102.5	[58]
S,N-Fe/N/C-CNT	1.25	102.7	[59]
CoTBrPP@bio-C	1	100	[44]
Fe/N/C@BMZIF	1	235	[60]
Cu@Fe-N-C	1	92	[61]
Fe _{SA} /FeO _{NC} /NSC	1	179.0	[62]