

Supporting Information

Prussian blue-derived FeNx/Fe-based N-doped carbon nanotubes catalysts with high ORR electrochemical performance

Zhenlu Zhao ^{‡ a b *}, Qidi Lu ^{‡ a}, and Xin Wang ^a

^a *School of Material Science and Engineering, University of Jinan, Jinan 250022, Shandong, China.*

^b *State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,
Changchun 130022, Jilin, China*

E-mail: mse_zhaozl@ujn.edu.cn

[‡] *Zhenlu Zhao and Qidi Lu contributed equally to this work.*

1. Chemicals and materials

Sodium ferricyanide ($\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, 99 wt.%, Shanghai Aladdin Biochemical Technology Co., LTD.). Hydrochloric acid (HCl, 36 wt.%~38 wt.%, Sinopod Chemical Reagent Co., LTD.), Ferric chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99 wt.%, Sinopod Chemical Reagent Co., LTD.). Ethanol ($\text{C}_2\text{H}_5\text{OH}$, Tianjin Fu yu Chemical Reagent Co., LTD.). Potassium hydroxide (KOH, Tianjin Da mao Chemical Reagent Co., LTD.) Melamine ($\text{C}_3\text{N}_6\text{H}_6$, 99 wt.%, McLean Reagent Co., LTD.) Commercial 20% Pt/C (Pt/C, 99 wt.%. All chemical reagents (analytical reagent grade) are not further purified prior to use. The deionized water (DI water) used in the experiment was manufactured in-house in our laboratory.

2. Materials characterization

The morphology of the materials can be characterized by Field Emission scanning electron microscopy (FESEM). The FESEM test was carried out on FEI QUANTAFEG 250 produced by FEI Company in the United States. The distribution of elements in catalyst samples can be analyzed using energy dispersion spectrometer (EDS). EDS test was conducted on JEOL 2100F produced by Bruker. Transmission electron microscopy (TEM) was used to characterize the morphologies of the samples, and LM1-125 produced by FEI Company in the United States was used for TEM test. X-ray diffractometer (XRD) is used to analyze the crystal structure and composition of the material. The XRD tests were performed on a D8-ADVANCE instrument manufactured by Bruker, Germany, with a sweep range of $10\text{-}90^\circ$ and a sweep speed of 5° min^{-1} . X-ray photoelectron spectroscopy (XPS) was used to study the atomic structure and chemical state on the surface of materials. XPS was tested using PX130031 produced by Bruker, Germany. High resolution Raman spectrometer (Raman) is used to measure the Raman vibration peaks of the catalyst materials and conduct quantitative analysis. Fully automated physical adsorption tests were used to analyze the specific surface area and pore size distribution of the samples. The sample is sintered in a tubular furnace, which is OTF-1200X-II produced by He fei Ke jing Material Technology Co., LTD.

3. Electrochemical characterization

The electrochemical tests were conducted using the CHI 760E electrochemical workstation and rotational equipment with a standard three-electrode system. A graphite rod and a 1M-KOH Hg/HgO electrode were employed as the counter and reference electrodes, respectively. The electrocatalyst inks were prepared by dispersing 5 mg electrocatalysts in a solution consisting of 20 μL 5% Nafion 117, 240 μL water, and 740 μL isopropanol. The working electrode was prepared by applying 10 μL of the electrocatalyst onto a rotating ring-disk electrode (RRDE, diameter = 4 mm) with a loading capacity of 0.5 mg per square centimeter.

Oxygen reduction reaction (ORR) tests were conducted in a 0.1 M KOH solution saturated with O_2 . All potentials were calibrated to the reversible hydrogen electrode (RHE) using the equation:

$$E (\text{vs. RHE}) = E (\text{Hg/HgO}) + 0.059 \cdot \text{pH} + 0.098$$

Linear sweep voltammetry (LSV) polarization curves were recorded at a scan rate of 5 mV per second. Long-term durability of the prepared electrocatalysts and Pt/C benchmark was assessed by performing chronoamperometry at 0.8 V and comparing LSV curves before and after thousands of cyclic voltammetry (CV) cycles. The electron transfer number (n) was calculated utilizing the Koutecký-Levich equations.

$$\frac{1}{j} = \frac{1}{j^l} + \frac{1}{j^k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j^k}$$

$$B = 0.62nFC_0D^{2/3}\nu^{-1/6}$$

The measured, diffusion-limited, and kinetic current density are denoted as j , j^l , and j^k respectively. The electrode's angular velocity (ω) is expressed in radians per second (rad s^{-1}), while the value of the Faraday constant (F) is 96485 C mol^{-1} . The saturated O_2 concentration (C_0) is $1.21 \times 10^{-6} \text{ mol cm}^{-3}$, and the diffusion coefficient of O_2 in 0.1 M KOH (D) is $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The kinetic viscosity (ν) is $0.01 \text{ cm}^2 \text{ s}^{-1}$. The RRDE measurements were conducted with a ring electrode potential of 1.2 V. The H_2O_2 yield ($\text{H}_2\text{O}_2\%$) and n of ORR were determined using the following equations:

$$n = \frac{4j^d}{j^d + j^r/N}$$

$$H_2O_2\% = \frac{200 j^r/N}{j^d + j^r/N}$$

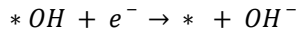
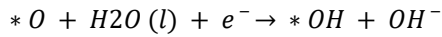
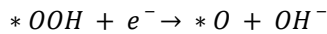
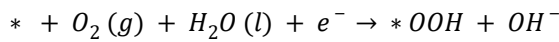
where N , j^d and j^r are the current collection efficiency of the Pt ring electrode (0.37), the disk current and the ring current, respectively.

4. Oxygen reduction reaction

Glassy carbon (GCE) was coated with catalyst ink using a 0.5 mg cm² loading quantity. The reference catalyst used was commercial Pt/C (20 wt%). The LSV curves were measured at a series of rotating electrode speeds (100, 400, 900, 1600 and 2500 rpm) at a scan rate of 2 mV s⁻¹ whereas the CV curves were measured in an O₂-saturated 0.1 M KOH aqueous solution at a scan rate of 2 mV s⁻¹ at a potential range of -0.8 to 0.2 V (E Hg/HgO). The reversible hydrogen electrode (RHE) was created from each potential using the formula:

$$E (\text{vs. RHE}) = E (\text{Hg/HgO}) + 0.059 \cdot pH + 0.098$$

In alkaline medium, the ORR could occur in the following 4 electron reaction pathway:



5. Supplementary Tables

Table S1. Comparison of ORR parameters for recent reported electrocatalysts in 0.1M KOH.

Catalysts	E _{onset} (V)	E _{1/2} (V)	Reference
FeN _x /Fe-NCNTs	0.96V	0.86V	This Work

Fe-CNSs-N	0.95V	0.83V	1
Fe-N/C-700	0.99V	0.85V	2
NHPC-900-1000	0.96V	0.83V	3
Fe-N-C/T-HT2	0.9V	0.85V	4
Fe/N/C-900	0.98V	0.81V	5

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