

## Supplementary Material

# Nanostructured Fe-N-C as Bifunctional Catalysts for Oxygen Reduction and Hydrogen Evolution

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**Abstract:** The development of electrocatalysts for energy conversion and storage devices is of paramount importance to promote sustainable development. Among the different families of materials, catalysts based on transition metals supported on a nitrogen-containing carbon matrix have been found to be effective catalysts toward oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) with high potential to replace conventional precious metal-based catalysts. In this work, we developed a facile synthesis strategy to obtain a Fe-N-C bifunctional ORR/HER catalysts, involving wet impregnation and pyrolysis steps. Iron (II) acetate and imidazole were used as iron and nitrogen sources, respectively, and functionalized carbon black pearls were used as conductive support. The bifunctional performance of the Fe-N-C catalyst toward ORR and HER was investigated by cyclic voltammetry, rotating ring disk electrode experiments, and electrochemical impedance spectroscopy in alkaline environment. ORR onset potential and half-wave potential were 0.95 V and 0.86 V, respectively, indicating a competitive performance in comparison with the commercial platinum-based catalyst. In addition, Fe-N-C had also a good HER activity, with an overpotential of 478 mV @10 mAcm<sup>-2</sup> and Tafel slope of 133 mVdec<sup>-1</sup>, demonstrating its activity as bifunctional catalyst in energy conversion and storage devices, such as alkaline microbial fuel cell and microbial electrolysis cells.

**Keywords:** PGM-free electrocatalysts; oxygen reduction; hydrogen evolution; energy conversion; bioelectrochemical systems

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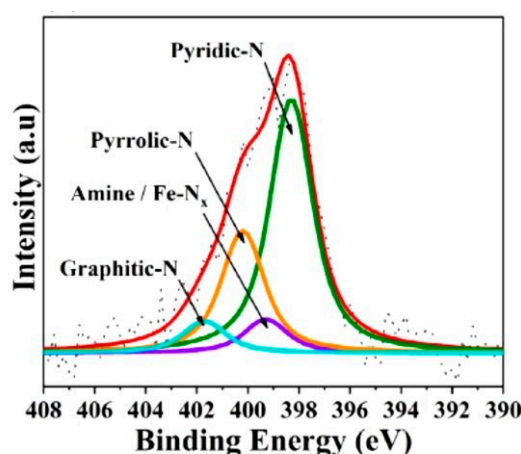


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X-ray photoelectron spectroscopy (XPS) was acquired by using an Omicron DAR 400 Al/Mg K $\alpha$  non-monochromatized X-ray source, and a VG-CLAM2 electron spectrometer. The C 1 s, N 1 s, and Fe 2 p spectra were analyzed by a deconvolution using KolXPD Software with a Voigtian peak fitting, Shirley and/or linear background and Doniach-Sun-jic convoluted with a gaussian for graphitic sp<sup>2</sup>-hybridized peak.

**Table S1.** Atomic percentage of the elements in Fe-N-C catalysts and relative content of the different types of nitrogen, estimated from XPS. .

Sample	C (At. %)	O (At. %)	N (At. %)	Graphitic-N (Rel. %)	Pyrrolic-N (Rel. %)	Pyridinic-N (Rel. %)	Amine/Fe-N <sub>x</sub> (Rel. %)	Fe (At. %)
Fe-N-C	70.74	27.24	1.90	7.17	27.67	57.52	7.64	0.12



**Figure S1.** N 1s XPS spectra for the Fe-N-C catalyst.

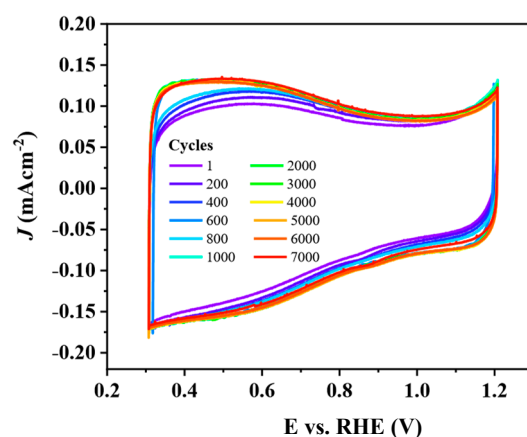
**Table S2.** Onset potential ( $E_{onset}$ ), half-wave potential ( $E_{1/2}$ ), limiting current density ( $J_{lim}$ ), number of electrons transferred ( $n$ ) and HO<sub>2</sub> percentage at 0.5 V vs. RHE over CV cycles in O<sub>2</sub>-saturated 0.1 M KOH.

Cycles	Fe-N-C				
	$E_{onset}$	$E_{1/2}$	$J_{lim}$	$n$	HO <sub>2</sub> (%)
1	0.95	0.85	-4.84	3.80	10.0
200	0.95	0.84	-4.49	3.80	10.0
400	0.95	0.84	-4.49	3.81	9.50
600	0.95	0.84	-4.47	3.81	9.50
800	0.95	0.84	-4.47	3.81	9.50
1000	0.95	0.84	-4.46	3.81	9.50

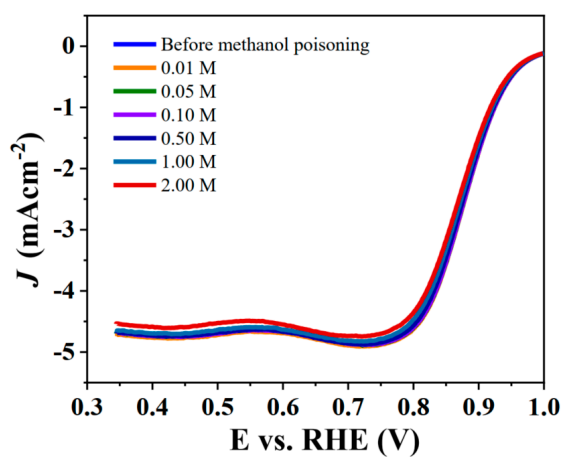
**Table S3.** Electrochemical parameters extrapolated from the Tafel analysis. .

Sample	Tafel slope*				Tafel slope*		
	$E_{1/2}$	$lcd$ zone ( $E > 0.80$ V)	$\alpha c$	$J_0$ (1 <sup>st</sup> )	$hcd$ zone ( $E < 0.80$ V)	$\alpha c$	$J_0$ (2 <sup>nd</sup> )
	$E$ vs. RHE (V)	(mV dec <sup>-1</sup> )	(1 <sup>st</sup> )	(mA cm <sup>-2</sup> )	(mV dec <sup>-1</sup> )	(2 <sup>nd</sup> )	(mA cm <sup>-2</sup> )
Fe-N-C	0.85	66.5	0.9	$7.74 \times 10^{-6}$	103	0.6	$1.21 \times 10^{-3}$

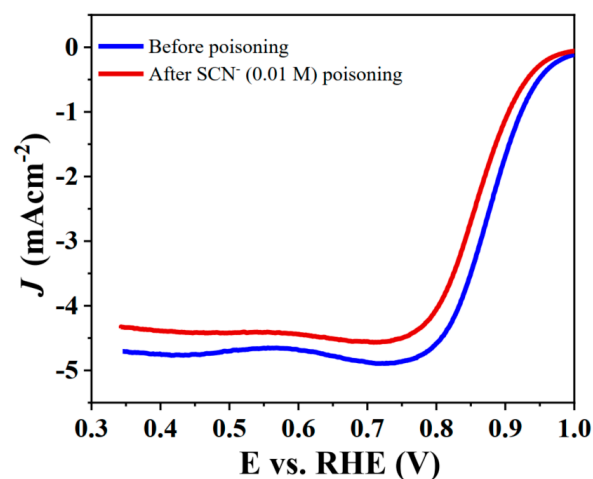
\*Absolute value; *hcd*: high current density; *lcd*: low current density.



**Figure 2.** Cyclic voltammograms in N<sub>2</sub>-saturated electrolyte at a scan rate of 5 mVs<sup>−1</sup> over 7000 cycles for the Fe-N-C sample.



(a)



(b)

**Figure S3.** LSV curves for the Fe-N-C catalyst in O<sub>2</sub>-saturated KOH 0.1 M electrolyte at a scan rate of 5 mVs<sup>−1</sup> and 1600 rpm before and after the addition of 0.01 – 2.00 M methanol (a) and 0.01 M KSCN in the electrolyte. .

**Table S4.** HER mechanism in alkaline environment

Mechanism	Alkaline Environment	Tafel Slope	Equation
Overall	$2\text{H}_2\text{O} + 2\text{e}^- + * \rightarrow \text{H}_2 + 2\text{OH}^-$	-	-
Volmer	$\text{H}_2\text{O} + \text{e}^- + * \rightarrow \text{H}^* + \text{OH}^-$	118 mVdec <sup>−1</sup>	1
Heyrovsky	$\text{H}_2\text{O} + \text{e}^- + \text{H}^* \rightarrow \text{H}_2 + \text{OH}^- + *$	40 mVdec <sup>−1</sup>	2
Tafel	$\text{H}^* + \text{H}^* \rightarrow \text{H}_2 + 2*$	30 mVdec <sup>−1</sup>	3

\*Indicates an adsorption active site on the catalyst surface.

**Table S5.** HER electrochemical parameters obtained from EIS data fitting.

E (V)	Rs ( $\Omega$ )	Rct ( $\Omega$ )	CPE (S.s <sup>n</sup> )	n
0.40	59.6	491	$3.8 \cdot 10^{-3}$	0.89
(E <sub>onset</sub> )	$\pm 0.41$	$\pm 31.42$	$\pm 1 \cdot 10^{-4}$	$\pm 0.01$
0.45 (E <sub>onset</sub> < E < $\eta_{10}$ )	60.48	173.5	$3.6 \cdot 10^{-4}$	0.88
	$\pm 0.35$	$\pm 6.22$	$\pm 1 \cdot 10^{-4}$	$\pm 0.02$
0.50 ( $\eta_{10}$ )	63.4	98.7	$3.4 \cdot 10^{-3}$	0.85
	$\pm 0.50$	$\pm 4.74$	$\pm 2 \cdot 10^{-4}$	$\pm 0.03$

**References.**

1. Chen, Z.; Qing, H.; Zhou, K.; Sun, D.; Wu, R. Metal-organic framework-derived nanocomposites for electrocatalytic hydrogen evolution reaction. *Prog. Mater. Sci.* **2020**, *108*, 100618, doi:10.1016/j.pmatsci.2019.100618.