Supporting Information

Enhancing Activity and Stability of Fe/Co-based Nitrogendoped Carbon with Richer Nitrogen and Metal-N Active Sites towards Oxygen Reduction Reaction

Zeqi Wu^a, Zhenlu Zhao^{a, b, *}

^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*

Methods

Chemicals and materials

Zinc nitrate $(Zn(NO_3)_2 \cdot 6H_2O)$, iron nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$, cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$, 2-methylimidazole, dopamine hydrochloride (DA), ethanol, methanol and potassium hydroxide (KOH, 99.99%) were purchased from Macklin. Carbon-supported Pt/C (20 wt.%) nanoparticles were purchased from Shanghai Maclean Biochemical Co. Nafion[®] solution (5 wt%) was purchased from Energy Chemical. The deionized water was made by the laboratory water purifier (18.25 M Ω cm). All the chemicals used in the synthesis of catalysts were analytical purity and no further purification was made.

Preparation of Fe/Co-NC

60 mg of Fe(NO₃)₃·9H₂O, 43 mg of Co(NO₃)₂·6H₂O and 3.6 g Zn(NO₃)₂·6H₂O was dissolved in 30 mL methanol. Another solution of 4.0 g 2-methylimidazole with 30 mL methanol was then added under magnetic stirring. The mixture was stirred for 24 h at

room temperature. After that, the precipitates, named Fe/Co-ZIF, were centrifuged, washed, and dried. The Fe/Co-ZIF powder was milled and then pyrolyzed in the tube furnace at 900 °C for 3h under an N₂ atmosphere. The heating rate and gas flow rate were set to be 3 °C/min and 50 mL/min, respectively.

Preparation of Fe/Co-NC RN x

200 mg Fe/Co-ZIF was dispersed in 20 mL methanol. 60 mg DA in 10 mL methanol was then rapidly added to the Fe/Co-ZIF dispersion at room temperature, and the mixture was stirred for 24 h. After that, the precipitates, named Fe/Co-ZIF@PDA III, were centrifuged, washed, and dried. By changing the PDA amount, Fe/Co-ZIF@PDA x particles were prepared, where x denotes the different weight ratio of DA to 200 mg of Fe/Co-ZIF (x = I, III, V represent 20 mg (10%), 60 mg (30%) and 100 mg (50%) of DA to 200 mg of Fe/Co-ZIF, respectively).

The preparation of Fe/Co-NC RN III was selected as an example to detail the carbonization of Fe/Co-ZIF@PDA particles. Briefly, the Fe/Co-ZIF@PDA III powder was milled and then pyrolyzed in the tube furnace at 900 °C for 3h under an N₂ atmosphere. The heating rate and gas flow rate were set to be 3 °C/min and 50 mL/min, respectively. The resulting product was denoted Fe/Co-NC RN III. Fe/Co-ZIF@PDA x (x = I, V) particles were also carbonized under the identical condition, and the corresponding products were denoted Fe/Co-NC RN x (x = I, V), respectively.

Characterization

The morphology and size of the catalysts were characterized by field emission scanning electron microscopy (SEM, Gemini300) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-F200). The crystal structure information was obtained by X-ray diffraction (XRD, Japan Rigaku Smart Lab SE) with Cu Ka radiation ($\lambda = 0.15$ nm) in the 2 θ range from 5° to 80°. The composition, chemical state, and molecular structure of elements on the surface of the sample were obtained by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB Xi⁺). The degree of

disorder and graphitization of the sample carbon were measured using a 532 nm laser as the excitation source using a Raman spectrometer (HR Evolution). Nitrogen adsorption-desorption measurements on MAC TriStar II 3flex. The pore size distribution and specific surface area of the sample were determined by Brunauer-Emmett-Teller (BET) method.

Electrochemical measurements

All the ORR electrochemical measurements were performed on the CHI 760E electrochemical workstation via a three-electrode cell with a Hg/HgO electrode as a reference electrode, a carbon rod as a counter electrode, and an electrocatalyst-coated rotating disk electrode or rotating ring disk electrode as a working electrode in oxygen-saturated 0.1 M KOH solution. A uniform electrocatalyst ink was prepared by ultrasonically dispersing 5.0 mg electrocatalyst powder in a mixed solution containing 1ml ethanol and 10.0 μ L Nafion for 0.5 h. Cyclic voltammetry curves (CV) and linear sweep voltammetry curves (LSV) are obtained at a sweep rate of 10 mV s⁻¹ and 2 mV s⁻¹ over a potential range of 0 to 1.2 V. Long-term stability and CH₃OH (3 M) toxicity tests were performed by measuring chronoamperometric response at 0.7 V and a rotating rate of 1600 rpm. To further calculate the electron transfer number (n), the Koutecky-Levich (K-L) equation is as follows:

$$J^{-1} = J_{k}^{-1} + B^{-1}\omega^{\frac{-1}{2}}$$
$$B = 0.2nFC_{0}D_{0}^{\frac{2}{3}}V^{\frac{-1}{6}}$$

where J and J_K are the measured and kinetic current densities, respectively, ω is the rotating speed, n is the electron transfer number, F is the Faraday constant (96,485 C mol⁻¹), C₀ is the bulk concentration of oxygen (1.2×10⁻⁶ mol cm⁻³), D₀ is the diffusion coefficient of oxygen (1.9×10⁻⁵ cm² s⁻¹), and V is the kinematic viscosity of the electrolyte (0.01 cm² s⁻¹).

The site densities of metal-N active sites were determined according to the method

described by Kucernak et al.¹ The method is based on the adsorption and reduction of nitrite (NO²⁻) on the central metal atoms. Equation is as follows:

$$SD(site g^{-1}) = \frac{Q_{strip}(Cg^{-1})}{n_{strip} \times F(Cmol^{-1})}$$

where Q_{strip} (C g⁻¹) is the excess coulometric charge associated with the stripping peak, F is the Faraday constant (96,485 C mol⁻¹), and n_{strip} is the number of electrons associated with the reduction of one nitrite per site ($n_{strip} = 5$).

Supplementary Figures



Figure S1. SEM (a) and TEM images (b, c) of Fe/Co-NC.



Figure S2. SEM images of (a) Fe/Co-NC RN I and (b) Fe/Co-NC RN V.



Figure S3. XRD patterns of (a) Fe/Co-NC RN I and (b) Fe/Co-NC RN V.



Figure S4. XPS survey spectra of (a) Fe/Co-NC and (b) Fe/Co-NC RN III.



Figure S5. Nitrogen contents of Fe/Co-NC and Fe/Co-NC RN III, according to XPS measurements.



Figure S6. C 1s XPS spectrum of Fe/Co-NC.



Figure S7. N 1s XPS spectrum of Fe/Co-NC.



Figure S8. Metal-N contents of Fe/Co-NC and Fe/Co-NC RN III, according to N 1s XPS spectrum.



Figure S9. Fe 2p XPS spectrum of Fe/Co-NC.



Figure S10. Co 2p XPS spectrum of Fe/Co-NC.



Figure S11. ORR LSV curves of (a) Fe/Co-NC, (b) commercial Pt/C before and after 10000 CV cycles.



Figure S12. LSV curves of Fe/Co-NC RN III at various rotating speeds.



Figure S13. ORR LSV curves before, during and after nitrite adsorption in an O_2 -saturated 0.5 M acetate buffer at pH 5.2. Catalyst loading: 0.28 mg cm⁻².



Figure S14. CV curves before and during nitrite adsorption within the nitrite reductive stripping region.



Figure S15. Methanol tolerance tests for commercial Pt/C and Fe/Co-NC RN III with the addition of 3 M methanol.

Supplementary Tables

Table S1. Elemental compositions of Fe/Co-NC and Fe/Co-NC RN III, according toXPS measurements.

Catalyst	C (at%)	N (at%)	O (at%)	Fe (at%)	Co (at%)
Fe/Co-NC	82.12	10.11	6.77	0.48	0.52
Fe/Co-NC RN III	80.75	11.23	7.05	0.50	0.47

Catalyst	Pyridinic N	Metal-N (%)	Pyrrolic N	Graphitic N
	(%)		(%)	(%)
Fe/Co-NC	44.55	26.36	11.26	17.83
Fe/Co-NC RN III	35.47	32.05	10.37	22.11

Table S3. Comparison of the ORR performances in alkaline media for ourelectrocatalyst and various reported cathode electrocatalysts.

	Catalyst	E _{1/2} of ORR (V)	Ref.
This work	Fe/Co-NC RN III	0.90	
Single-atom catalyst	S,N-Fe/N/C-CNT	0.85	2
	NiN ₄ /GHSs/FeN ₄	0.83	3
	FeNi SAs/NC	0.84	4
	meso/micro-FeCo-N _x -CN	0.886	5
	Fe/N-G-SAC	0.89	6
	Co-N,B-CSs	0.83	7
Metal-free	N-GRW	0.84	8
	B,N-carbon	0.84	9
	NPCSs	0.83	10
	2D-PPCN	0.85	11
	GH-BGQD	0.87	12
	NKCNPs	0.79	13
	Co ₃ O _{4-x} HoNPs@HPNCS	0.834	14
	Co ₃ O ₄ -NP/N-rGO	0.76	15
Metal oxides	Co@Co ₃ O ₄ /NC	0.80	16

	Co ₂ FeO ₄ /NCNTs	0.80	17
	ZnCo ₂ O ₄ /N-CNT	0.87	18
Metal nitrides	Ni ₃ FeN/Co,N-CNF	0.81	19
	Fe ₃ Pt/Ni ₃ FeN	0.93	20
	Ni-Fe-MoNNTs	0.72	21
Metal selenides	NiSe ₂ /CoSe ₂ -N	0.81	22
	Ni _x Co _{0.85-x} Se	0.78	23
	N-CoSe ₂ /3D MXene	0.79	24
Perovskites	Pb ₂ Ru ₂ O _{6.5}	0.81	25
	LaNi _{0.85} Mg _{0.15} O ₃	0.69	26
	S _{5.84%} -LaCoO ₃	0.704	27
	Pt-SCFP/C-12	0.81	28

Supplementary References

- 1. D. Malko, A. Kucernak and T. Lopes, *Nat. Commun.*, 2016, 7, 13285.
- P. Chen, T. Zhou, L. Xing, K. Xu, Y. Tong, H. Xie, L. Zhang, W. Yan, W. Chu and C. J. A. C. Wu, *Angew. Chem.*, 2017, **129**, 625-629.
- 3. J. Chen, H. Li, C. Fan, Q. Meng, Y. Tang, X. Qiu, G. Fu and T. J. A. M. Ma, *Adv. Mater.*, 2020, **32**, 2003134.
- 4. D. Yu, Y. Ma, F. Hu, C. C. Lin, L. Li, H. Y. Chen, X. Han and S. J. A. E. M. Peng, *Adv. Energy Mater.*, 2021, **11**, 2101242.
- 5. S. Li, C. Cheng, X. Zhao, J. Schmidt and A. J. A. C. I. E. Thomas, *Angew. Chem. Int. Ed.*, 2018, **57**, 1856-1862.
- M. Xiao, Z. Xing, Z. Jin, C. Liu, J. Ge, J. Zhu, Y. Wang, X. Zhao and Z. J. A. M. Chen, *Adv. Mater.*, 2020, **32**, 2004900.
- 7. Y. Guo, P. Yuan, J. Zhang, Y. Hu, I. S. Amiinu, X. Wang, J. Zhou, H. Xia, Z. Song and Q. J.

A. n. Xu, ACS Nano, 2018, 12, 1894-1901.

- H. B. Yang, J. Miao, S.-F. Hung, J. Chen, H. B. Tao, X. Wang, L. Zhang, R. Chen, J. Gao and H. M. J. S. a. Chen, *Sci. Adv.*, 2016, 2, e1501122.
- T. Sun, J. Wang, C. Qiu, X. Ling, B. Tian, W. Chen and C. J. A. S. Su, *Adv. Sci.*, 2018, 5, 1800036.
- S. Chen, L. Zhao, J. Ma, Y. Wang, L. Dai and J. J. N. e. Zhang, *Nano energy*, 2019, 60, 536-544.
- W. Lei, Y.-P. Deng, G. Li, Z. P. Cano, X. Wang, D. Luo, Y. Liu, D. Wang and Z. J. A. C. Chen, ACS Catal., 2018, 8, 2464-2472.
- T. V. Tam, S. G. Kang, M. H. Kim, S. G. Lee, S. H. Hur, J. S. Chung and W. M. J. A. E. M. Choi, *Adv. Energy Mater.*, 2019, 9, 1900945.
- 13. Q. Wang, Y. Lei, Y. Zhu, H. Wang, J. Feng, G. Ma, Y. Wang, Y. Li, B. Nan, Q. J. A. a. m. Feng and interfaces, *ACS Appl. Mater. Interfaces*, 2018, **10**, 29448-29456.
- D. Ji, L. Fan, L. Tao, Y. Sun, M. Li, G. Yang, T. Q. Tran, S. Ramakrishna and S. J. A. C. Guo, *Angew. Chem.*, 2019, **131**, 13978-13982.
- X. Han, G. He, Y. He, J. Zhang, X. Zheng, L. Li, C. Zhong, W. Hu, Y. Deng and T. Y. J. A. E. M. Ma, *Adv. Energy Mater.*, 2018, 8, 1702222.
- A. Aijaz, J. Masa, C. Rösler, W. Xia, P. Weide, A. J. Botz, R. A. Fischer, W. Schuhmann and M. J. A. C. I. E. Muhler, *Angew. Chem. Int. Ed.*, 2016, 55, 4087-4091.
- X. T. Wang, T. Ouyang, L. Wang, J. H. Zhong, T. Ma and Z. Q. J. A. C. Liu, *Angew. Chem.*, 2019, **131**, 13425-13430.
- 18. Z.-Q. Liu, H. Cheng, N. Li, T. Y. Ma and Y.-Z. J. A. M. Su, Adv. Mater., 2016, 28, 3777-3784.
- Q. Wang, L. Shang, R. Shi, X. Zhang, G. I. Waterhouse, L.-Z. Wu, C.-H. Tung and T. J. N. E. Zhang, *Nano Energy*, 2017, 40, 382-389.
- Z. Cui, G. Fu, Y. Li and J. B. J. A. C. I. E. Goodenough, *Angew. Chem. Int. Ed.*, 2017, 56, 9901-9905.
- C. Zhu, Z. Yin, W. Lai, Y. Sun, L. Liu, X. Zhang, Y. Chen and S. L. J. A. E. M. Chou, *Adv. Energy Mater.*, 2018, 8, 1802327.
- X. Zheng, X. Han, Y. Cao, Y. Zhang, D. Nordlund, J. Wang, S. Chou, H. Liu, L. Li and C. J. A. M. Zhong, *Adv. Mater.*, 2020, **32**, 2000607.
- X. Zheng, J. Zhang, J. Wang, Z. Zhang, W. Hu and Y. J. S. C.-M. Han, *Sci. China Mater.*, 2020, 63, 347-355.
- Z. Zeng, G. Fu, H. B. Yang, Y. Yan, J. Chen, Z. Yu, J. Gao, L. Y. Gan, B. Liu and P. J. A. M. L. Chen, ACS Mater. Lett., 2019, 1, 432-439.
- J. Park, M. Risch, G. Nam, M. Park, T. J. Shin, S. Park, M. G. Kim, Y. Shao-Horn, J. J. E. Cho and E. Science, *Energy Environ. Sci.*, 2017, 10, 129-136.
- J. Bian, R. Su, Y. Yao, J. Wang, J. Zhou, F. Li, Z. L. Wang and C. J. A. A. E. M. Sun, ACS Appl. Energy Mater., 2019, 2, 923-931.
- J. Ran, T. Wang, J. Zhang, Y. Liu, C. Xu, S. Xi and D. J. C. o. M. Gao, *Chem. Mater.*, 2020, 32, 3439-3446.
- X. Wang, J. Sunarso, Q. Lu, Z. Zhou, J. Dai, D. Guan, W. Zhou and Z. J. A. E. M. Shao, *Adv. Energy Mater.*, 2020, 10, 1903271.