

One-step preparation of eggplant-derived hierarchical porous graphitic biochar as efficient oxygen reduction catalyst in microbial fuel cells

Zhengtai Zha^{a,b}, Zhi Zhang^{a,b,*}, Ping Xiang^{a,b}, Hongyi Zhu^{a,b}, Bangmei Zhou^{a,b}, Zhulong Sun^{a,b}, Shun Zhou^{a,b}

^a College of Environment and Ecology, Chongqing University, Chongqing, 400045, China

^b Key Laboratory of Three Gorges Reservoir Region's Eco-Environment, Ministry of Education, Chongqing University, Chongqing, 400045, China

*Corresponding author. E-mail address: zhangzhicqu@cqu.edu.cn (Z. Zhang).

Text S1. Conversion of potential between Ag/AgCl electrode and reversible hydrogen electrode (RHE)

All the electrochemical measurements were performed with a three-electrode system in 50 mM PBS solution. The reference electrode Ag/AgCl was filled with 4 M KCl gel solution. The potentials could be converted to vs. a reversible hydrogen electrode (RHE) which is calculated from Eq. (S1).

$$E_{RHE} = E_{vs. Ag/AgCl} + 0.0591 * pH + 0.199 \quad (S1)$$

Where E_{RHE} would be the measured potential vs. a reversible hydrogen electrode, $E_{vs. Ag/AgCl}$ is the experimentally tested potential vs. Ag/AgCl reference electrode. 0.199 V is the formal potential of an Ag/AgCl electrode with 4 M KCl filling solution at 25 °C vs. NHE according to the Phychemi Co., Ltd.

Test. S2 Electrode preparation method

The anode material is carbon felt (2 × 2 cm), soaked in acetone overnight, then thoroughly washed with deionized water, and dried in an oven at 60°C for using. Cathode material was carbon cloth (project area: 7 cm²) including a gas diffusion layer, carbon-based layer, and catalyst layer (0.5 mg/cm²). The gas diffusion layer was fabricated by coating polytetrafluoroethylene (PTFE) solution (60 wt%, Hesen, Shanghai, China) on the carbon-based layer and annealing at 370 °C for 15 min in a muffle furnace; this process was repeated four times. The catalyst ink was prepared by sonicating a mixture comprising the catalyst (3.5 mg), nafion solution (25 μL),

isopropanol (15 μL), and deionized water (5 μL) for 20 min. The uniform catalyst ink was brushed on the carbon cloth and dried at 28 $^{\circ}\text{C}$ for 24h. In addition, Pt/C cathode (20 wt%, 0.5 mg/cm^2) was fabricated by the same operation process as a reference to probe the performance of the EPGC catalysts.

Table S1 Nutrient solution formula used in MFCs.

Phosphate buffer solution (g / L)		Trace metal solution (mg / L)		Vitamin solution (mg / L)	
Component	Concentration	Component	Concentration	Component	Concentration
NH ₄ Cl	0.31	Nitrilotriacetic acid	1.5	Biotin	2.0
KCl	0.13	MgSO ₄ ·7H ₂ O	3.0	folic acid	2.0
NaH ₂ PO ₄ ·2H ₂ O	2.75	MnSO ₄ ·2H ₂ O	0.5	pyridoxine HCl	10.0
Na ₂ HPO ₄ ·12H ₂ O	11.466	NaCl	1.0	riboflavin	5.0
		FeSO ₄ ·7H ₂ O	0.1	thiamin	5.0
		CaCl ₂ ·2H ₂ O	0.1	nicotinic acid	5.0
		CoCl ₂ ·6H ₂ O	0.1	Pantothenic acid	5.0
		ZnSO ₄	0.1	Vitamin B12	0.1
		CuSO ₄ ·5H ₂ O	0.01	paminobenzoic acid	5.0
		AlK(SO ₄) ₂ ·12H ₂ O	0.01	thioctic acid	5.0
		H ₃ BO ₃	0.01		
		Na ₂ MoO ₄ ·2H ₂ O	0.01		
		NiCl ₂ ·6H ₂ O	0.024		
		NaWO ₄ ·2H ₂ O	0.025		

Table S2 Chemical composition of the samples and N1s components (values given in % of total amount N) based on XPS measurements

Samples	at.% (C)	at.% (O)	at.% (N)	Pyridinic N (%)	Pyrrolic N (%)	Graphitic N (%)	Oxidized N (%)
EPGC-700-2	85.35	8.82	5.83	43.73	38.67	6.93	10.67
EPGC-800-1	85.96	9.62	4.43	46.10	35.13	9.42	9.35
EPGC-800-2	86.37	10.01	3.62	67.40	20.88	7.89	3.83
EPGC-800-3	89.82	7.52	2.66	58.91	30.63	4.68	5.78
EPGC-900-2	90.55	7.63	1.82	62.94	25.74	8.32	3.00

Table S3 Comparison of the structure and performance of EPGC-800-2 and other carbon-based ORR catalysts

Catalysts	Specific surface area (m ² /g)	I_D/I_G	Onset potential (V vs Ag/AgCl)	half-wave potential (V vs Ag/AgCl)	n	Ref.
EPGC-800-2	1137	0.76	0.153	-0.022	3.90	This study
NC/Fe ₈ Co ₂	561.02		-0.02	-0.12	3.87-3.93	[1]
PR-C (1:3.5)	416.7	1.27	0.087	-0.048	3.2	[2]
CE-Fe-MWNT	680	1.05	-0.007	-0.133	3.83	[3]
PAC-800	1273.8	1.05	0.03	-0.13	3.72-3.96	[4]
e-BAC	114	2.26	-0.200	-0.3		[5]
Fe ₃ O ₄ @N-mC	26.73	1.24		-0.257	3.76	[6]
NC-3	609.1	1.13	0.132	-0.041	3.34-3.71	[7]
TGC-900	651.78	1.04	-0.027	-0.154	3.48-3.84	[8]
Mn-Fe@g-C ₃ N ₄	268.6	1.14	0.197	-0.174	3.94	[9]
ZIF-8	1416		0.11	-0.32	3.83	[10]
CP-M-Z	636.99	2.64	0.16	-0.128	3.87-3.93	[11]
CN800	143		0.215	-0.096	3.1	[12]
HC-900	908.9	1.29	-0.015	-0.129	3.65-3.93	[13]

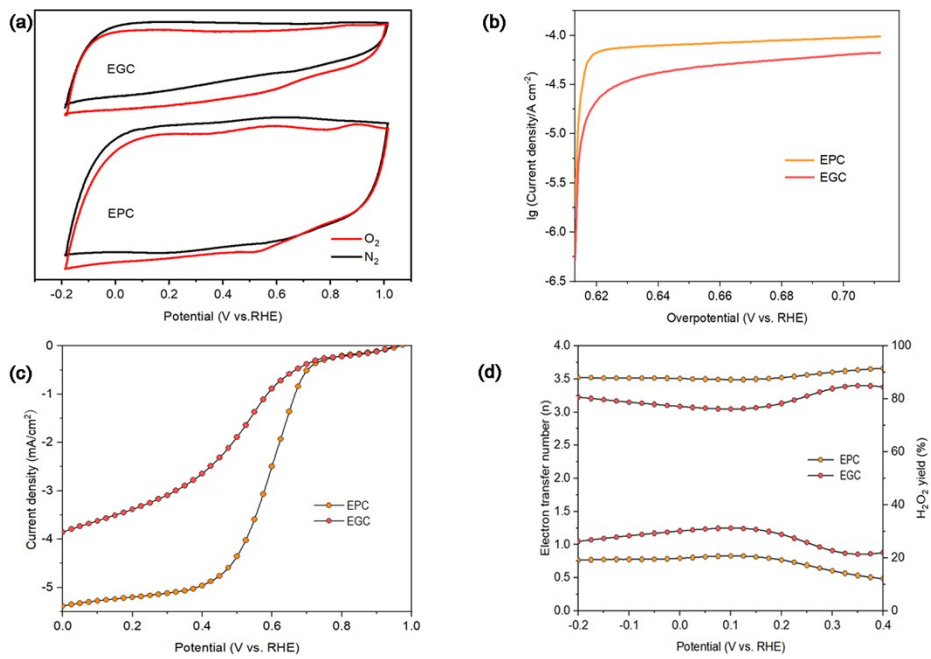


Fig. S1 (a) CV curves in N_2 - and O_2 -saturated 50 mM PBS solutions at 5 mV/s, (b) Tafel plots, (c) LSV curves in O_2 -saturated 50 mM PBS with 1600 rpm at 5 mV/s, (d) electron transfer numbers (n) and H_2O_2 yield of EPC and EGC.

Reference

- [1] C. Han, X. Bo, J. Liu, M. Li, M. Zhou, L. Guo, Fe, Co bimetal activated N-doped graphitic carbon layers as noble metal-free electrocatalysts for high-performance oxygen reduction reaction, *J. Alloys Compd.* 710 (2017) 57–65.
- [2] W. Wang, S. Liu, Y. Liu, W. Jing, R. Zhao, Z. Lei, Phenolic resin/chitosan composite derived nitrogen-doped carbon as highly durable and anti-poisoning electrocatalyst for oxygen reduction reaction, *Int. J. Hydrogen Energy.* 42 (2017) 26704–26712.
- [3] J. Zhang, S. Wu, X. Chen, M. Pan, S. Mu, Egg derived nitrogen-self-doped carbon/carbon nanotube hybrids as noble-metal-free catalysts for oxygen reduction, *J. Power Sources.* 271 (2014) 522–529.
- [4] P. Fu, L. Zhou, L. Sun, B. Huang, Y. Yuan, Nitrogen-doped porous activated carbon derived from cocoon silk as a highly efficient metal-free electrocatalyst for the oxygen reduction reaction, *RSC Adv.* 7 (2017) 13383–13389.
- [5] S. Marzorati, A. Goglio, S. Fest-Santini, D. Mombelli, F. Villa, P. Cristiani, A. Schievano, Air-breathing bio-cathodes based on electro-active biochar from pyrolysis of Giant Cane stalks, *Int. J. Hydrogen Energy.* 44 (2019) 4496–4507.
- [6] H. Zhou, Y. Yang, S. You, B. Liu, N. Ren, D. Xing, Oxygen reduction reaction activity and the microbial community in response to magnetite coordinating nitrogen-doped carbon catalysts in bioelectrochemical systems, *Biosens. Bioelectron.* 122 (2018) 113–120.
- [7] B, Jianting Liu A , et al. "A novel hard-template method for fabricating tofu-gel based N self-doped porous carbon as stable and cost-efficient electrocatalyst in microbial fuel cell." *International Journal of Hydrogen Energy* 44.48(2019):26477-26488.
- [8] Liu J , Wei L , Wang H , et al. Biomass-derived N-doped porous activated carbon as a high-performance and cost-effective pH-universal oxygen reduction catalyst in fuel cell[J]. *International Journal of Hydrogen Energy*, 2020.
- [9] A, Kengqiang Zhong , et al. "Highly conductive skeleton Graphitic-C 3 N 4 assisted Fe-based metal-organic frameworks derived porous bimetallic carbon nanofiber for enhanced oxygen-reduction performance in microbial fuel cells." *Journal of Power Sources* 467.
- [10] Xue W , Zhou Q , Li F , et al. Zeolitic imidazolate framework-8 (ZIF-8) as robust catalyst for oxygen reduction reaction in microbial fuel cells[J]. *Journal of Power Sources*, 2019, 423(MAY 31):9-17.
- [11] Yang, W., Dong, Y., Li, J., Fu, Q., Zhang, L., 2020. Templating synthesis of hierarchically meso/macroporous N-doped microalgae derived biocarbon as oxygen reduction reaction catalyst for microbial fuel cells. *Int. J. Hydrogen Energy*.
- [12] Wang X , Yuan C , Shao C , et al. Enhancing oxygen reduction reaction by using metal-free nitrogen-doped carbon black as cathode catalysts in microbial fuel cells

treating wastewater[J]. Environmental Research, 182.

[13] Wenyuan, Jiahuan, Tang, et al. Hierarchically structured carbon materials derived from lotus leaves as efficient electrocatalyst for microbial energy harvesting.[J]. The ence of the total environment, 2019, 666:865-874.