Supporting information for

Controllable design of multi-metallic aerogels as efficient electrocatalysts for methanol fuel cells

Lanqing Li[#], Wei Gao[#], Jianqi Ye, Haoxin Fan, Dan Wen*

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering,

Northwestern Polytechnical University, Xi'an, 710072, P. R. China

[#] These authors contributed equally to this work.

*Corresponding author should be addressed to D. Wen (<u>dan.wen@nwpu.edu.cn</u>)



Figure S1. Energy dispersive spectrum (EDS) of PtNi nanotubular aerogels.



Figure S2. XRD spectrum of PtNi nanowire aerogels.



Figure S3. Effect of HCl concentration with (a) 5, (b) 10, (c) 20, (d) 60 mM on the nanotubular structure during the post treatment.



Figure S4. TEM images of samples before (a, b, c) and after (d, e, f) acid treatment when the molar ratio of Ni/Pt in the precursor is 9:1 (a, d), 36:1 (b, e) and pure Ni (c, f).



Figure S5. TEM images for growing pathway from the solid nanowire to the nanotubular structure of the PtNi-2 sample after post treatment of etching and replacing for (a) 10 s, (b) 1 min, and (c) 30 min.



Figure S6. High-resolution XPS spectra for (a) Ni 2p and (b) Pt 4f in PtNi nanowire aerogels.



Figure S7. Mass activities and specific activities of commercial Pt/C and as-prepared PtNi-x aerogels at 0.9 V in ORR process.



Figure S8. LSV curves of PtNi template aerogels in 0.1 M KOH solution.



Figure S9. (a) Polarization curves of PtNi-2 aerogels at a set of rotation rates (400, 625, 900, 1225, 1600, 2025 and 2500 rpm), (b) Koutecky–Levich plots for the oxygen reduction on PtNi-2 aerogels at different potentials (0.2V, 0.3 V, 0.5 V, 0.6 V) in O₂-saturated 0.1 M KOH solution.



Figure S10. ORR performance of Pt/C and Au-PtNi nanotubular aerogels.



Figure S11. MOR performance of Pt/C and Au-PtNi nanotubular aerogels.

ICP results	Atomic ratio (Pt:Ni)	Pt (µg/mL)	Ni (µg/mL)
PtNi-0	1.76:1	6.93	1.21
PtNi-1	2.34:1	7.41	0.94
PtNi-2	2.88:1	7.26	0.77
PtNi-3	2.88:1	8.73	0.93

Table S1. ICP-OES results of PtNi-x aerogels

Samples	Pt loading	Onset potential	Half-wave potential	j_k at 0.9 V	Mass	Specific
	(µg)	(V vs RHE)	(V vs RHE)	(mA/cm ²)	activity	activity
					(A/mg _{Pt})	(mA/cm_{pt}^2)
Pt/C	3.2	0.98	0.87	1.79	0.11	0.15
PtNi-0	5.78	1.02	0.90	5.89	0.20	0.41
PtNi-1	6.18	1.03	0.93	11.02	0.35	0.62
PtNi-2	6.05	1.03	0.93	12.95	0.42	0.72
PtNi-3	7.28	1.02	0.91	5.19	0.14	0.34

Table S2. Performance comparison of different catalysts towards ORR

		Half-wave	Mass activity	Specific activity	Ref
Samples	Electrolyte	potential (V vs	(A mg ⁻¹ _{Pt})	(m A ann ²)	
		RHE)		$(\text{IIIA CIII}^-\text{Pt})$	
PtNi nanotubular					
a ana a a l	0.1 M KOH	0.93	0.42 at 0.9 V vs RHE	0.72 at 0.9 V vs RHE	This work
aerogei					
Fe ₃ Pt/Ni ₃ FeN	0.1 M KOH	0.93	0.35 at 0.9 V vs RHE	/	[1]
Fe ₃ Pt/N@C	0.1 M KOH	0.89	0.43 at 0.9 V vs RHE	/	[2]
	0.1.N.W.O.W.	0.01	0.05 · 0.0 M		[2]
Au-Pd-Pt aerogels	0.1 M KOH	0.91	0.37 at 0.9 V vs RHE	0.88 at 0.9 V vs RHE	[3]
Pt-Ni@PtD/G	0.1 M HClO ₄	0.83	0.061 at 0.9 V vs RHE	0.098 at 0.9 V vs RHE	[4]
Nanoporous Pt	0.1 M HClO ₄	0.8*	0.3 at 0.8 V vs RHE	1	[5]
_					
PtPd/CNWs	0.1 M HClO ₄	0.87	0.23 at 0.9 V vs RHE	0.43 at 0.9 V vs RHE	[6]
PtCu RDNFs	0.1 M HClO ₄	0.91	0.18 at 0.85 V vs RHE	0.48 at 0.85 V vs RHE	[7]
Pd4-s-Pt1/C	0.1 M HClO₄	0.90*	0.33 at 0.9 V vs RHE	0.74 at 0.9 V vs RHE	[8]
					[1]
ZIF-67-Pt/RGO	0.5 M H ₂ SO ₄	0.90*	0.21 at 0.9 V vs RHE	/	[9]
Pt@Co SAs-ZIF-					
NC	0.5 M H ₂ SO ₄	0.92	0.48 at 0.9 V vs RHE	0.64 at 0.9 V vs RHE	[10]

Table S3. Comparison for the electrochemical activities of the recent reported ORR electrocatalysts

* estimated value from the literature figures.

Reference:

[1] Z. Cui, G. Fu, Y. Li, J.B. Goodenough, Ni₃FeN-Supported Fe3 Pt Intermetallic Nanoalloy as a High-Performance Bifunctional Catalyst for Metal-Air Batteries, Angew Chem. Int. Ed. Engl. 56(33) (2017) 9901-9905.

[2] D. Chen, Z. Li, Y. Zhou, X. Ma, H. Lin, W. Ying, X. Peng, Fe₃Pt Intermetallic Nanoparticles Anchored on N-doped Mesoporous Carbon for the Highly Efficient Oxygen Reduction Reaction, Chem. Commun. 56(36) (2020) 4898-4901.

[3] R. Du, W. Jin, R. Hübner, L. Zhou, Y. Hu, A. Eychmüller, Engineering Multimetallic Aerogels for pH - Universal HER and ORR Electrocatalysis, Adv. Ener. Mater. 10(12) (2020) 1903857.

[4] X. Lyu, Y. Jia, X. Mao, D. Li, G. Li, L. Zhuang, X. Wang, D. Yang, Q. Wang, A. Du, X. Yao, Gradient-Concentration Design of Stable Core-Shell Nanostructure for Acidic Oxygen Reduction Electrocatalysis, Adv. Mater. 32(32) (2020) e2003493.

[5] B. Geboes, J. Ustarroz, K. Sentosun, H. Vanrompay, A. Hubin, S. Bals, T. Breugelmans, Electrochemical Behavior of Electrodeposited Nanoporous Pt Catalysts for the Oxygen Reduction Reaction, ACS Catal. 6(9) (2016) 5856-5864.

[6] X. Deng, S. Yin, X. Wu, M. Sun, Z. Li, Z. Xie, Y. Liang, Q. Huang, Scalable Preparation of PtPd/carbon Nanowires in the Form of Membrane as Highly Stable Electrocatalysts for Oxygen Reduction Reaction, Int. J. Hydrogen Ener. 44(5) (2019) 2752-2759.

[7] H. J. Niu, H. Y. Chen, G. L. Wen, J. J. Feng, Q. L. Zhang, A. J. Wang, One-pot Solvothermal Synthesis of Three-dimensional Hollow PtCu Alloyed Dodecahedron Nanoframes with Excellent Electrocatalytic Performances for Hydrogen Evolution and Oxygen Reduction, J. Colloid Interface Sci. 539 (2019) 525-532.

[8] G. Zhang, W. Lu, L. Cao, X. Qin, F. Ding, S. Tang, Z.-G. Shao, B. Yi, Large faceted Pd nanocrystals supported small Pt nanoparticles as highly durable electrocatalysts for oxygen reduction, J. Power Sources. 326 (2016) 23-34.

[9] W. Wu, Z. Zhang, Z. Lei, X. Wang, Y. Tan, N. Cheng, X. Sun, Encapsulating Pt Nanoparticles inside a Derived Two-Dimensional Metal-Organic Frameworks for the Enhancement of Catalytic Activity, ACS Appl. Mater. Interfaces 12(9) (2020) 10359-10368.

[10] L. Liang, H. Jin, H. Zhou, B. Liu, C. Hu, D. Chen, Z. Wang, Z. Hu, Y. Zhao, H.-W. Li, D. He, S. Mu, Cobalt Single Atom Site Isolated Pt Nanoparticles for Efficient ORR and HER in Acid Media, Nano

Energy 88 (2021) 106221.