

Supplementary Information

A Perspective on Protective Carbon Shells for Improved Stability of Alkaline Water Oxidation Electrocatalysts

Lettie A. Smith,[†] Kenta Kawashima,[†] Raul A. Marquez,[†] and C. Buddie Mullins^{†,§,¶,⊥,▽,}*

[†] Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, United States.

[§] McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States.

[¶] Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States.

[⊥] Center for Electrochemistry, The University of Texas at Austin, Austin, Texas 78712, United States.

[▽] H2@UT, The University of Texas at Austin, Austin, Texas 78712, United States.

* Corresponding author: mullins@che.utexas.edu

Table 1. Summary of Example Carbon Core-Shell OER Electrocatalysts: Their Properties and Carbon Corrosion

sample	NP size (nm)	carbon layer thickness (nm)	Overpotential (mV) @ 10 mA·cm ⁻²	long-term test	duration of long-term test	post-characterization	carbon corrosion ?	ref.
Fe ₃ C@C-N	10-40	-	420	CA, 1.70 V vs RHE	> 13.8 h	XRD, TEM, CO ₂ detection	Yes	¹
Fe ₃ C@C	-	-	-	CA, 1.70 V vs RHE	> 13.8 h	-	Yes	¹
Fe ₃ C (no carbon layer)	-	-	-	CA, 1.70 V vs RHE	<1.5 h	-	Yes	¹
FO ₈₀₀	30 to 40	~5	330	CA, 1.57 V vs RHE	> 50 h	SEM, XPS	Likely	²
FeNi@N-CNT	CNT, 40 nm diameter	~7	300	Chrono galvanostatic measurements, CA, 1.56 V vs RHE	10 h	XRD, TEM, XPS	Likely	³
Fe/Fe ₃ C-A@CNT	5 to 10	1 to 2	292	CP, 50 mA·cm ⁻²	12 h	-	-	⁴
Fe/Fe ₃ C-C@CNT	>200	9.31	342	CP, 50 mA·cm ⁻²	12 h	-	-	⁴
Fe/Fe ₃ C-P@CNT	200	0	341	CP, 50 mA·cm ⁻²	12 h	-	-	⁴
Ni ₃ Fe-Fe ₃ C@NCNTs (also referred to as NF-FC@NCNTs)	~5	2-2.5	171	CP, 10 mA·cm ⁻²	~300 h	SEM, TEM, XRD, Raman, XPS	Likely	⁵
C@CoP ₂ /CC	50-100	2.2	234	CA, 1.52 V vs RHE	80 h	XRD, XPS, SEM	-	⁶
Co/CoOx@NS-NCNTs	~50	~50	360	CA, 1.7 V vs RHE	5 h	-	-	⁷

Fe ₃ C@NG800-0.2	≥ 4	0-25	361	CA, 1.59 V vs RHE	20 h	-	-	8
Co@Co ₃ O ₄ /NC-1	2-10	~8	330	CP, 10 mA·c m ⁻²	~50 h	-	-	9
CoNP@NC/N-G-700	35	2.8	390	CA, 1.57 V vs RHE	1.38 h	TEM	No	10

References

- (1) Abbas, S. A.; Ma, A.; Seo, D.; Jung, H.; Lim, Y. J.; Mehmood, A.; Nam, K. M. Synthesis of Fe₃C@C Core–Shell Catalysts with Controlled Shell Composition for Robust Oxygen Evolution Reaction. *Appl. Surf. Sci.* **2021**, *551*, 149445. <https://doi.org/10.1016/j.apsusc.2021.149445>.
- (2) Bandal, H. A.; Pawar, A. A.; Kim, H. Transformation of Waste Onion Peels into Core–Shell Fe₃C@N-Doped Carbon as a Robust Electrocatalyst for Oxygen Evolution Reaction. *Electrochimica Acta* **2022**, *422*, 140545. <https://doi.org/10.1016/j.electacta.2022.140545>.
- (3) Tao, Z.; Wang, T.; Wang, X.; Zheng, J.; Li, X. MOF-Derived Noble Metal Free Catalysts for Electrochemical Water Splitting. *ACS Appl. Mater. Interfaces* **2016**, *8* (51), 35390–35397. <https://doi.org/10.1021/acsami.6b13411>.
- (4) Gao, T.; Yu, S.; Chen, Y.; Li, X.; Tang, X.; Wu, S.; He, B.; Lan, H.; Li, S.; Yue, Q.; Xiao, D. Regulating the Thickness of the Carbon Coating Layer in Iron/Carbon Heterostructures to Enhance the Catalytic Performance for Oxygen Evolution Reaction. *J. Colloid Interface Sci.* **2023**, *642*, 120–128. <https://doi.org/10.1016/j.jcis.2023.03.067>.
- (5) Liu, T.; Xiang, Y.; Tan, Z.; Hong, W.; He, Z.; Long, J.; Xie, B.; Li, R.; Gou, X. One-Step Growth of Ni₃Fe–Fe₃C Heterostructures Well Encapsulated in NCNTs as Superior Self-Supported Bifunctional Electrocatalysts for Overall Water Splitting. *J. Alloys Compd.* **2023**, *949*, 169825. <https://doi.org/10.1016/j.jallcom.2023.169825>.
- (6) Alsabban, M. M.; Yang, X.; Wahyudi, W.; Fu, J.-H.; Hedhili, Mohamed. N.; Ming, J.; Yang, C.-W.; Nadeem, M. A.; Idriss, H.; Lai, Z.; Li, L.-J.; Tung, V.; Huang, K.-W. Design and Mechanistic Study of Highly Durable Carbon-Coated Cobalt Diphosphide Core–Shell Nanostructure Electrocatalysts for the Efficient and Stable Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2019**, *11* (23), 20752–20761. <https://doi.org/10.1021/acsami.9b01847>.
- (7) Zhang, P.; Cai, Z.; You, S.; Wang, F.; Dai, Y.; Zhang, C.; Zhang, Y.; Ren, N.; Zou, J. Self-Generated Carbon Nanotubes for Protecting Active Sites on Bifunctional Co/CoOx Schottky Junctions to Promote Oxygen Reduction/Evolution Reactions via Efficient Valence Transition. *J. Colloid Interface Sci.* **2019**, *557*, 580–590. <https://doi.org/10.1016/j.jcis.2019.09.060>.
- (8) Jiang, H.; Yao, Y.; Zhu, Y.; Liu, Y.; Su, Y.; Yang, X.; Li, C. Iron Carbide Nanoparticles Encapsulated in Mesoporous Fe–N-Doped Graphene-Like Carbon Hybrids as Efficient Bifunctional Oxygen Electrocatalysts. *ACS Appl. Mater. Interfaces* **2015**, *7* (38), 21511–21520. <https://doi.org/10.1021/acsami.5b06708>.
- (9) Ajaz, A.; Masa, J.; Rösler, C.; Xia, W.; Weide, P.; Botz, A. J. R.; Fischer, R. A.; Schuhmann, W.; Muhler, M. Co@Co₃O₄ Encapsulated in Carbon Nanotube-Grafted Nitrogen-Doped Carbon Polyhedra as an Advanced Bifunctional Oxygen Electrode. *Angew. Chem. Int. Ed.* **2016**, *55* (12), 4087–4091. <https://doi.org/10.1002/anie.201509382>.
- (10) Zhong, X.; Jiang, Y.; Chen, X.; Wang, L.; Zhuang, G.; Li, X.; Wang, J. Integrating Cobalt Phosphide and Cobalt Nitride-Embedded Nitrogen-Rich Nanocarbons: High-Performance Bifunctional Electrocatalysts for Oxygen Reduction and Evolution. *J. Mater. Chem. A* **2016**, *4* (27), 10575–10584. <https://doi.org/10.1039/C6TA03820D>.