Supporting information

Electronic Tuning of Ni-Fe-Co Oxide/Hydroxide as Highly Active Electrocatalysis for Rechargeable Zinc−Air Batteries

Xiaolong Guo[a,*], Xinyu Zhang[a], Yong Wu[c], Yuci Xin[a], Dongmei Li[a], Yuxin Zhang[b,*], Peng Yu [a,*]

a)Chongqing Key Laboratory of Photo-Electric Functional Materials, College of Physics and Electronic Engineering, Chongqing Normal University, Chongqing 401331, China

b) College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

c) Institute of Materials & Laboratory for Microstructure, Shanghai University, Shanghai 200072, China

*Corresponding author

E-mail addresses: guoxiaolong@cqnu.edu.cn (X. Guo) ; zhangyuxin@cqn.edu.cn (Y. Zhang), pengyu@cqnu.edu.cn (P. Yu)

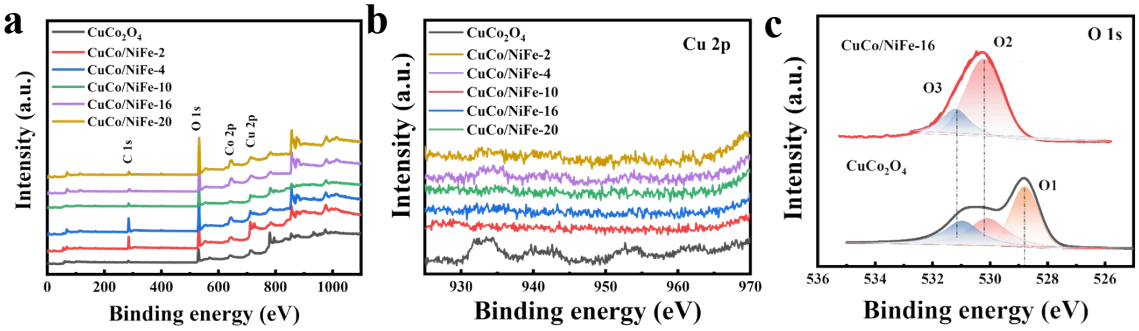

Fig. S1 (a) XPS full spectrum of the electrocatalysts. XPS spectra of (b) Cu 2p and (c) O 1s for as-prepared catalysts.

Table. S1 The fitted O ions ratio in the XPS.

Catalysts	O1(at.%)	O2(at.%)	O3 (at.%)
$CuCo_2O_4$	39.18	33.62	27.20
CuCo/NiFe-2	28.36	34.51	37.13
CuCo/NiFe-4	11.82	37.85	50.33
CuCo/NiFe-10	0	29.94	70.06
CuCo/NiFe-16	0	26.42	73.58
CuCo/NiFe-20	0	54.28	45.72

Table. S2 OER catalytic performance comparison for as-prepared catalysts.

Catalysts	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Interface resistance （ohm）
$CuCo_2O_4$	342	68	5.90
CuCo/NiFe -2	297	55	10.50
CuCo/NiFe-4	292	43	3.10
CuCo/NiFe-10	284	39	3.20
CuCo/NiFe-16	251	31	2.50
CuCo/NiFe-20	295	40	5.23

Table. S3 Comparison of OER activity of $CuCo_2O_4$-based electrocatalysts in alkaline media.

Catalysts	Method	Electrolyte	Onset overpotential (mV)	Tafel slope (mV/dec)	Overpotential (mV)	Ref.
CuCoO nanowire	Hydrothermal	1 M KOH	250	68	270 (20 mA cm^{-2})	[1]
s$CuCo_2O_4$/rGo nanoparticle	Hydrothermal	1 M KOH	-	64	360 (10 mA cm^{-2})	[2]
$CuCo_2O_4$@ CQD Nanowires	Hydrothermal	1 M KOH	230	64	290 (20 mA cm^{-2})	[3]
$CuCo_2O_4$ Polyhedron	Hydrothermal	1 M KOH	330	90.3	420 (10 mA cm^{-2})	[3]
$CuCo_2O_4$ Nanochain	Hydrothermal	1 M KOH	270	63.3	351 (10 mA cm^{-2})	[4]
$CuCo_2O_4$ nanoparticle	Hydrothermal	1 M KOH	-	67	400 (10 mA cm^{-2})	[4]
$CuCo_2O_4$ Nanosheet	Electrodepositing	1 M KOH	240	64	260 (20 mA cm^{-2})	[5]
$CuCo_2O_4$ Nanosheet	Hydrothermal	1 M KOH	-	117	294 (20 mA cm^{-2})	[6]
$CuCo_2O_4$/NF	Hydrothermal	1 M KOH	-	50	296 (20 mA cm^{-2})	[7]
$CuCo_2O_4$	Hydrothermal	1 M KOH	-	64	360 (10 mA cm^{-2})	[8]
$CuCo_2O_4$/Nr GO	Hydrothermal	1 M KOH	-	101	460 (10 mA cm^{-2})	[9]
CuCo/NiFe -16	Hydrothermal	1 M KOH	230	31	251 (10 mA cm^{-2})	Present work

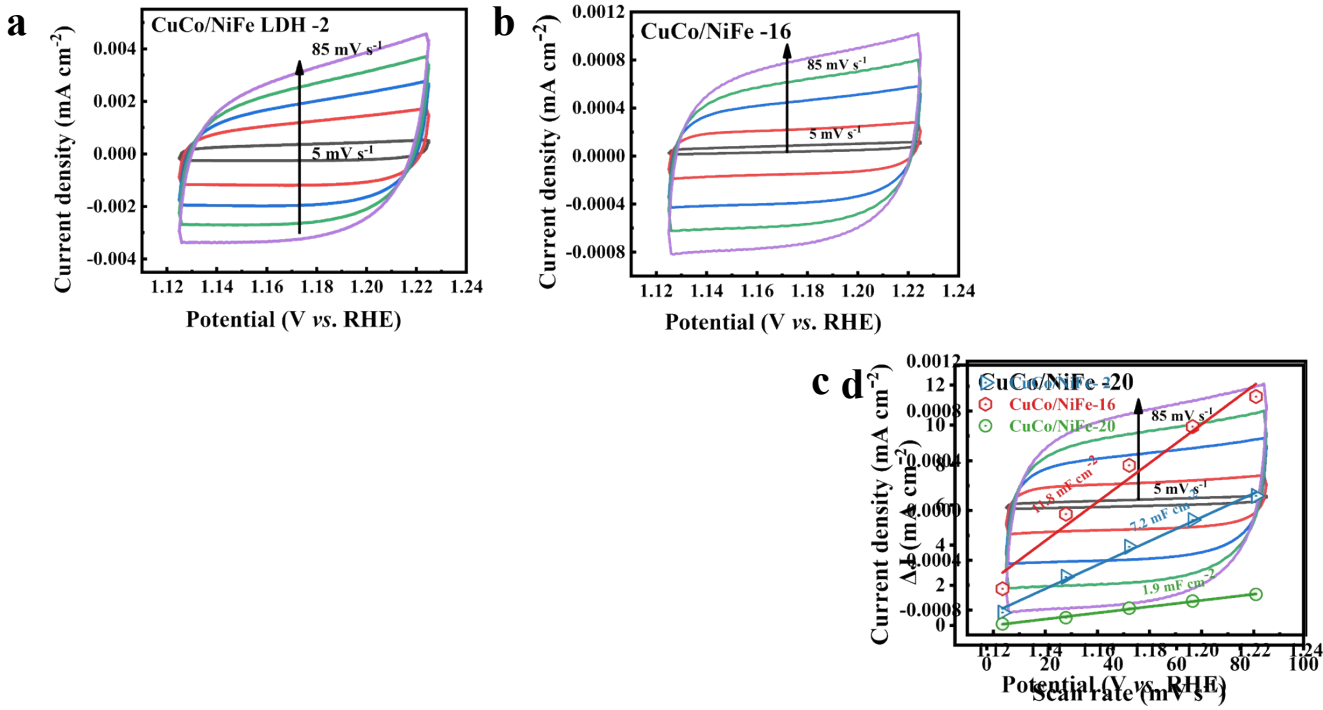

Fig. S2 (a-c) CV curves of CuCo/NiFe-2, CuCo/NiFe-16 and CuCo/NiFe-20 catalysts. (d) The corresponding double layer capacitance.

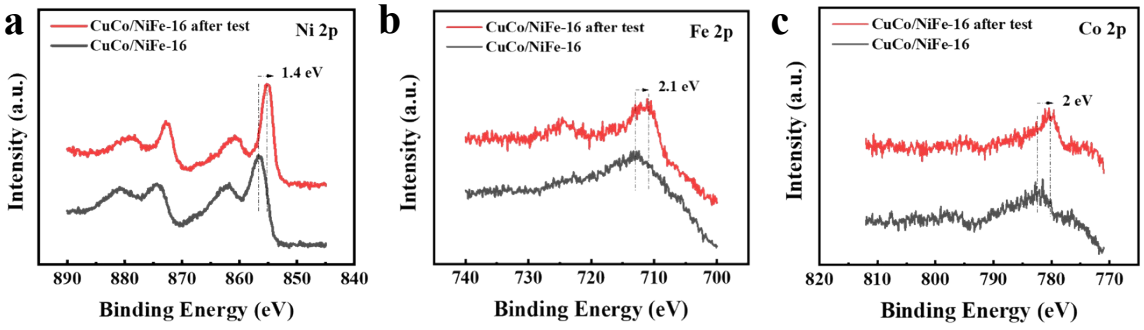

Fig. S3 XPS spectra of the CuCo/NiFe-16 after long time reaction (a) Ni 2p, (b) Fe 2p, (c) Co 2p.

After OER test, all $2p_{3/2}$ peak centers occur shift with various degree（Ni $2p_{3/2}$: ~1.4 eV; Fe $2p_{3/2}$: ~2.1 eV; Co $2p_{3/2}$: ~2 eV）(**Fig. S**3). The shifts after OER indicate that both Ni, Fe and Co ions probably participated in the OER process. According to the LSV curves (**Fig. 4**a), the catalysts firstly experience the oxidation process, where NiFe LDH and $CuCo_2O_4$ oxidized to NiFeOOH and CoOOH [10, 11], respectively, and then occur OER reaction. However, the obtained valence state of metal cation will recover after OER reaction due to the unstable high valence state. Moreover, the recovering of valences are not completely consistent with the valences before OER.

References

[1] M. Kuang, P. Han, Q. Wang, J. Li, G. Zheng, CuCo Hybrid Oxides as Bifunctional Electrocatalyst for Efficient Water Splitting, Adv. Funct. Mater. 26 (2016) 8555-8561.

[2] S.K. Bikkarolla, P. Papakonstantinou, $CuCo_2O_4$ nanoparticles on nitrogenated graphene as highly efficient oxygen evolution catalyst, J. Power Sources 281 (2015) 243-251.

[3]G. Wei, J. He, W. Zhang, X. Zhao, S. Qiu, C. An, Rational Design of Co(II) Dominant and Oxygen Vacancy Defective $CuCo_2O_4$@CQDs Hollow Spheres for Enhanced Overall Water Splitting and Supercapacitor Performance, Inorg. Chem. 57 (2018) 7380-7389.

[4] A. Karmakar, S.K. Srivastava, Interconnected Copper Cobaltite Nanochains as Efficient Electrocatalysts for Water Oxidation in Alkaline Medium, ACS. Appl. Mater. Interfaces 9 (2017) 22378-22387.

[5] S.M. Pawar, B.S. Pawar, P.T. Babar, A.T.A. Ahmed, H.S. Chavan, Y. Jo, S. Cho, J. Kim, B. Hou, A.I. Inamdar, S.N. Cha, J.H. Kim, T.G. Kim, H. Kim, H. Im, Nanoporous $CuCo_2O_4$ nanosheets as a highly efficient bifunctional electrode for supercapacitors and water oxidation catalysis, Appl. Surf. Sci. 470 (2019) 360-367.

[6] A.T.A. Ahmed, B. Hou, H.S. Chavan, Y. Jo, S. Cho, J. Kim, S.M. Pawar, S. Cha, A.I. Ina mdar, H. Kim, H. Im, Self-Assembled Nanostructured $CuCo_2O_4$ for Electrochemical Energy Storage and the Oxygen Evolution Reaction via Morphology Engineering, Small 14 (2018) 1800742.

[7] X. Q. Du, X. S. Zhang, Z. F. Xu, Z. Yang, Y. Q. Gong, $CuCo_2O_4$ microflowers catalyst with oxygen evolution activity comparable to that of noble metal, International Journal of Hydrogen Energy, 43 (10) (2018) 5012-5018.

[8] Y. K. Zhao, X. C. Zhou, Y. Ding, J. W. Huang, M. Zheng, W. C. Ye, A study of photocatalytic, chemical, and electrocatalytic water oxidation on ACo_2O_4 (A=Ni, Cu, Zn) samples through doping different metal ions, Journal of Catalysis, 338 (2016) 30-37.

[9] S. K. Bikkarolla and P. Papakonstantinou, $CuCo_2O_4$ nanoparticles on nitrogenated graphene as highly efficient oxygen evolution catalyst, Journal of Power Sources, 281 (2015) 243-251.

[10] S. H. Hsu, S. F. Hung, H. Y. Wang, F. X. Xiao, L. Zhang, H. Yang, H. M. Chen, J. M. Lee, B. Liu, Small Method, 2 (2018) 1800001.

[11] J. Zhang, J. Liu, L. Xi, Y. Yu, N. Chen, S. Sun, W. Wang, K. M. Lange, B. Zhang, J. Am. Chem. Soc., 140 (2018) 3876-3879.