Direct electrodeposition of NiFe-based high-entropy compound on nickel foam advanced electrocatalysts for oxygen evolution reaction

Yibin Yang,* Jitao Yang, Yiqin Duan, Xinghua Huang, Qichao Qu, Yuhao Zhang, Lijuan Dong, Zhihao Duan, Mingzhu Wu, Ying Li*

Chemical Pollution Control Chongqing Applied Technology Extension Center of Higher Vocational Colleges, Chongqing Industry Polytechnic University, Chongqing 401120, PR China

AUTHOR INFORMATION

Corresponding Author

Name: Yibin Yang, Ying Li

E-mail: yangyb@cqipu.edu.cn; yingli@cqipu.edu.cn

Notes

The authors declare no competing financial interest.

Methods：

When employing the exhaust gas collection method to measure oxygen production, dissolved gas in the electrolyte can introduce errors. Therefore, cyclic voltammetry (CV) is used to investigate the quantity of reacting species. In a CV curve, the total current density $i=i_c+i_f$ consists of both capacitive current (i_c) and faradaic current (i_f). Since the TOF calculation for the OER should reflect only the faradaic contribution, the capacitive current must be subtracted. Additionally, oxidation/reduction peaks from elements such as Ni and Fe should be excluded from the integration range to ensure that only the OER faradaic current is considered.

The capacitive current is proportional to the scan rate: $i_c=C_{dl}\cdot v$.
The faradaic reaction rate can be expressed as: $r=i_f/(nF)$, where n=4 for the OER.

Given that the OER occurs exclusively on the catalyst surface, the number of active surface sites must be estimated. This is achieved by determining the relative electrochemically active surface area (ECSA):

$$\mathrm{ECSA}=C_{dl}/C_s$$

Where C_s is the specific capacitance, typically taken as 40 μF cm^{-2} for a flat metal oxide surface.

Assuming all surface metal atoms are active sites, and using an approximate surface metal atom density $\rho=1.5\times10^{15}$ atoms cm^{-2}, the number of active sites is:

$$N_{\mathrm{sites}}=\rho\times\mathrm{ECSA}$$

Finally, the turnover frequency (TOF) is calculated as:

$$\mathrm{TOF}=i_J\times N_A/(n\times F\times N_{\mathrm{sites}})$$

where N_A is Avogadro's number and F is the Faraday constant.

In summary, the TOF calculation follows this rationale: first, isolate the OER faradaic current by subtracting both capacitive and non-OER faradaic contributions; second, estimate the number of surface active sites using ECSA and an assumed surface atom density; and finally, normalize the reaction rate to the number of active sites to obtain the TOF.

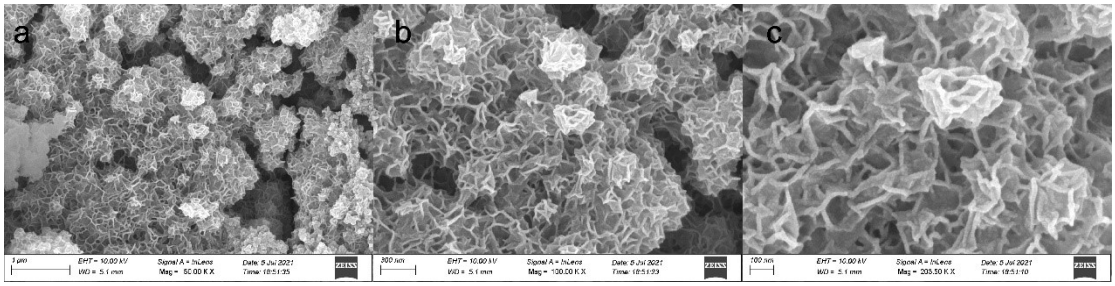

Figure S1. Scanning electron microscopy (SEM) images of the NiFe-2:1 electrocatalyst taken at different magnifications.

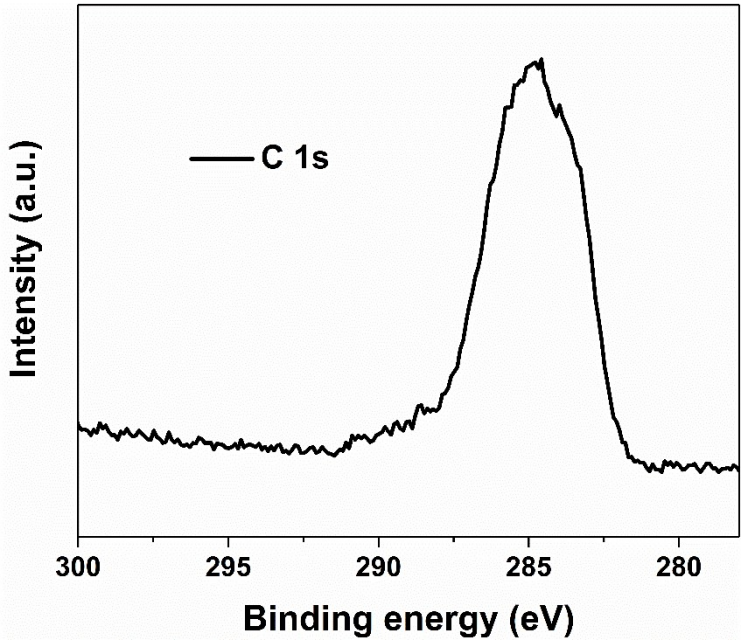

Figure S2. High-resolution XPS C 1s spectrum.

Table S1 Comparison of catalytic performance of Mn doped CoFe LDH to recently reported high performance metal oxide/hydroxide OER catalysts.

Elecatrocatalysts	electrolyte	j ($mA\ cm^{-2}$)	η (mV)	Tafel slope ($mV\ dec^{-1}$)	Ref.
NiFe-2:1 hydroxides@NF	1.0 M KOH	10	232	56.70	This work
$Co_3Fe_{1.5}$-LDH/NF	1.0 M KOH	10	284	45	1
$SrCo_{0.4}Fe_{0.2}W_{0.4}O_{3-\delta}$	1.0 M KOH	10	300	-	2
CoFe-LDH/rGO	0.1 M KOH	10	325	-	3
$LaFe_xNi_{1-x}O_3$	1.0 KOH	10	302	53	4
$NdFe_{1-x}Ni_xO_3$	1.0 KOH	10	310	76	5
$La_{1-x}Pr_xCoO_3$	1.0 M KOH	10	312	50	6
Ni_6Fe_2W LDH/CP	1.0 KOH	10	264	44.5	7
D-$IrTe_2$ HNSs	0.5 M H_2SO_4	10	298	-	8
6H-$SrIrO_3$	0.5 M H_2SO_4	10	248	-	9
$Fe_{0.33}Co_{0.67}OOH$ PNSAs/CFC	0.1 M KOH	10	266	30	10
RuNiFe LDHs	1 M KOH	10	246	67.2	11

Table S2 Equivalent circuit fitting parameters for the EIS data of the electrocatalysts

electrocatalysts	Rs	Rct	CPE-T	CPE-P	χ^2
NiFe-3:1	1.708	0.3144	0.2786	0.8382	0.022037
NiFe-2:1	1.843	0.2942	0.2283	0.0188	0.025288
NiFe-1:1	1.668	0.3085	0.24320	0.8282	0.000708
NiFe-1:2	1.809	0.3468	0.2150	0.8413	0.024436
NiFe-1:3	2.218	0.4213	0.1313	0.8270	0.027471

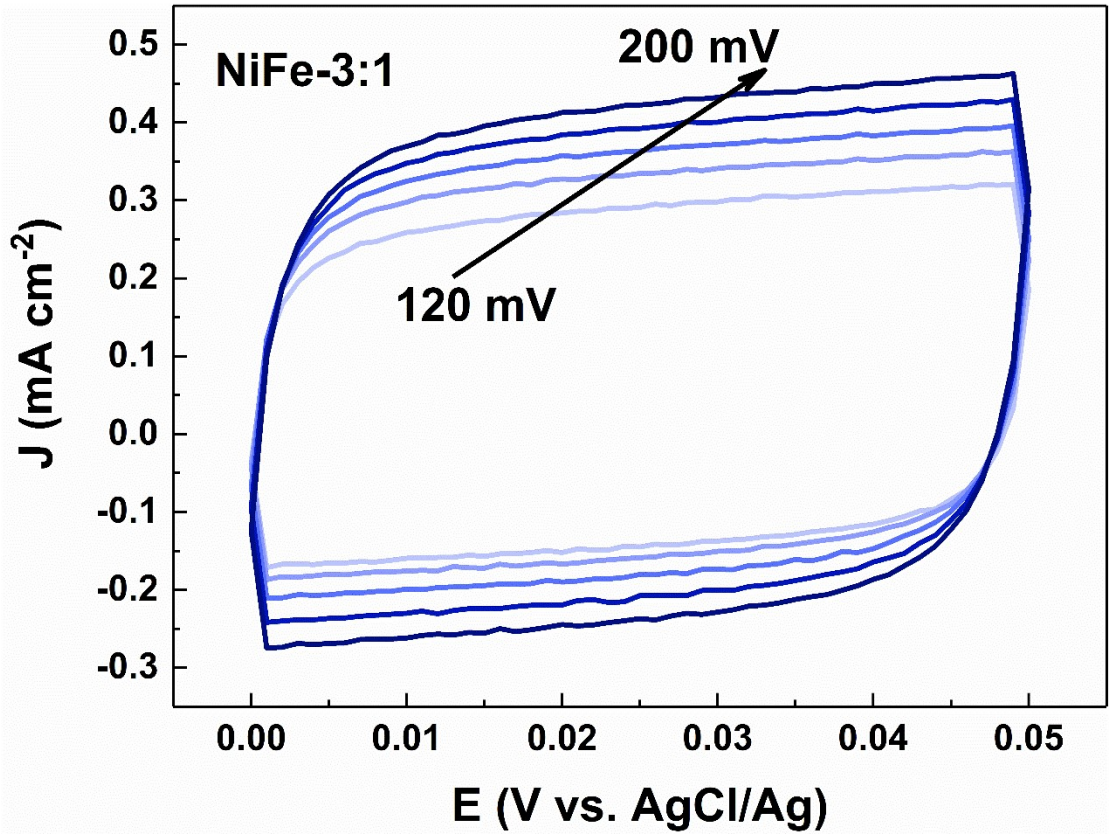

Figure S3. CV curves of different samples at various scan rate of NiFe-3:1.

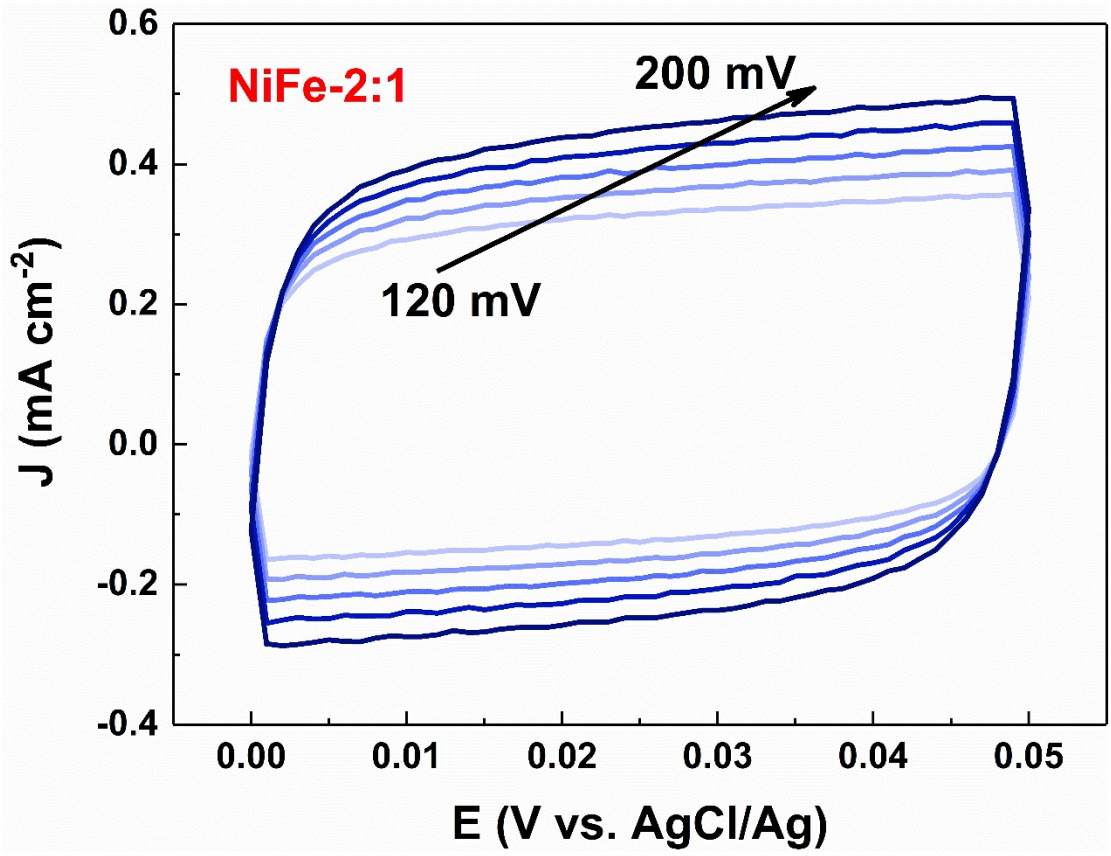

Figure S4. CV curves of different samples at various scan rate of NiFe-2:1.

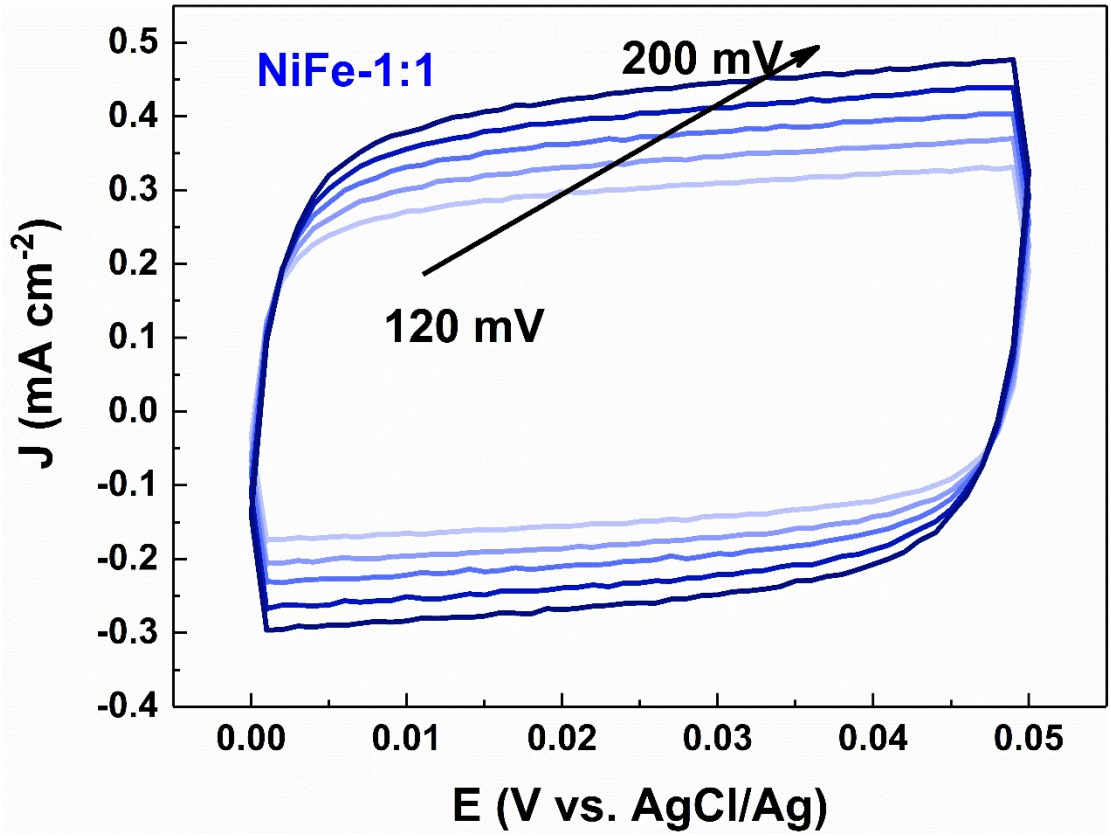

Figure S5. CV curves of different samples at various scan rate of NiFe-1:1.

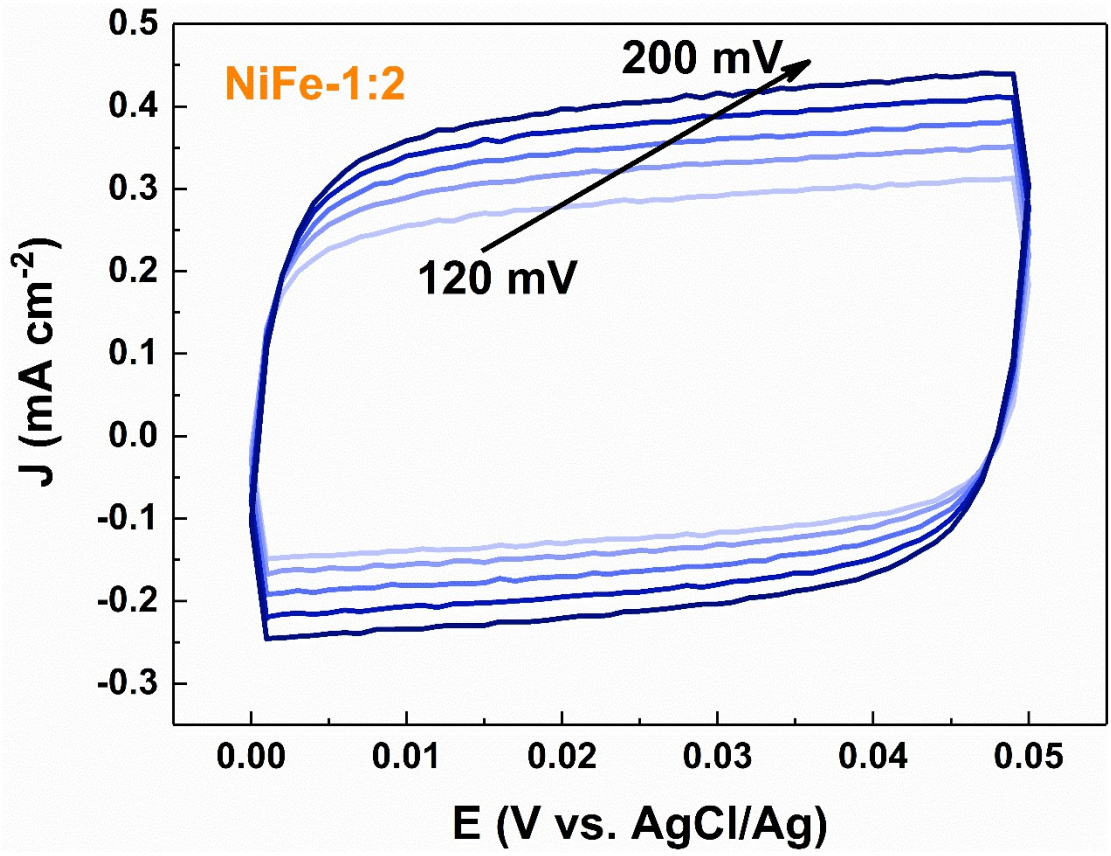

Figure S6. CV curves of different samples at various scan rate of NiFe-1:2.

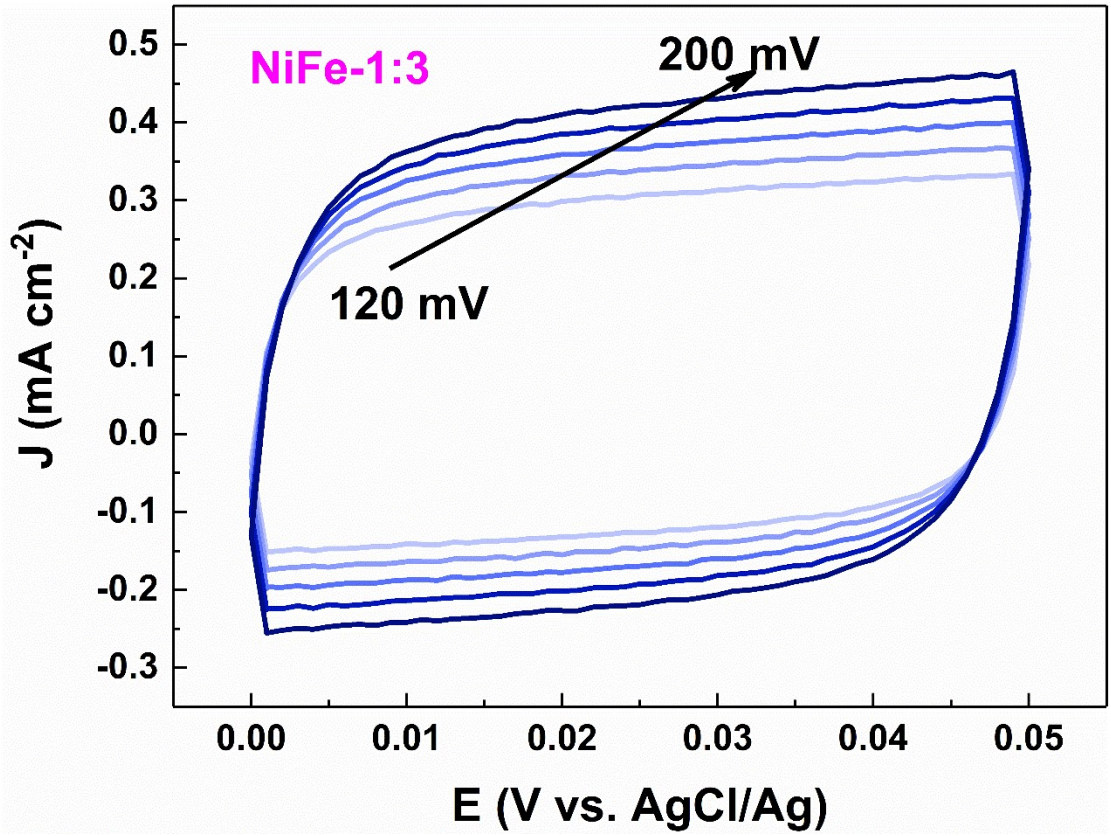

Figure S7. CV curves of different samples at various scan rate of NiFe-1:3.

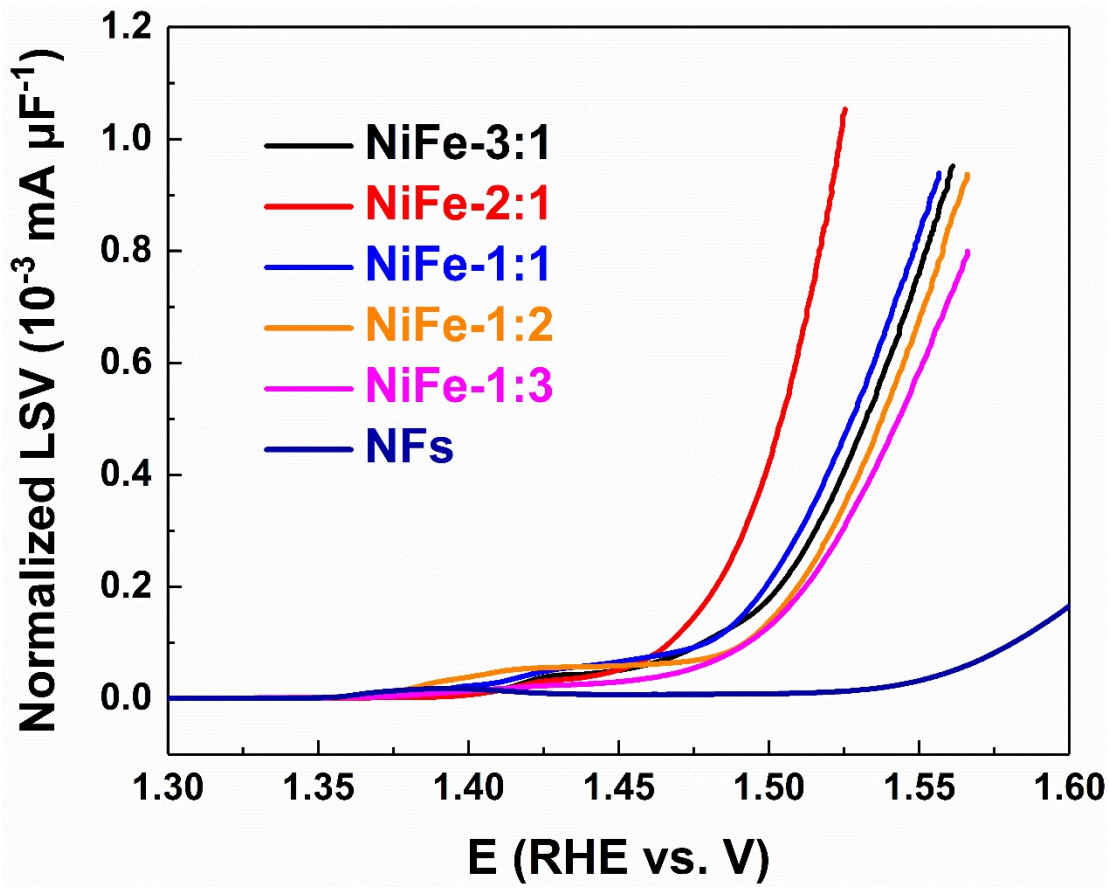

Figure S8 C_{dl} normalized LSV curves of NiFe-3:1, NiFe-2:1, NiFe-1:1, NiFe-1:2 NiFe-1:3 and NFs.

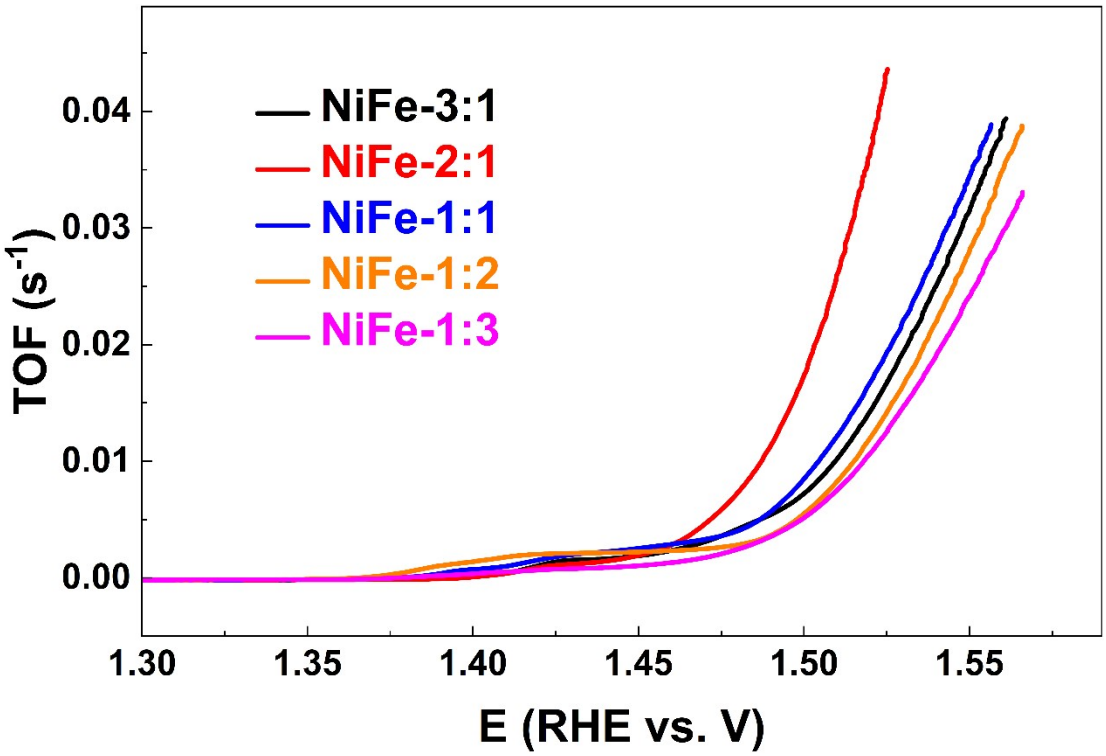

Figure S9 TOF curves of NiFe-3:1, NiFe-2:1, NiFe-1:1 and NiFe-1:2 NiFe-1:3, respectively.

References:

1. Han, L.; Dong, C.; Zhang, C.; Gao, Y.; Zhang, J.; Gao, H.; Wang, Y.; Zhang, Z., Dealloying-directed synthesis of efficient mesoporous CoFe-based catalysts towards the oxygen evolution reaction and overall water splitting. *Nanoscale* **2017,** *9*, 16467-16475.
2. G. Chen, Z. Hu, Y. Zhu, Z.-G. Chen, Y. Zhong, H.-J. Lin, C.-T. Chen, L. H. Tjeng, W. Zhou, Z. Shao. Ultrahigh-performance tungsten-doped perovskites for the oxygen evolution reaction. *J. Mater. Chem. A* **2018**, 6, 9854-9859.
3. Han, X.; Yu, C.; Yang, J.; Zhao, C.; Huang, H.; Liu, Z.; Ajayan, P. M.; Qiu, J., Mass and charge transfer coenhanced oxygen evolution behaviors in CoFe-layered double hydroxide assembled on graphene. *Adv. Mater. Inter.* **2016,** *3,* 1500782.
4. Wang, H.; Wang, J.; Pi, Y.; Shao, Q.; Tan, Y.; Huang, X. Double Perovskite LaFexNi1-xO3 Nanorods Enable Efficient Oxygen Evolution Electrocatalysis. *Angew. Chem. Int. Ed.* **2019**, *58* (8), 2316-2320.
5. Khreif, Y.; Omari, M.; Makhloufi, S. Synthesis and catalytic properties of Ni-doped NdFeO3. *Inorg. Chim. Acta* **2024**, *566*.
6. Xie, R.; Nie, Z.; Hu, X.; Yu, Y.; Aruta, C.; Yang, N. Pr-Doped LaCoO3 toward Stable and Efficient Oxygen Evolution Reaction. *ACS Appl. Energy Mater.* **2021**, *4* (9), 9057-9065.
7. Xu, J.; Wang, M.; Yang, F.; Ju, X.; Jia, X., Self-supported porous Ni-Fe-W hydroxide nanosheets on carbon fiber: a highly efficient electrode for oxygen evolution reaction. *Inorg. Chem.,* **2019,** *58*, 13037-13048.
8. Y. Pi, Y. Xu, L. Li, T. Sun, B. Huang, L. Bu, Y. Ma, Z. Hu, C. W. Pao, X. Huang, Adv. Funct. Mater. 2020, 30, 2004375.
9. L. Yang, G. Yu, X. Ai, W. Yan, H. Duan, W. Chen, X. Li, T. Wang, C. Zhang, X. Huang, J. S. Chen, X. Zou, Nat. Commun. 2018, 9, 5236.
10. Ye, S.-H.; Shi, Z.-X.; Feng, J.-X.; Tong, Y.-X.; Li, G.-R., Activating CoOOH porous nanosheet arrays by partial iron substitution for efficient oxygen evolution reaction. *Angew. Chem. Int. Ed.* **2018,** *57* (10), 2672-2676.
11. Yang, Yang, Wang, Wen-Jie, Yang, Yi-Bin, Guo, Peng-Fei, Zhu, Bing. Wang, Kuan, Wang, Wei-Tao, He, Zhen-Hong, Liu, Zhao-Tie, Ru-doped NiFe layered double hydroxide as a highly active electrocatalyst for oxygen evolution reaction. J. Electrochem. Soc. 2022, 2, 024503.