Supporting information

Mn-Incorporated High-Entropy Quaternary Sulfide CoNiFeMnS for Efficient Electrocatalytic Oxygen Evolution Reaction

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Microstructural Characterization

Scanning electron microscope (SEM, Zeiss Ultra Plus, Zeiss, Germany) and transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) are used to characterize the morphology and structure of electrocatalyst. And the dispersion of elements was confirmed by dispersive X-ray spectroscope (EDS) maps equipped in the SEM. The X-ray photoelectron spectroscope (XPS, ESCALAB 250 Xi X-ray, Thermo Fisher Scientific, America) was used to characterize the elemental chemical state of the sample. The crystallinity and purity of the material is assessed by X-ray diffractometer (XRD, Ultra IV, Rigaku, Japan). The fourier transform infrared (FT-IR, Nexus670, Nicolet, America) spectrometer measurements to complete the chemical composition of substances analyzation. The nitrogen adsorption-desorption isotherms use the typical Brunauer-Emmett-Teller (BET) measurement and the pore distribution curves were collected through an SSA-7000 analyzer.

Electrochemical measurements

All the electrochemical measurements were carried out in 1 M KOH solution at room temperature using CHI 660E electrochemical workstation. Glassy carbon electrode (5 mm in diameter) coated with catalysts was used as working electrode. Graphite rod and Ag/AgCl electrode were used as counter electrode (CE) and reference electrode (RE), respectively. The catalyst ink was prepared by dispersing 5 mg of catalyst into the mixture solution of 240 μl H_2O, 240 μl isopropyl alcohol, 20 μl 5% nafion solution. The loading of catalyst is 0.4 mg cm^{-2}.

The linear scanning voltammetry (LSV) curves were recorded at a scan rate of 10

mV s^{-1} with 80% iR-compensation. Cyclic voltammetry (CV) curves were measured in non-Faradic region at different scan rates of 20, 40, 60, 80, and 100 mV s^{-1}, respectively. Electrochemical impedance spectroscopy (EIS) was obtained with an amplitude of 500 mV in the frequency range of 100 kHz to 0.1 Hz. A chronoamperometric test was conducted at the current density of 10 mA cm^{-2} to evaluate the stability. All measured potentials were converted relative to the reversible hydrogen electrode (RHE) according to the following equation:

$$E(RHE) = E(Ag/AgCl) + 0.059 * pH + 0.097\ V \quad (1)$$

Besides, the overpotential (η) was obtained by the following formula:

$$\eta = E(RHE) - 1.23\ V \quad (2)$$

The OER process in alkaline solution involves four steps as described in Equations (1)-(4). The first step is adsorption of OH^- on active site leading to generation of *OH, followed by adsorption of OH^- onto *OH and dissociation into *O intermediate and H_2O. Then, adsorption of OH^- onto *O results in the generation of *OOH, and the adsorption of OH^- onto *OOH results their dissociation into H_2O and O_2.

$$OH^- + * \rightarrow *OH + e^- \quad (3)$$

$$*OH + OH^- \rightarrow *O + H_2O + e^- \quad (4)$$

$$*O + OH^- \rightarrow *OOH + e^- \quad (5)$$

$$*OOH + OH^- \rightarrow * + O_2 + H_2O + e^- \quad (6)$$

High-entropy materials (HEMs) should contain near-equimolar ratios of five or more metals. The ideal configurational entropy (S_{conf}) of an HEM can be approximated as:

$$S_{conf} \approx -R\sum x_i \ln(x_i) \quad (7)$$

where x_i is the mole fraction of each metal relative to the total metal content and R is the ideal gas constant, and one definition of an HEM is a material in which $S_{conf} \geq 1.5R$[1-2]. MOFs contain large numbers of nonmetal atoms and there are therefore inherent shortcomings in the application of Equation 7 to HEMOF and HES; however, considering the S_{conf} based on metal composition alone was deemed sufficient for comparison between different HEMOFs in the context of this work.

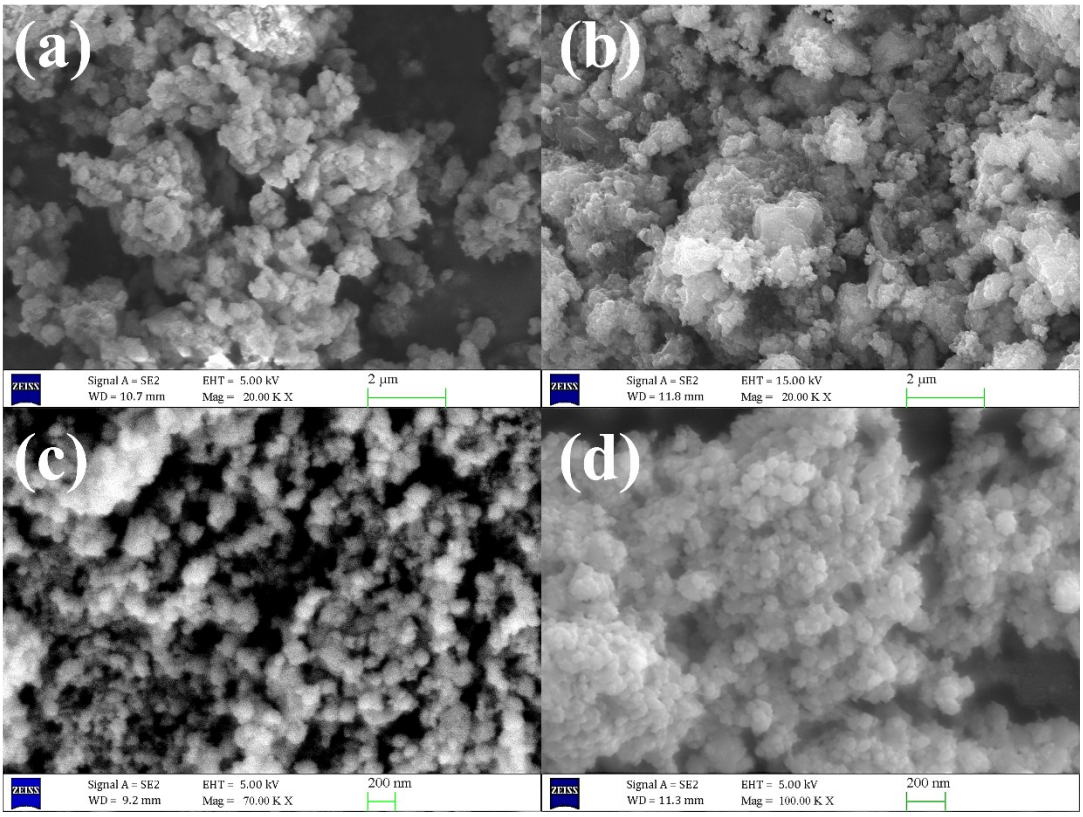


Figure S1. The SEM images of (a) CoS, (b)CoFeS, (c) CoNiFeS, and (d) CoNiFeMnS electrocatalysts.

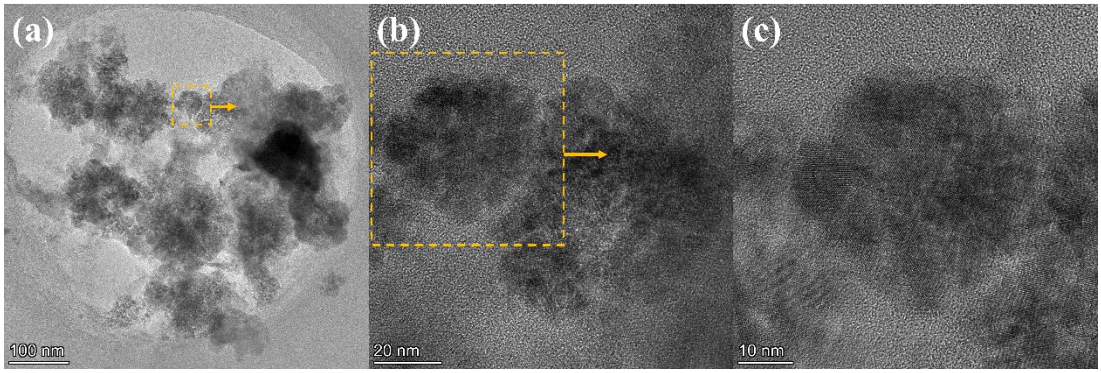


Figure S2. TEM and HRTEM images of CoNiFeMnS electrocatalysts.

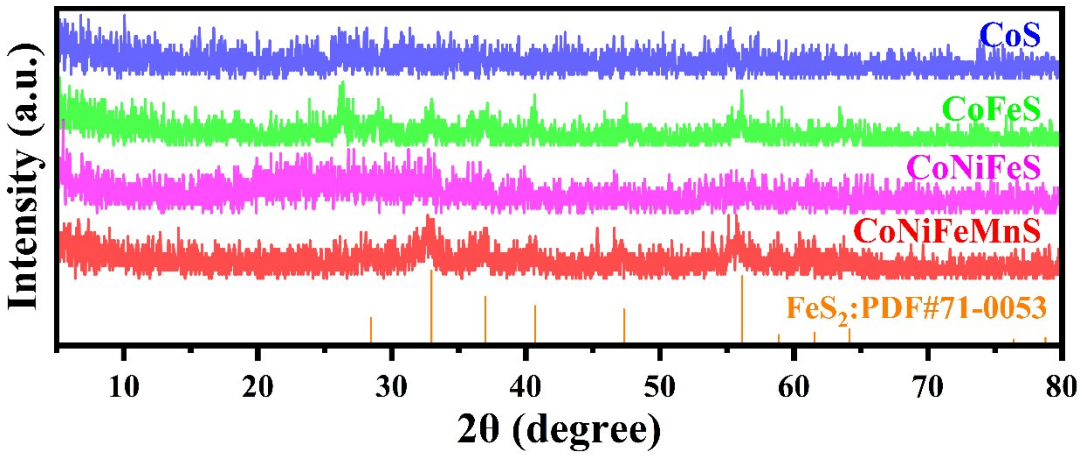


Figure S3. The XRD patterns of (a) CoS, (b) CoFeS, (c) CoNiFeS, (d) CoNiFeMnS electrocatalysts.

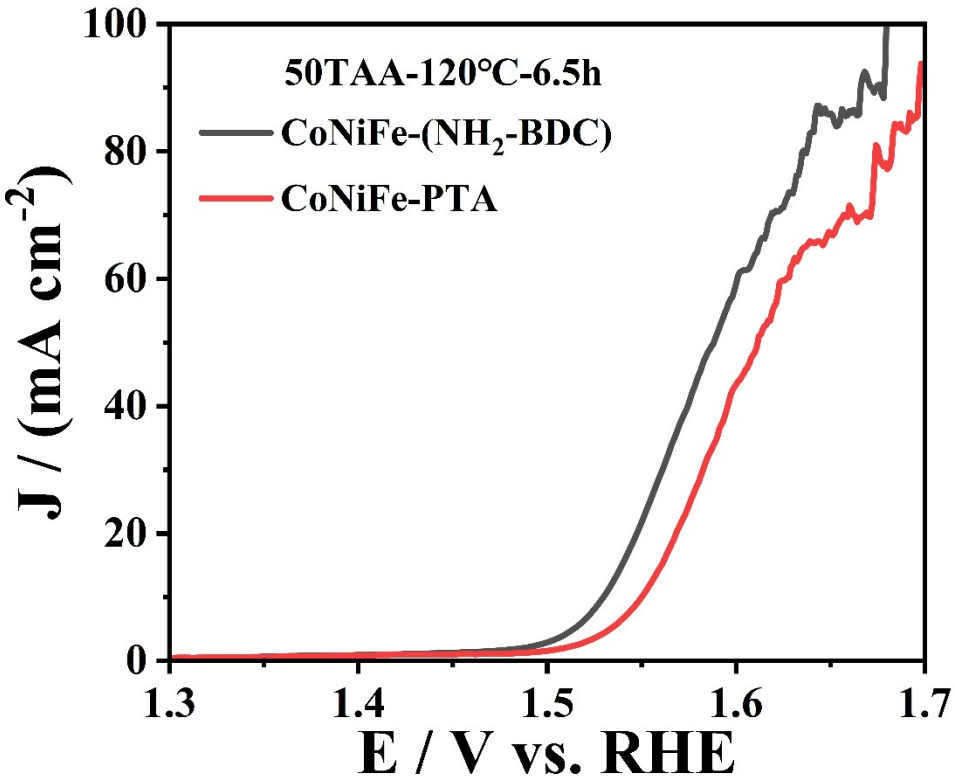


Figure S4. LSV performing comparation of different ligands in CoNiFe combination.

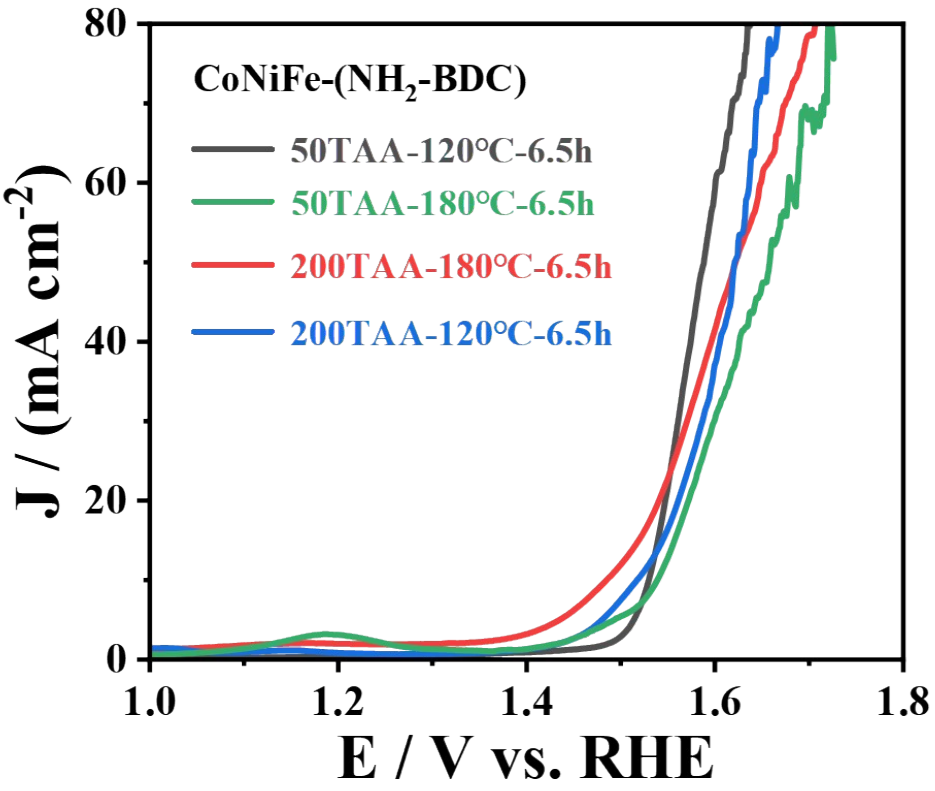


Figure S5. LSV performing comparation of different temperature reaction and TAA amount in the combination of CoNiFe with NH_2-BDC ligand.

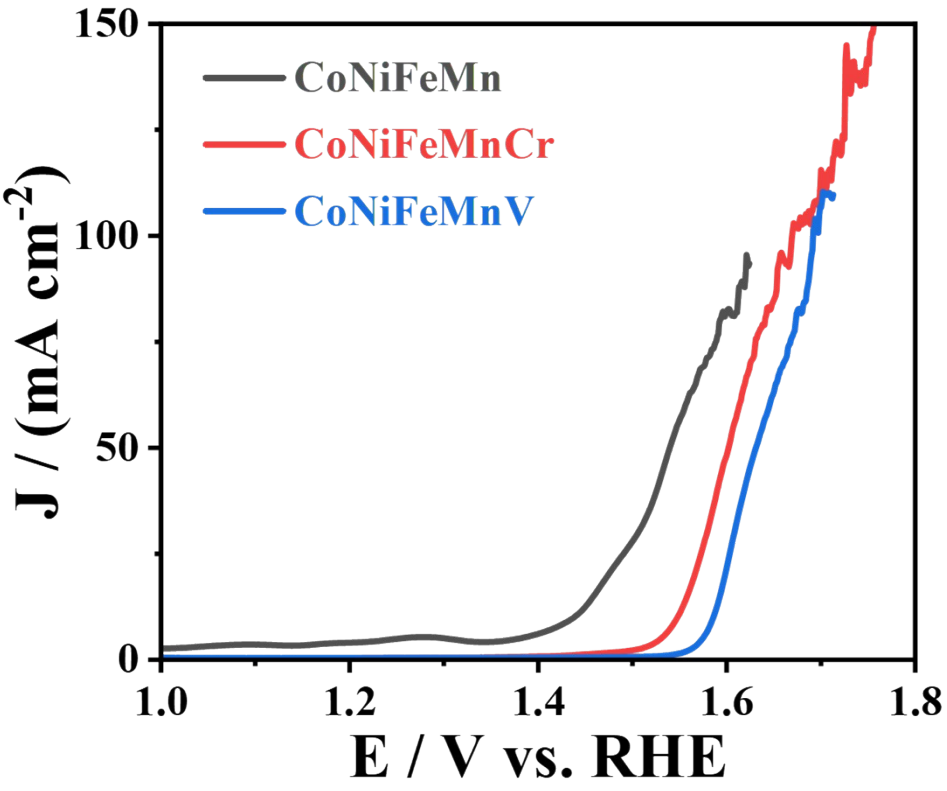


Figure S6. LSV performing comparation of different CoNiFeMnX combination.

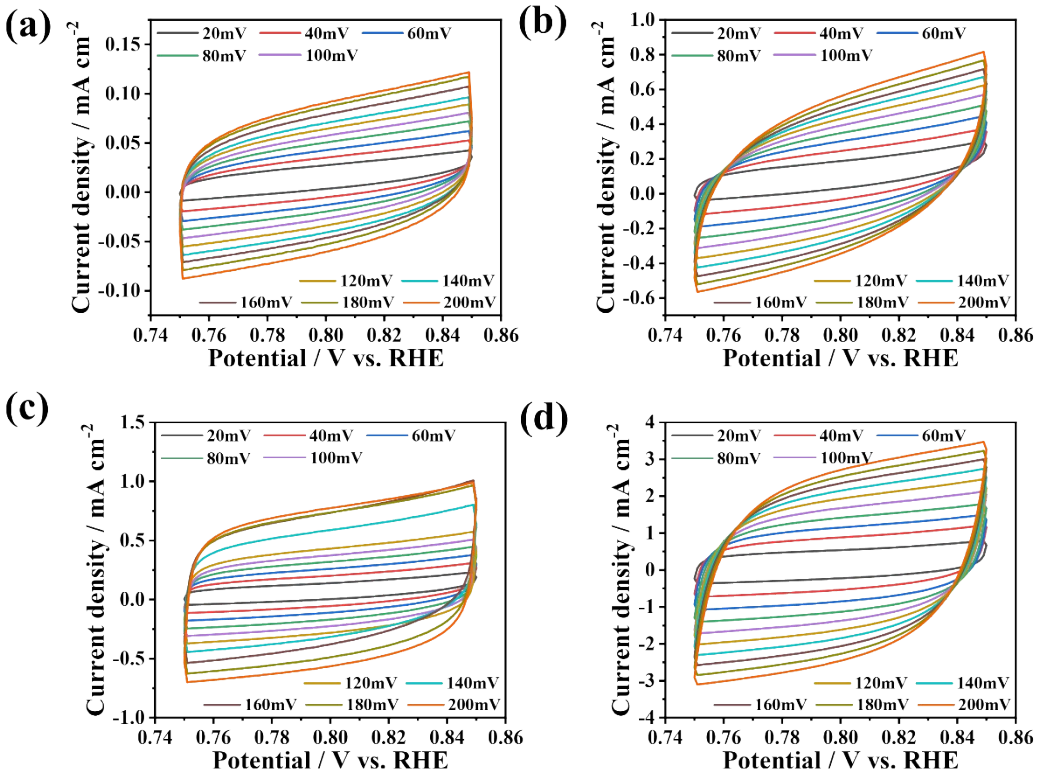


Figure S7. Stability performance at 10 mA cm^{-2} current density of (a) Ni-MOF, (b) NiCo-MOF, (c) NiFe-MOF, (d) NiCoFe-MOF electrocatalysts.

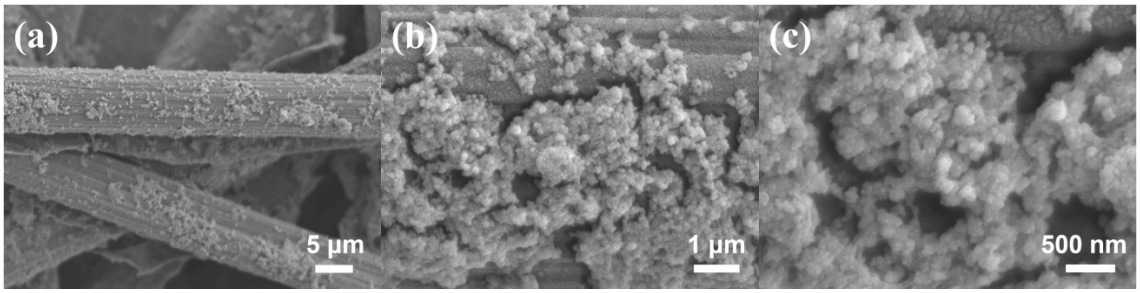


Figure S8. (a-c) The SEM images in different magnification of the CoNiFeMnS after long-term test.

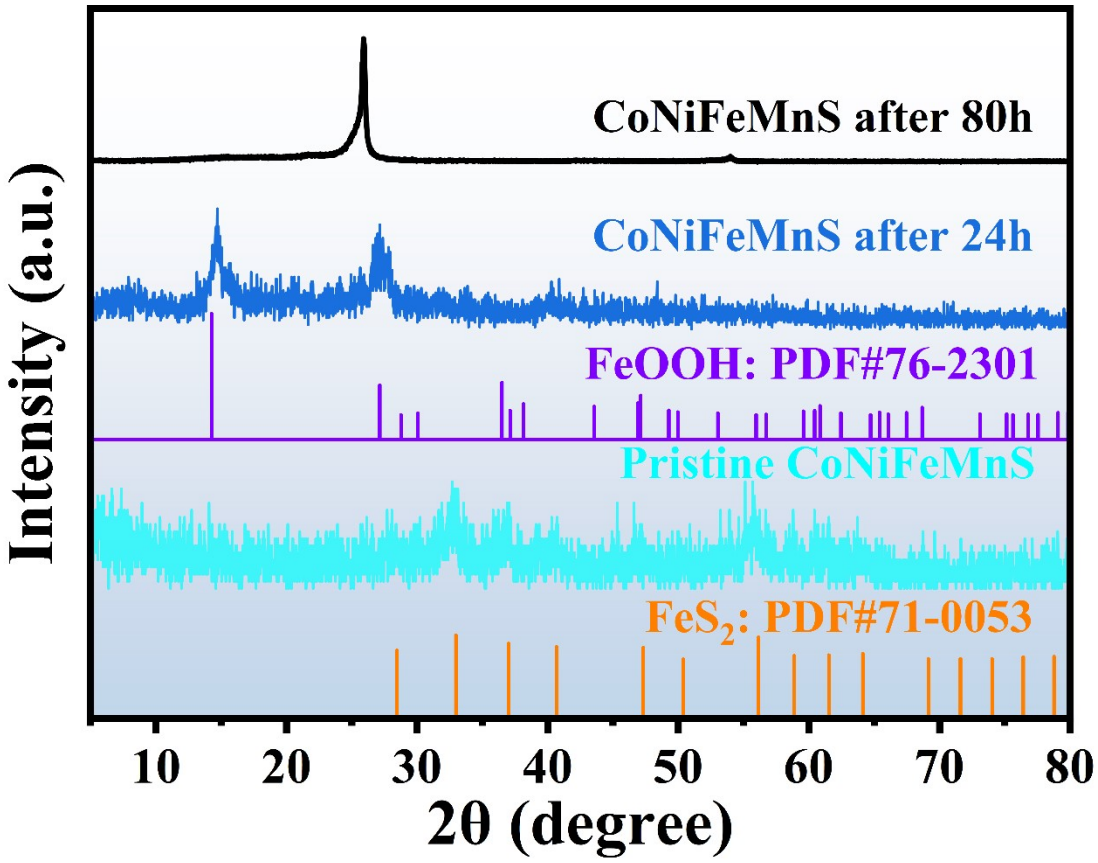
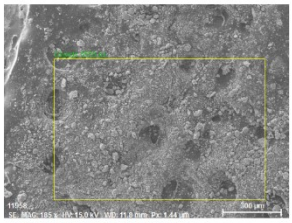


Figure S9. The XRD pattern of CoNiFeMnS pristine, after 24 and 80 hours OER.

Application Note
Company / Department



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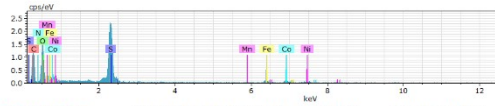

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El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	41.81	37.63	52.33	8.82
O	8	K-series	33.02	29.73	31.03	6.63
S	16	K-series	15.08	13.57	7.07	0.64
Ni	28	K-series	5.61	5.05	1.44	0.53
Co	27	K-series	5.58	5.02	1.42	0.49
N	7	K-series	4.99	4.50	5.36	2.63
Fe	26	K-series	4.15	3.74	1.12	0.36
Mn	25	K-series	0.84	0.76	0.23	0.15
		Total:	111.09	100.00	100.00	

Spectrum: Objects 6556.xls

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	41.81	37.63	52.33	8.82
O	8	K-series	33.02	29.73	31.03	6.63
S	16	K-series	15.08	13.57	7.07	0.64
Ni	28	K-series	5.61	5.05	1.44	0.53
Co	27	K-series	5.58	5.02	1.42	0.49
N	7	K-series	4.99	4.50	5.36	2.63
Fe	26	K-series	4.15	3.74	1.12	0.36
Mn	25	K-series	0.84	0.76	0.23	0.15
		Total:	111.09	100.00	100.00	

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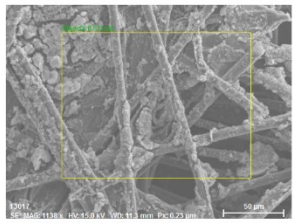

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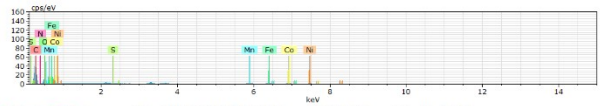

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El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	55.14	56.02	70.84	6.38
O	8	K-series	22.02	22.37	21.23	2.87
Ni	28	K-series	4.96	5.04	1.30	0.21
Co	27	K-series	4.94	5.02	1.29	0.20
Mn	25	K-series	4.78	4.86	1.34	0.18
Fe	26	K-series	3.60	3.66	0.99	0.15
N	7	K-series	2.49	2.53	2.75	0.64
S	16	K-series	0.50	0.51	0.24	0.05
		Total:	98.43	100.00	100.00	

Spectrum: Objects 6731.xls

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	55.14	56.02	70.84	6.38
O	8	K-series	22.02	22.37	21.23	2.87
Ni	28	K-series	4.96	5.04	1.30	0.21
Co	27	K-series	4.94	5.02	1.29	0.20
Mn	25	K-series	4.78	4.86	1.34	0.18
Fe	26	K-series	3.60	3.66	0.99	0.15
N	7	K-series	2.49	2.53	2.75	0.64
S	16	K-series	0.50	0.51	0.24	0.05
		Total:	98.43	100.00	100.00	

7/25/2018

Figure S10. Pristine and post-OER EDS Elemental Mapping of CoNiFeMnS

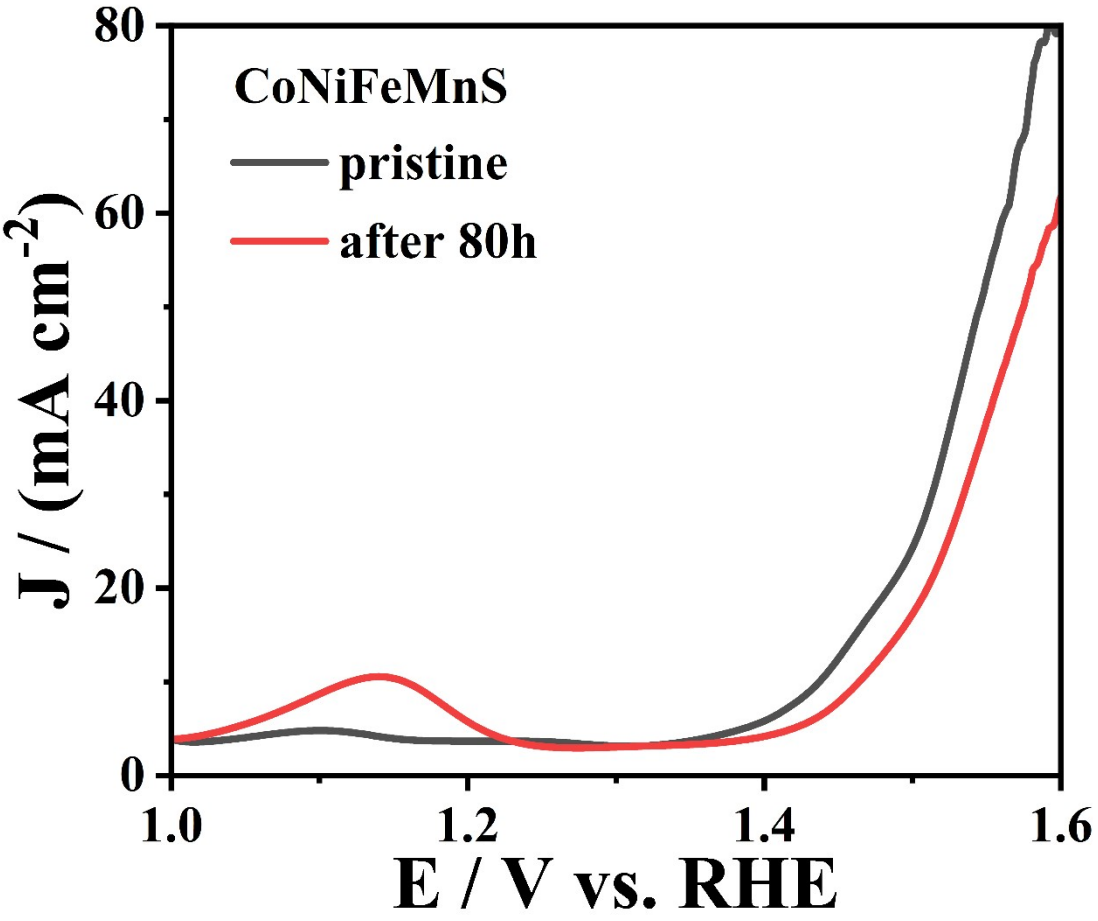

Figure S11. The LSV pattern of CoNiFeMnS pristine and after 80h OER.

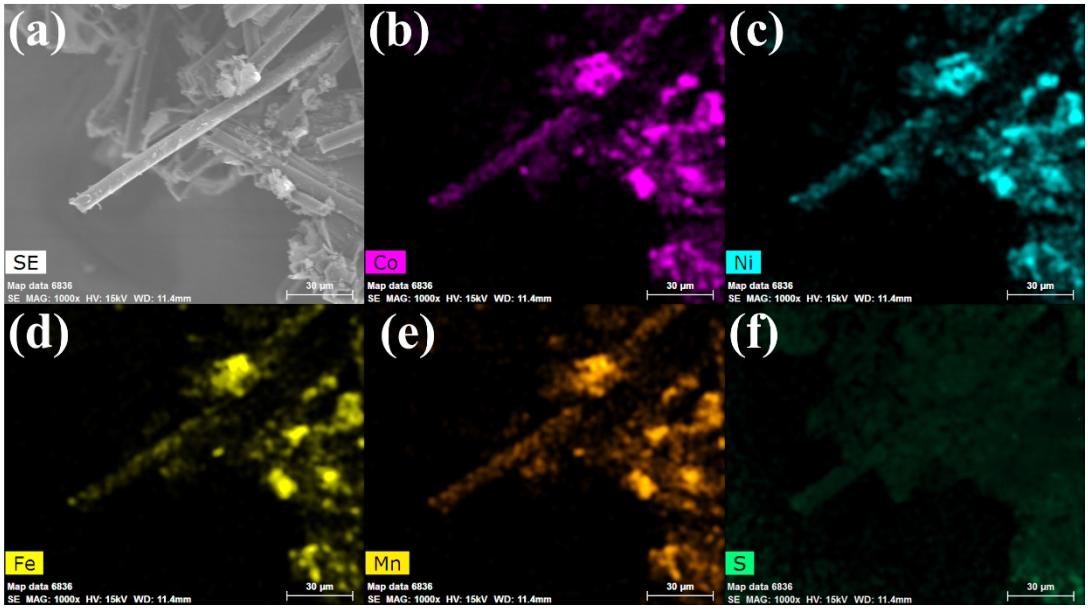

Figure S12. EDS elemental mapping of CoNiFeMnS after 80 h OER test at 10 mA cm^{-2}: (a) SEM image, (b) Co, (c) Ni, (d) Fe, (e) Mn, (f) S.

The metal elements maintain uniform distribution, and the sulfur element only shows an extremely weak diffuse signal close to the background.

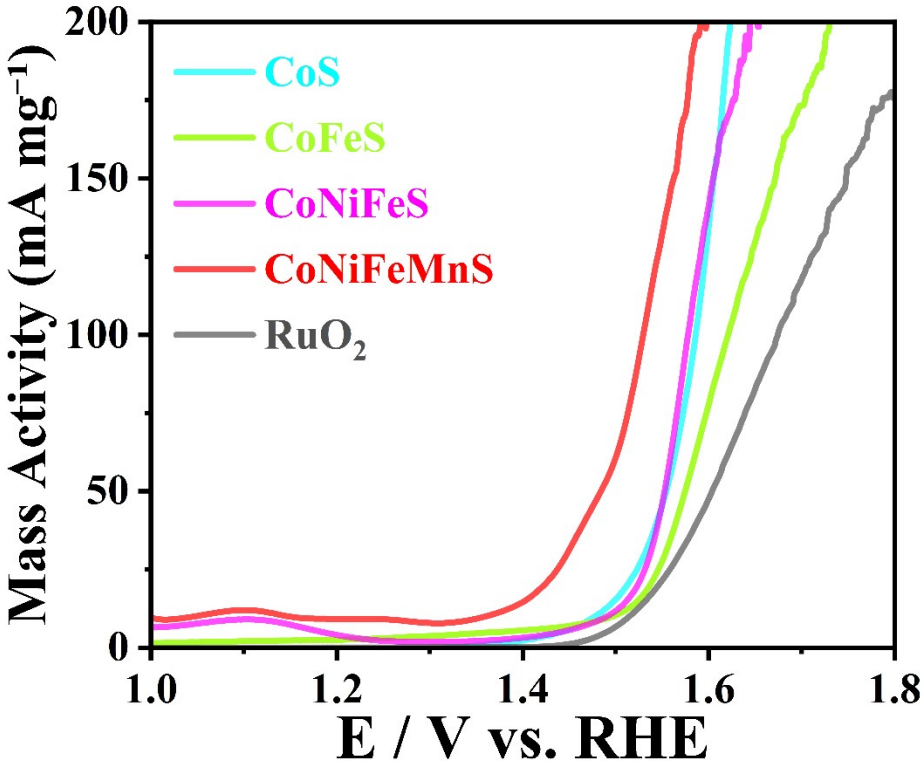

Figure S13. Mass Activity pattern of electrocatalysts for OER.

Table S1. The overpotentials(η_{10}) of OER@10 mA cm^{-2} compared and reported of similar catalysts which conduct in 1.0 M KOH solutions.

Catalyst	Tafel slope for OER (mV dec^{-1})	η_{10} for OER (mV vs RHE)	Reference
CoNiFeMnS	65.19	208	This work
(MgMnFeCoNi)Sx	56.2	270	[3]
(FeCoNiCrCuAl)S@La-HCS	51.75	246	[4]
(FeCoNiCrCuAl)S@HCS	61.51	253	[5]
HES-1	85	313	[6]
CoZnCdCuMnS@CF	69.8	220	[7]
Ru-HES	75	266	[8]
(NiCoFe-2)MoO4	62.4	264	[9]
NiCoFeCuS	57.97	264	[10]

Table S2. Atomic ratio content of pristine CoNiFeMnS elements in XPS results.

element	Atomic %
C 1s	38.59
Co 2p	7.87
Fe 2p	7.2
Mn 2p	7.89
Ni 2p	3.82
S 2p	34.64

Atomic ratio content of pristine CoNiFeS elements in XPS results.

element	Atomic %
C 1s	40.81
Co 2p	9.67
Fe 2p	7.71
Ni 2p	9.75
S 2p	32.06

Table S3. CoNiFeMnS pristine and post 80h OER in EDS results.

Element	Atomic % (Pristine CoNiFeMnS)	Atomic % (Post-80h OER CoNiFeMnS)
C	52.33	70.84
O	31.03	21.23
N	5.36	2.75
Co	1.42	1.29
Ni	1.44	1.30
Fe	1.12	0.99
Mn	0.23	1.34
S	7.07	0.24

Reference

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