

## Supplementary Material

# Three factors make bulk high-entropy alloys as effective electrocatalysts for oxygen evolution

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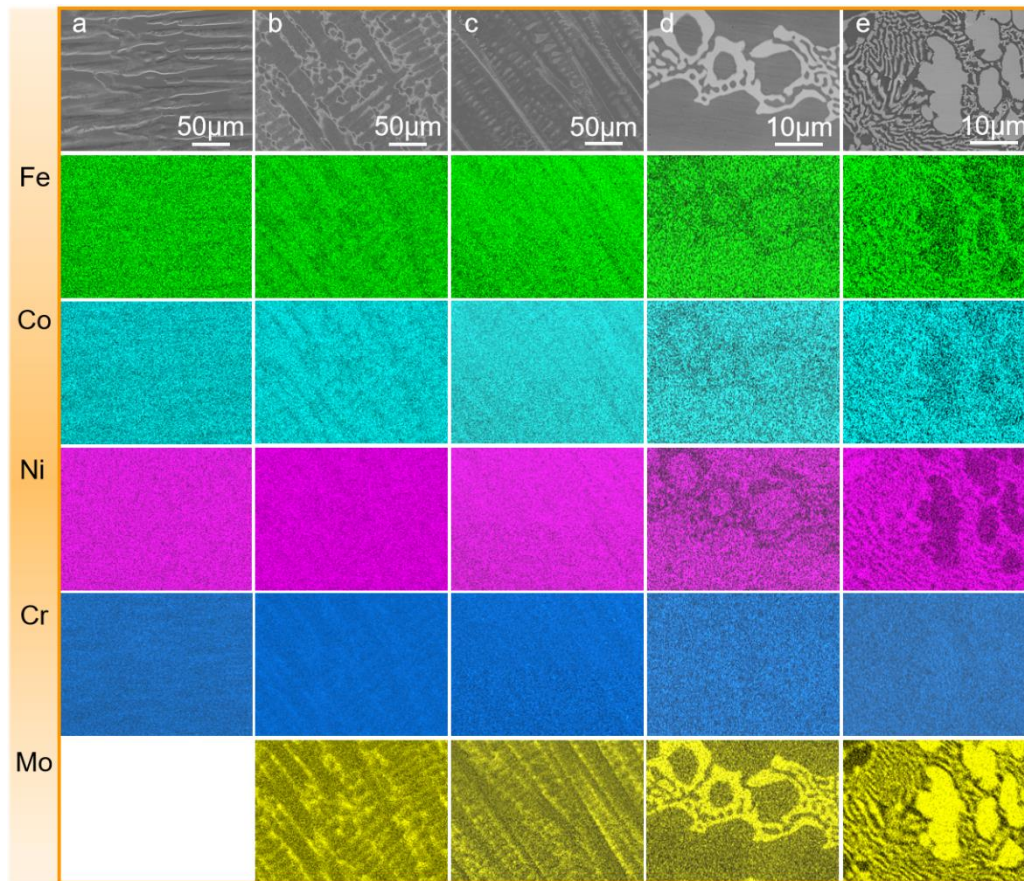
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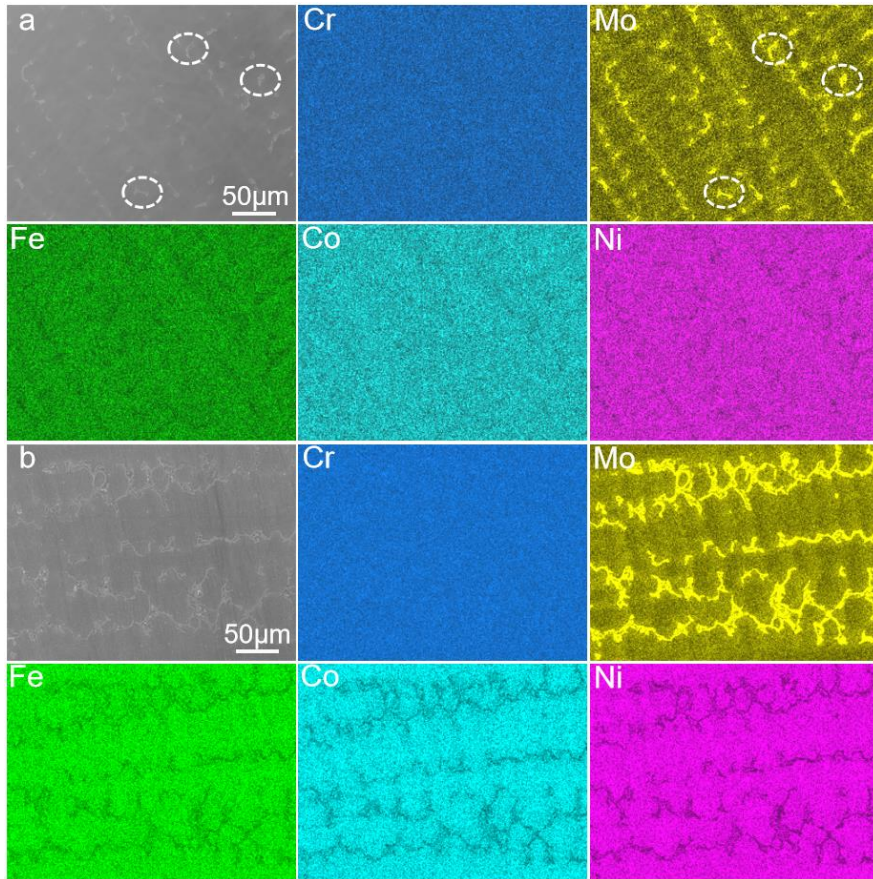
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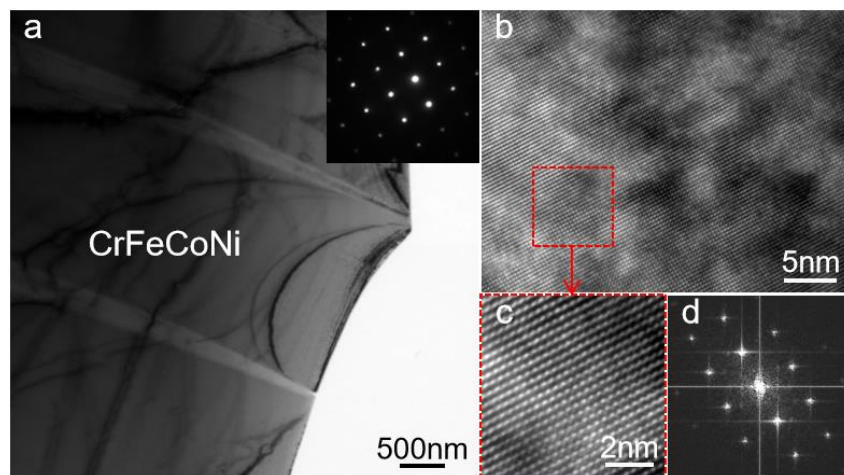
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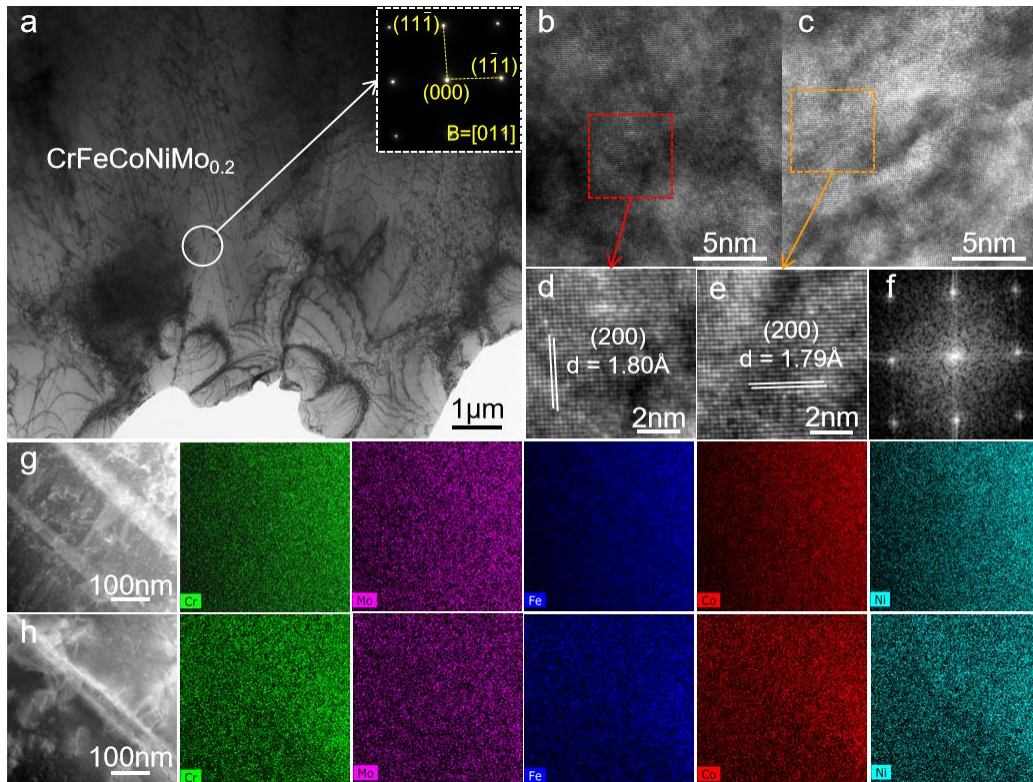
**Figure S1.** SEM images (top panel) and EDS elemental mapping. (a) CrFeCoNi; (b) CrFeCoNiMo<sub>0.1</sub>; (c) CrFeCoNiMo<sub>0.2</sub>; (d) CrFeCoNiMo<sub>0.5</sub>; (e) CrFeCoNiMo. Note that: the non-uniform distribution in (b) and (c) is not caused by phase separation but by dendrites specific to the cast alloy. This structure is formed due to nonequilibrium cooling and does not change the f.c.c. structure.



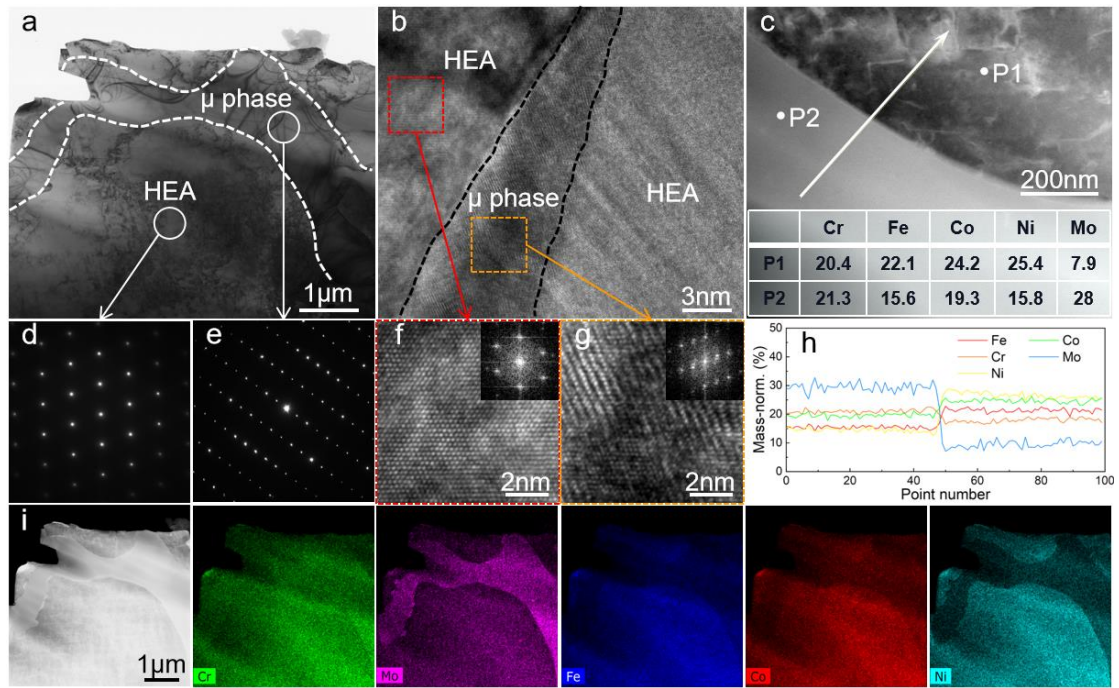
**Figure S2.** SEM images and EDS elemental mapping. (a) CrFeCoNiMo<sub>0.3</sub>. The white dashed circles marked the  $\mu$  phase. (b) CrFeCoNiMo<sub>0.4</sub>. It follows that the excessive addition of Mo leads to an increase in the volume fraction of the  $\mu$  phase.



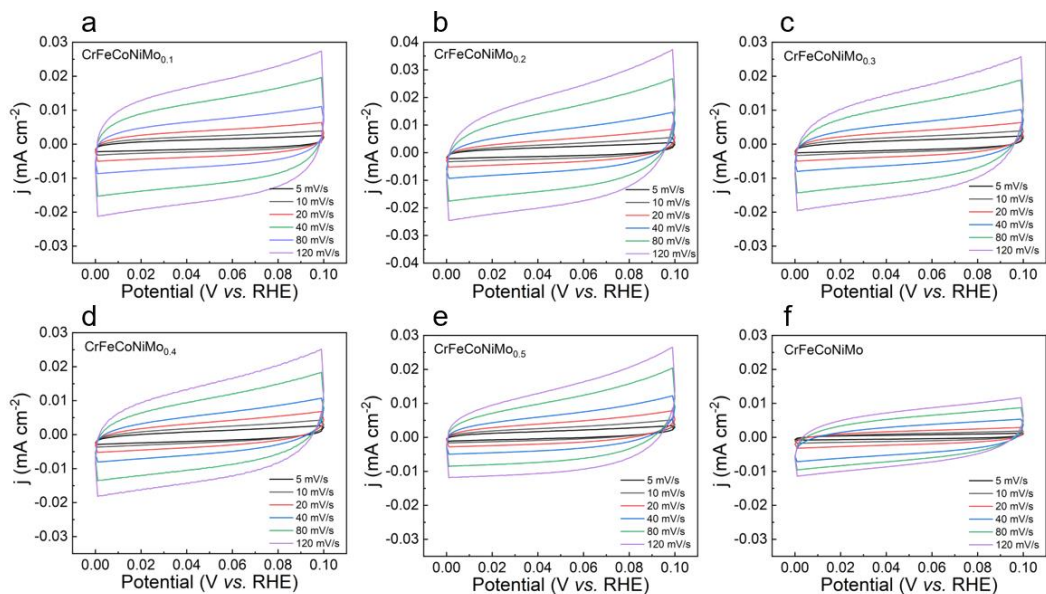
**Figure S3.** TEM images of CrFeCoNi HEA. (a) TEM bright-field image. The inset is the SAED pattern. (b) HRTEM image. (c) Magnified image of the red dashed box in (b). (d) is the FFT pattern of (c). The results indicate that the CrFeCoNi consisted of a single f.c.c. phase.



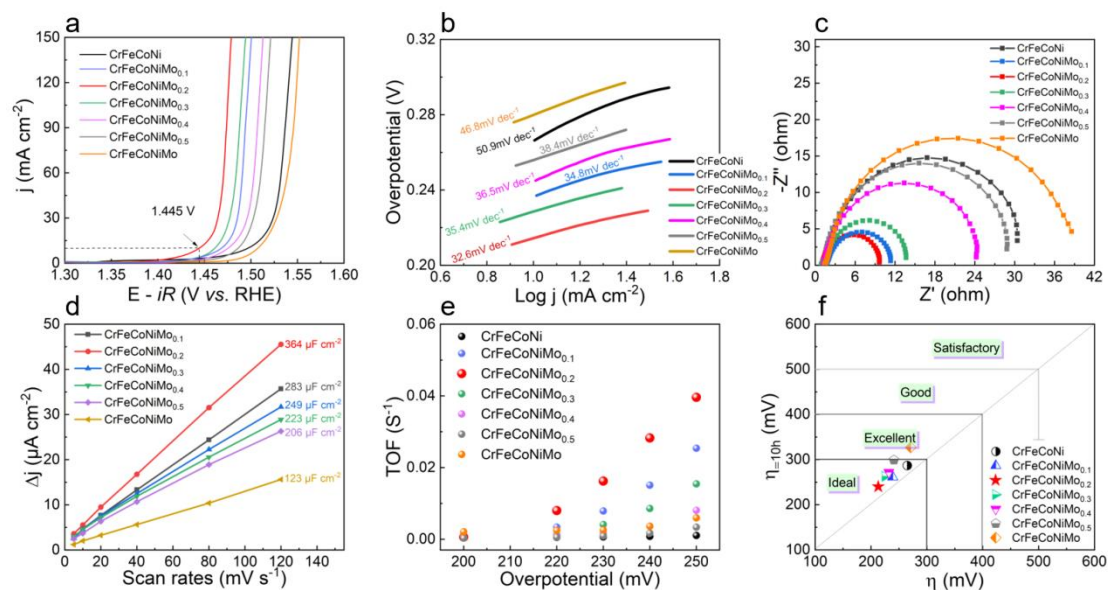
**Figure S4.** TEM images of CrFeCoNiMo<sub>0.2</sub> HEA. (a) TEM bright-field image. The inset is the SAED pattern. (b) and (c) are the HRTEM images of the regions with relatively high and low Mo content in the structure, respectively. (d) and (e) correspond to the enlarged HRTEM image in the red dashed and yellow dashed box in (b) and (c), respectively. f, is the FFT pattern of (d) and (e). Due to the identical FFT pattern of (d) and (e), only one is shown here. (g) and (h) are the HAADF-TEM images. (g) corresponds to high Mo content and (h) corresponds to low Mo contents.



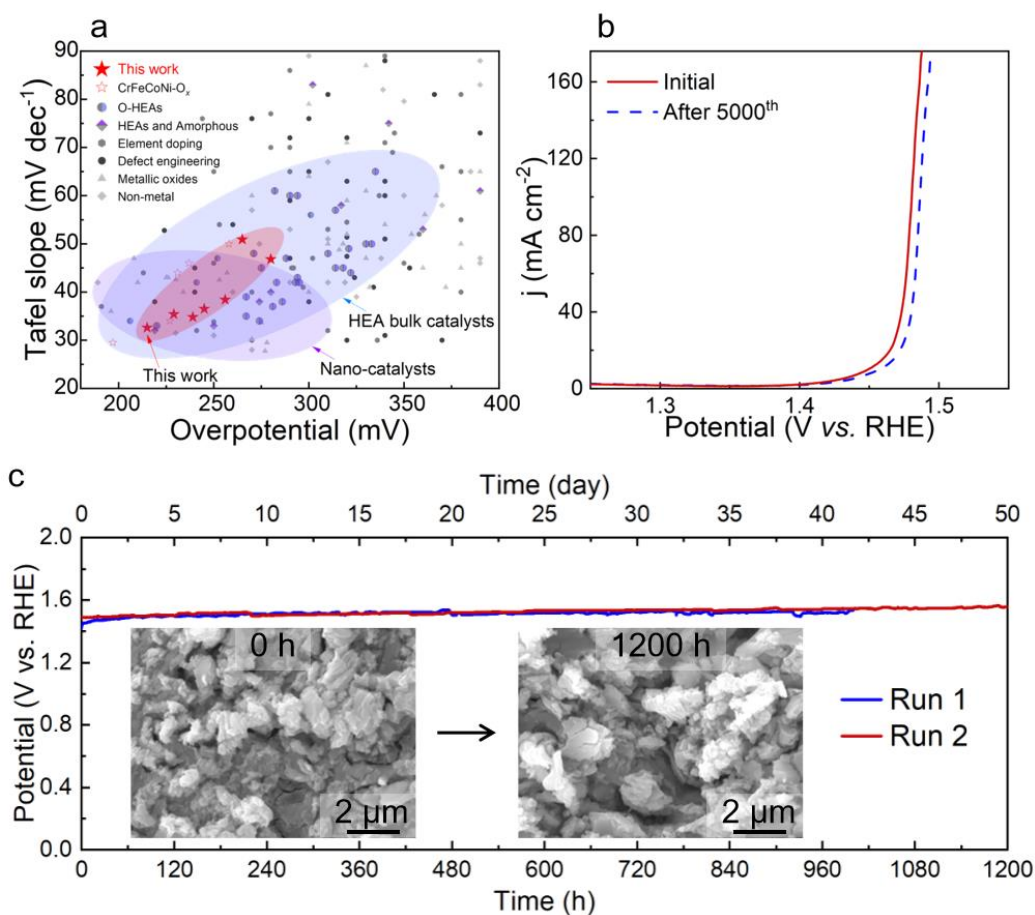
**Figure S5.** TEM images of CrFeCoNiMo HEA. (a) Microscopic morphology of the region containing the  $\mu$  and f.c.c. phases. (b) HRTEM image. The interface between HEA and  $\mu$ -phase is marked by the black dashed line. (c) TEM image at the interface between  $\mu$  and f.c.c. phases. The table in (c) show the atomic ratios of Cr, Fe, Co, Ni, and Mo elements in  $\mu$  and f.c.c. phases. (d) and (e) are the SAED patterns corresponding to  $\mu$  and f.c.c. phase in (a), respectively. (f) and (g) are the enlargement of HRTEM images corresponding to  $\mu$  and f.c.c. phase in (b), respectively. The inset both show the corresponding FFT patterns. (h) The EDX-line analysis of the white lines in (c). (i) TEM image and the corresponding elemental mappings of Cr, Fe, Co, Ni, Mo elements.



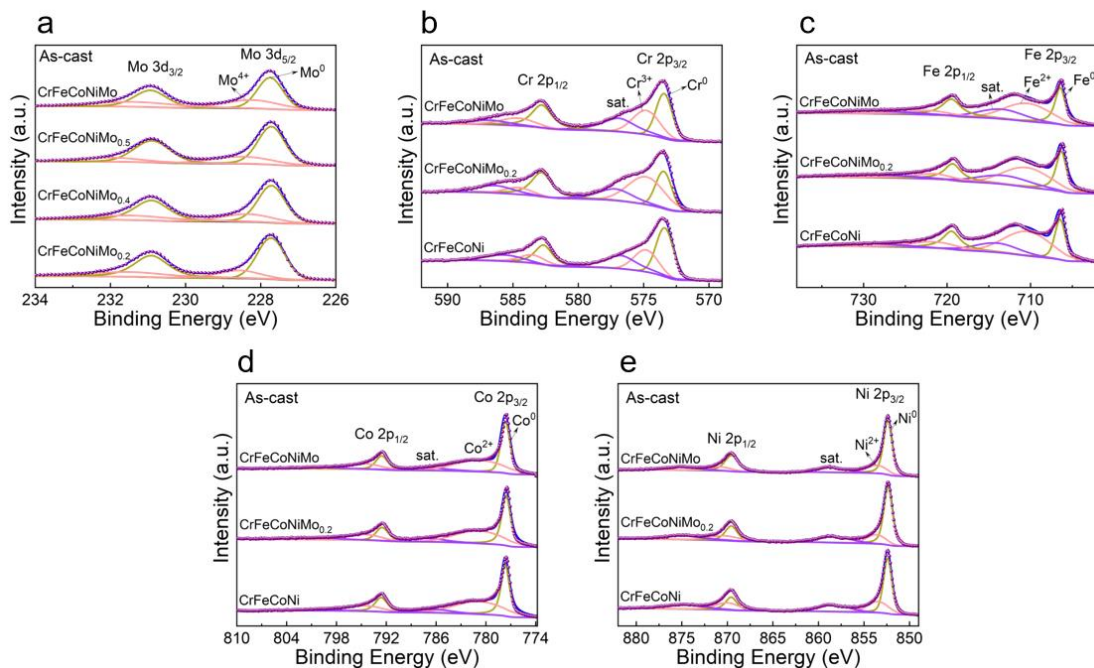
**Figure S6.** CV curves at different scan rates in the non-Faraday interval of 0-0.1 V. (a) CrFeCoNiMo<sub>0.1</sub>. (b) CrFeCoNiMo<sub>0.2</sub>. (c) CrFeCoNiMo<sub>0.3</sub>. (d) CrFeCoNiMo<sub>0.4</sub>. (e) CrFeCoNiMo<sub>0.5</sub>. (f) CrFeCoNiMo. The scan rates are 5, 10, 20, 40, 80, 120 mV s<sup>-1</sup>.



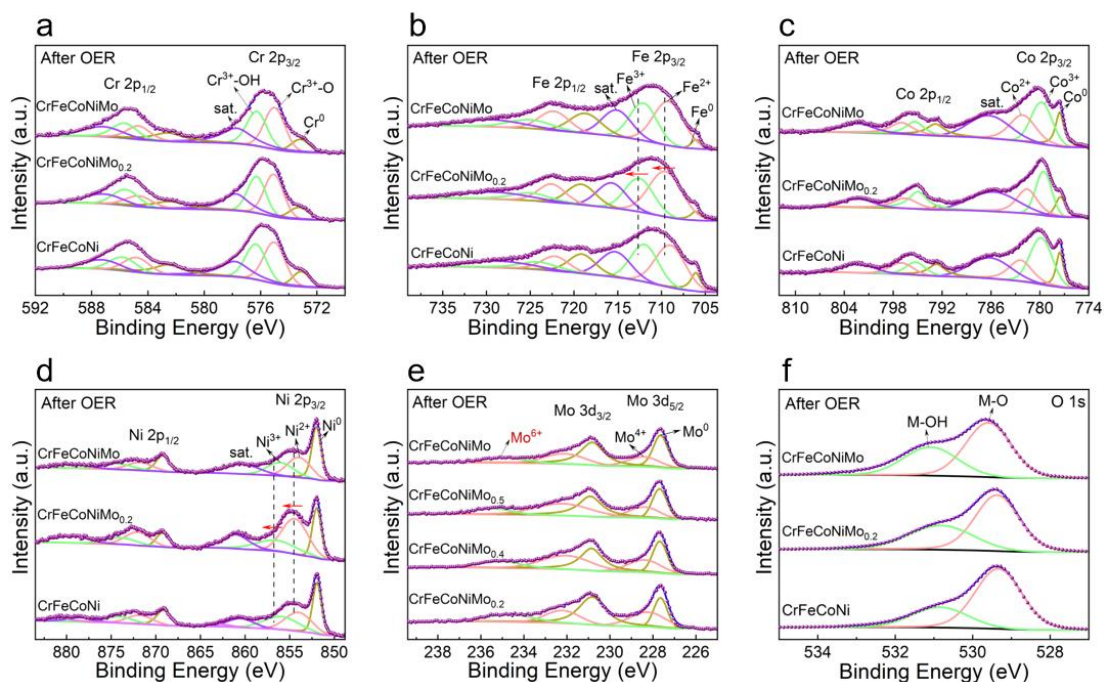
**Figure S7.** OER performance of CrFeCoNiMo<sub>x</sub>. (a) OER polarization curves. (b) Tafel slopes. (c) EIS Nyquist plots. (d)  $C_{dl}$  curves. (e) TOF curves. (f) Classification of the HEAs based on OER performance.



**Figure S8.** OER performance comparison and electrochemical stability. (a) The OER performance comparison showing the overpotential at 10 mA cm<sup>-2</sup> with Tafel slope in 1.0 M KOH. (b) OER polarization curves after 5000th CVs of CrFeCoNiMo<sub>0.2</sub> electrocatalyst. (c) Long-term stability testing of CrFeCoNiMo<sub>0.2</sub> at a constant current density of 10 mA cm<sup>-2</sup>. The inset shows the SEM image of the surface after stability test.

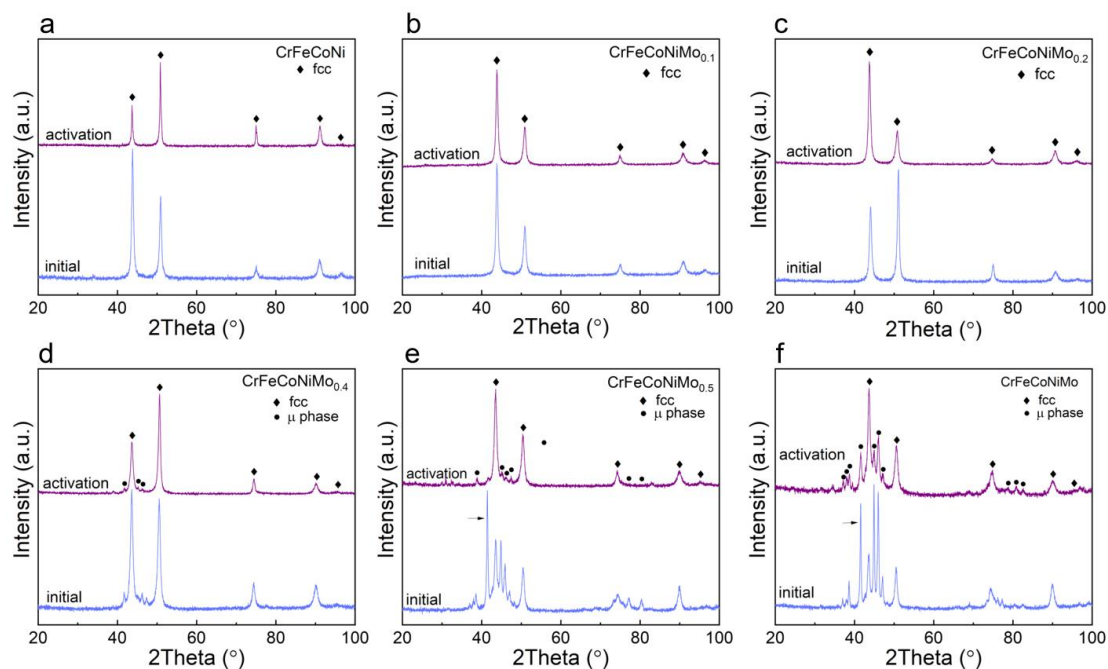


**Figure S9.** High-resolution XPS spectra of as-cast samples. (a) Mo 3d. (b) Cr 2p. (c) Fe 2p. (d) Co 2p. (e) Ni 2p.

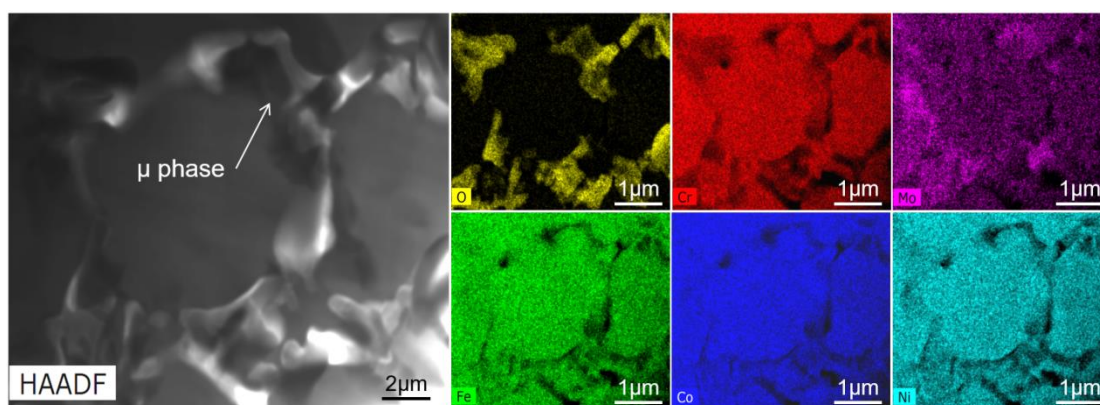


**Figure S10.** High-resolution XPS spectra after OER. (a) Cr 2p. (b) Fe 2p. (c) Co 2p. (d) Ni 2p. (e) Mo 3d. (f) O 1s.

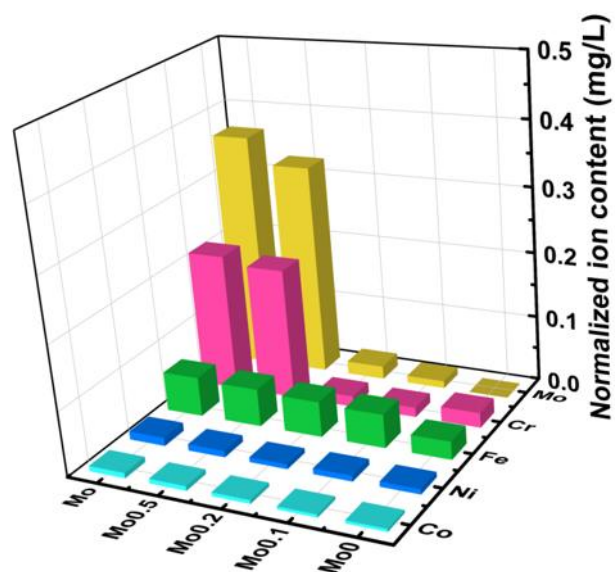




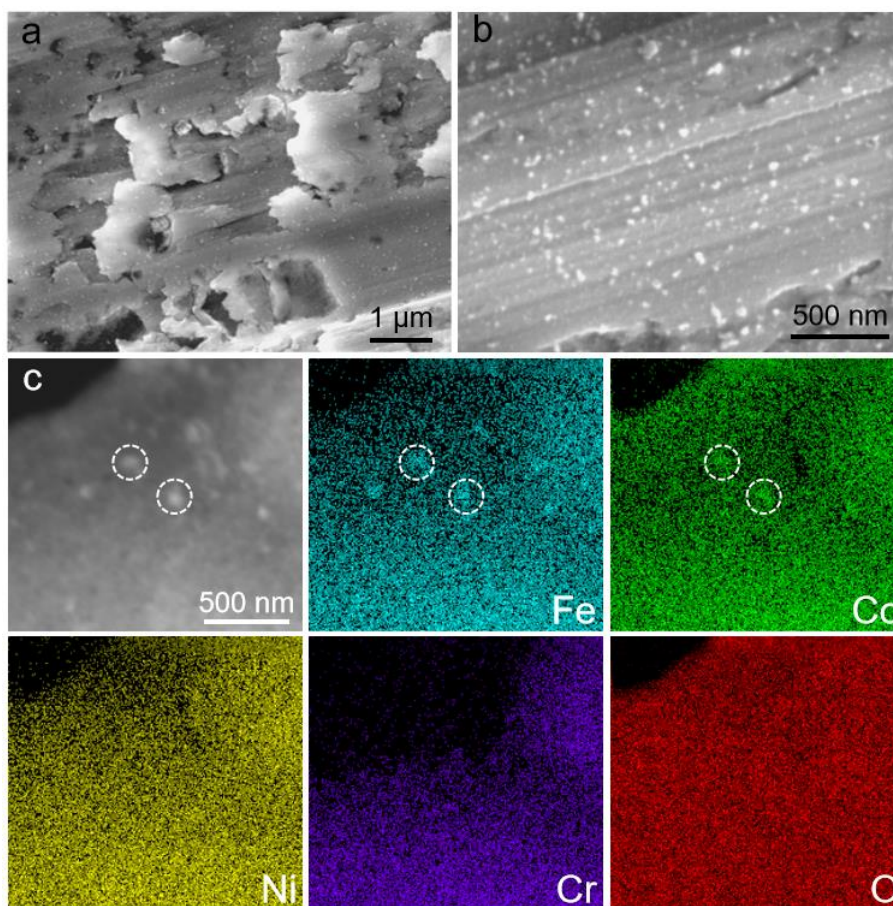
**Figure S11.** XRD patterns of CrFeCoNiMo<sub>x</sub> HEAs before and after electrochemical activation. (a) CrFeCoNi. (b) CrFeCoNiMo<sub>0.1</sub>. (c) CrFeCoNiMo<sub>0.2</sub>. (d) CrFeCoNiMo<sub>0.4</sub>. (e) CrFeCoNiMo<sub>0.5</sub>. (f) CrFeCoNiMo. The analysis of CrFeCoNiMo<sub>x</sub> ( $x = 0.4, 0.5, 1$ ) show that the intensity of the diffraction peak corresponding to  $\mu$  phase decreased after activation, indicating that the  $\mu$  phase is corroded in alkaline solution.



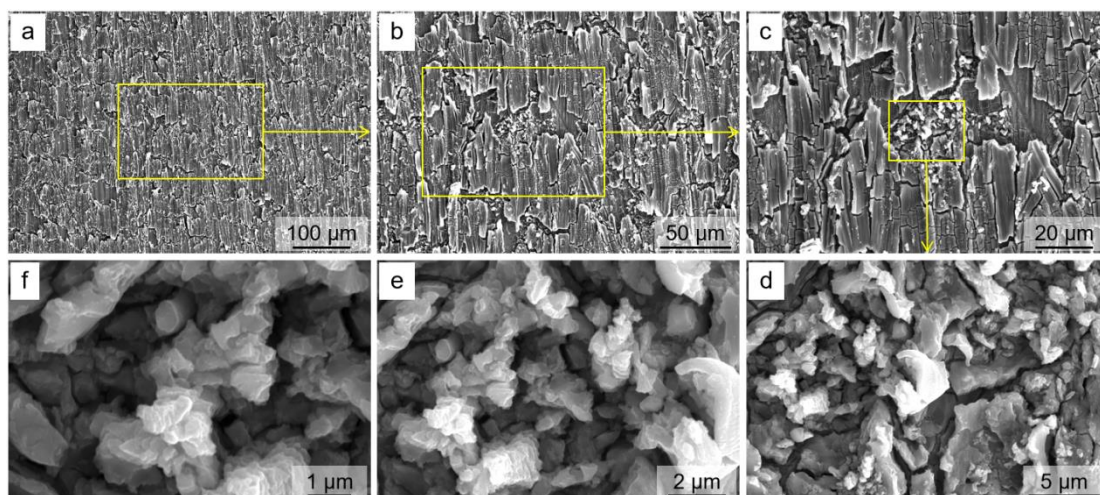
**Figure S12.** TEM-HAADF images of CrFeCoNiMo electrocatalysts after electrocatalytic testing. The Cr, Fe, Co, Ni and Mo elements in the  $\mu$  phase show significant chemical shedding after OER testing. The content of O element on  $\mu$  phase is much higher than on the substrate. It indicates that  $\mu$  phase is corroded.



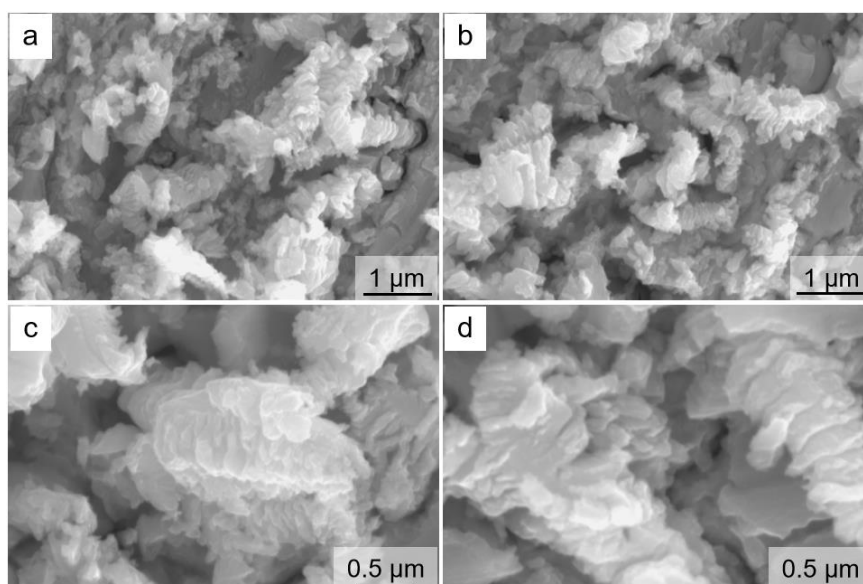
**Figure S13.** The ICP-OES results of each element in the electrolyte.



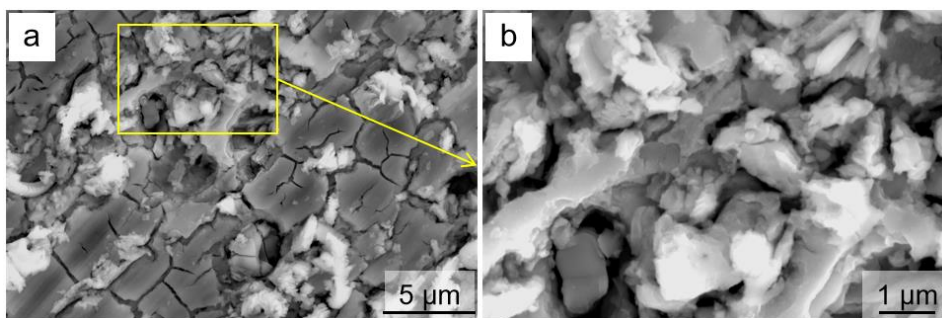
**Figure S14.** SEM and TEM images of CrFeCoNi after electrochemical activation. (a) and (b) are SEM images at different magnifications. The formation of nanoparticles on the catalyst surface can be clearly observed in (b). (c) TEM images and elemental mapping.



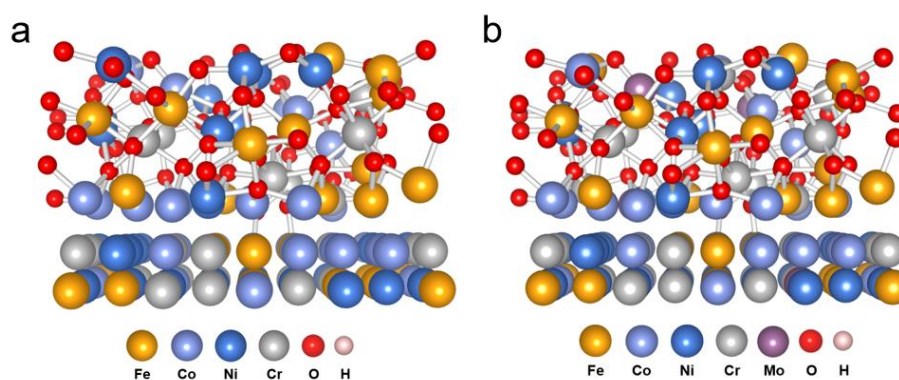
**Figure S15.** SEM images of CrFeCoNiMo<sub>0.2</sub> after electrochemical activation. From (a) to (f) is the stepwise amplification of the multi-metal oxide formed on the surface.



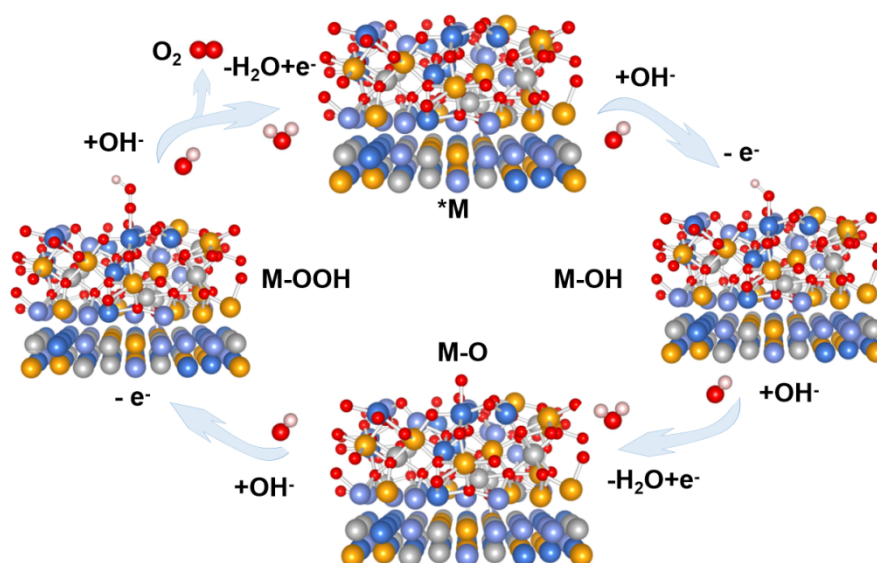
**Figure S16.** SEM images of the characteristic morphology of multi-metal oxides on the CrFeCoNiMo<sub>0.2</sub> surface.



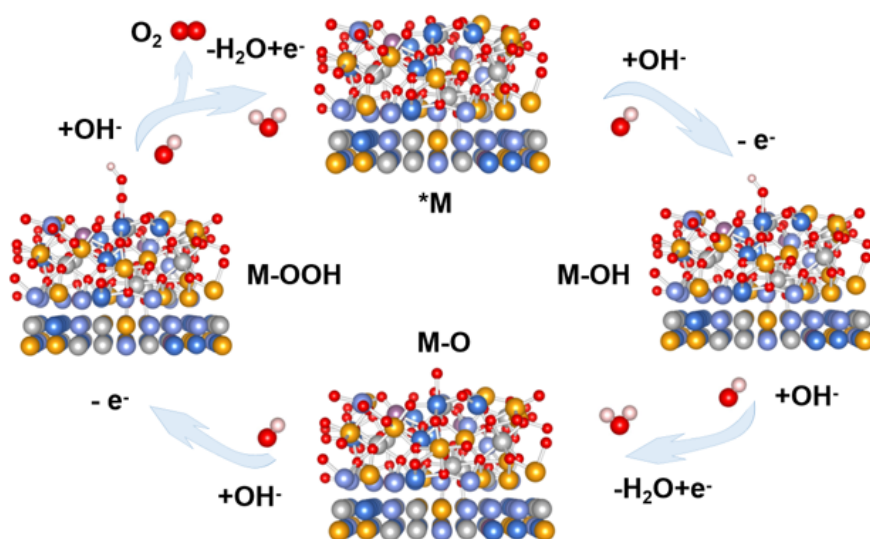
**Figure S17.** SEM images of oxides on the surface of CrFeCoNiMo. (a) Distribution of oxides on the surface. (b) Enlarged view of the yellow box in (a). Compared with CrFeCoNiMo<sub>0.2</sub>, the oxide formed on the surface of CrFeCoNiMo is reduced and unshaped.



**Figure S18.** Optimized models considered for DFT calculations. (a) CrFeCoNi. (b) CrFeCoNiMo<sub>0.2</sub>.



**Figure S19.** Multistep OER reactions on different atomic configurations of CrFeCoNi.



**Figure S20.** Multistep OER reactions on different atomic configurations of CrFeCoNiMo<sub>0.2</sub>. The groups located in the upper part of the model are oxygen-containing intermediates

**Table S1.** The electrocatalytic OER performance of this work and the performance data reported for other catalysts, including high entropy materials, amorphous materials and containing high value metal materials.

Number	Catalyst	Substrate	Electrolyte	$\eta$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Ref.
1	CrFeCoNi			265	50.9	
2	CrFeCoNiMo <sub>0.1</sub>			239	34.8	
3	CrFeCoNiMo <sub>0.2</sub>			215	32.6	
4	CrFeCoNiMo <sub>0.3</sub>	Integrated	1.0 M KOH	229	35.4	This work
5	CrFeCoNiMo <sub>0.4</sub>			245	36.5	
6	CrFeCoNiMo <sub>0.5</sub>			256	38.4	
7	CrFeCoNiMo			280	46.8	
High-entropy materials						
8	Fe-Co-Ni-Cr-Nb	Self-supported	0.1 M KOH	288	27	[1]
9	FeCoCrNi			221	38.7	
10	FeCrNi	CCs	1.0 M KOH	255	42.6	[2]
11	CoCrNi			304	51.4	
12	MnFeCoNi/MO <sub>x</sub>	Self-supported	1.0 M KOH	302	83.7	[3]
13	CoFeLaNiPt	HOPG/GC	0.1 M KOH	377		[4]
14	FeCoNiP			280 @ 100 mA cm <sup>-2</sup>	60	
15	FeCoNiP <sub>0.5</sub> S <sub>0.5</sub>	Self-supported	1.0 M KOH	258 @ 100 mA cm <sup>-2</sup>	49	[5]
16	FeCoNiS			300 @ 100 mA cm <sup>-2</sup>	80	
17	AlNiCoRuMo			245	54.5	
18	AlNiCoRuCu	GC	1.0 M KOH	265	57	[6]
19	AlNiCoRu			270	68.3	
20	AlNiCoFeMo	Al precursor	1.0 M KOH	240	46	[7]

21	CoCrFeNiAl	Self-supported	1.0 M KOH	240	57	[8]
22	Co-Cu-Fe-Mo	Cu foil		199	48.8	
23	Co-Cu-Mo	Cu foil	1.0 M KOH	273	57.5	[9]
24	Co-Fe-Mo	CCC		253	51.2	
25	Al-Ni-Co-Ir-Mo	Al precursor	1.0 M KOH	233	55.2	[10]
26	CoCrFeMnNi	Self-supported	1.0 M NaOH			[11]
27	(CoCuFeMnNi) <sub>3</sub> O <sub>4</sub>	MWCNT	1.0 M KOH	350	59.5	[12]
28	FeNiMnCrCu			466 @ 40 mA cm <sup>-2</sup>	58	
29	FeCoNiCrAl	Self-supported	1.0 M NaOH	580 @ 40 mA cm <sup>-2</sup>	75	[13]
30	(CrFeCoNi) <sub>97</sub> O <sub>3</sub>			196	29	
31	(CrFeCoNiCu) <sub>97</sub> O <sub>3</sub>	Integrated	1.0 M KOH	211	27	[14]
32	(CrFeCoNiMn) <sub>99</sub> O <sub>1</sub>			271	35	
33	(FeCoNi) <sub>3</sub> O <sub>4-x</sub>	Self-supported	1.0 M KOH	229		[15]
34	FeCoNiMnCu	self-assembled		280	59	[16]
35	AlCoFeMoCr	GC	1.0 M KOH	260	52.4	[17]
36	FeCoNiMn			266	64.5	
37	FeCoNiSn	CFP	1.0 M KOH	264	68.2	[18]
38	FeCoNiCu			258	73.9	
39	FeVNbTiZrOF	CC	1.0 M KOH	348	110.3	[19]
40	(CoNiMnZnFe) <sub>3</sub> O <sub>3.2</sub>	CFP	1.0 M KOH	336	47.5	[20]
41	MnFeCoNiCu	CC	1.0 M KOH	263	43	[21]
42	CoFeNiMnMoPi	PTFE film	1.0 M KOH	270	74	[22]
43	K <sub>0.8</sub> Na <sub>0.2</sub> (MgMnFeCoNi)F <sub>3</sub>			314	55	
44	K(MgMnFeCoNi)F <sub>3</sub>	GC	1.0 M KOH	369	61	[23]
45	Na(MgMnFeCoNi)F <sub>3</sub>			334	57	
<b>Amorphous/glass materials</b>						
46	NiFeP	Self-supported	1.0 M KOH	219	32	[24]
47	Ni <sub>1.5</sub> Sn@triMPO <sub>4</sub>	triMPO <sub>4</sub>	1.0 M KOH	240	45.2	[25]
48	(Fe <sub>73.5</sub> Si <sub>13.5</sub> B <sub>9</sub> Nb <sub>3</sub> Cu <sub>1</sub> ) <sub>91.5</sub> Ni <sub>8.5</sub>	Self-supported	1.0 M KOH	230	130	[26]
49	Fe <sub>40</sub> Ni <sub>20</sub> Co <sub>20</sub> P <sub>15</sub> C <sub>5</sub>	Self-supported	1.0 M KOH	278	40	[27]
50	Ni <sub>40</sub> Fe <sub>40</sub> P <sub>20</sub>			270	35	
51	Ni <sub>70</sub> Pd <sub>10</sub> P <sub>20</sub>	Self-supported	1.0 M KOH	345	42	[28]
52	Ni <sub>40</sub> Pd <sub>40</sub> P <sub>20</sub>			340	46	
53	Ni-Fe-P	Cu foil	30 wt.% KOH	309	79.4	[29]
<b>Containing high valance metal materials</b>						
54	NiFeMo	Ni foam	1.0 M KOH	220	35	[30]
55	(Ni <sub>x</sub> Fe <sub>y</sub> Co <sub>6-x-y</sub> )Mo <sub>6</sub> C	Ni foam	1.0 M KOH	212	55.1	[31]
56	FeCoMoS			238	51	
57	CoMoS	NG	1.0 M KOH	300	77	[32]
58	FeCoMo	GC	1.0 M KOH	277	27.7	[33]
59	NiFe-MoO <sub>x</sub>	Self-supported	1.0 M KOH	276	55	[34]
60	Co@WC <sub>1-x</sub>	NCNTs	0.1 M KOH	330	90	[35]
61	Mo-CoP	CC	1.0 M KOH	305	56	[36]
62	FeCoMoW			212		
63	NiFeMoW			205		
64	NiFeMo	CP/Ni foam	1.0 M KOH	201		[37]
65	NiFeW			202		
66	G-FeCoW			191		
67	A-FeCoW	Au foam	1.0 M KOH	232		[38]

68	FeNi-Mo <sub>2</sub> C	carbon layers	1.0 M KOH	288	38.8	[39]
79	Co <sub>0.76</sub> Fe <sub>0.18</sub> Mo <sub>0.06</sub> O <sub>1.35</sub>	GC	1.0 M KOH	250	57	[40]
70	Fe-Mo-Te	GC	1.0 M KOH	300	45.6	[41]
71	P/Mo-Co <sub>3</sub> O <sub>4</sub>	CC	1.0 M KOH	265		[42]

Note: Unless otherwise denoted, the overpotential in the table corresponds to a current density of 10 mA cm<sup>-2</sup>.

### Supplementary References

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