Supplementary information

High-valence metals improve oxygen evolution reaction performance by modulating 3*d* metal oxidation cycle energetics

In the format provided by the authors and unedited

Supplementary Information for

High-valence metals improve OER performance by modulating 3d metal oxidation

cycle energetics

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Supplementary Figure 24. XRD patterns of NiFeX and FeCoX oxyhydroxide catalysts.



Supplementary Figure 25. The particle size distribution of NiFeMo and FeCoMoW catalysts.



Supplementary Figure 26. EXAFS and Fourier-transformed EXAFS spectra of FeCoMoW catalyst. (a) Mo K-edge and (b) W L₃-edge ploted in k-space, with k-weight = 3. (c) Mo K-edge and (d) W L₃-edge ploted in R-space, with k-weight = 3.



Supplementary Figure 27. Time-dependent Fe L-edges sXAS scans of FeCoMoW and NiFe catalysts . Each scan interval is 30 seconds.



Supplementary Figure 28. Analysis of Fe L-edge sXAS of NiFeX samples for Fe^{3+} and Fe^{2+} . Data are fitted using a linear combination of the XAS spectra from the two reference Fe oxides (FeO for Fe²⁺ and Fe(OH)₃ for Fe³⁺).



Supplementary Figure 29. Analysis of Fe L-edge sXAS of FeCoX samples for Fe^{3+} and Fe^{2+} . Data are fitted using a linear combination of the XAS spectra from the two reference Fe oxides (FeO for Fe²⁺ and Fe(OH)₃ for Fe³⁺).



Supplementary Figure 30. ⁵⁷**Fe Mössbauer spectra of different catalyst: (a)** FeCo and **(b)** FeCoMoW.



Supplementary Figure 31. Analysis of Fe K-edge XANES of NiFeMo sample for Fe^{3+} and Fe^{2+} . Data are fitted using a linear combination of the XANES spectra from the two reference Fe oxides (FeO for Fe²⁺ and Fe(OH)₃ for Fe³⁺).



Supplementary Figure 32. The *in-situ* sXAS studies of Co oxidation states of FeCoMoW and FeCo catalysts during OER, comparing with two reference samples (CoO for Co^{2+} , and EuCoO_3^1 for Co^{3+}).



Supplementary Figure 33. The *in-situ* Co K-edge XANES spectra of (a, b) FeCoMoW and (c, d) FeCo catalysts.



Supplementary Figure 34. *Ex-situ* Co L-edge XAS of FeCoMoW and FeCo catalysts before and after OER, comparing with two reference samples (CoO for Co^{2+} , and $EuCoO_3^{-1}$ for Co^{3+}).



Supplementary Figure 35. The *in-situ* W L₃-edge XANES spectra of FeCoW catalyst.



Supplementary Figure 36. OER polarization curves of NiFeMo, NiFe, and the state-of-the-art NiFe catalysts. The state-of-the-art NiFe was synthesized according to the literature² and tested on our platform. All tests were carried out on Ni foam electrode in 1M KOH and at room temperature. The overpotentials at 10 mA·cm⁻² are: 180 mV (NiFeMo), 225 mV(NiFe), 190 mV (repeated state-of-the-art NiFe).



Supplementary Figure 37. Comparison of overpotential and covalent radii of the dopant for (a)NiFeX and (b) FeCoX catalysts.



Supplementary Figure 38. Performance of NiFeX and FeCoX catalysts in 30% KOH electrolyte at 85 °C. (a, b) OER polarization curves on nickel foam measured with a 5 mV·s⁻¹ scan rate, with 95% *iR*-correction. (c, d) Turnover frequency trends as a function of potential for catalysts on nickel foam measured with a 5 mV·s⁻¹ scan rate, with 95% *iR*-correction.



Supplementary Figure 39. Mass activities of catalysts in alkaline 30% KOH electrolyte at 85°C. The mass activities were calculated based on total loading mass of catalysts.



Supplementary Figure 40. Chronopotentiometric durability. The electrolyser setup held at 300 mA·cm⁻² for 120 h in 30% KOH electrolyte at 85 °C by using NiFeMo oxyhydroxide catalysts and commercial Ru electrode as anode and cathode, respectively.



Supplementary Figure 41. Cyclic voltammetry curves of NiFeMo catalyst in 30% KOH electrolyte at 85 °C.

Elements	Samples	Bader charge (a.u.)		
	FeCo	1.73 ± 0.02		
	FeCoMo	1.64 ± 0.20		
Ea	FeCoW	1.58 ± 0.23		
Fe	FeCoNb	1.58 ± 0.22		
	FeCoRe	1.67 ± 0.15		
	FeCoTa	1.57 ± 0.22		
	FeCo	1.53 ± 0.04		
	FeCoMo	1.42 ± 0.12		
Co	FeCoW	1.41 ± 0.12		
Co	FeCoNb	1.39 ± 12		
	FeCoRe	1.41 ± 0.10		
	FeCoTa	1.45 ± 0.12		
	NiFe	1.74 ± 0.03		
	NiFeMo	1.63 ± 0.20		
Fa	NiFeW	1.58 ± 0.23		
re	NiFeNb	1.57 ± 0.21		
	NiFeRe	1.67 ± 0.15		
	NiFeTa	1.57 ± 0.21		
Ni	NiFe	1.77 ± 0.02		
	NiFeMo	1.69 ± 0.07		
	NiFeW	1.69 ± 0.07		
	NiFeNb	1.73 ± 0.07		
	NiFeRe	1.73 ± 0.05		
	NiFeTa	1.70 ± 0.07		

Supplementary Table 1. Statistical analysis of Bader charge of FeCoX and NiFeX for Fe, Co, Ni within the oxyhydroxide framework.

	FeCo	FeCoMo	FeCoW	FeCoNb	FeCoTa	FeCoRe	FeCoMoW
ΔG_1 (*+H ₂ O \rightarrow OH*+H ⁺ +e ⁻)	2.09	1.70	1.72	1.80	1.86	1.94	1.69
ΔG ₂ (OH*→O*+H ⁺ +e ⁻)	1.71	1.56	1.58	1.61	1.62	1.65	1.59
ΔG ₃ (O*+OH ⁻ →OOH*+e ⁻)	0.63	0.85	0.83	0.75	0.74	0.61	0.81
ΔG_4^a $(OOH^* \rightarrow ^* + O_2 + H^+ + e^-)$	0.49	0.81	0.79	0.76	0.70	0.72	0.83
Overpotential	0.86	0.47	0.49	0.57	0.63	0.71	0.46

Supplementary Table 2. Gibbs energies (eV) of the elementary steps of OER on FeCoX systems.

^a ΔG_4 is calculated based on the experimental reaction energy, $\Delta G_4 = 4*1.23 \text{ eV} - \Delta G_1 - \Delta G_2 - \Delta G_3$ to avoid direct calculation of the O-O bonds.

-	NiFe	NiFeMo	NiFeW	NiFeNb	NiFeTa	NiFeRe	NiFeMoW
ΔG_1	1.68	1.61	1.62	1.64	1.66	1.69	1.70
$(*+H_2O \rightarrow OH^*+H^++e^-)$							
ΔG_2	2.14	1.76	1.78	1.84	1.95	1.97	1.77
(OH* → O*+H++e ⁻)							
$\Delta G_3 (O^*+OH^-)$	0.57	0.78	0.75	0.73	0.70	0.64	0.68
→OOH*+e ⁻)							
ΔG_4^a	0.53	0.77	0.77	0.71	0.61	0.62	0.77
$(OOH^* \rightarrow ^* + O_2 + H^+ + e^-)$							
Overpotential	0.91	0.53	0.55	0.61	0.72	0.74	0.54

Supplementary Table 3. Gibbs energies (eV) of the elementary steps of OER on NiFeX systems.

^a ΔG_4 is calculated based on the experimental reaction energy, $\Delta G_4 = 4*1.23 \text{ eV} - \Delta G_1 - \Delta G_2$

 $-\Delta G_3$ to avoid direct calculation of the O-O bonds.

Samples	Fe ²⁺ molar ratio (%)	Overpotential (mV) ^a	Overpotential (mV) ^b	
NiFe	0 ± 0	248	217	
NiFeMo	$29.6~\pm 6.36$	201	163	
NiFeW	33.3 ± 2.82	202	172	
NiFeTa	44.5 ± 1.68	216	193	
NiFeRe	17.8 ± 2.04	218	179	
NiFeNb	38.8 ±2.24	224	199	
NiFeMoW	51.9	205	174	
FeCo	0.38	266	222	
FeCoMo	34.2 ± 1.41	233	197	
FeCoW	51.1 ±3.36	217	169	
FeCoTa	$37.5\ \pm 1.91$	242	175	
FeCoRe	19.6 ± 0.92	238	191	
FeCoNb	28.2 ± 2.13	238	178	
FeCoMoW	55.2 ± 1.18	212	167	

Supplementary Table 4. Summary of electrochemical characterization parameters and surface and bulk Fe²⁺ ratio of different samples.

^a obtained at the current density of 10 mA cm⁻² tested in 1 M KOH electrolyte at 25°C.

^b obtained at the current density of 200 mA cm⁻² tested in 30% KOH electrolyte at 85°C.

Supplementary Note

Time-dependent Fe L-edges XAS measurements

We sought to evaluate possible beam damage resulting from XAS, a series of time-dependent Fe L-edges XAS measurements for FeCoMoW vs. control samples (without high-valence metals) were performed and shown in Supplementary Figure 27. The probe spot was irradiated over different periods, and the XAS spectra were recorded. The spectra of FeCoMoW show the same lineshape as one another, and have a significant Fe²⁺ character, meaning that Fe²⁺ content is constant as a function of different irradiation times; while the Fe in NiFe is dominated by Fe³⁺ in the case of brief scans at its Fe L-edge (Supplementary Figure 27b). This suggests that the Fe L-edge data are not materially impacted by beam damage, and that Fe in FeCoMoW is indeed mostly Fe²⁺.

In-situ XAS study of high-valence metal

We also characterized the oxidation of high-valence W during OER, the results in Supplementary Figure 35 showed that the onset energy of the sample before and during OER is the same as that of WO₃, indicating that the oxidation state did not change, i.e. +6. And the Whiteline intensity increase is during the OER, which is ascribed to the local symmetry distortion³. Under the positive potential during OER, the OH adsorption is enhanced, and therefore the adsorbates distort local WO₆ symmetry.

Supplementary References

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