Electronic Supplementary Information

Capturing the Active Sites of Multimetallic (Oxy)Hydroxides for Oxygen Evolution Reactions

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FIGURES



Fig. S1. The cell (a) was filled with 1.0 M KOH electrolyte and bubbled with hydrogen for 30 min. Then the Pt foils (exposed area, $1.0 \times 1.0 \text{ cm}^2$) were applied as both working and counter electrodes and the Hg/HgO or Ag/AgCl electrode as the reference electrodes. Then CVs (b, c) were carried out at a scan rate of 1.0 mV·s⁻¹ and the average of the two interconversion point values was taken as the thermodynamic potential.¹

The pH of 1.0 M KOH (13.7) was measured by using a pH meter (PHS-3, LEICI), which was calibrated with the standard references of pH = 4, 6 and 13. As read from **Fig. S1b~c**, the potential values can be converted by the following equations: $E_{RHE} = E_{Hg/HgO} + 0.926$ and $E_{RHE} = E_{Ag/AgCI} + 1.037$.



Fig. S2. (a-d) Atomic structures of various Cr and/or Fe substituted β -NiOOH models for DFT calculations. The (101) surfaces are exposed and covered by OH groups in alkaline media. The H, O, Cr, Fe and Ni atoms are shown in white, red, green, cyan and blue colours, respectively. Of note: model (d) was used to fit FTs for *operando* Fe-sub- β -NiOOH under the applied potential of 0.70 V.



Fig. S3. Scaling relations between calculated binding energies of OOH*, O* and OH* species on various metal sites of the Cr and/or Fe substituted β -NiOOH models described in **Table S7**. The dashed lines are linear fitting of the data points, and the fitting equations are given.



Fig. S4. Overall XPS surveys of NiFeCr/NF and NiFe/NF.



Fig. S5. HRTEM (a), SAED patterns (b) and EDS mapping (c: Fe, d: Ni, e: O) of NiFe (oxy)hydroxide catalyst on TEM copper grid.



Fig. S6. (a) SEM for NiFeCr/CF and relevant Ni (b), Fe (c), Cr (d), O (e) EDS mappings and statistics (f).



Fig. S7. (a) SEM for NiFe/CF and relevant Ni (b), Fe (c), O (d) mappings and EDS statistics (e).



Fig. S8. Reversal LSV scans (a) at the scanning rate of 5.0 mV \cdot s⁻¹ in 1.0 M KOH electrolyte with 80 % iR-compensation and the derived Tafel slopes (b).



Fig. S9. Color change on NiFe/NF (left: black) and NiFeCr/NF (right: gray) electrodes during water oxidation in 1 M KOH under the applied potential of 1.6 V vs RHE without iR-compensation



Fig. S10. CVs of NiFe/NF (a) and NiFeCr/NF (d) at the scanning rates from 100^{800} mV·s⁻¹ in 1.0 M KOH without iR-compensation; (b, e) The relevant plots of the redox peak current densities vs. the square root of scanning rates; (c, f) The relevant plots of the redox peak potentials vs. the logarithm of scanning rates.



Fig. S11. CVs of NiFe/NF and NiFeCr/NF in 0.1 M (a) and 1.0 M (c) ultrapure KOH electrolyte; CVs of NiFe/NF and NiFeCr/NF in 0.1 M (b) and 1.0 M (d) unpurified KOH electrolyte; Scanning rate of $50.0 \text{ mV} \cdot \text{s}^{-1}$ and without iR-compensation



Fig. S12. LSVs of Cr/CF, FeCr/CF, NiCr/NF, NiFe/NF and NiFeCr/NF at the scanning rate of 5.0 mV·s⁻¹ in 1.0 M KOH electrolyte with 80 % iR-compensation.

Cr/CF control sample was fabricated on copper foam substrate in the depositing bath of 6 mM $Cr(NO_3)_3 \cdot 9H_2O$ via the same electrodeposition protocols in the manuscript. FeCr/CF control sample was fabricated on copper foam substrate in the depositing bath of 3 mM Fe(NO_3)_3 \cdot 9H_2O and 6 mM $Cr(NO_3)_3 \cdot 9H_2O$. NiCr/NF control sample was fabricated on nickel foam substrate in the depositing bath of 12 mM $Ni(NO_3)_2 \cdot 6H_2O$ and 6 mM Cr(NO_3)_3 \cdot 9H_2O. NiCr and FeCr control samples were not tested for XAS because they show very poor OER activities, which also indicates the significant OER observed at NiFeCr is resulted from the synergistic effect from Ni, Fe and Cr dependently.



Fig. S13. XPS of O1s (a), Fe2p (b), Ni2p (c) and overall survey (d, insert: Cr2p) of NiFe/NF and NiFeCr/NF after OER.



Fig. S14. CVs of NiFe/NF electrode in 1.0 M KOH electrolyte before and after addition of 0.5 mM $Cr(NO_3)_3$ ·9H₂O at the scanning rate of 50 mV·s⁻¹ without iR-compensation. CVs were carried in an H-cell separated with Nafion 117 membrane so as to get rid of the enhancement from the counter electrode.



Fig. S15. TEM morphology of defective NiFeCr sheet after OER peeled from NF substrate.



Fig. S16. Cyclic voltammetries on NiFeCr/NF (red) and NiFe/NF (black) under various scanning rates and the relevant calculation for electrochemical surface areas.



Fig. S17. ECSA normalised LSVs from Fig. 2a.



Fig. S18. LSVs of NiFe/NF and NiFeCr/NF at the scanning rate of 5.0 mV·s⁻¹ in 0.1 M KOH electrolyte with 60 % iR-compensation.



Fig. S19. Raman of NiFe (black) and NiFeCr (red) (oxy)hydroxide compounds on SPE (gold substrate).



Fig. S20. XANES data of Fe (a), Ni (b) and Cr (c) K-edge on pristine NiFe, NiFeCr catalysts and the relevant hydroxide references; FTs from EXAFS of Fe (d), Ni (e) and Cr (f) on pristine NiFe, NiFeCr catalysts and the relevant hydroxide references.

The Ni(OH)₂, Fe(OH)₃ and Cr(OH)₃ references were synthesized via coprecipitation approach. For example, 3 mmol Ni(NO₃)₃· Θ ²O (or hydrated Fe, Cr nitrate salts) were dissolved in 250 ml Ar-saturated H₂O. Then 0.1 M KOH was slowly dropped into the solution with 500 rpm stirring till the pH of the suspension was adjusted to 10 and the suspension was washed and centrifuged with water and ethanol three times. The precipitate was carefully collected and dried in the vacuum oven at 60 $^{\circ}$ C for 48 hours. Finally, the dried solids were ground into powder. For XAS analysis, 5.0 mg reference powder was mixed with 95.0 mg cellulose (99.5 %, Sigma) and filled in a polymer XAS holder sealed with Kapton tap.



Fig. S21. EXAFS K space of Fe (a) and Ni (b) and Cr (c) in NiFe and NiFeCr catalysts (solid: measured, circle: fitting).



Fig. S22. Structures of OH*, O* and OOH* reaction intermediates (in the black circles) on (a) oxyhydroxide and (b) on the defective oxyhydroxide. The H, O, Cr, Fe and Ni atoms are shown in white, red, green, cyan and blue colours, respectively.

TABLES

	XPS	EDS	ICP
Ni in NiFe	6.6	4.0	6.0
Fe in NiFe	2.0	3.0	2.8
Ni in NiFeCr	6.2	6.7	6.0
Fe in NiFeCr	1.0	2.0	1.1
Cr in NiFeCr	1.1	2.7	2.6

Table S1. Elemental contributions on NiFe and NiFeCr electrode

From XSP fitting, as the Ni⁰ on the substrate, Ni content should contribute more than the real content in NiFeCr and NiFe hydroxide thin film.

Table 52. Onset overpotential and Tale slope values						
	Forward	Backward	Average			
NiFe onset	260 mV	270 mV	265 mV			
NiFe Tafel	50 mV∙dec⁻¹	46 mV·dec⁻¹	48 mV·dec⁻¹			
NiFeCr onset	240 mV	240 mV	240 mV			
NiFeCr Tafel	41 mV∙dec⁻¹	31 mV·dec⁻¹	36 mV·dec⁻¹			

 Table S2. Onset overpotential and Tafel slope values

Table S3. EIS parameters of NiFe/NF and NiFeCr/NF

	R _s /Ω	$Q_1/S \cdot s^n$	<i>n</i> ₁	C _{dl1} /F	R_{ct1}	$Q_2/S \cdot s^n$	<i>n</i> ₂	C _{dl2} /F	R _{ct2}
NiFe	2.74	0.04	0.69	0.0057	0.38	0.012	0.88	0.0075	59.93
NiFeCr	2.90	0.09	0.49	0.0016	0.26	0.011	0.93	0.0084	39.45

Materials	η/mV	j/mA∙cm⁻²	iR	Electrolyte	Ref
NiFeCr/NF	240	onset	Correcton	1 M KOH	this work
NiFeCr/NF	260	100	Correction	1 M KOH	2
NiFe/NF	265	onset	Correcton	1 M KOH	this work
NiFe/NF	290	100	Correction	1 M KOH	2
Ru	290	10	No	1 M NaOH	3
Ir	390	10	No	1 M NaOH	3
NiFe LDH	225	10	Correction	1 M KOH	4
NiFe ₂ O ₄	410	5		0.1 M KOH	5
$Co_{3-x}C_xO_4$	350	10	Correction	1 M NAOH	6
NiV LDH	310	10		1 M KOH	7
CoFe LDH	325	10	Correction	0.1 M KOH	8
CoMn LDH	324	10	Correction	1 M KOH	9
NiFeV LDH	230	10	Correction	1 M KOH	10
CoFeW LDH	191	10	Correction	1 М КОН	11
NiFePi	290	10	Correction	1 M KOH	12

Table S4. Comparison between this work and other benchmark catalysts

Table S5. ICP-OES survey for Cr content in KOH electrolyte

	•			
	KOH before OER	KOH after OER		
Cr content/µg·L⁻¹	6.78	144		

1.0 ml fresh 1.0 M KOH was collected and diluted into 10 ml for a blank control; After OER, another 1.0 ml 1.0 M KOH was collected and diluted into 10 ml. The diluted electrolyte samples were then tested in ICP-OES system.

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Ni Pristine NiFe Ni-O 6 2.06 0.006 Ni-M 6 3.13 0.008 Fe Pristine NiFe Fe-O 6 1.97 0.007 Fe-M 6 3.17 0.014 Ni in Pristine NiFeCr Ni-O 6 2.05 0.001 Ni-M 6 3.14 0.004 Fe in Pristine NiFeCr Fe-O 6 1.96 0.006 Fe-M 6 3.05 0.006
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Ni-M 6 3.14 0.004 Fe in Pristine NiFeCr Fe-O 6 1.96 0.006 Fe-M 6 3.05 0.006
Fe in Pristine NiFeCr Fe-O 6 1.96 0.006 Fe-M 6 3.05 0.006
Fe-M 6 3.05 0.006
Cr in Pristine NiFeCr Cr-O 6 1.94 0.002
Cr-M 6 3.00 0.006
Ni in NiFe 0.70 Ni-O 5* 1.88 0.002
Ni-M 6 2.81 0.001
Fe in NiFe 0.70 Fe-O 5 [*] 2.01 0.002
Fe-M 6 3.22 0.016
Ni in NiFeCr 0.70 Ni-O 5 [*] 2.04 0.013
Ni-M 6 3.04 0.001
Fe in NiFeCr 0.70 Fe-O 5 [*] 1.97 0.006
Fe-M 6 2.98 0.013
Cr in NiFeCr 0.70 Cr-O 5 [*] 1.79 0.002
Cr-M 6 2.75 0.022

Table S6. Fitting parameters of EXAFS spectra including coordination number (CN), interatomic distance (R), Debye-Waller factor (σ^2), and energy shift (E₀)

* The unsaturated CN number is due to the oxygen trap (vacancy) for active intermediate

Table S7. Calculated binding energies of OH*, O* and OOH* intermediates (ΔE_{OH*} , ΔE_{O^*} , ΔE_{OOH*}), theoretical OER overpotential (η^{OER}), and rate-limit step (RLS) for various metal sites on the Cr and Fe doped NiOOH (101) surface. The values of RuO₂(110) surface are also listed for comparison. The atomic structures of all the models are shown in **Fig. S22**.

site	system	ΔE_{OH^*}	ΔE_{O^*}	ΔE_{OOH*}	η^{OER}	RLS
		(eV)	(eV)	(eV)	(∨)	
	a-(Cr, Fe, Ni)	0.72	1.99	3.11	0.25	OOH*
Cr	b-(Cr, Fe, Ni)	1.18	2.56	3.80	0.37	OOH*
	c-(Cr, Ni)	1.02	2.24	3.45	0.34	OOH*
Cr near vacancy	(Cr, Fe, Ni)	0.67	1.61	3.59	1.11	OOH*
	a-(Cr, Fe, Ni)	1.17	3.30	3.61	0.54	0*
Fe	b-(Cr, Fe, Ni)	1.17	3.45	3.70	0.68	0*
	d-(Fe, Ni)	1.39	3.99	4.32	1.01	0*
	a-(Cr, Fe, Ni)	1.97	4.62	4.07	1.14	OH*
Ni	b-(Cr, Fe, Ni)	2.00	4.68	4.6	1.17	OH*
	c-(Cr, Ni)	2.01	4.47	4.55	1.18	OH*
	d-(Fe, Ni)	1.70	4.38	4.34	1.09	OH*
Ru	RuO ₂ (110)	0.33	2.31	3.65	0.40	OOH*

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