

Supplementary information for:

Investigation of mixed-metal (oxy)fluorides as a new class of water oxidation electrocatalysts

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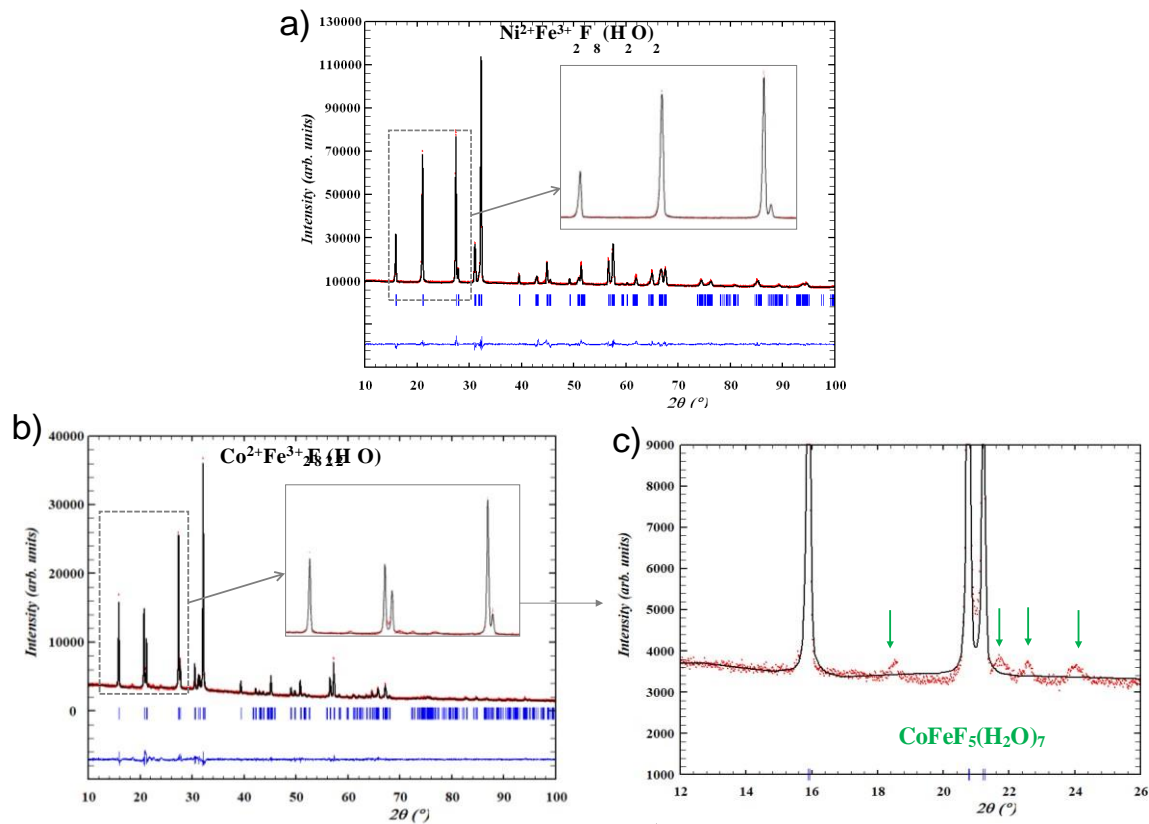


Figure S1: Rietveld refinement of the X-ray patterns of a) $\text{NiFe}_2\text{F}_8(\text{H}_2\text{O})_2$, b) and c) $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$ using the structural model of $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ (ICSD-38366). Vertical markers give Bragg peak positions of the C2/m space group.

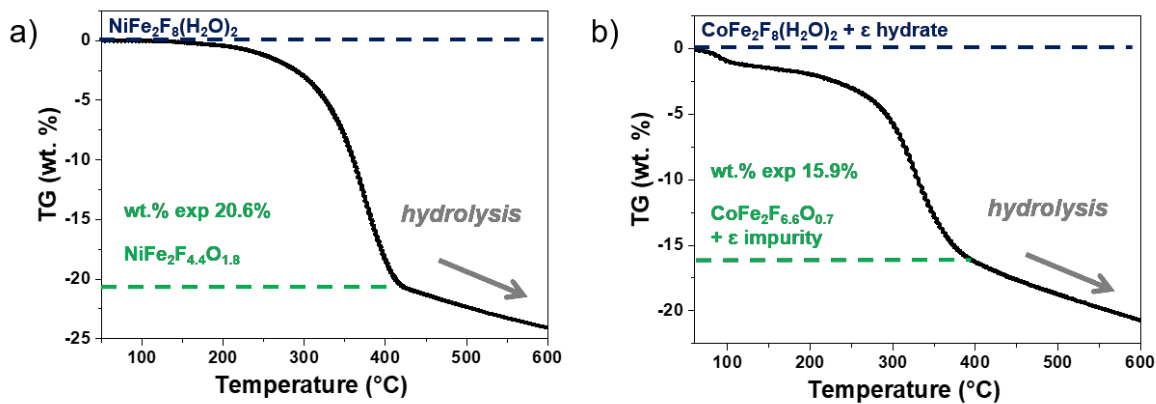


Figure S2: TGA analysis under dry air of a) $\text{Ni}^{2+}\text{Fe}^{3+}_2\text{F}_8(\text{H}_2\text{O})_2$ and b) $\text{Co}^{2+}\text{Fe}^{3+}_2\text{F}_8(\text{H}_2\text{O})_2$

Table S1: Summary of temperature domains for $M^{2+}M^{3+}_2F_8(H_2O)_2$ phases (M= Ni and Co).

Phases	Temperature domain		
	Crystallized phase	Amorphous phase	Oxide, formula
$NiFe_2F_8(H_2O)_2$	$T < 340^\circ C$	$340 \leq T \leq 380$	$380^\circ C < T, NiFe_2O_4$
$CoFe_2F_8(H_2O)_2$	$T < 300^\circ C$	$300 \leq T \leq 340$	$340^\circ C < T, CoFe_2O_4$

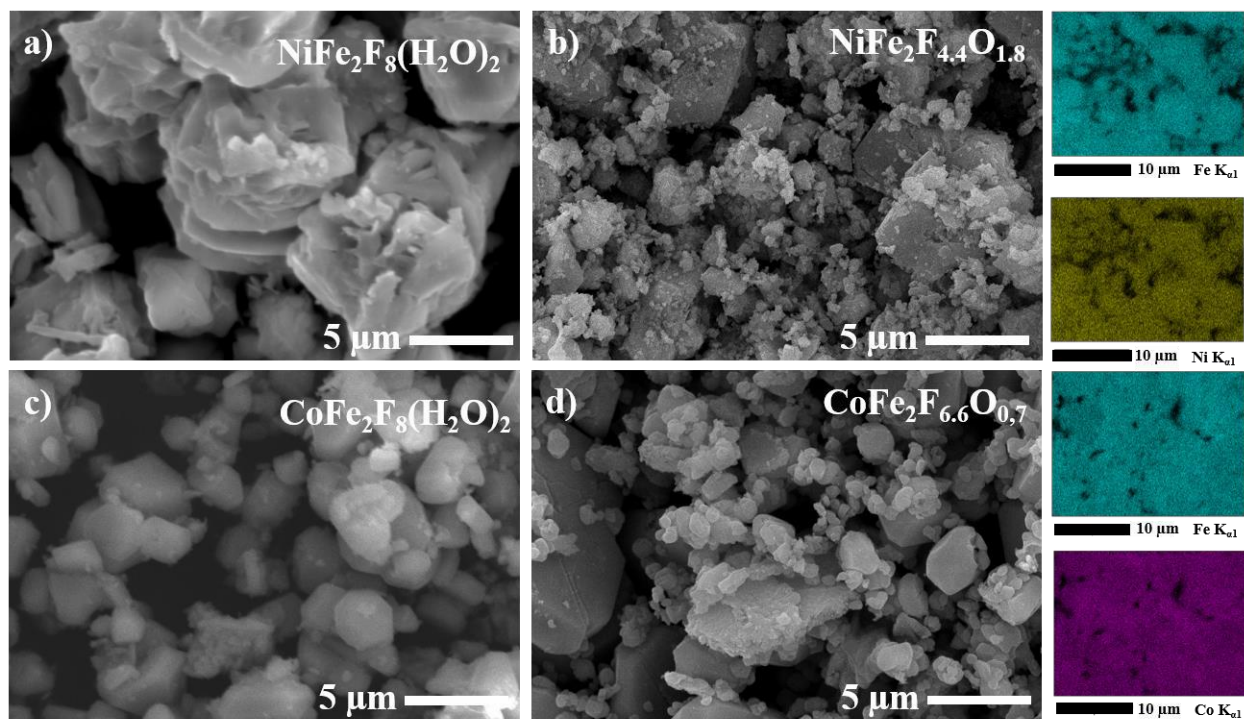


Figure S3: SEM images of a) $Ni^{2+}Fe^{3+}_2F_8(H_2O)_2$ and b) $Co^{2+}Fe^{3+}_2F_8(H_2O)_2$ powders before (a, c) and after calcination (b, d)) under air. On the right: Corresponding EDS mapping on the calcined powders.

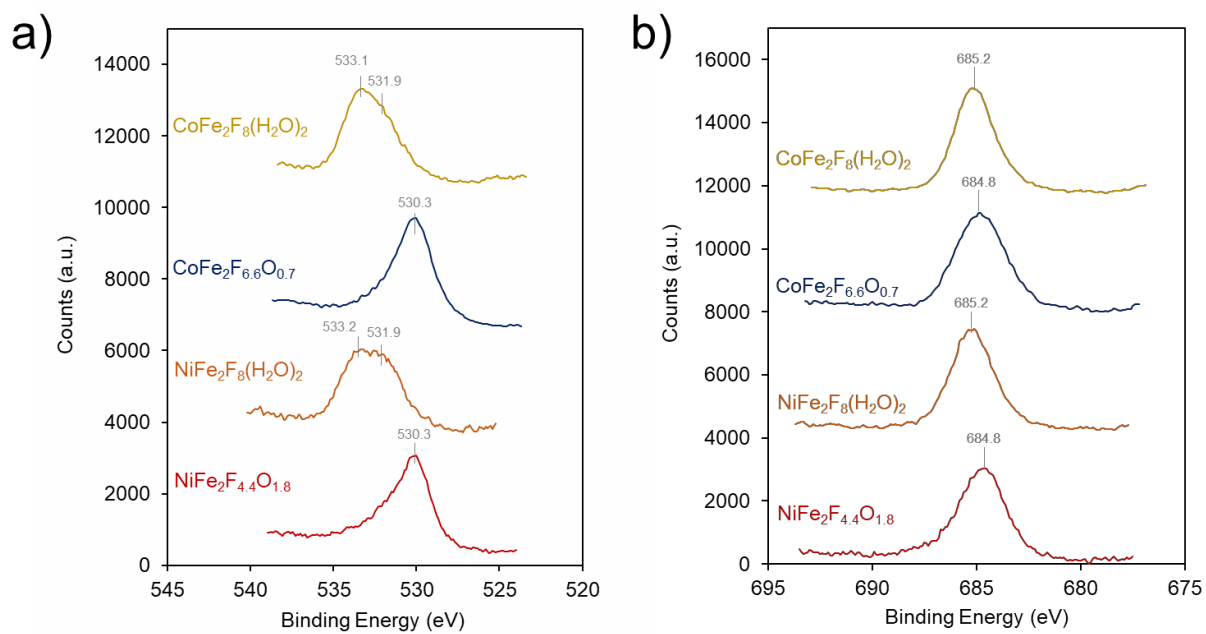


Figure S4: O1s a) and F1s b) XPS of the investigated (oxy)fluorides.

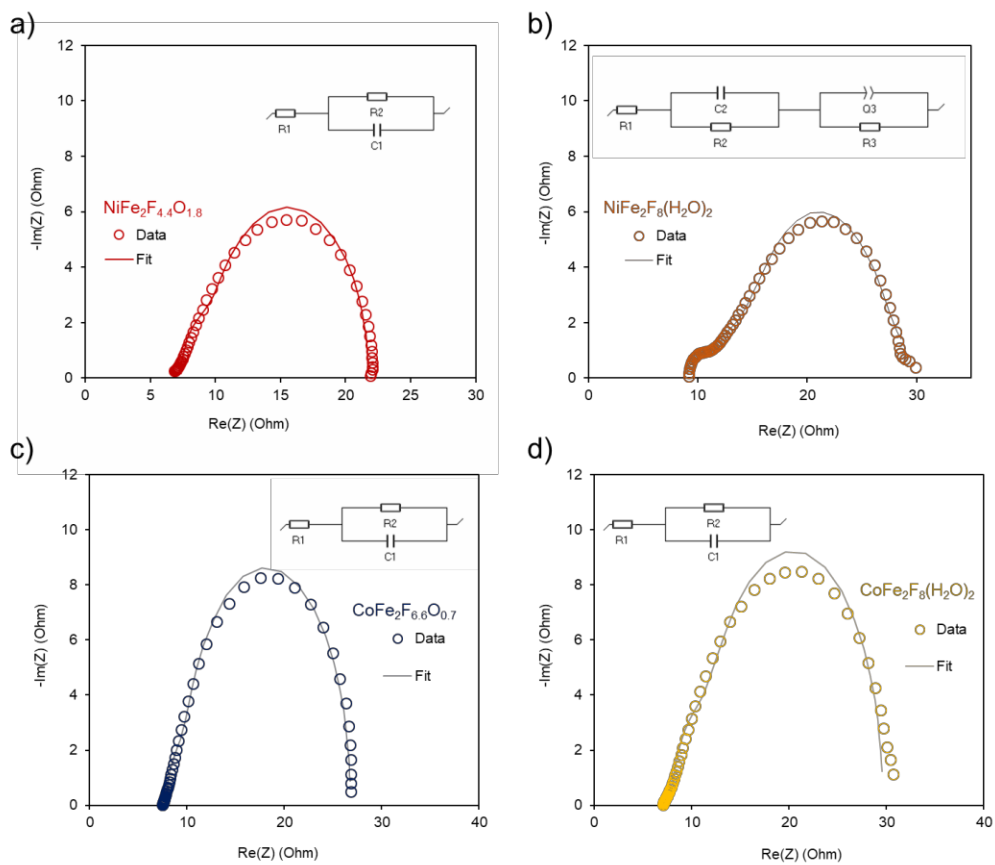


Figure S5: Example of EIS Fitting performed using a Randles circuit for (oxy)fluorides except for $\text{NiFe}_2\text{F}_8(\text{H}_2\text{O})_2$, which needed an extra constant phase and resistive element, indicating that charge transfer through the material was, in part, limiting the system performance. R = resistive element, C = capacitive element, Q = constant phase element.

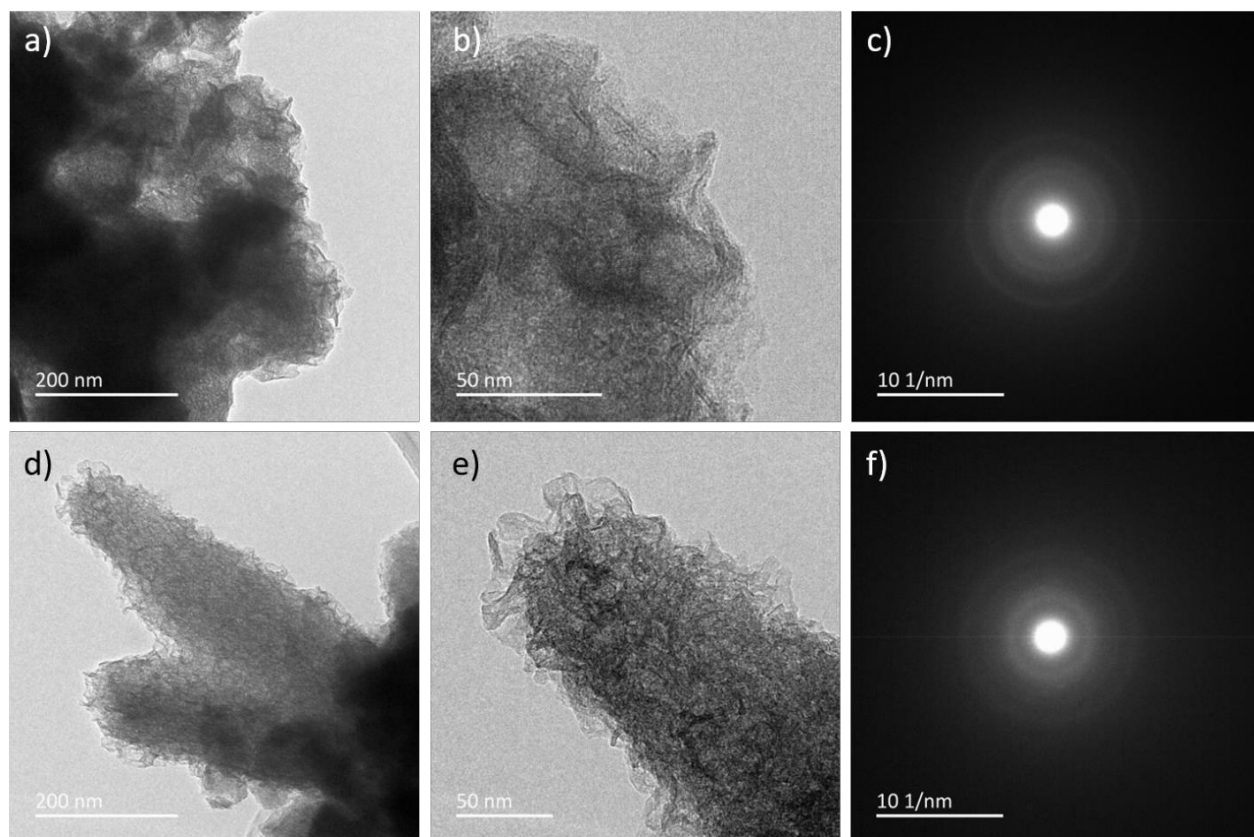


Figure S6: TEM micrographs of a), b) NiFe₂F_{4.4}O_{1.8} and d), e) CoFe₂F_{6.6}O_{0.7} after catalysis. c) and f) Corresponding SAED.

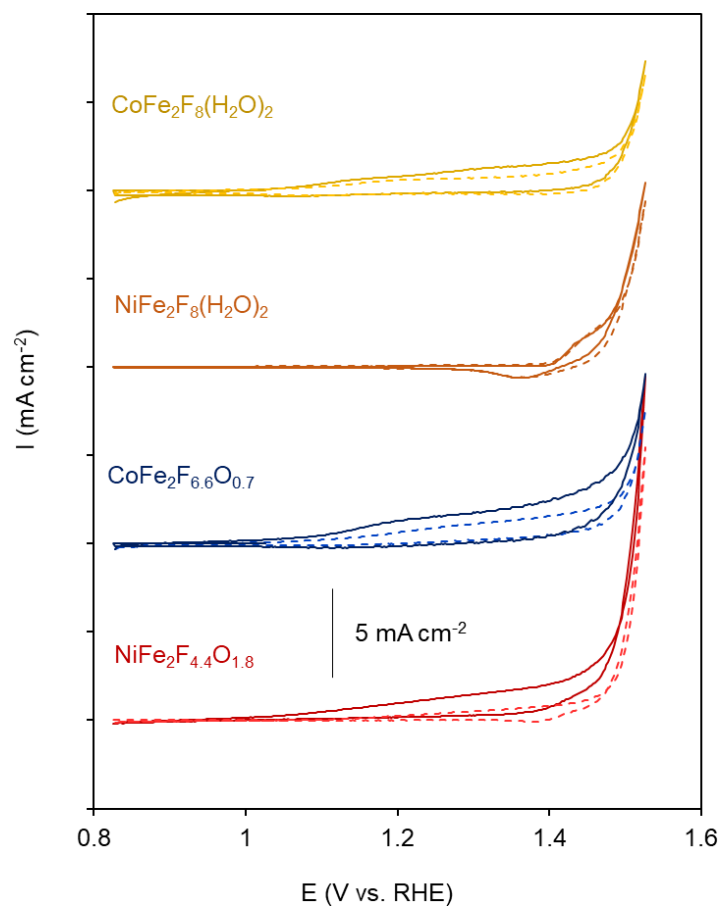


Figure S7: Cyclic voltammograms of (oxy)fluorides in 1.0 M KOH without (dotted lines) and with the addition of 10 mM methanol.

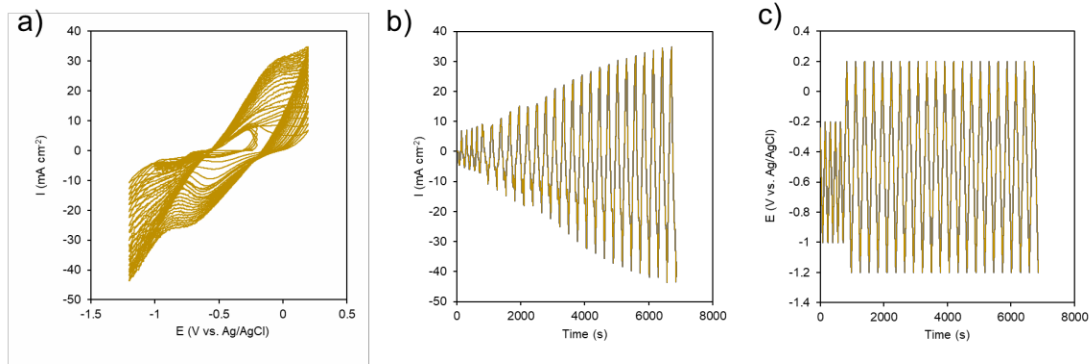


Figure S8: Electrodeposition of CoS_x HER catalyst, depicted in current vs voltage a), current vs. time b) and voltage vs. time c).

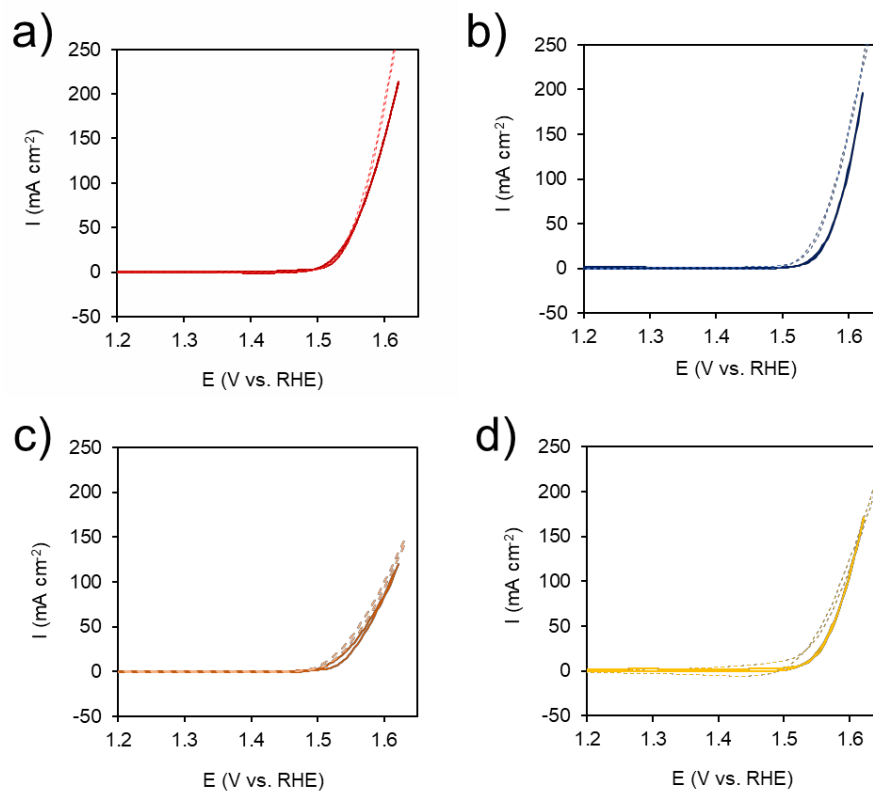


Figure S9: Cyclic voltammometry experiments were repeated without the use of a nafion binder (dotted line) and compared to those performed with nafion in the catalyst in (normal line) for $\text{NiFe}_2\text{F}_{4.4}\text{O}_{1.8}$ and a), $\text{CoFe}_2\text{F}_{6.6}\text{O}_{0.7}$ (b), $\text{NiFe}_2\text{F}_8(\text{H}_2\text{O})_2$ (c) and $\text{CoFe}_2\text{F}_8(\text{H}_2\text{O})_2$ (d)