Supporting information

Mapping the performance of amorphous ternary metal oxide water oxidation catalysts containing aluminum

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Explanation of Tafel parameters in this work

When it comes to quantifying and comparing the electrocatalytic activity of different catalysts, one of the straight-forward methods is to relate to Tafel parameters. The Tafel parameters are derived from the well-known Butler-Volmer kinetic equation (S1), which describes the variation of current density with overpotential for a specific electrochemical reaction

$$J = J_o * \{\exp(\alpha n f \eta) - \exp[(1-\alpha) n f \eta]\} \qquad \text{(S1)}$$

where J is the current density, J_0 is the exchange current density, α is the transfer coefficient, $f = F/RT$ (F is Faraday constant), n is the number of electrons involved in the electrochemical reaction, and η is the overpotential.

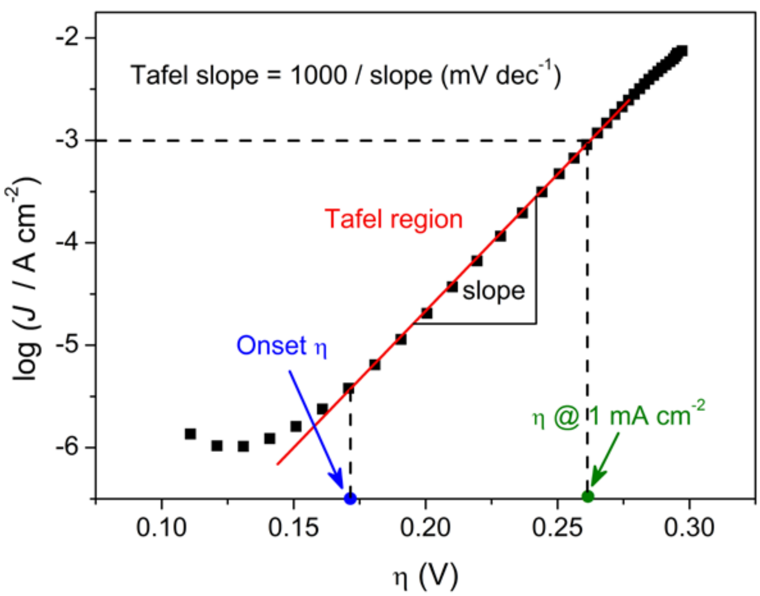
At high positive overpotentials, equation S1 can be simplified as

$$J = J_o \cdot \exp(\alpha n f \eta) \qquad \text{(S2)}$$

which gives

$$\log J = \log J_o + \alpha n f \eta * \log e \qquad \text{(S3)}$$

Equation S3 is a simplified form of the Butler-Volmer equation, and called the Tafel equation. According to equation S3, log$J$ and η exhibit a linear relationship in the overpotential range when the current density is governed by the kinetics at the electrode surface. The reciprocal of the linear slope is the Tafel slope, and the onset of this linear range is the onset overpotential of catalysis. The overpotential required to achieve a current density of 1 mA cm^{-2} is η @1 mA cm^{-2}. A schematic profile of these parameters is presented in Scheme S1.



Scheme S1. Schematic Tafel parameters

Thin film preparation

All the films prepared in this study were obtained by mixing the appropriate amounts of precursors in order to obtain a solution this is 15 % wt/wt in precursor (taking into account the respective purity of each precursor), as indicated in Table S1. The solutions were then spin-coated onto clean F-doped SnO_2 (FTO) glass substrates (following a detergent-water-acetone-ethanol wash sequence, and dried by air and then exposed to ozone for 15 minutes before use). The mixed precursors were sonicated for 1-2 min to achieve homogeneous mixing, followed by spin-coating on FTO-coated glass substrates at a rate of 3000 RPM for 1 min (Laurell model WS-650MZ-23NPP-Lite). The coated substartes were then exposed to UV light using an Atlantic Ultraviolet G18T5VH/U ozone producing lamp (lamp output = 18.4 W, UV output = 5.8 W).

As a representative example , the preparation for the $Al_{0.4}Fe_{0.2}Ni_{0.4}O_x$ thin film used 0.0550 g of aluminium di(sec-butoxide)acetoacetic ester chelate (min 8.4% Al), 0.8000 g of Fe(III) 2-ethylhexanoate (50% *w/w* in mineral spirits), and 0.0796 g og Ni(II) 2-ethylhexanoate (78% *w/w* in 2-ethylhexanoic acid) which were mixed into 0.7916 g of hexanes.

Table S1. Amounts (in grams) of the aluminum, iron, nickel and cobalt precursors and solvent (hexane) required to make one gram solutions of 15 wt%.

Nominal composition	Amount of precursors (g)				Hexanes (g)	UV exposure time (hrs)*
	Aluminum di(sec-butoxide)acetoacetic ester chelate (min 8.4% Al)	Fe(III) 2-ethylhexanoate (50% *w/w* in mineral spirits)	Ni(II) 2-ethylhexanoate (78% *w/w* in 2-ethylhexanoic acid)	Co(II) 2-ethylhexanoate (65% *w/w* in mineral spirits)		
$Al_{0.6}Fe_{0.2}Ni_{0.2}O_x$	0.0832	0.0803	0.0405	-----	0.7960	48
$Al_{0.4}Fe_{0.4}Ni_{0.2}O_x$	0.0502	0.1453	0.0367	-----	0.7679	48
$Al_{0.4}Fe_{0.2}Ni_{0.4}O_x$	0.0541	0.0784	0.0791	-----	0.7884	48
$Al_{0.2}Fe_{0.6}Ni_{0.2}O_x$	0.0229	0.1990	0.0335	-----	0.7447	48
$Al_{0.2}Fe_{0.4}Ni_{0.4}O_x$	0.0245	0.1421	0.0717	-----	0.7616	48
$Al_{0.2}Fe_{0.2}Ni_{0.6}O_x$	0.0264	0.0765	0.1159	-----	0.7811	48
$Al_{0.33}Fe_{0.33}Ni_{0.34}O_x$	0.0421	0.1220	0.0635	-----	0.7724	48
$Al_{0.6}Co_{0.2}Fe_{0.2}O_x$	0.0832	0.0803	-----	0.0424	0.7942	48
$Al_{0.4}Co_{0.4}Fe_{0.2}O_x$	0.0541	0.0783	-----	0.0827	0.7849	48
$Al_{0.4}Co_{0.2}Fe_{0.4}O_x$	0.0502	0.1452	-----	0.0383	0.7663	48
$Al_{0.2}Co_{0.6}Fe_{0.2}O_x$	0.0264	0.0765	-----	0.1211	0.7760	48
$Al_{0.2}Co_{0.4}Fe_{0.4}O_x$	0.0245	0.1421	-----	0.0750	0.7584	48
$Al_{0.2}Co_{0.2}Fe_{0.6}O_x$	0.0229	0.1989	-----	0.0350	0.7432	48
$Al_{0.33}Co_{0.33}Fe_{0.34}O_x$	0.0420	0.1252	-----	0.0641	0.7687	48
$Al_{0.6}Co_{0.2}Ni_{0.2}O_x$	0.0905	-----	0.0441	0.0461	0.8193	48
$Al_{0.4}Co_{0.4}Ni_{0.2}O_x$	0.0587	-----	0.0429	0.0898	0.8086	48
$Al_{0.4}Co_{0.2}Ni_{0.4}O_x$	0.0587	-----	0.0859	0.0449	0.8105	48

$Al_{0.2}Co_{0.6}Ni_{0.2}O_x$	0.0286	-----	0.0418	0.1312	0.7984	48
$Al_{0.2}Co_{0.4}Ni_{0.4}O_x$	0.0286	-----	0.0837	0.0875	0.8002	48
$Al_{0.2}Co_{0.2}Ni_{0.6}O_x$	0.0286	-----	0.1256	0.0437	0.8021	48
$Al_{0.33}Co_{0.33}Ni_{0.34}O_x$	0.0480	-----	0.0723	0.0734	0.8063	48
$Al_{0.8}Fe_{0.2}O_x$	0.1137	0.0823	-----	-----	0.8040	48
$Al_{0.6}Fe_{0.4}O_x$	0.0767	0.1486	-----	-----	0.7745	48
$Al_{0.4}Fe_{0.6}O_x$	0.0468	0.2031	-----	-----	0.7502	48
$Al_{0.2}Fe_{0.8}O_x$	0.0215	0.2486	-----	-----	0.7299	48
$Al_{0.8}Co_{0.2}O_x$	0.1240	-----	-----	0.0474	0.8287	48
$Al_{0.6}Co_{0.4}O_x$	0.0905	-----	-----	0.0922	0.8174	48
$Al_{0.4}Co_{0.6}O_x$	0.0587	-----	-----	0.1346	0.8067	48
$Al_{0.2}Co_{0.8}O_x$	0.0286	-----	-----	0.1749	0.7965	48
$Al_{0.8}Ni_{0.2}O_x$	0.1240	-----	0.0453	-----	0.8307	48
$Al_{0.6}Ni_{0.4}O_x$	0.0905	-----	0.0882	-----	0.8213	48
$Al_{0.4}Ni_{0.6}O_x$	0.0588	-----	0.1289	-----	0.8124	48
$Al_{0.2}Ni_{0.8}O_x$	0.0286	-----	0.1674	-----	0.8039	48

*Using an Atlantic Ultraviolet G18T5VH/U ozone producing lamp. Lamp output = 18.4 W, UV output = 5.8 W

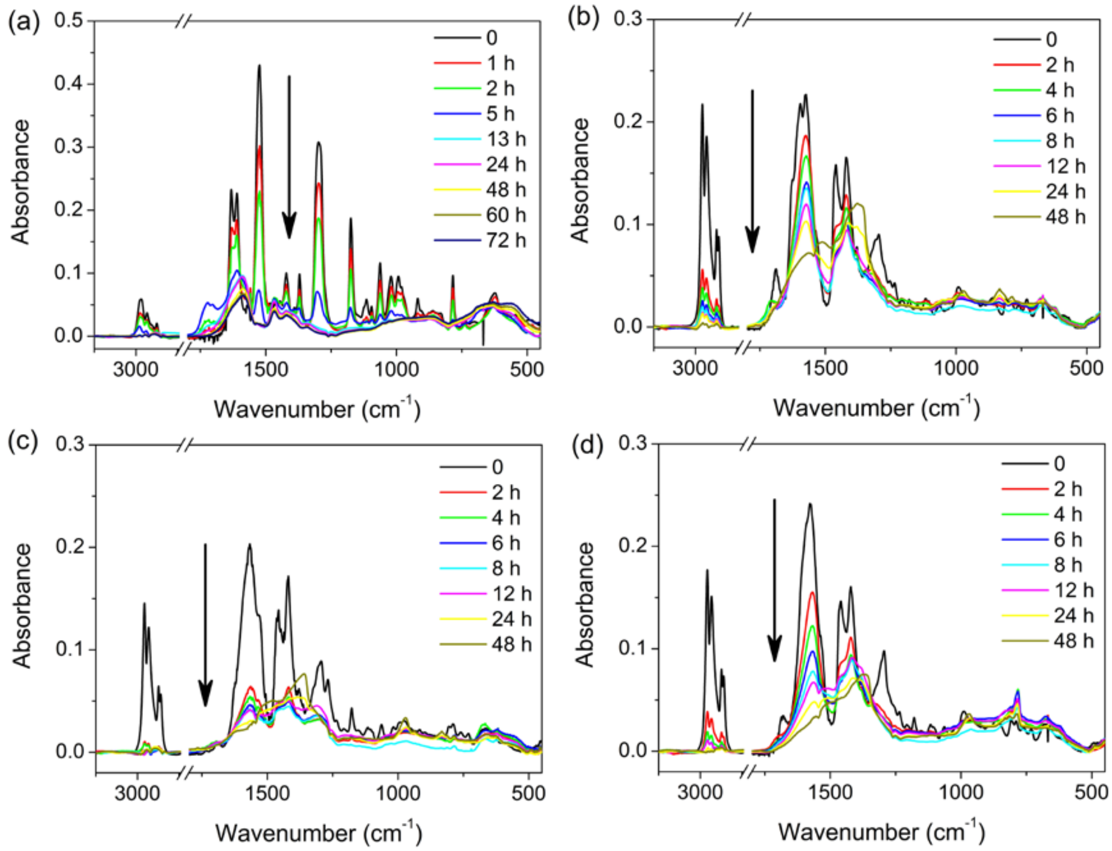


Figure S1. Change of IR spectra of films of (a) Al_2O_3, (b) $Al_{0.2}Fe_{0.2}Ni_{0.6}O_x$, (c) $Al_{0.2}Co_{0.6}Fe_{0.2}O_x$, and (d) $Al_{0.2}Co_{0.2}Ni_{0.6}O_x$ precursors on KBr pellets with photolysis time. The absorption due to the 2-ethylhexanoate ligands (C-H vibrations 3000-2800 cm^{-1}, coordinated carboxylate vibrations 1700-1400 cm^{-1}) disappears after 48 h. The bands around 1560 and 1420 cm^{-1} are probably due to the vibrations related to CO_3^{2-}. The small bands at 961 and 781 cm^{-1} were probably due to the out of plane bending vibration of residual C-H and bending vibration of carboxyl, respectively.

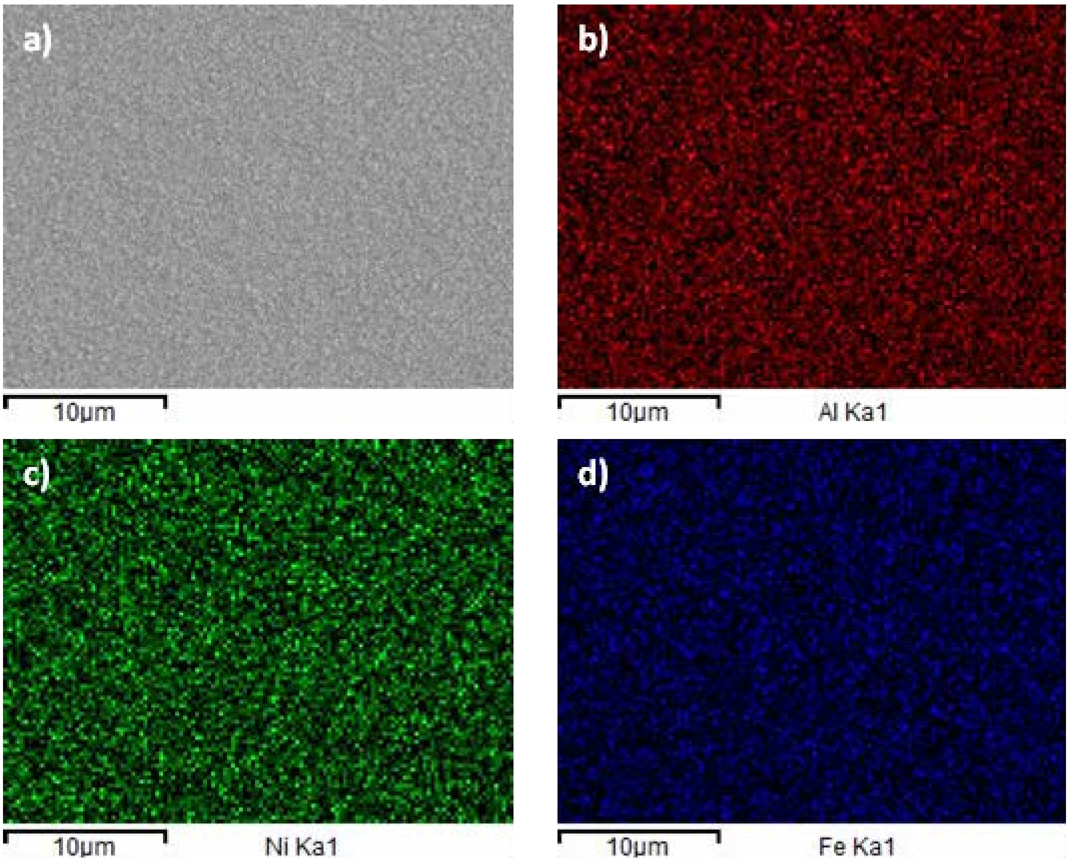


Figure S2. a) SEM image of an $Al_{40}Fe_{20}Ni_{40}O_x$ film on FTO and b)-d) EDXS elemental mapping images showing Al K α_1 (red), Ni K α_1 (green) and Fe K α_1 (blue), respectively.

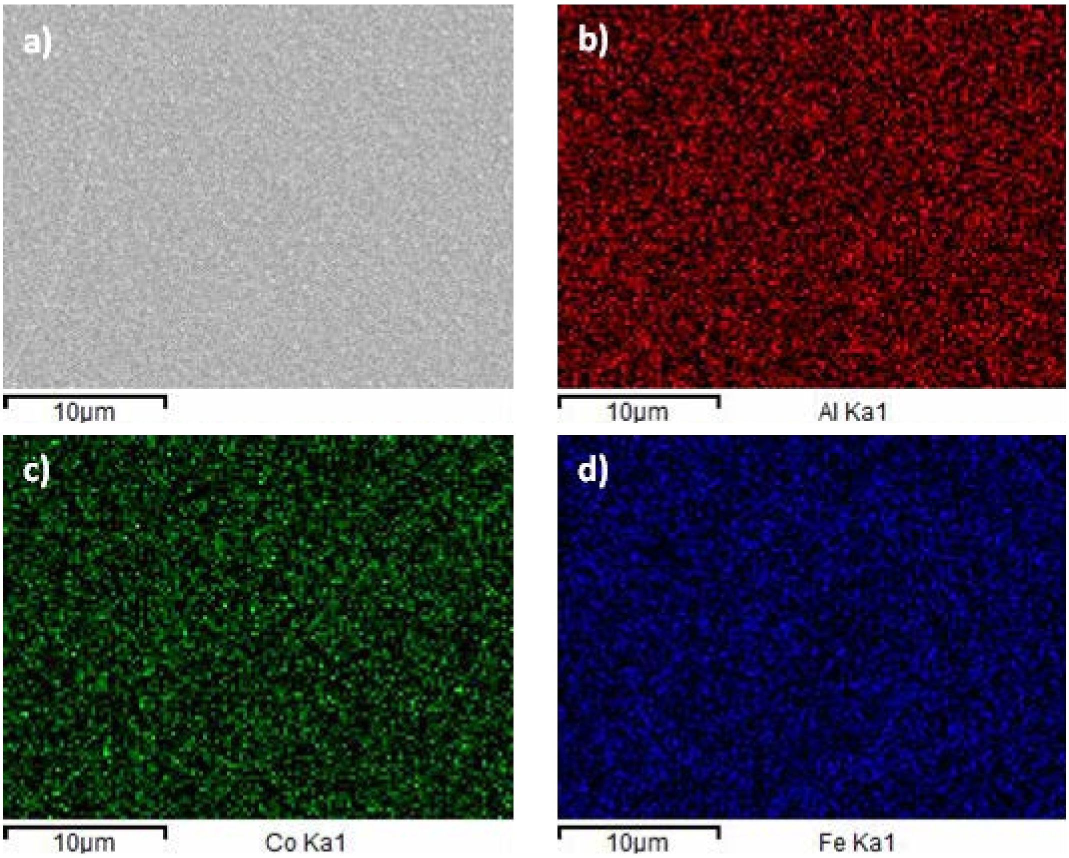


Figure S3. a) SEM image of an $Al_{20}Co_{60}Fe_{20}O_x$ film on FTO and b)-d) EDXS elemental mapping images showing Al K α_1 (red), Co K α_1 (green) and Fe K α_1 (blue), respectively.

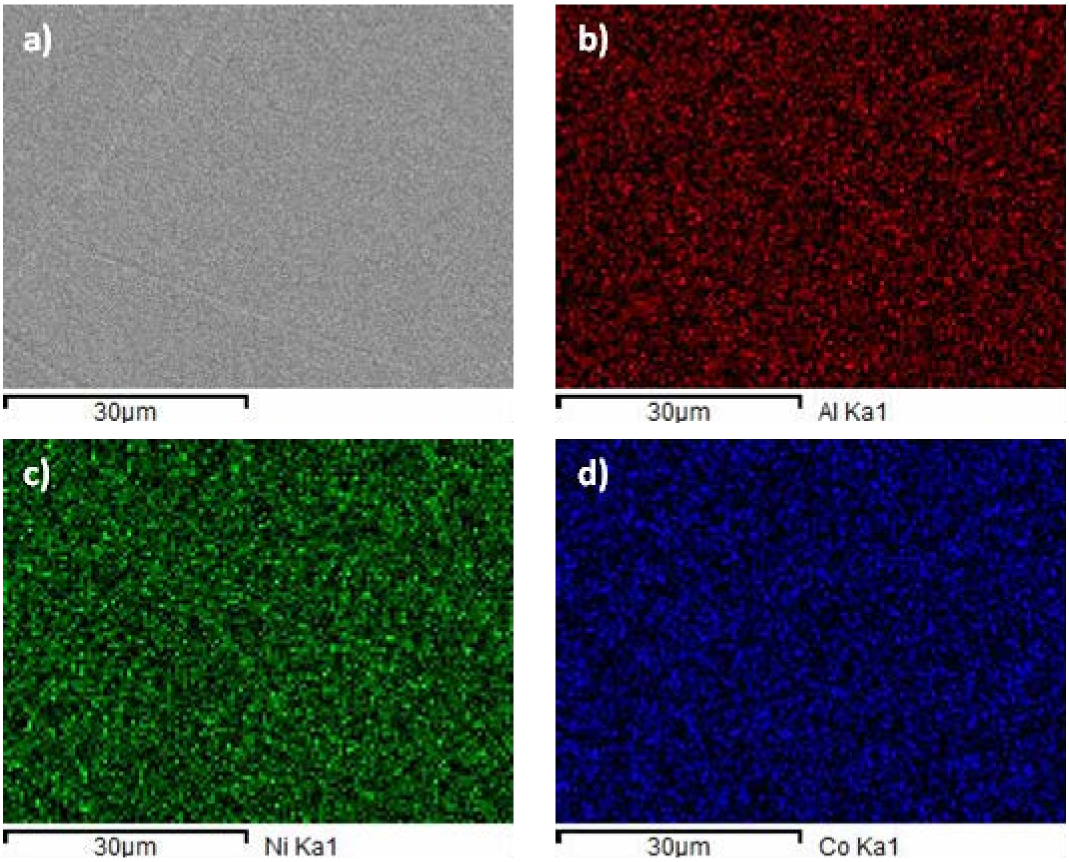


Figure S4. a) SEM image of an $Al_{20}Co_{20}Ni_{60}O_x$ film on FTO and b)-d) EDXS elemental mapping images showing Al K α_1 (red), Ni K α_1 (green) and Co K α_1 (blue), respectively.

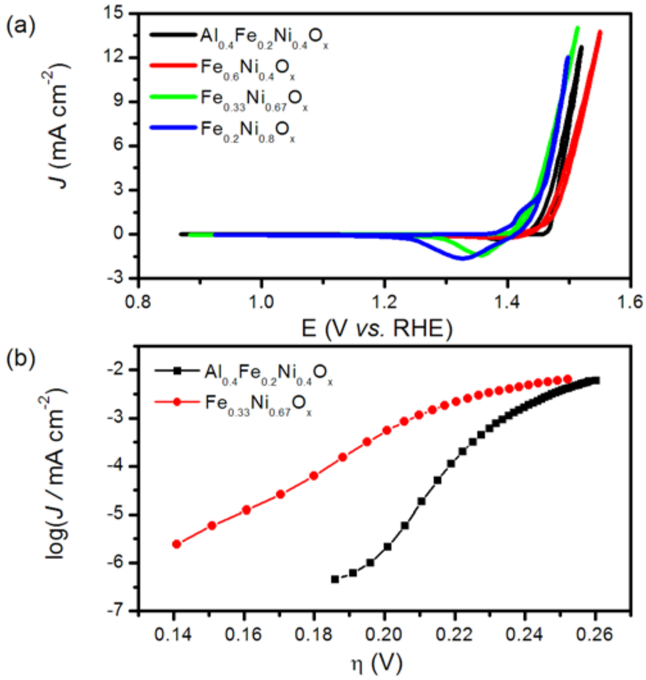


Figure S5. Cyclic voltammograms (after iR correction) of several Al/Fe/Ni series compositions deposited on FTO and recorded in 0.1 M KOH at a scanning rate of 10 mV s^{-1}.

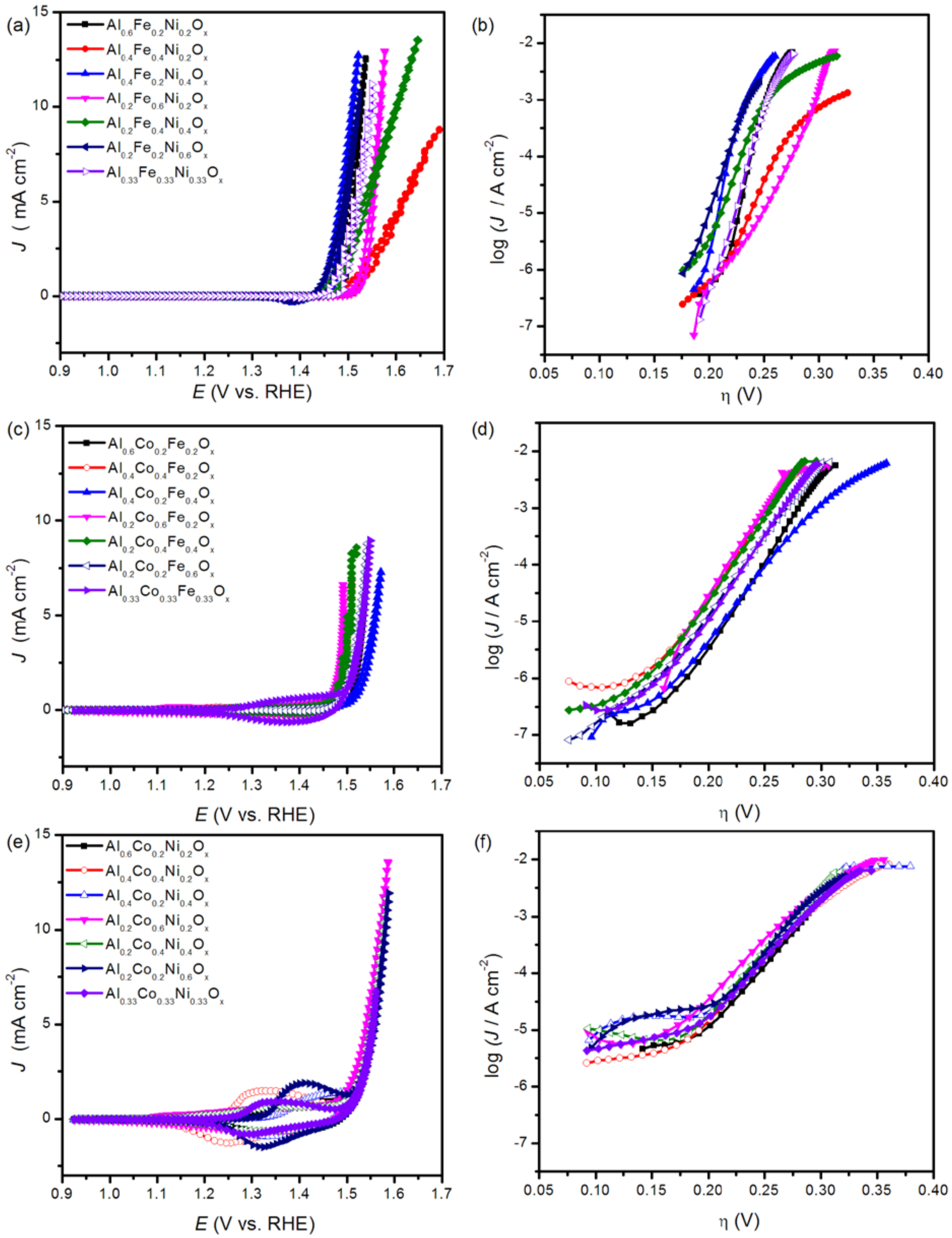


Figure S6. Cyclic voltammograms (left column) and Tafel plots (right column) of (a-b) Al/Fe/Ni, (c-d) Al/Co/Fe, and (e-f) Al/Co/Ni ternary metal oxide films in 0.1 M KOH.

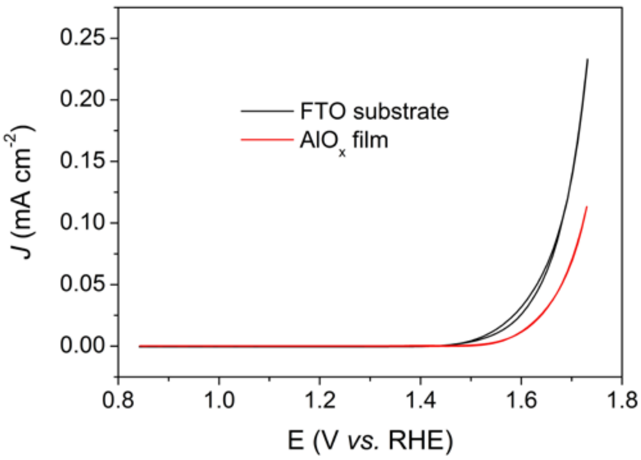


Figure S7. Cyclic voltammograms for aluminum oxide deposited on FTO, and the bare FTO substrate itself (recorded in 0.1 M KOH at a scanning rate of 10 mV s^{-1}).

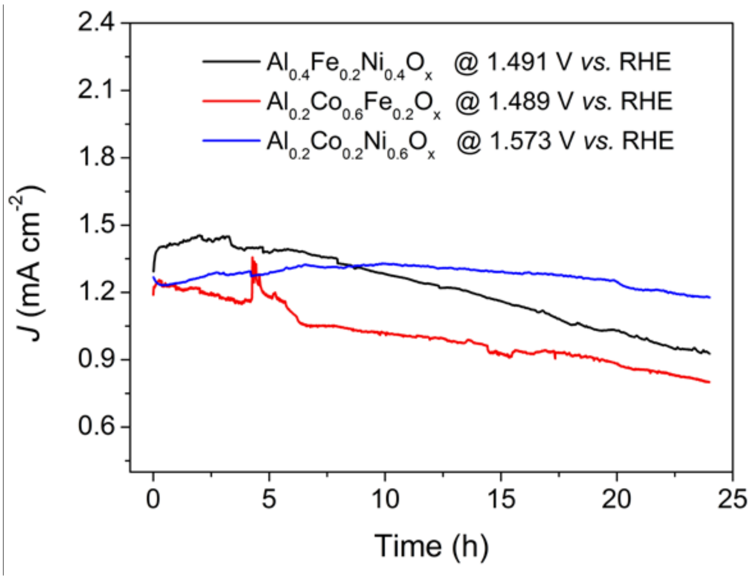


Figure S8. Temporal stability of $Al_{0.4}Fe_{0.2}Ni_{0.4}O_x$, $Al_{0.2}Co_{0.6}Fe_{0.2}O_x$, $Al_{0.2}Co_{0.2}Ni_{0.6}O_x$ in 0.1 M KOH at 25 ^{o}C.

Table S2. Cation content of several ternary materials determined by ICP-OES.

Composition	Al	Co	Fe	Ni
$Al_{0.6}Fe_{0.2}Ni_{0.2}O_x$	0.62	-	0.19	0.18
$Al_{0.4}Fe_{0.2}Ni_{0.4}O_x$	0.42	-	0.21	0.37
$Al_{0.2}Fe_{0.2}Ni_{0.6}O_x$	0.23	-	0.21	0.56
$Al_{0.33}Fe_{0.33}Ni_{0.33}O_x$	0.36	-	0.33	0.30
$Al_{0.2}Co_{0.6}Fe_{0.2}O_x$	0.22	0.58	0.20	-
$Al_{0.2}Co_{0.4}Fe_{0.4}O_x$	0.22	0.39	0.39	-
$Al_{0.4}Co_{0.4}Ni_{0.2}O_x$	0.43	0.39	-	0.18
$Al_{0.2}Co_{0.2}Ni_{0.6}O_x$	0.22	0.21	-	0.56

Table S3. Tafel parameters of all amorphous catalysts investigated in this study.

Composition	Tafel slope (mV dec^{-1})	Onset η of catalysis (V)	η @ 0.5 mA cm^{-2}	η @ 1 mA cm^{-2}
$Al_{0.6}Fe_{0.2}Ni_{0.2}O_x$	10.8 (0.7)	0.222 (0.008)	0.249 (0.012)	0.253 (0.011)
$Al_{0.4}Fe_{0.4}Ni_{0.2}O_x$	22.2 (0.7)	0.2210 (0.0001)	0.285 (0.006)	0.304 (0.013)
$Al_{0.4}Fe_{0.2}Ni_{0.4}O_x$	11.0 (0.8)	0.2010 (0.0001)	0.230 (0.002)	0.236 (0.002)
$Al_{0.2}Fe_{0.6}Ni_{0.2}O_x$	26.6 (0.6)	0.2409 (0.0001)	0.293 (0.002)	0.298 (0.001)
$Al_{0.2}Fe_{0.4}Ni_{0.4}O_x$	17.4 (1.9)	0.208 (0.003)	0.2435 (0.0005)	0.251 (0.004)
$Al_{0.2}Fe_{0.2}Ni_{0.6}O_x$	16.7 (0.9)	0.196 (0.007)	0.228 (0.002)	0.233 (0.003)
$Al_{0.33}Fe_{0.33}Ni_{0.33}O_x$	14.7 (1.2)	0.213 (0.003)	0.247 (0.001)	0.2541 (0.0001)
$Fe_{0.8}Ni_{0.2}O_x$	34.2 (0.9)	0.241 (0.001)	0.301 (0.002)	0.312 (0.002)
$Fe_{0.67}Ni_{0.33}O_x$	26.4 (0.2)	0.211 (0.001)	0.267 (0.004)	0.276 (0.005)
$Fe_{0.6}Ni_{0.4}O_x$	26.8 (1.4)	0.191 (0.001)	0.240 (0.006)	0.250 (0.008)
$Fe_{0.5}Ni_{0.5}O_x$	25.5 (0.9)	0.181 (0.001)	0.231 (0.001)	0.239 (0.001)
$Fe_{0.4}Ni_{0.6}O_x$	24.1 (2.0)	0.174 (0.009)	0.217 (0.002)	0.226 (0.001)
$Fe_{0.33}Ni_{0.67}O_x$	23.3 (1.2)	0.171 (0.001)	0.201 (0.003)	0.210 (0.003)
$Fe_{0.2}Ni_{0.8}O_x$	30.0 (0.7)	0.151 (0.001)	0.199 (0.002)	0.208 (0.002)
$Al_{0.8}Fe_{0.2}O_x$	32.8 (2.2)	0.331 (0.001)	0.413 (0.006)	0.430 (0.007)
$Al_{0.6}Fe_{0.4}O_x$	24.0 (1.2)	0.326 (0.007)	0.405 (0.002)	0.420 (0.002)
$Al_{0.4}Fe_{0.6}O_x$	24.9 (1.7)	0.296 (0.007)	0.378 (0.002)	0.387 (0.001)
$Al_{0.2}Fe_{0.8}O_x$	35.2 (1.8)	0.281 (0.001)	0.373 (0.004)	0.383 (0.006)
$Al_{0.8}Ni_{0.2}O_x$	40.4 (1.3)	0.220 (0.003)	0.263 (0.004)	0.276 (0.002)
$Al_{0.6}Ni_{0.4}O_x$	43.2 (1.6)	0.199 (0.001)	0.236 (0.008)	0.248 (0.008)
$Al_{0.4}Ni_{0.6}O_x$	36.6 (1.5)	0.198 (0.002)	0.217 (0.004)	0.228 (0.005)
$Al_{0.2}Ni_{0.8}O_x$	39.6 (2.1)	0.209 (0.003)	0.233 (0.002)	0.245 (0.004)
$Al_{0.6}Co_{0.2}Fe_{0.2}O_x$	32.8 (0.7)	0.1909 (0.0001)	0.266 (0.006)	0.276 (0.006)
$Al_{0.4}Co_{0.4}Fe_{0.2}O_x$	34.1 (1.4)	0.178 (0.003)	0.250 (0.011)	0.260 (0.011)
$Al_{0.4}Co_{0.2}Fe_{0.4}O_x$	38.8 (1.1)	0.168 (0.003)	0.282 (0.002)	0.2966 (0.0004)
$Al_{0.2}Co_{0.6}Fe_{0.2}O_x$	31.2 (1.6)	0.174 (0.005)	0.243 (0.004)	0.254 (0.005)
$Al_{0.2}Co_{0.4}Fe_{0.4}O_x$	35.1 (0.7)	0.161 (0.007)	0.238 (0.011)	0.248 (0.011)
$Al_{0.2}Co_{0.2}Fe_{0.6}O_x$	36.6 (1.0)	0.146 (0.014)	0.265 (0.012)	0.277 (0.011)
$Al_{0.33}Co_{0.33}Fe_{0.33}O_x$	34.9 (0.6)	0.171 (0.001)	0.260 (0.006)	0.270 (0.006)
$Co_{0.8}Fe_{0.2}O_x$	36.6 (2.1)	0.178 (0.004)	0.238 (0.004)	0.249 (0.003)
$Co_{0.67}Fe_{0.33}O_x$	36.04 (0.06)	0.173 (0.003)	0.237 (0.001)	0.247 (0.001)
$Co_{0.6}Fe_{0.4}O_x$	37.2 (0.6)	0.163 (0.011)	0.243 (0.012)	0.253 (0.013)
$Co_{0.5}Fe_{0.5}O_x$	38.0 (0.9)	0.168 (0.003)	0.2459 (0.0004)	0.257 (0.001)
$Co_{0.4}Fe_{0.6}O_x$	37.7 (0.6)	0.178 (0.003)	0.258 (0.006)	0.269 (0.005)
$Co_{0.33}Fe_{0.67}O_x$	37.5 (0.6)	0.151 (0.007)	0.251 (0.011)	0.262 (0.011)
$Co_{0.2}Fe_{0.8}O_x$	36.3 (0.2)	0.178 (0.003)	0.275 (0.002)	0.287 (0.003)
$Al_{0.8}Co_{0.2}O_x$	40.7 (0.6)	0.201 (0.001)	0.293 (0.001)	0.309 (0.001)
$Al_{0.6}Co_{0.4}O_x$	41.9 (1.8)	0.201 (0.001)	0.292 (0.006)	0.307 (0.007)
$Al_{0.4}Co_{0.6}O_x$	40.4 (3.1)	0.191 (0.001)	0.280 (0.009)	0.293 (0.011)
$Al_{0.2}Co_{0.8}O_x$	43.5 (0.1)	0.171 (0.014)	0.272 (0.001)	0.286 (0.001)
$Al_{0.6}Co_{0.2}Ni_{0.2}O_x$	44.6 (1.3)	0.206 (0.007)	0.271 (0.002)	0.285 (0.002)

$Al_{0.4}Co_{0.4}Ni_{0.2}O_x$	44.4 (0.9)	0.1920 (0.0005)	0.267 (0.003)	0.282 (0.005)
$Al_{0.4}Co_{0.2}Ni_{0.4}O_x$	46.8 (1.9)	0.207 (0.005)	0.269 (0.003)	0.283 (0.003)
$Al_{0.2}Co_{0.6}Ni_{0.2}O_x$	47.9 (2.3)	0.1732 (0.0002)	0.257 (0.002)	0.272 (0.002)
$Al_{0.2}Co_{0.4}Ni_{0.4}O_x$	44.7 (0.3)	0.188 (0.007)	0.263 (0.001)	0.277 (0.001)
$Al_{0.2}Co_{0.2}Ni_{0.6}O_x$	40.1 (1.2)	0.2093 (0.0001)	0.255 (0.002)	0.267 (0.003)
$Al_{0.33}Co_{0.33}Ni_{0.33}O_x$	47.7 (2.0)	0.197 (0.007)	0.271 (0.001)	0.286 (0.002)
$Co_{0.8}Ni_{0.2}O_x$	46.5 (1.1)	0.1730 (0.0001)	0.256 (0.005)	0.270 (0.006)
$Co_{0.67}Ni_{0.33}O_x$	42.9 (3.2)	0.19035 (0.00001)	0.246 (0.001)	0.258 (0.003)
$Co_{0.6}Ni_{0.4}O_x$	49.1 (0.5)	0.188 (0.008)	0.261 (0.003)	0.276 (0.002)
$Co_{0.5}Ni_{0.5}O_x$	52.7 (2.4)	0.177 (0.007)	0.267 (0.009)	0.285 (0.010)
$Co_{0.4}Ni_{0.6}O_x$	52.7 (1.2)	0.183 (0.002)	0.2697 (0.0001)	0.286 (0.001)
$Co_{0.33}Ni_{0.67}O_x$	54.5 (0.5)	0.172 (0.014)	0.267 (0.009)	0.285 (0.008)
$Co_{0.2}Ni_{0.8}O_x$	50.0 (1.0)	0.1920 (0.0002)	0.259 (0.001)	0.272 (0.001)
FeO_x	33.7 (3.0)	0.279 (0.015)	0.370 (0.021)	0.387 (0.023)
NiO_x	42.3 (1.6)	0.203 (0.018)	0.239 (0.010)	0.273 (0.004)
CoO_x	44.7 (2.9)	0.189 (0.003)	0.260 (0.006)	0.251 (0.011)

Table S4. ICP-OES composition of $Al_{0.4}Fe_{0.2}Ni_{0.4}O_x$ samples after different treatments.

Treatment	Al	Fe	Ni
Fresh	0.42	0.21	0.37
In 0.1 M KOH for 2 h	0.20	0.28	0.52
In 0.1 M KOH for 24 h	0.18	0.27	0.55
CV in 0.1 M KOH for 2 h (0-0.9 V vs. NHE)	0.27	0.26	0.47
CV in 0.1 M KOH for 24 h (0-0.9 V vs. NHE)	0.27	0.26	0.47