

Supplementary Information

Geometric distortions in nickel (oxy)hydroxide electrocatalysts by redox inactive iron ions

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Bond Angle Calculations:

Lines drawn between the two oxygen atoms and the two metal atoms in a di- μ -oxo bridged M_1 - M_2 motif yields right-angle triangles. Knowledge of the bond distances involved (R_{M_1-O} , R_{M_2-O} and $R_{M_1-M_2}$) enables the application of trigonometry to calculate θ_{O-M_1-O} . In this work, θ_{O-M-O} values were calculated using Equation S1:

$$\theta_{O-M_1-O} = 2\cos^{-1} \left[\frac{R_{M_1-O}^2 - R_{M_2-O}^2 + R_{M_1-M_2}^2}{2R_{M_1-M_2}R_{M_1-O}} \right] \quad (S1)$$

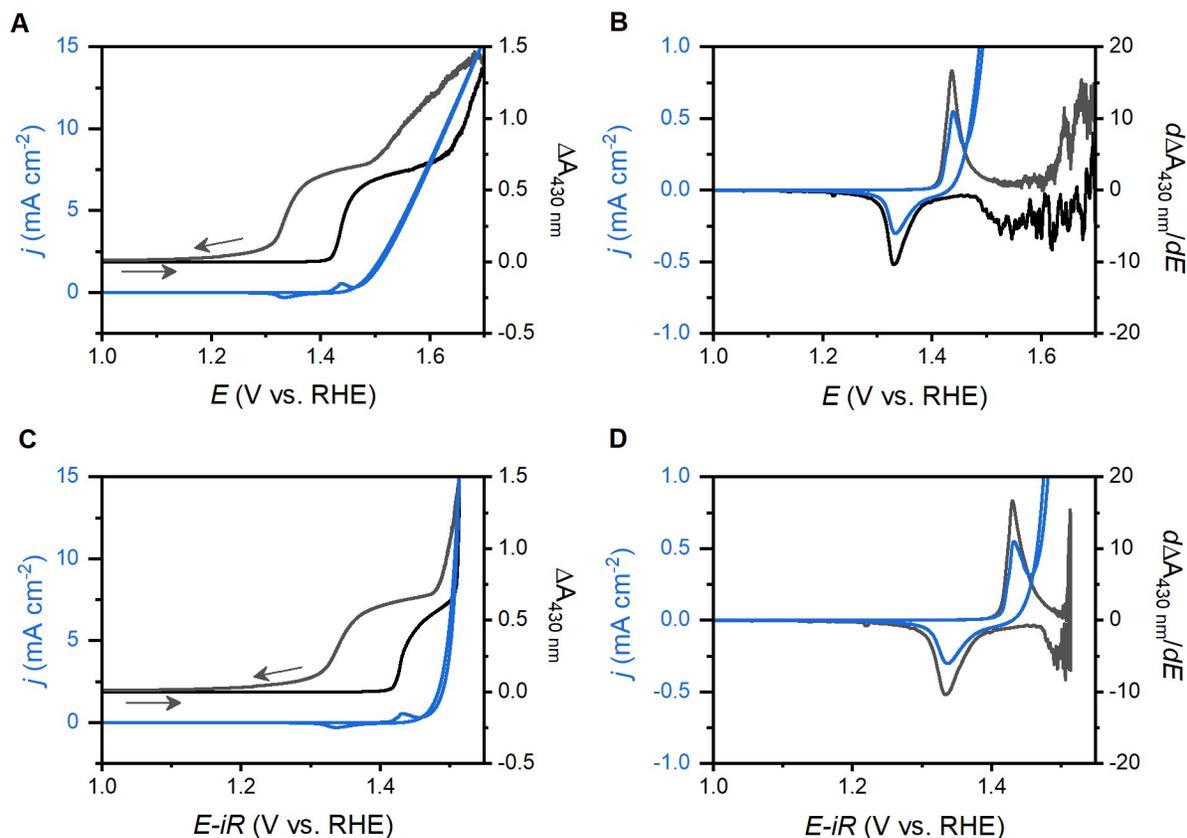


Figure S1. Spectroelectrochemical cyclic voltammetry experiments for 88% Ni (A-B) before and (C-D) after numeric correction for solution resistance. Panels (A) and (C) compare the current to the change in absorbance, and panels (B) and (D) show the derivative of the absorbance. The voltage was swept at 1 mV s⁻¹ in 1 M KOH and solution resistance was 12 Ω . Derivative plots were smoothed using an 8 mV weighted average window.

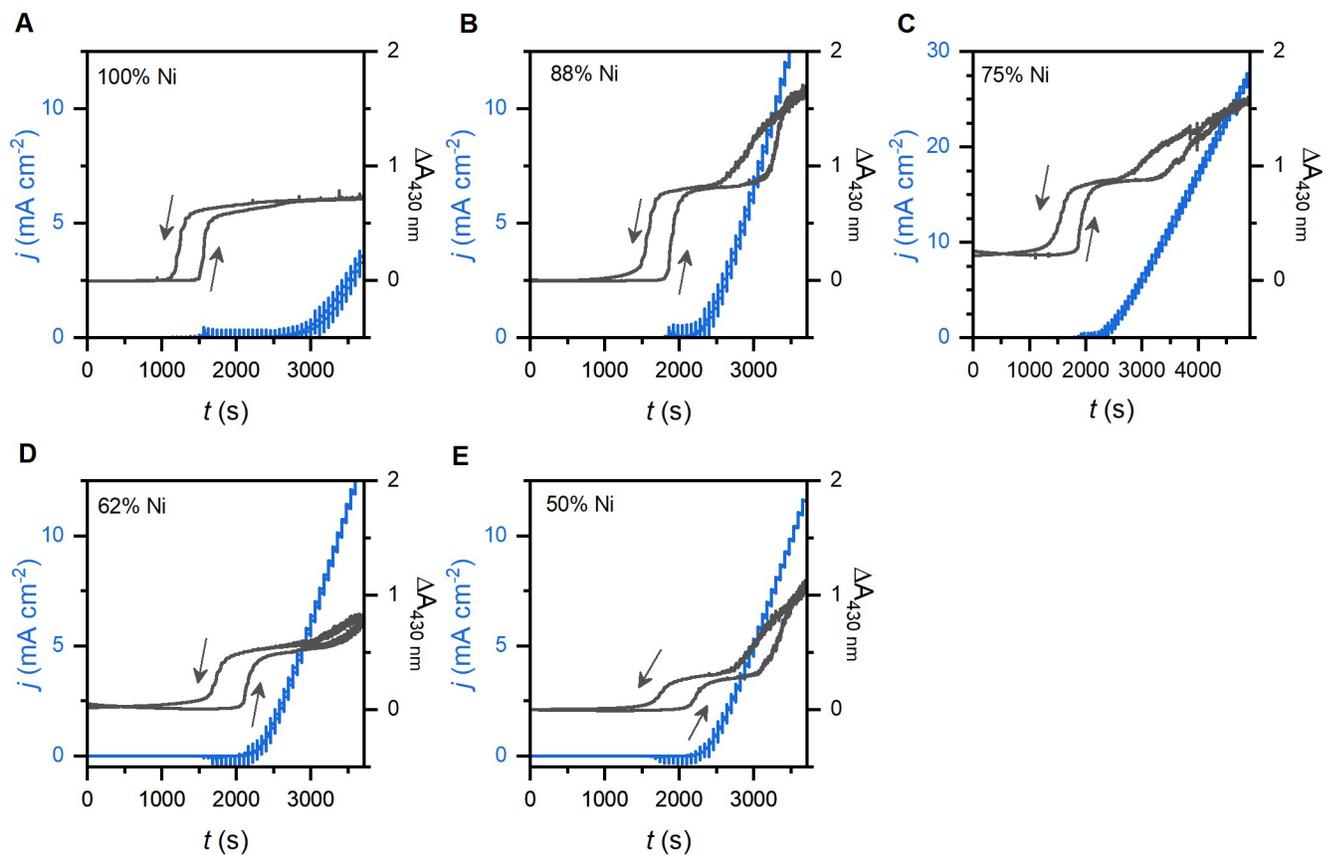


Figure S2. Staircase voltammetry experiments used to generate Tafel plots. The transient current density (blue traces; left axes) and $\Delta A_{430\text{ nm}}$ values (grey traces; right axes) recorded for (A) 100% Ni, (B) 88% Ni, (C) 75% Ni, (D) 62% Ni and (E) 50% Ni. Experiments employed 60 second, 10 mV steps from 1.0 to 1.7 V vs. RHE (no resistance compensation).

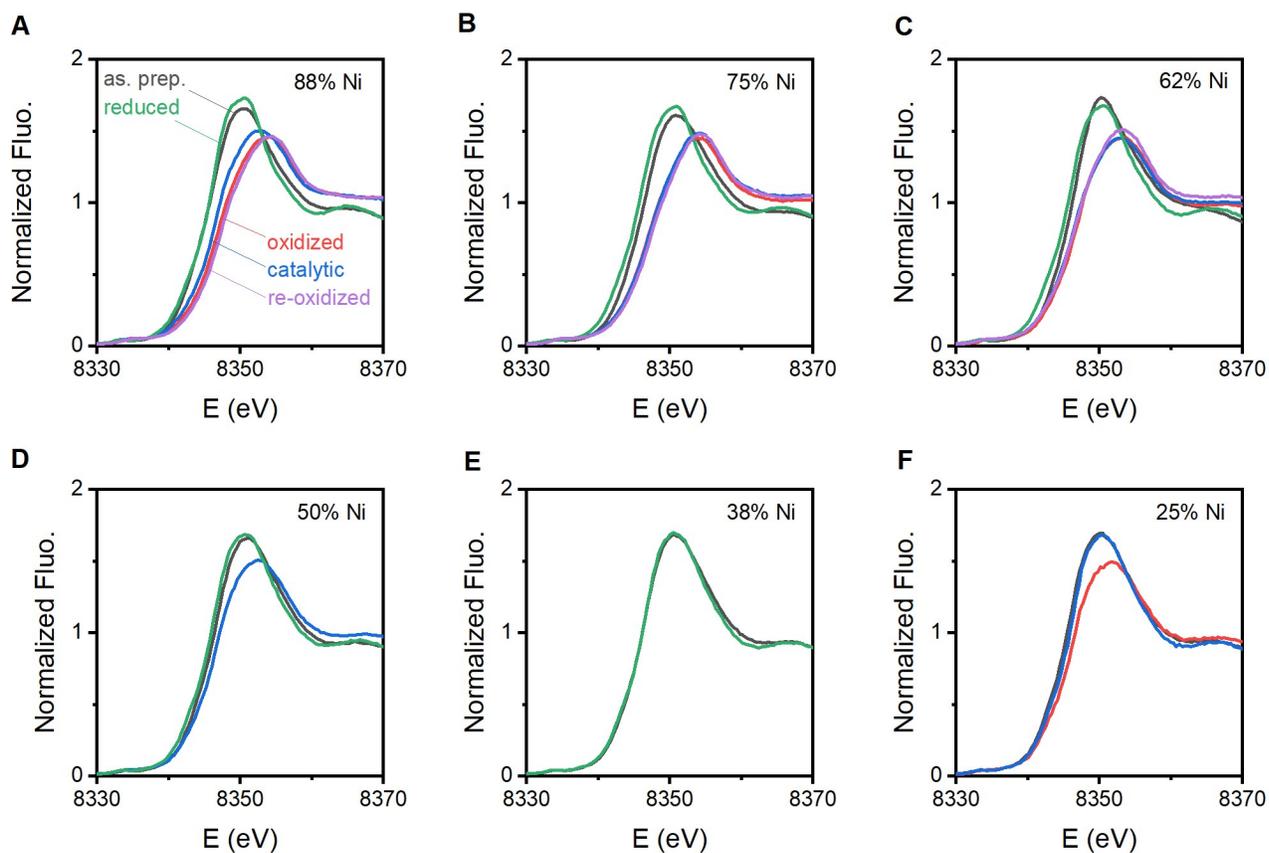


Figure S3. X-ray absorption near-edge spectra for the Ni K-edges. Data shown for as-prepared (black), oxidized (red), catalytic (blue), reduced (green) and re-oxidized (purple) samples of (A) 88% Ni, (B) 75% Ni, (C) 62% Ni, (D) 50% Ni, (E) 38% Ni, and (F) 25% Ni.

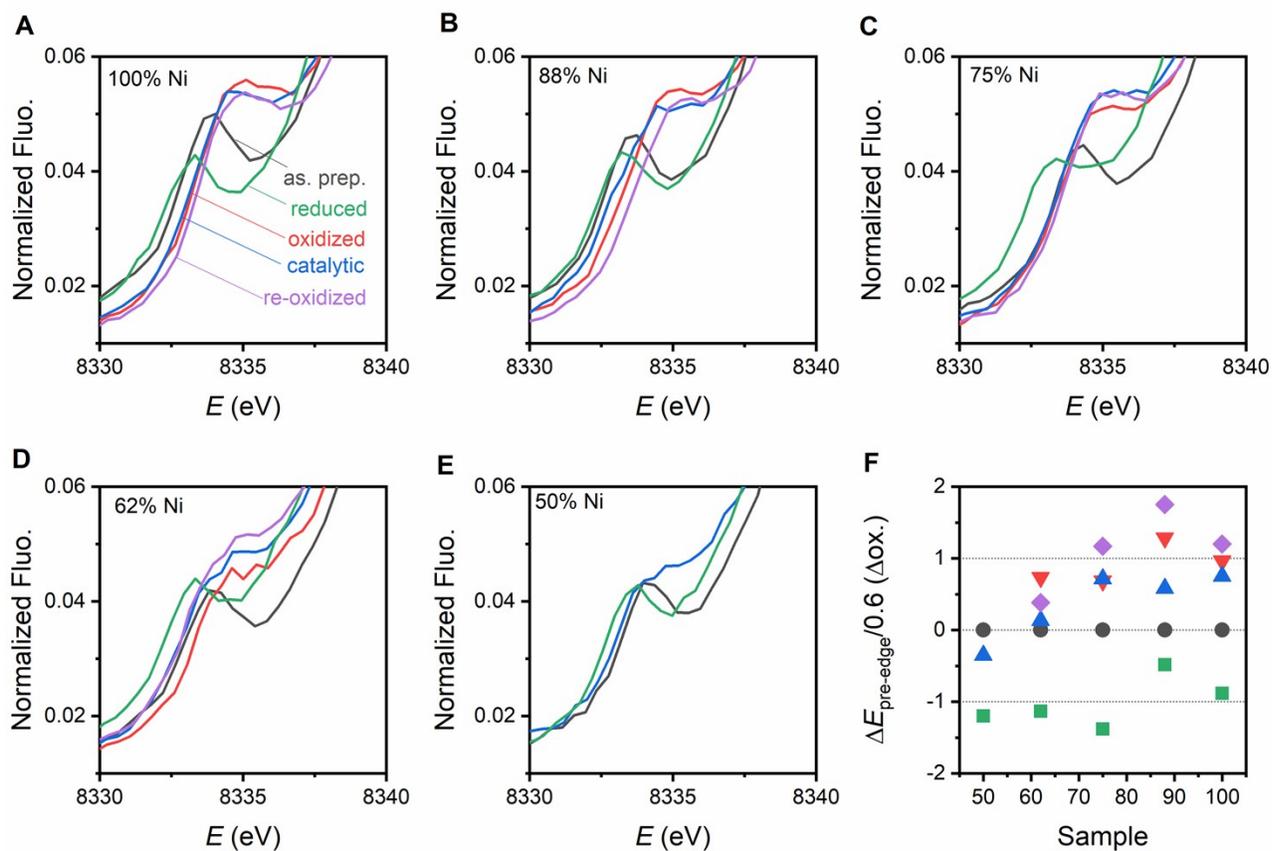


Figure S4. Pre-edge region for the Ni K-edge XAS spectra. Data shown for as-prepared (black), oxidized (red), catalytic (blue), reduced (green) and re-oxidized (purple) samples of (A) 100% Ni, (B) 88% Ni, (C) 75% Ni, (D) 62% Ni, and (E) 50% Ni. (F) Approximate nickel oxidation states for the samples shown, relative to the as-prepared sample.

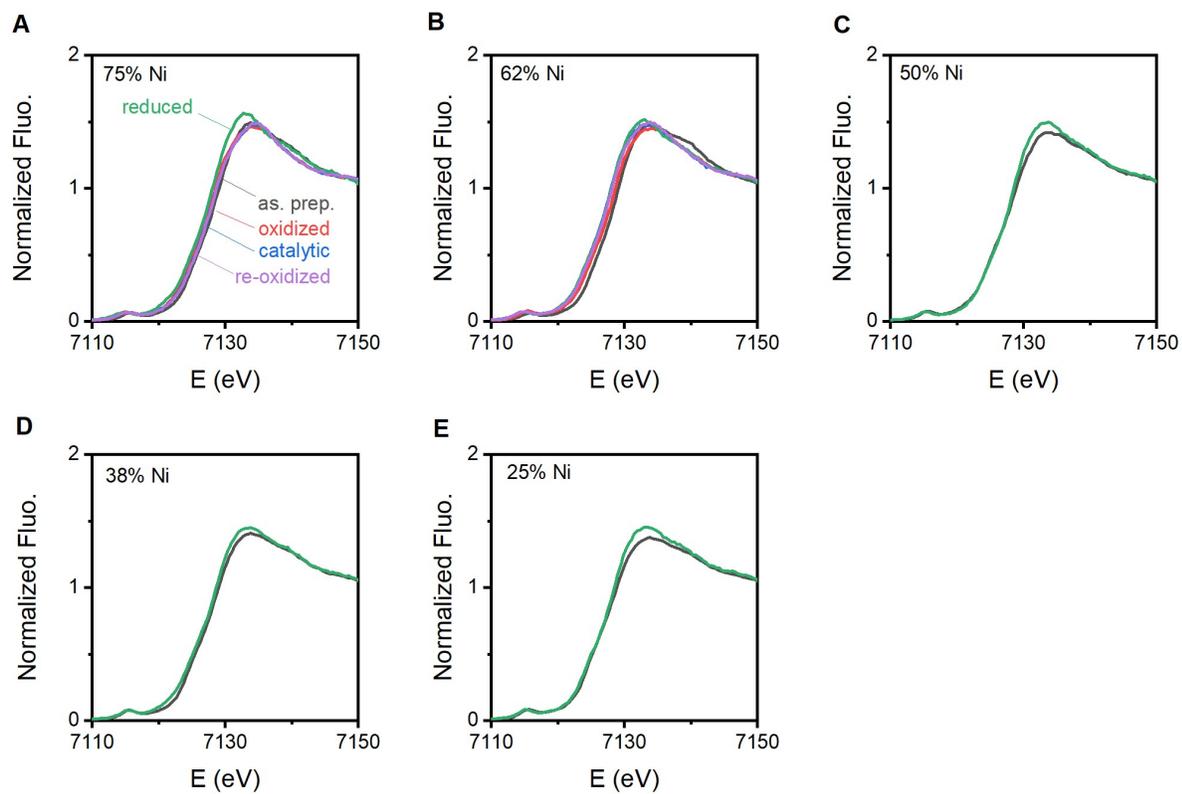


Figure S5. X-ray absorption near-edge spectra for the Fe K-edges. Data shown for as-prepared (black), oxidized (red), catalytic (blue), reduced (green) and re-oxidized (purple) samples of (A) 75% Ni, (B) 62% Ni, (C) 50% Ni, (D) 27% Ni, (E) and 25% Ni.

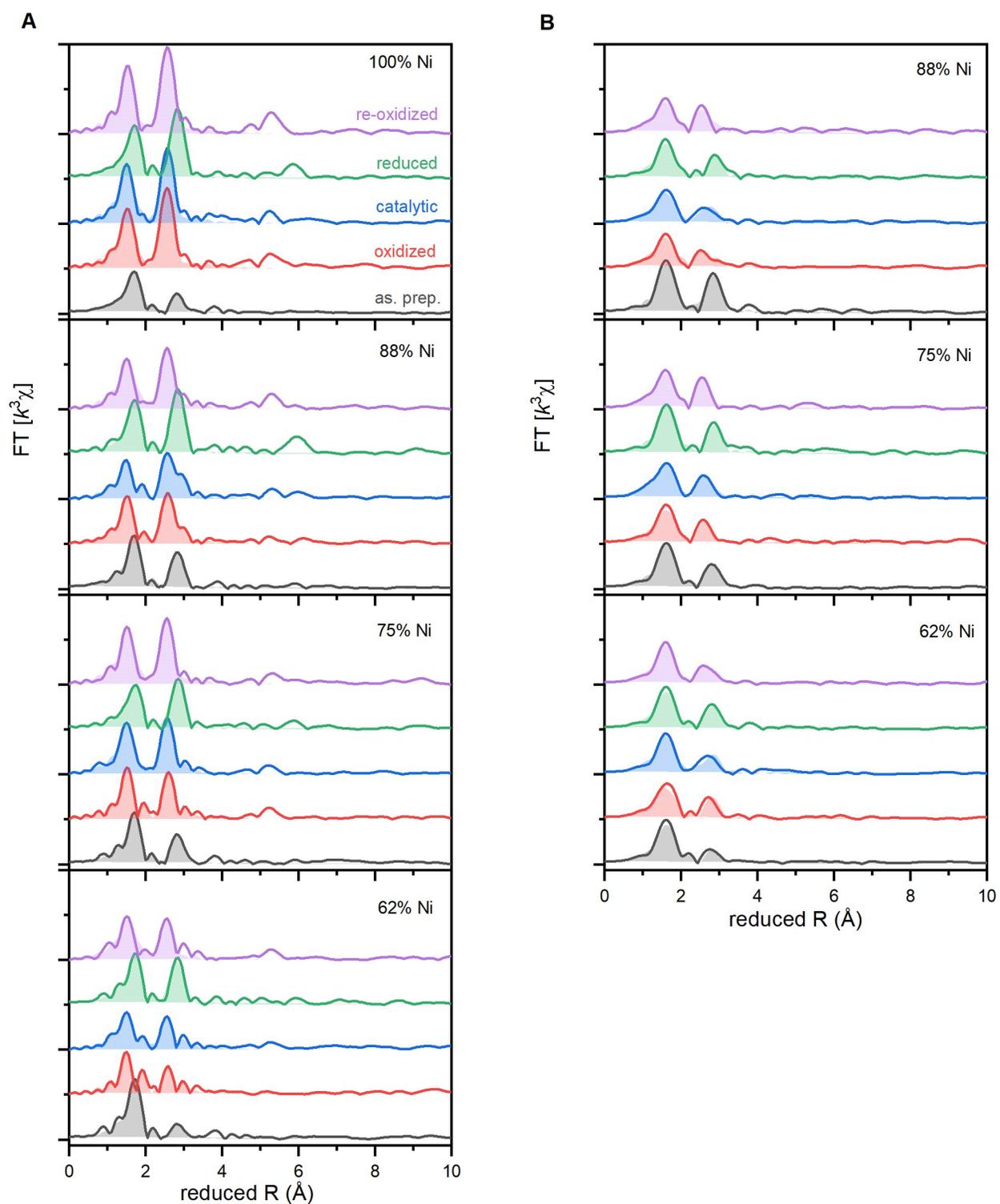


Figure S6. Expanded view of Fourier-transformed X-ray absorption fine-structure spectra shown in the main text. Data shown for the (A) Ni K-edge and (B) Fe K-edge. All panels contain data for as-prepared (black), oxidized (red), catalytic (blue), reduced (green) and re-oxidized (purple) films. Solid lines represent the experimental data and shading the EXAFS simulations

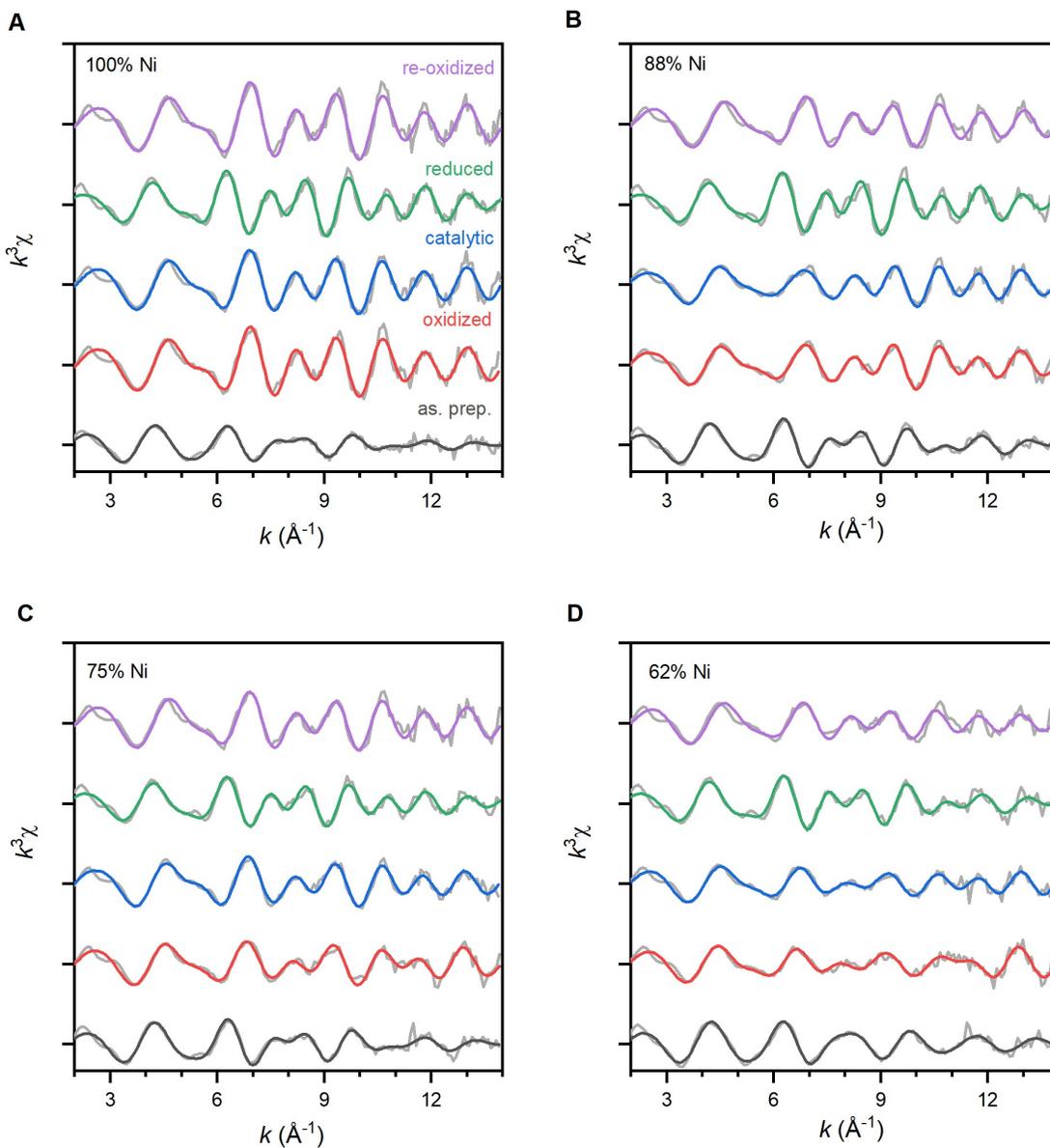


Figure S7. The k -3 weighted X-ray absorption fine-structure spectra (grey lines) and the mathematical fits (coloured lines) for the Ni K-edge of (A) 100% Ni, (B) 88% Ni, (C) 75% Ni, and (D) 62% Ni. All panels contain data for as-prepared (black), oxidized (red), catalytic (blue), reduced (green) and re-oxidized (purple) films. Fits shown correspond to the parameters given in Tables 1 and S3.

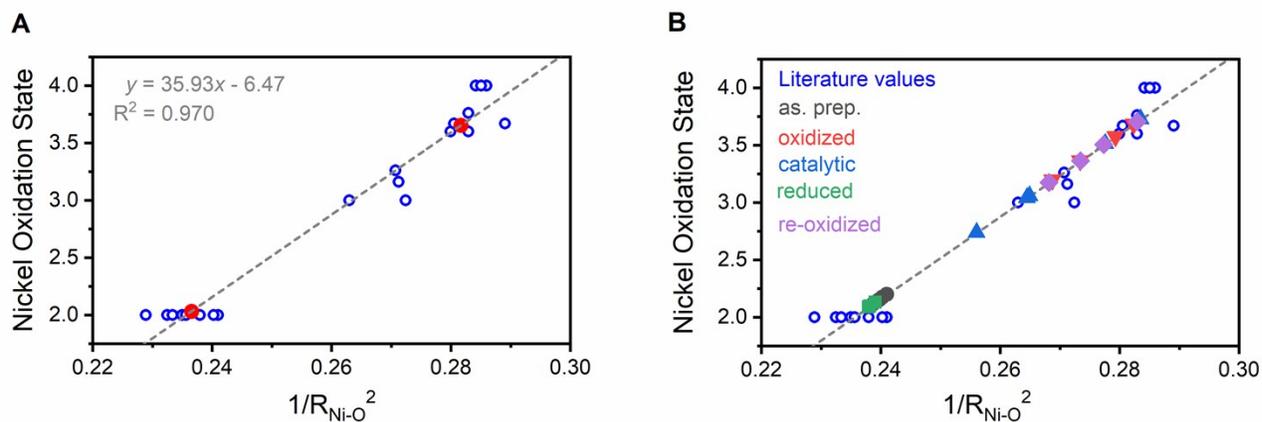


Figure S8. Calibration curves relating nickel-oxygen bond length to nickel oxidation state. Comparison of Ni-O bond lengths from the literature to (A) the two nickel-oxygen bond-lengths observed in EXAFS simulations and (B) the weighted average $R_{\text{Ni-O}}$ values for each composition-voltage combination. Literature values for calibration curve are tabulated in reference 12.

Table S1. EXAFS simulation parameters for the minimal fit description of Ni K-edge spectra with idealized octahedral coordination.^a

% Ni	$N_{\text{Ni-O1}}$	$R_{\text{Ni-O1}}$	$N_{\text{Ni-O2}}$	$R_{\text{Ni-O2}}$	$\sigma_{\text{Ni-O}}$	$N_{\text{Ni-M1}}$	$R_{\text{Ni-M1}}$	$N_{\text{Ni-M2}}$	$R_{\text{Ni-M2}}$	$\sigma_{\text{Ni-M}}$	R_f
100 ^b			6	2.041 (0.004)	0.084 (0.003)			2.3 (0.7)	3.054 (0.008)	0.086 (0.012)	14.7
88 ^b			6	2.043 (0.003)	0.070 (0.003)			4.4 (0.8)	3.071 (0.005)	0.085 (0.007)	13.9
75 ^b			6	2.043 (0.004)	0.072 (0.003)			4.8 (1.2)	3.064 (0.006)	0.099 (0.009)	16.0
62 ^b			6	2.048 (0.003)	0.062 (0.003)			3.7 (1.9)	3.060 (0.013)	0.116 (0.019)	10.6
50 ^b			6	2.037 (0.004)	0.074 (0.003)			6.9 (1.6)	3.050 (0.006)	0.111 (0.009)	17.1
38 ^b			6	2.047 (0.003)	0.070 (0.003)			6.4 (1.4)	3.057 (0.006)	0.111 (0.008)	15.8
25 ^b			6	2.045 (0.003)	0.073 (0.003)			6.1 (1.6)	3.042 (0.007)	0.115 (0.010)	18.5
13 ^b			6	2.046 (0.003)	0.071 (0.003)			7.3 (2.0)	3.065 (0.008)	0.124 (0.010)	17.8
100 ^c			6	1.883 (0.004)	0.077 (0.003)	4.7 (0.4)	2.829 (0.002)			0.060 (0.004)	12.3
88 ^c	4.4 (0.2)	1.884 (0.005)	1.5	2.107 (0.068)	0.068 (0.005)	4.7 (1.3)	2.844 (0.005)	2.4 (1.1)	3.101 (0.011)	0.078 (0.008)	9.5
75 ^c	4.4 (0.2)	1.882 (0.005)	1.6	2.092 (0.058)	0.058 (0.005)	3.8 (1.1)	2.862 (0.005)	1.2 (0.8)	3.083 (0.021)	0.072 (0.010)	18.7
62 ^c	3.5 (0.2)	1.892 (0.005)	2.5	2.096 (0.048)	0.048 (0.006)	2.2 (0.8)	2.884 (0.007)	1.4 (0.7)	3.066 (0.016)	0.061 (0.016)	20.8
100 ^d	6	1.880 (0.003)			0.081 (0.003)	3.9 (0.4)	2.834 (0.002)			0.055 (0.004)	15.1
88 ^d	4.0 (0.2)	1.882 (0.007)	2	2.080 (0.017)	0.070 (0.006)	3.9 (1.0)	2.844 (0.005)	2.8 (1.0)	3.100 (0.008)	0.073 (0.008)	8.0
75 ^d	5.3 (0.3)	1.883 (0.005)	0.7	2.113 (0.054)	0.078 (0.006)	5.5 (1.1)	2.847 (0.004)	1.8 (0.8)	3.077 (0.014)	0.078 (0.006)	12.2
62 ^d	4.3 (0.3)	1.889 (0.008)	1.8	2.092 (0.023)	0.078 (0.007)	2.0 (0.2)	2.861 (0.005)	1.0 (0.3)	3.049 (0.013)	0.052 (0.006)	19.4
50 ^d	2.8 (0.4)	1.887 (0.016)	3.2	2.058 (0.017)	0.087 (0.010)	3.1 (0.8)	2.860 (0.008)	3.5 (0.9)	3.048 (0.008)	0.083 (0.009)	20.9
25 ^d	2.6 (0.2)	1.894 (0.012)	3.4	2.067 (0.011)	0.073 (0.010)	2.7 (0.8)	2.859 (0.016)	4.8 (1.5)	3.044 (0.094)	0.094 (0.013)	10.3
100 ^e			6	2.045 (0.004)	0.070 (0.003)			6.5 (0.7)	3.085 (0.002)	0.072 (0.004)	8.8
88 ^e			6	2.050 (0.004)	0.070 (0.003)			5.9 (0.8)	3.094 (0.003)	0.070 (0.005)	9.5
75 ^e			6	2.044 (0.006)	0.081 (0.005)			4.8 (0.8)	3.080 (0.004)	0.074 (0.007)	17.1
62 ^e			6	2.050 (0.005)	0.072 (0.004)			5.8 (1.1)	3.065 (0.005)	0.087 (0.007)	18.3
50 ^e			6	2.046 (0.005)	0.077 (0.004)			6.8 (1.5)	3.055 (0.006)	0.098 (0.008)	16.0
38 ^e			6	2.047 (0.004)	0.075 (0.004)			5.9 (1.2)	3.062 (0.005)	0.096 (0.008)	17.0
25 ^e			6	2.046 (0.004)	0.066 (0.003)			6.4 (1.4)	3.056 (0.006)	0.101 (0.008)	22.4
100 ^f			6	1.880 (0.004)	0.069 (0.003)	5.1 (0.5)	2.832 (0.002)			0.061 (0.005)	13.0
88 ^f			6	1.891 (0.007)	0.090 (0.005)	2.8 (0.5)	2.830 (0.004)			0.050 (0.009)	20.0
75 ^f			6	1.888 (0.005)	0.080 (0.005)	3.1 (0.5)	2.833 (0.003)			0.051 (0.008)	17.5
62 ^f			6	1.902 (0.008)	0.099 (0.006)	2.0 (0.6)	2.847 (0.006)			0.054 (0.014)	34.2

^a $S_0^2 = 0.90$, σ_i group fitted with similar shells per sample/voltage combination ^b as-prepared samples, ^c oxidized samples, ^d catalytic samples, ^e reduced samples, ^f re-oxidized samples

Table S2: EXAFS simulation parameters for the minimal fit description of Fe K-edge spectra with idealized octahedral coordination.^a

% Ni	$N_{\text{Fe-O1}}$	$R_{\text{Fe-O1}}$	$\sigma_{\text{Fe-O1}}$	$N_{\text{Fe-M1}}$	$R_{\text{Fe-M1}}$	$N_{\text{Fe-M2}}$	$R_{\text{Fe-M2}}$	$\sigma_{\text{Fe-M2}}$	R_f
88 ^b	6	1.994 (0.004)	0.078 (0.003)			3.9 (0.6)	3.09	0.07	13.3
75 ^b	6	1.986 (0.004)	0.089 (0.004)			3.9 (1.0)	3.066	0.095	14.2
62 ^b	6	1.984 (0.005)	0.097 (0.004)			2.4 (1.1)	3.06	0.1	18.8
50 ^b	6	1.974 (0.005)	0.107 (0.004)			4.0 (1.3)	3.044	0.108	18.6
38 ^b	6	1.974 (0.006)	0.110 (0.004)			4.5 (1.7)	3.034	0.122	19.6
25 ^b	6	1.970 (0.006)	0.115 (0.005)			3.3 (1.3)	3.039	0.109	21.0
13 ^b	6	1.973 (0.006)	0.108 (0.004)			2.9 (1.1)	3.035	0.101	18.5
0 ^c	6	1.966 (0.005)	0.107 (0.004)			5.0 (1.9)	3.029	0.131	34.4
88 ^c	6	1.959 (0.008)	0.117 (0.006)	1.7 (0.7)	2.874 (0.010)	1.6 (0.7)	3.042 (0.014)	0.036 (0.029)	21.5
75 ^c	6	1.974 (0.007)	0.108 (0.006)	3.8 (2.4)	2.940 (0.024)	1.3 (1.0)	3.126 (0.095)	0.096 (0.029)	17.1
62 ^c	6	1.967 (0.008)	0.112 (0.006)	1.2 (0.7)	2.833 (0.046)	3.5 (1.8)	3.021 (0.015)	0.083 (0.026)	28.1
0 ^c	6	1.971 (0.006)	0.101 (0.005)			5.8 (2.7)	3.04 (0.014)	0.131 (0.020)	30.5
88 ^d	6	1.961 (0.009)	0.112 (0.007)	1.8 (0.9)	2.857 (0.032)	2.7 (1.7)	3.016 (0.025)	0.082 (0.042)	20.4
75 ^d	6	1.956 (0.008)	0.107 (0.006)	3.0 (1.9)	2.887 (0.027)	2.1 (0.9)	3.040 (0.039)	0.082 (0.043)	9.2
62 ^d	6	1.966 (0.007)	0.100 (0.006)	1.5 (0.6)	2.872 (0.018)	2.3 (1.0)	3.039 (0.012)	0.051 (0.027)	17.5
50 ^d	6	1.968 (0.007)	0.103 (0.006)	1.1 (0.6)	2.863 (0.037)	2.6 (1.4)	3.037 (0.016)	0.066 (0.042)	18.6
25 ^d	6	1.980 (0.006)	0.093 (0.005)	1.8 (0.4)	2.949 (0.017)	1.8 (0.5)	3.115 (0.020)	0.06	34.9
88 ^e	6	1.979 (0.007)	0.105 (0.006)			1.1 (0.5)	3.103 (0.009)	0.028 (0.031)	29.7
75 ^e	6	1.993 (0.005)	0.082 (0.005)			3.0 (0.9)	3.099 (0.007)	0.073 (0.015)	16.1
62 ^e	6	1.983 (0.007)	0.098 (0.006)			4.6 (1.7)	3.062 (0.010)	0.104 (0.015)	17.4
50 ^e	6	1.986 (0.006)	0.095 (0.005)			2.4 (0.9)	3.064 (0.009)	0.072 (0.018)	16.6
38 ^e	6	1.976 (0.008)	0.106 (0.006)			2.7 (1.2)	3.061 (0.012)	0.090 (0.020)	20.5
25 ^e	6	1.974 (0.007)	0.106 (0.006)			2.3 (0.9)	3.056 (0.010)	0.075 (0.019)	27.1
88 ^f	6	1.951 (0.010)	0.116 (0.008)	2.5 (1.1)	2.868 (0.013)	2.1 (0.8)	3.029 (0.020)	0.056 (0.026)	29.1
75 ^f	6	1.960 (0.009)	0.107 (0.007)	3.2 (1.7)	2.893 (0.019)	1.6 (0.7)	3.058 (0.046)	0.068 (0.035)	9.4
62 ^f	6	1.972 (0.008)	0.098 (0.006)	2.0 (1.1)	2.896 (0.023)	2.2 (1.2)	3.050 (0.023)	0.068 (0.032)	11.6

^a $S_0^2 = 0.90$, σ_{Fe} group fitted with similar shells per sample/voltage combination, ^b as-prepared samples, ^c oxidized samples, ^d catalytic samples, ^e reduced samples, ^f re-oxidized samples

Table S3. EXAFS simulation parameters for the Ni K-edge of as-prepared, oxidized and re-oxidized samples from the Fe-Ni (oxy)hydroxide series.^a

% Ni	$N_{\text{Ni-O1}}$	$R_{\text{Ni-O1}}$	$N_{\text{Ni-O2}}$	$R_{\text{Ni-O2}}$	$N_{\text{Ni-M1}}$	$R_{\text{Ni-M1}}$	$N_{\text{Ni-M2}}$	$R_{\text{Ni-M2}}$	R_f
100 ^b			4.8 (0.3)	2.040 (0.004)			1.4 (0.2)	3.054 (0.008)	15.3
88 ^b			5.8 (0.3)	2.042 (0.004)	1.6 (0.9)	3.011 (0.034)	2.6 (0.8)	3.105 (0.023)	13.5
75 ^b			5.6 (0.3)	2.043 (0.004)	1.6 (0.6)	3.007 (0.026)	2.0 (0.6)	3.113 (0.024)	15.5
62 ^b			6.6 (0.3)	2.047 (0.003)	1.1 (0.4)	2.995 (0.029)	1.3 (0.4)	3.122 (0.027)	13.3
50 ^b			5.7 (0.3)	2.037 (0.004)	2.2 (0.4)	2.989 (0.015)	2.5 (0.4)	3.111 (0.015)	17.2
38 ^b			5.9 (0.3)	2.046 (0.003)	1.3 (0.3)	2.952 (0.018)	2.6 (0.3)	3.086 (0.010)	16.2
25 ^b			5.9 (0.3)	2.045 (0.003)	1.0 (0.3)	2.919 (0.021)	2.3 (0.3)	3.063 (0.009)	19.1
13 ^b			6.1 (0.3)	2.047 (0.003)	1.8 (0.3)	2.989 (0.013)	2.4 (0.3)	3.124 (0.011)	16.7
100 ^c	4.5 (0.3)	1.882 (0.004)			5.4 (0.3)	2.833 (0.003)	0.9 (0.4)	3.084 (0.021)	9.6
88 ^c	3.8 (0.4)	1.884 (0.007)	0.8 (0.4)	2.077 (0.041)	3.2 (0.3)	2.841 (0.006)	1.3 (0.4)	3.110 (0.017)	10.5
75 ^c	4.1 (0.4)	1.883 (0.006)	1.2 (0.4)	2.091 (0.027)	3.3 (0.4)	2.862 (0.006)	0.9 (0.5)	3.079 (0.024)	20.1
62 ^c	3.7 (0.4)	1.891 (0.007)	2.5 (0.4)	2.102 (0.013)	2.5 (0.4)	2.883 (0.008)	1.7 (0.5)	3.067 (0.014)	25.3
100 ^d	5.3 (0.3)	1.880 (0.003)			5.6 (0.2)	2.832 (0.002)			12.5
88 ^d	4.2 (0.4)	1.882 (0.006)	0.8 (0.4)	2.068 (0.040)	4.1 (0.3)	2.836 (0.004)	1.2 (0.3)	3.079 (0.014)	7.4
75 ^d	4.6 (0.4)	1.883 (0.006)	0.5 (0.4)	2.062 (0.078)	4.9 (0.3)	2.839 (0.003)	1.4 (0.4)	3.046 (0.013)	8.6
62 ^d	3.9 (0.3)	1.892 (0.006)	1 (0.4)	2.088 (0.032)	3.1 (0.3)	2.858 (0.005)	1.4 (0.4)	3.071 (0.012)	14.5

^a $S_0^2 = 0.90$, brackets represent error in values

^b as prepared samples; $\sigma_{\text{Ni-O}} = 0.070 \pm 0.002 \text{ \AA}$; $\sigma_{\text{Ni-M}} = 0.066 \text{ \AA}$

^c oxidized samples; $\sigma_{\text{Ni-O}} = 0.059 \pm 0.004 \text{ \AA}$; $\sigma_{\text{Ni-M}} = 0.066 \text{ \AA}$

^d re-oxidized samples; $\sigma_{\text{Ni-O}} = 0.064 \pm 0.004 \text{ \AA}$; $\sigma_{\text{Ni-M}} = 0.066 \text{ \AA}$

Table S4. EXAFS simulation parameters for the Fe K-edge of the Fe-Ni (oxy)hydroxide series.^a

% Ni	$N_{\text{Fe-O1}}$	$R_{\text{Fe-O1}}$	$N_{\text{Fe-O2}}$	$R_{\text{Fe-O2}}$	$N_{\text{Fe-M1}}$	$R_{\text{Fe-M1}}$	$N_{\text{Fe-M2}}$	$R_{\text{Fe-M2}}$	R_f
88 ^b	3.8 (2.3)	1.970 (0.024)	2.1 (2.3)	2.047 (0.049)	1.1 (0.3)	2.914 (0.016)	4.5 (0.3)	3.091 (0.004)	5.7
75 ^b	3.3 (2.0)	1.961 (0.026)	1.8 (2.0)	2.042 (0.052)	1.0 (0.3)	2.929 (0.022)	2.9 (0.3)	3.083 (0.009)	5.3
62 ^b	3.7 (0.5)	1.951 (0.011)	1.9 (0.5)	2.080 (0.024)	1.0 (0.5)	3.007 (0.036)	1.0 (0.5)	3.127 (0.041)	15.2
50 ^b	2.4 (0.6)	1.918 (0.019)	2.5 (0.6)	2.037 (0.021)	1.3 (0.3)	2.925 (0.018)	2.5 (0.3)	3.079 (0.010)	8.5
38 ^b	1.7 (0.6)	1.898 (0.024)	3.0 (0.5)	2.023 (0.016)	1.3 (0.3)	2.933 (0.018)	2.0 (0.3)	3.084 (0.013)	12.1
25 ^b	2.0 (0.7)	1.908 (0.023)	2.4 (0.6)	2.027 (0.022)	1.1 (0.3)	2.936 (0.023)	1.9 (0.3)	3.083 (0.015)	14.5
13 ^b	0.9 (0.4)	1.856 (0.040)	3.7 (0.4)	1.993 (0.011)	0.8 (0.4)	2.937 (0.039)	1.7 (0.4)	3.068 (0.020)	11.0
0 ^b	0.3 (0.1)	1.606 (0.026)	3.8 (0.2)	1.965 (0.004)	1.6 (0.2)	2.953 (0.012)	1.9 (0.3)	3.109 (0.012)	17.7
88 ^c	2.1 (2.3)	1.930 (0.051)	1.7 (2.2)	2.019 (0.074)	2.4 (0.4)	2.881 (0.011)	2.2 (0.4)	3.055 (0.013)	13.2
75 ^c	2.3 (0.7)	1.906 (0.024)	2.9 (0.7)	2.039 (0.023)	2.0 (0.4)	2.920 (0.019)	1.1 (0.5)	3.067 (0.039)	15.4
62 ^c	3.0 (0.5)	1.909 (0.014)	2.6 (0.5)	2.064 (0.021)	1.0 (0.4)	2.857 (0.027)	2.5 (0.4)	3.027 (0.012)	23.9
0 ^c	2.8 (1.4)	1.931 (0.029)	2.0 (1.3)	2.036 (0.045)	1.5 (0.4)	2.929 (0.019)	2.5 (0.4)	3.093 (0.013)	17.1
88 ^d	1.2 (0.4)	1.847 (0.034)	3.6 (0.4)	1.993 (0.014)	1.5 (0.3)	2.853 (0.016)	2.3 (0.4)	3.014 (0.012)	9.9
75 ^d	2.3 (0.9)	1.898 (0.027)	2.6 (0.9)	2.017 (0.027)	2.3 (0.4)	2.878 (0.013)	1.9 (0.4)	3.030 (0.019)	9.5
62 ^d	3.5 (0.8)	1.940 (0.016)	1.4 (0.8)	2.061 (0.048)	1.7 (0.3)	2.871 (0.014)	2.7 (0.4)	3.039 (0.010)	10.2
50 ^d	3.0 (0.9)	1.926 (0.020)	2.1 (0.8)	2.045 (0.033)	1.1 (0.3)	2.865 (0.020)	2.5 (0.4)	3.038 (0.010)	13.5
25 ^d	4.3 (0.2)	1.982 (0.005)			1.8 (0.4)	2.952 (0.014)	1.8 (0.4)	3.116 (0.017)	27.5
88 ^e	2.6 (0.7)	1.920 (0.020)	2.7 (0.7)	2.047 (0.023)	1.7 (0.3)	2.901 (0.012)	3.4 (0.4)	3.090 (0.007)	16.3
75 ^e	1.7 (1.8)	1.930 (0.052)	4.1 (1.8)	2.020 (0.024)	0.9 (0.3)	2.936 (0.027)	3.4 (0.4)	3.104 (0.008)	11.3
62 ^e	2.6 (0.9)	1.929 (0.022)	2.8 (0.8)	2.045 (0.024)	1.5 (0.4)	2.964 (0.024)	2.6 (0.4)	3.102 (0.015)	14.7
50 ^e	3.7 (1.2)	1.965 (0.020)	1.3 (1.2)	2.070 (0.064)	0.9 (0.3)	2.888 (0.023)	2.9 (0.4)	3.066 (0.008)	7.3
38 ^e	3.3 (0.5)	1.937 (0.013)	1.9 (0.5)	2.077 (0.028)	0.7 (0.4)	2.943 (0.048)	2.1 (0.4)	3.082 (0.019)	13.0
25 ^e	3.5 (0.5)	1.939 (0.012)	1.7 (0.5)	2.084 (0.030)	1.0 (0.3)	2.888 (0.022)	2.8 (0.4)	3.061 (0.009)	14.2
88 ^f	3.3 (0.3)	1.906 (0.008)	2.1 (0.3)	2.075 (0.016)	2.9 (0.3)	2.876 (0.007)	2.2 (0.3)	3.041 (0.011)	21.5
75 ^f	1.5 (0.5)	1.862 (0.028)	3.6 (0.5)	1.996 (0.013)	3.1 (0.3)	2.889 (0.007)	1.7 (0.3)	3.048 (0.016)	10.0
62 ^f	0.9 (0.5)	1.861 (0.047)	4.0 (0.5)	1.992 (0.012)	1.9 (0.3)	2.889 (0.013)	2.2 (0.3)	3.043 (0.013)	4.3

^a $S_0^2 = 0.90$, brackets represent error in values, $\sigma_{\text{Ni-O}} = 0.070 \pm 0.002 \text{ \AA}$; $\sigma_{\text{Ni-M}} = 0.066 \text{ \AA}$

^b as prepared samples

^c oxidized samples

^d catalytic samples

^e reduced samples

^f re-oxidized samples

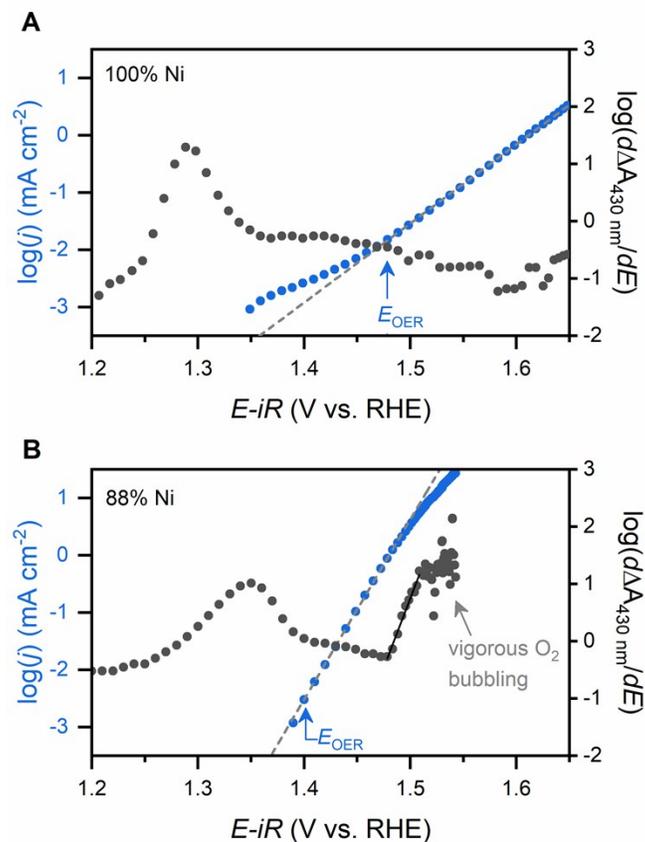


Figure S9. Comparison between steady state electrochemical currents and optical absorbance values acquired by staircase voltammetry on (A) 100% Ni and (B) 88% Ni. The points labelled as E_{OER} signify the onset of linearity in Tafel plots; significant scatter in absorbance data occurs as current densities approach 10 mA cm^{-2} due to O_2 bubble formation.

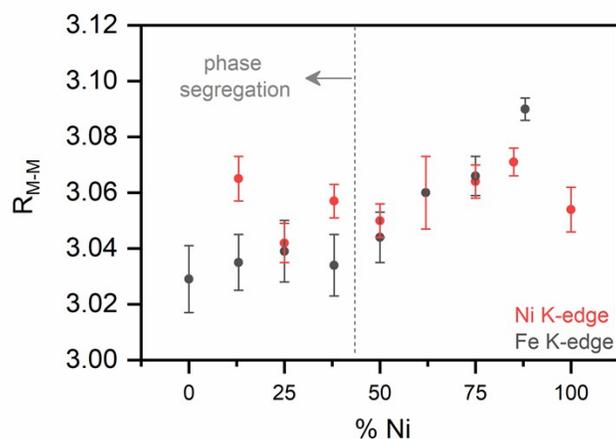


Figure S10. Average distance between metal atoms in di- μ -oxo bridged M-M motifs in as-prepared films as a function of compositions. Data shown was determined by the minimal-fit model (Tables S1 and S2) on the Ni K-edge (red points) and the Fe K-edge (black points). Error bars represent estimated error in the EXAFS simulations.