

Supplementary Information to Atomic-scale understanding of oxide growth and dissolution kinetics of Ni-Cr alloys

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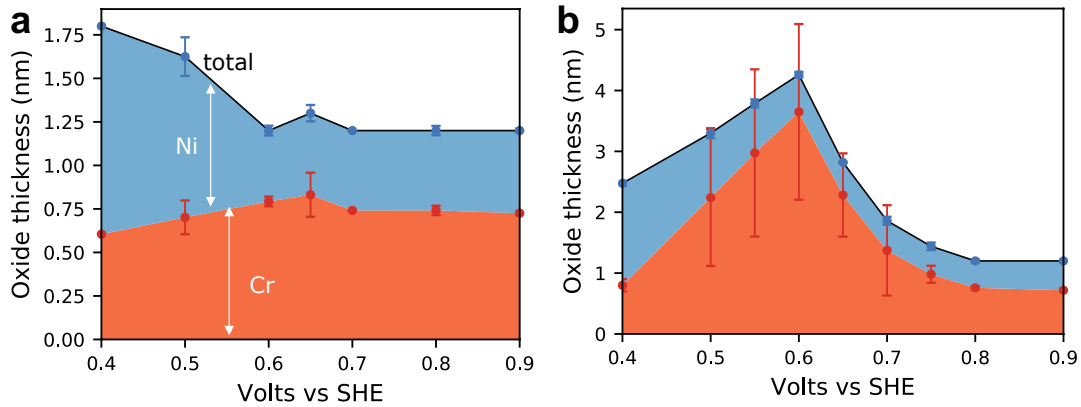


FIG. S1. Oxide thickness as a function of voltage (a) without reprecipitation near neutral pH at 400K; (b) with reprecipitation under pH=2 at 500 K. Error bars are standard deviations of (a) 3 and (b) 5 independent runs.

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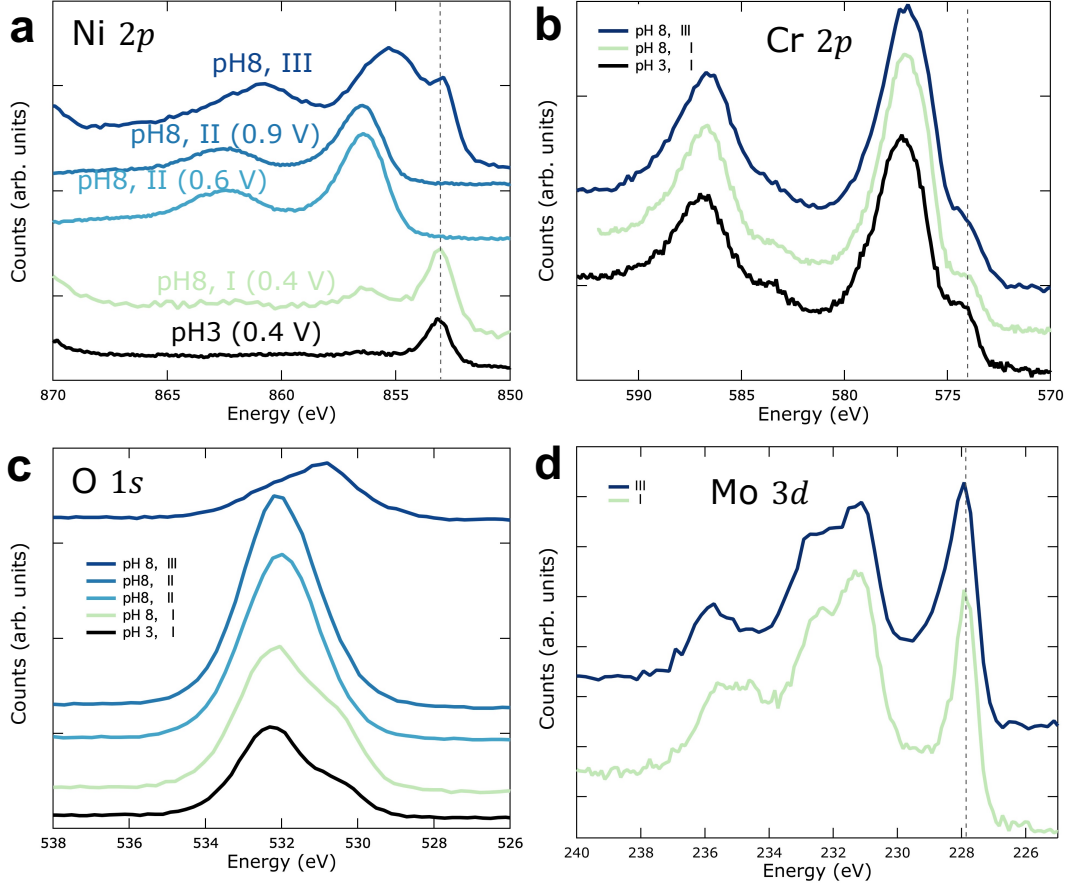


FIG. S2. X-ray photoelectron spectroscopy (XPS) spectra of Alloy 22 surface film polarized in pH 3 and pH 8 solutions at 90 °C(363K) for (a) Ni 2*p*, (b) Cr 2*p*, (c) O 1*s*, and (d) Mo 3*d*. Dashed grey lines represent position of metallic peak.

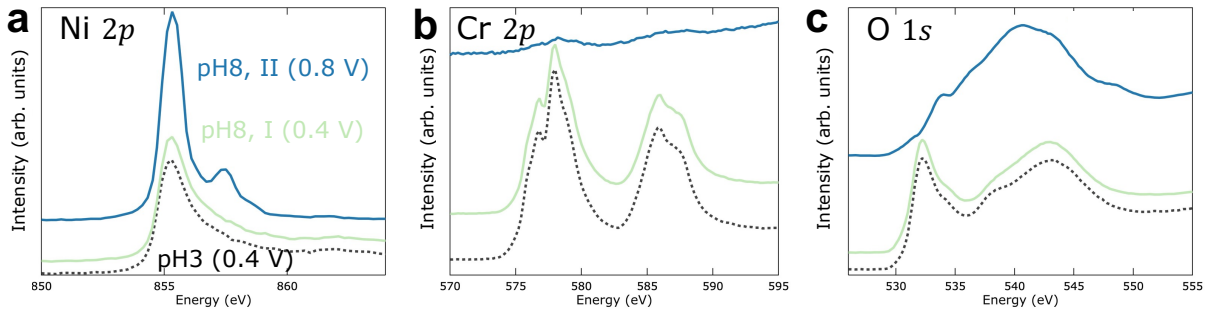


FIG. S3. Ni 2*p*, Cr 2*p*, and O 1*s* total electron yield X-ray absorption (XAS) spectra of the Ni%80-Cr%20 substrates displayed in Figures 3, 5. Samples were held at 0.4 V vs the standard hydrogen electrode (SHE) (green) and 0.8 V vs SHE (blue) in pH 8 solution and 0.4 V vs SHE (dashed black) in pH 3 solution for 60,000 seconds. The spectra at 0.4V vs SHE for pH 3 (black) and pH 8 (green) are not significantly different from one another. In regime II, for samples held at 0.8 V vs SHE (blue) in pH 8 solution, both the Ni and oxygen spectra display new peaks and the Cr signature is very weak indicating a thick nickel oxide layer.

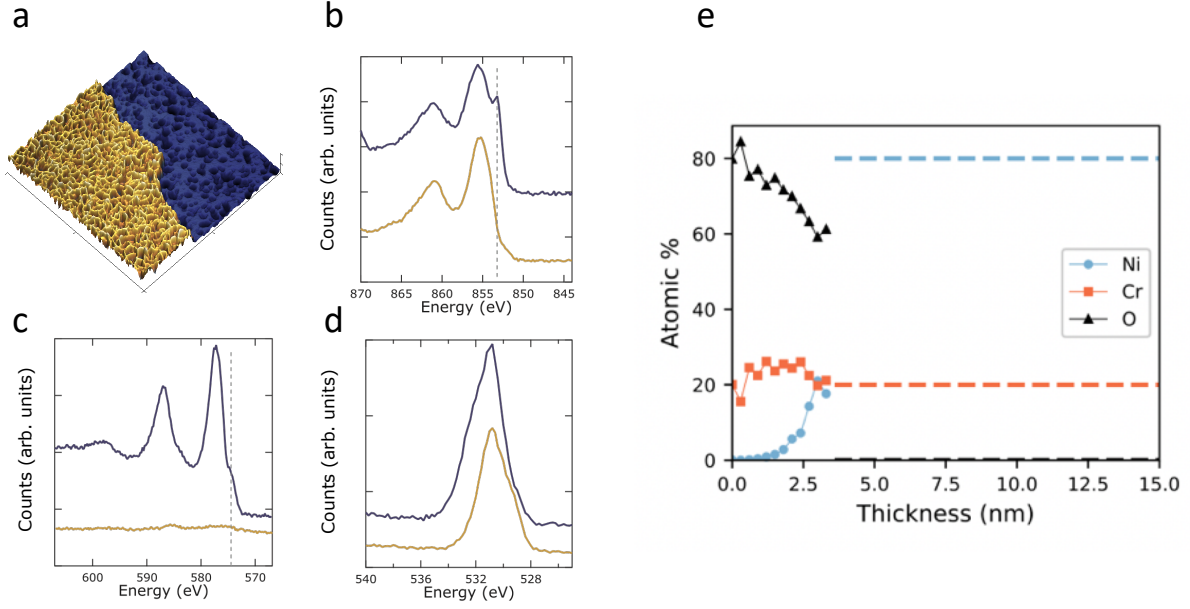


FIG. S4. Oxide film in regime (III) created by a potentiodynamic scan that stopped just as the nickel was beginning to dissolve. (a) AFM image displaying an area where the top Ni-rich oxide delaminated exposing the underlying Cr-rich oxide so that they can be compared. Image is $10\ \mu\text{m} \times 10\ \mu\text{m}$, with z-scale of 700 nm. (b-d) XPS comparing the Ni-rich oxide consistent with regime (II) (gold) with the Cr-rich oxide consistent with regime (III) (blue). The Ni (b), Cr (c) and O (d) windows are shown. (e) Simulated depth profile on the onset of Ni oxide dissolution at 0.77 V from Figure 2(c).

Regime I							
Formula	Ni_3O_4	$\text{Ni}_3\text{O}_4(\text{S})$	CrNi_2O_4	$\text{Cr}_2\text{Ni}_3\text{O}_6$	$\text{Cr}_2\text{Ni}_5\text{O}_8$	CrNiO_3	CrO_3
%	36	4	1	40	10	3	7
Regime II(a), < 2 nm to alloy/oxide interface							
Formula	Ni_3O_4	$\text{Ni}_3\text{O}_4(\text{S})$	CrNi_2O_4	$\text{Cr}_2\text{Ni}_3\text{O}_6$	$\text{Cr}_2\text{Ni}_5\text{O}_8$	CrNiO_3	CrO_3
%	18	5	3	42	6	11	16
Regime II(a), > 2 nm to alloy/oxide interface							
Formula	NiO	Ni_3O_4	$\text{Ni}_3\text{O}_4(\text{S})$	$\text{Cr}_2\text{Ni}_3\text{O}_6$	$\text{Cr}_2\text{Ni}_5\text{O}_8$	CrNiO_3	
%	9	78	2	3	3	2	
Regime II(b), < 2 nm to alloy/oxide interface							
Formula	$\text{Ni}_3\text{Cr}_3\text{O}_8$	$\text{Cr}_2\text{Ni}_3\text{O}_6$	$\text{Cr}_3\text{Ni}_4\text{O}_8$	CrNiO_3	$\text{Cr}_{1.94}\text{O}_3$	CrO_2	CrO_3
%	4	22	1	4	7	17	45
Regime II(b), > 2 nm to alloy/oxide interface							
Formula	NiCr_2O_4	Cr_3O_4	CrO_2	CrO_3			
%	3	3	26	68			

TABLE S1. Detailed composition near neutral pH as determined by simulations

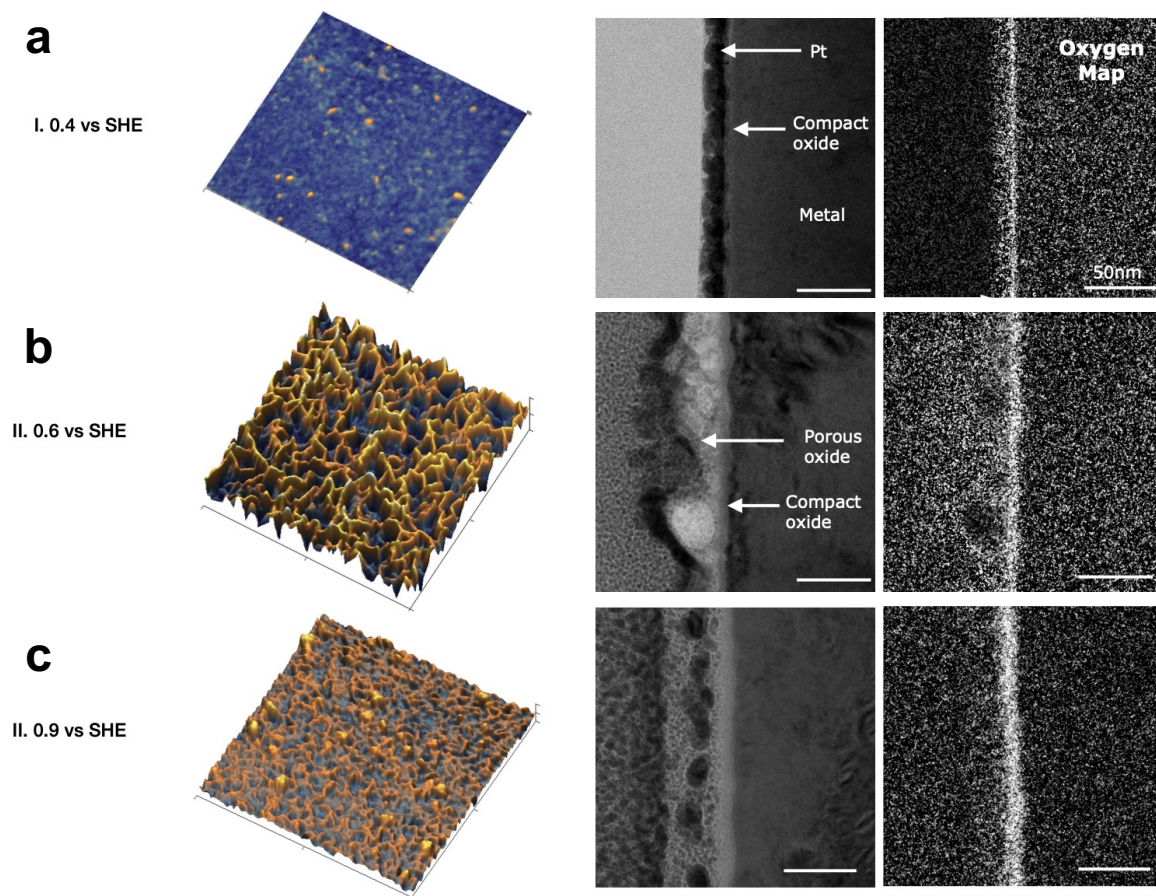


FIG. S5. TEM cross-sections and EELS oxygen maps of Alloy 22 at 0.4 V regime (I) (top row), 0.6 V regime (II) (middle row), and 0.9 V regime (II) (bottom row) in pH 8 solution.

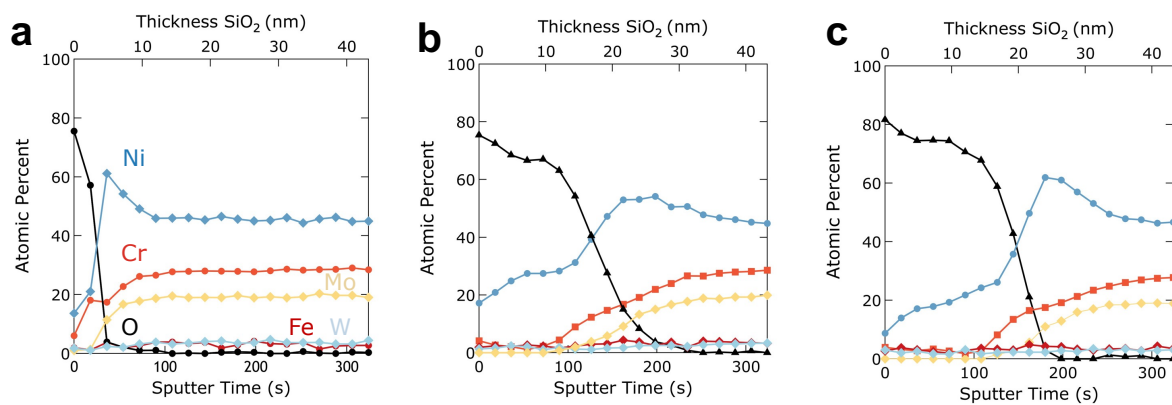


FIG. S6. Auger depth profiles of Alloy 22 at (a) 0.4 V regime (I), (b) 0.6 V regime (II) , and (c) 0.9 V regime (II) vs SHE in pH 8 solution

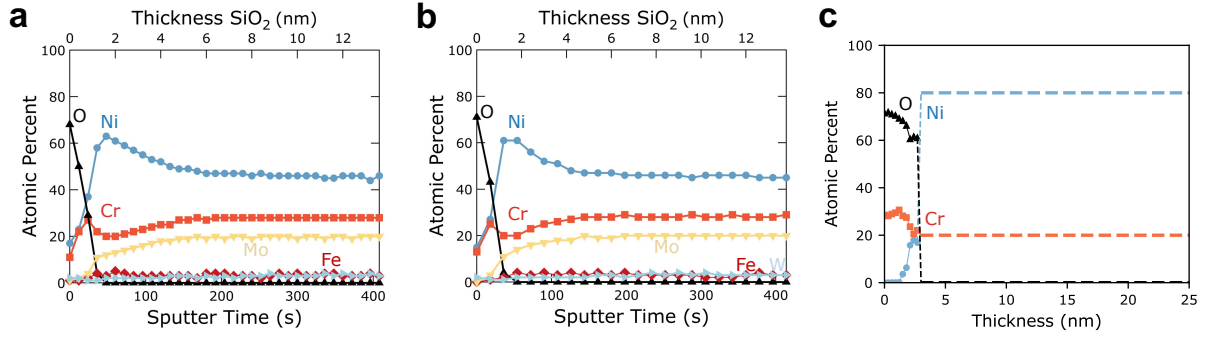


FIG. S7. Auger depth profiles of Alloy 22 at (a) 0.4 V and (b) 0.7 V in pH 3 solution, alongside (c) the simulated depth profile at 0.65 V in pH 2 solution.

pH=2, < 2 nm to alloy/oxide interface							
Formula	$\text{Ni}_3\text{Cr}_3\text{O}_8$	$\text{Cr}_2\text{Ni}_3\text{O}_6$	$\text{Cr}_3\text{Ni}_4\text{O}_8$	CrNiO_3	$\text{Cr}_{1.94}\text{O}_3$	CrO_2	CrO_3
%	3	25	2	7	26	3	32
pH=2, > 2 nm to alloy/oxide interface							
Formula	NiCr_2O_4	Cr_3O_4	$\text{Cr}_{1.94}\text{O}_3$	CrO_3			
%	3	3	18	74			

TABLE S2. Detailed composition at pH=2 as determined by simulations

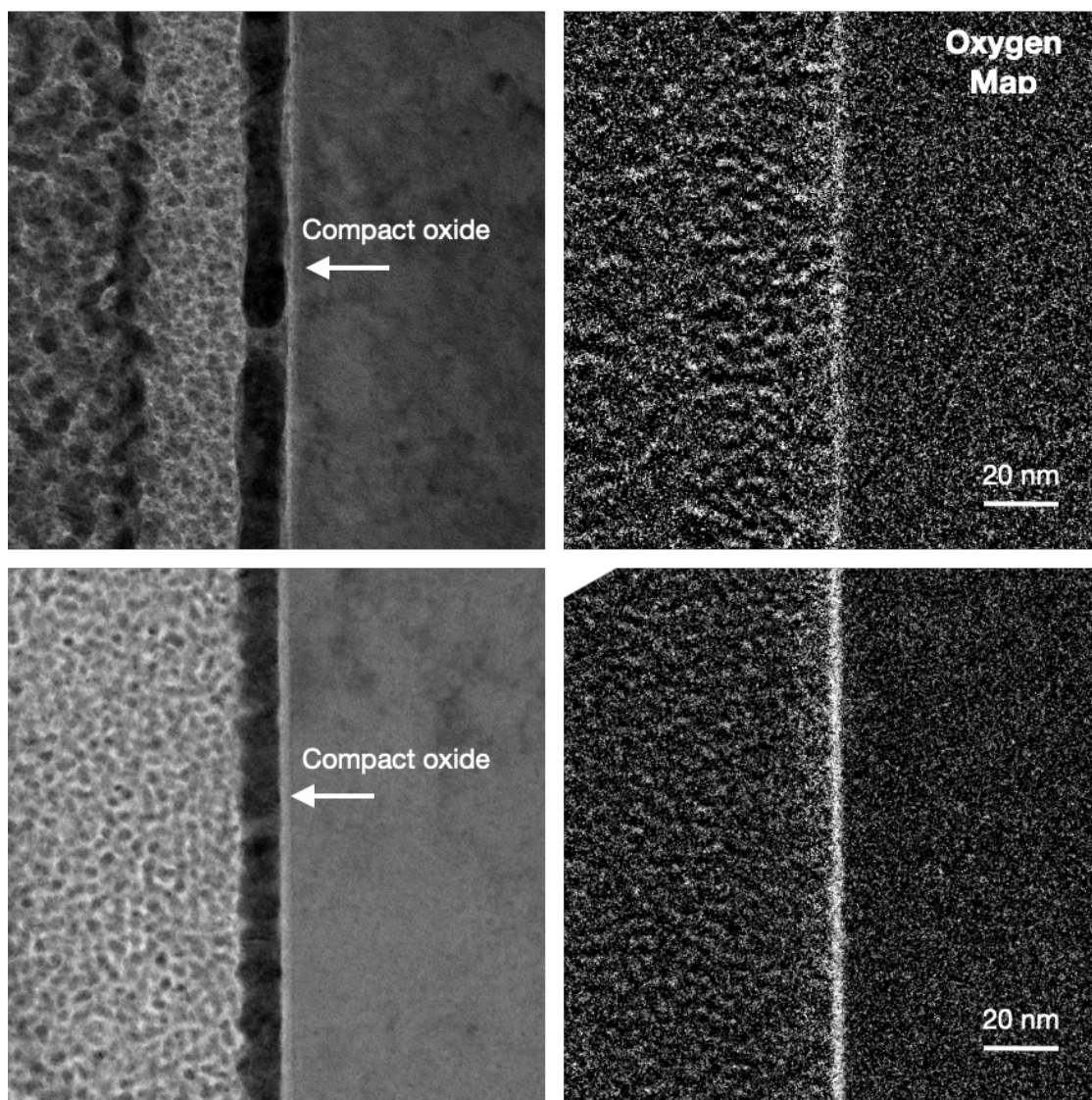


FIG. S8. Cross-sectional TEM images and Oxygen EELS maps of Alloy 22 potentiostatically held at 0.4 (top row) and 0.7 V (bottom row) vs SHE for 60,000s in pH 3 solution. At both voltages the oxide forms a compact film

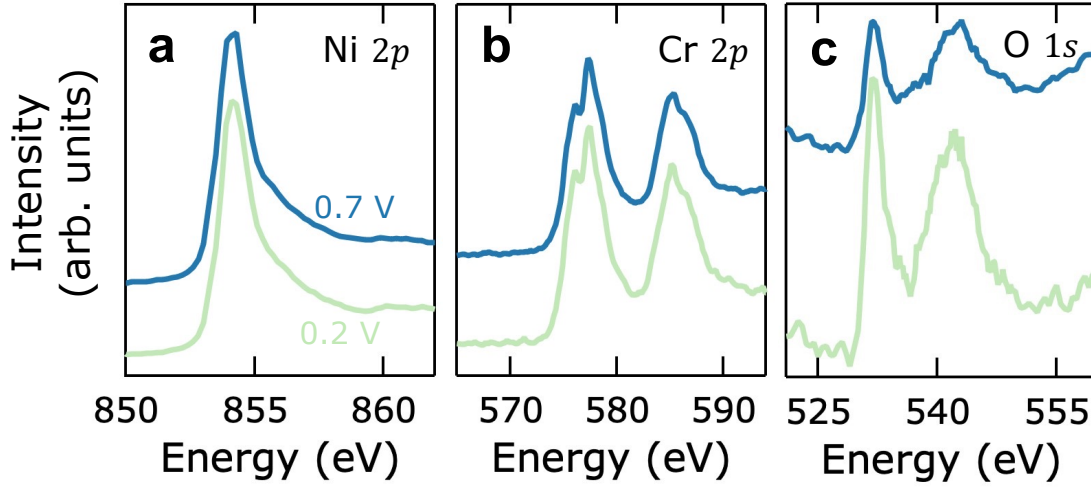


FIG. S9. Ni 2p, Cr 2p, and O 1s XAS spectra of 70% Ni-30% C sputter deposited thin films held at 0.2 V vs SHE (green) and 0.7 V vs SHE (blue) for 300 seconds in pH 3 solution. The spectra do not change significantly as a function of voltage, and no new peaks form that are suggestive of a phase change. at 25 °C(298K).

Formula	Energy above hull	Description
NiO	0 meV	Rock salt
Ni ₇ O ₈	0 meV	All Ni in octahedral sites
Ni ₃ O ₄	0 meV	All Ni in octahedral sites
Ni ₃ O ₄ (S)	49 meV	Spinel
CrO ₃ (T)	0 meV	All Cr in tetrahedral sites
CrO ₃	80 meV	All Cr in octahedral sites
CrO ₂	0 meV	All Cr in octahedral sites
Cr ₂ O ₃	0 meV	All Cr in octahedral sites
Cr _{1.94} O ₃	9 meV	All Cr in octahedral sites
Cr ₃ O ₄	0 meV	Spinel
Cr ₁₅ O ₁₆	0 meV	All Cr in octahedral sites, variant of NiO
NiCrO ₃	241 meV	Ni in tetrahedral sites and Cr in octahedral sites
NiCr ₂ O ₄	0 meV	Spinel with Ni in tetrahedral and Cr in octahedral sites
CrNi ₂ O ₄	31 meV	Spinel with Cr in tetrahedral and Ni in octahedral sites
CrNi ₂ O ₄ (I)	14 meV	Spinel with tetrahedral sites all Ni
CrNi ₂ O ₄ (II)	7 meV	Spinel with tetrahedral sites all Ni
Ni ₃ Cr ₃ O ₈	0 meV	Spinel with tetrahedral sites all Ni
CrNiO ₃	27 meV	All cations in octahedral sites, variant of Cr ₂ O ₃
Cr ₃ Ni ₄ O ₈	81 meV	All cations in octahedral sites, variant of NiO
Cr ₂ Ni ₃ O ₆	52 meV	All cations in octahedral sites, variant of NiO
Cr ₂ Ni ₅ O ₈	81 meV	All cations in octahedral sites, variant of NiO
CrNi ₃ O ₄	26 meV	All cations in octahedral sites, variant of NiO
O ₂	0 meV	Empty oxygen lattice

TABLE S3. Basis structures for the composition analysis of simulated configurations

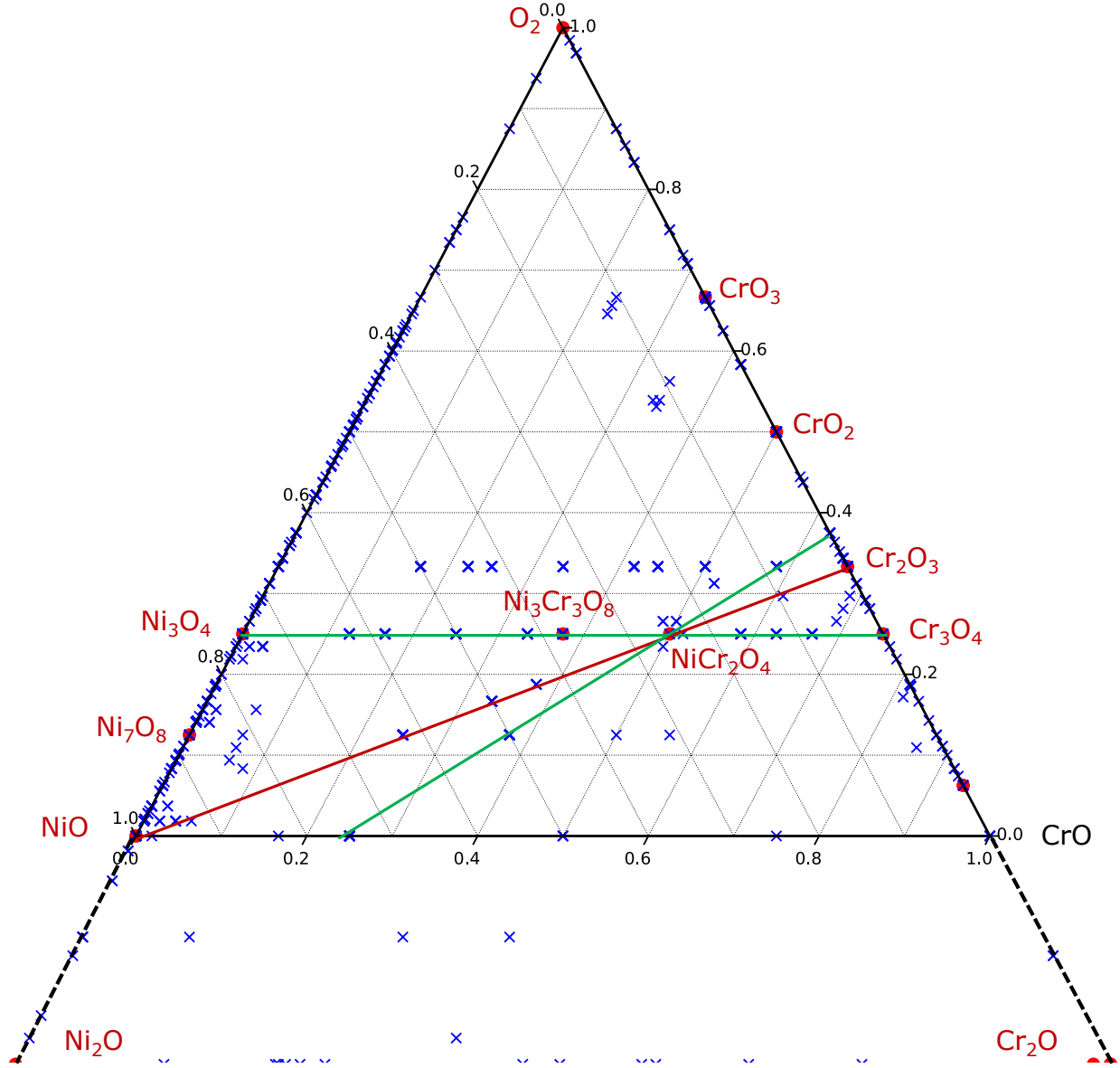


FIG. S10. Compositions sampled by DFT in the Ni-Cr-O ternary composition space. Red points are on the energy convex hull and blue crosses are above the hull. The two green lines enclose most of the low-energy bulk compounds possibly in a passivation film.

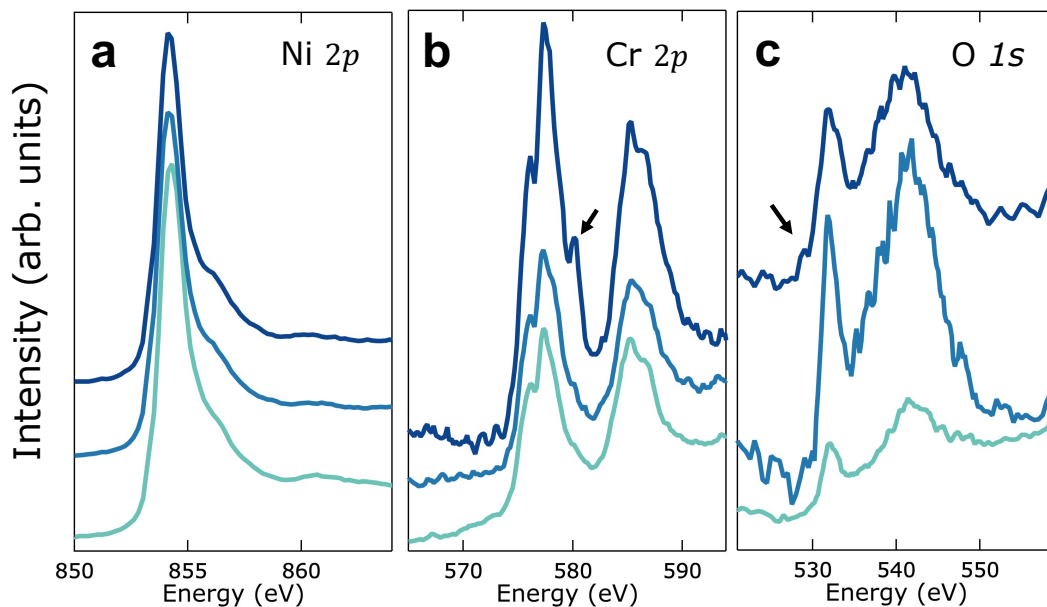


FIG. S11. Ni 2*p*, Cr 2*p*, and O 1*s* XAS spectra of Ni₇₀-Cr₃₀ sputter deposited thin films held at 0.5, 0.7, and 0.9V vs SHE (light to dark) for 300 seconds in pH 8 solution with 0.1M NiCl₂. In contrast to Figure 7, the presence of 0.1 M NiCl₂ in the pH 8 solution suppresses nickel dissolution and prevents the formation of new nickel oxides. This observation suggests that the newly observed oxygen peak at 529 eV is linked to changes in the chromium spectra (at 580 eV), not the nickel oxide. Furthermore, this experiment demonstrates that the formation of nickel oxide in regime (II) is not solely driven by high nickel ion concentrations in the solution, but also necessitates a redox reaction.

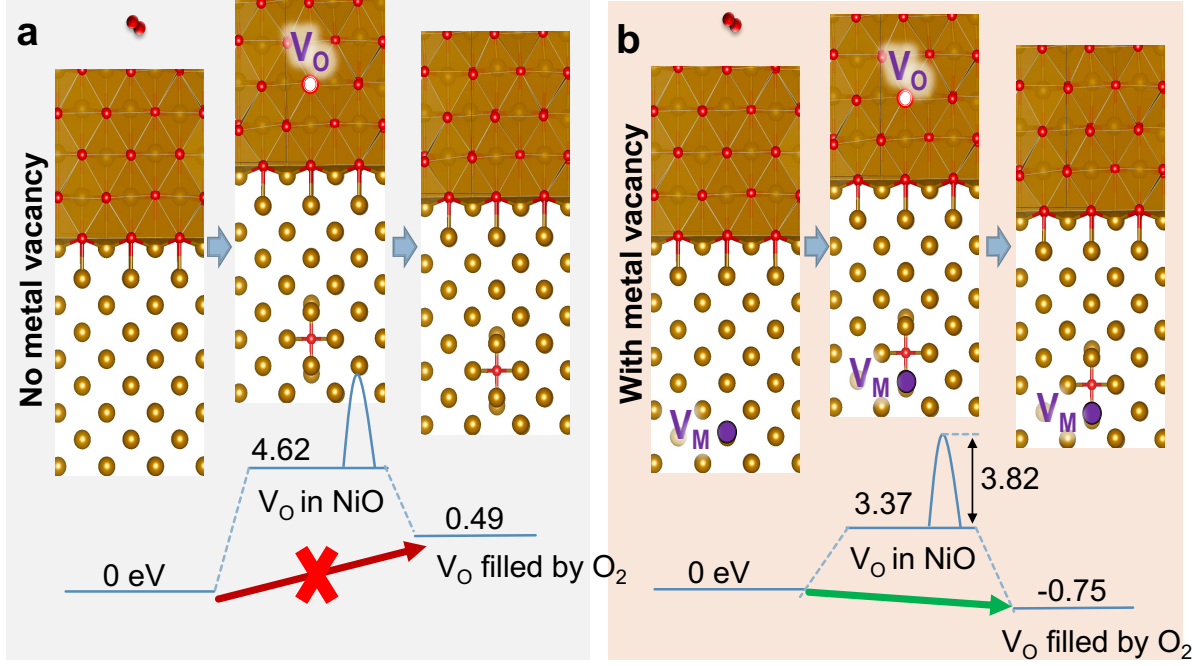


FIG. S12. Energetics of O-vacancy mediated inward growth. Red spheres are oxygen; brown spheres are Ni metal atoms; brown octahedra are NiO₆. The figures show a few inevitable steps of inward growth and their energies in eV: first a pair of O vacancy (V_O in NiO) and O interstitial (in Ni metal) is formed; then the O vacancy diffuses in NiO; finally the O vacancy is filled on the surface by O₂. The formation energy of the O vacancy is significantly lowered by the presence of a Ni metal vacancy (V_M) which better accommodates the O interstitial, but it is still 3.37 eV. The diffusion barrier of O vacancy in NiO is 3.82 eV. High formation energy and high diffusion barrier of the O vacancy make inward growth unlikely near room temperature. These energetics are computed in bulk Ni and NiO with the SCAN functional.

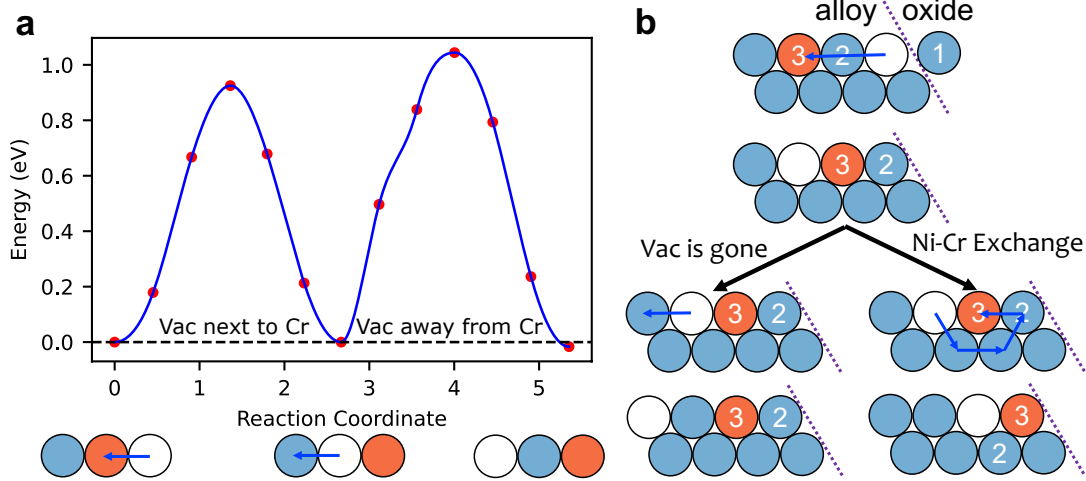


FIG. S13. (a) Diffusion barriers as a vacancy (white) moves past a Cr (orange) in the Ni (blue) face-centered cubic (FCC) lattice calculated with the PBE functional. The energies of the local minima also show that there is no nearest-neighbor adhesion between Cr and the vacancy. (b) Schematic demonstrating vacancy hops (blue arrows) with and without Ni-Cr exchange. The large number of steps needed for Ni-Cr exchange (right branch) compared to vacancy diffusion away from the interface (left branch), makes exchange a low probability event in the alloy. In the absence of a vacancy, the Ni-Cr exchange barrier is 6.1 eV, prohibitively high in the temperature range of interest. For these reasons, Ni-Cr exchange within the alloy is not considered in the model with the implication that the initially formed oxide tracks the composition of the underlying alloy.

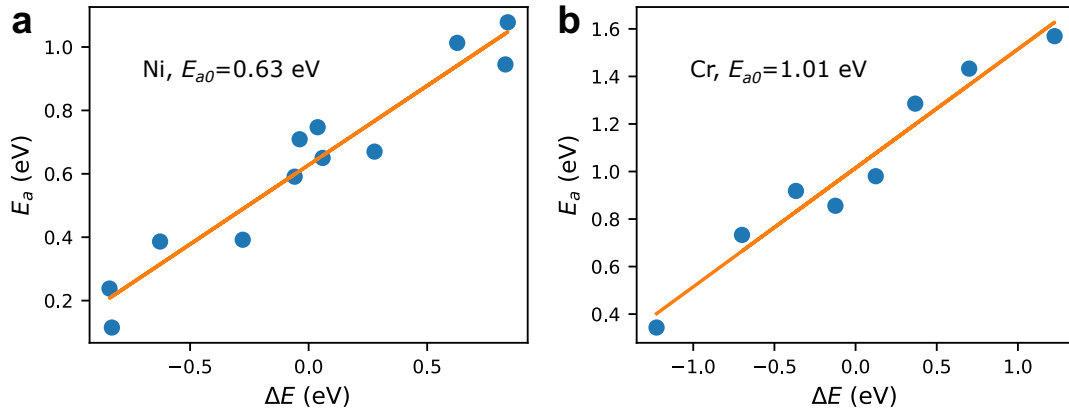


FIG. S14. Brønsted-Evans-Polanyi (BEP) relation for (a) Ni and (b) Cr hopping in the FCC close packed oxygen lattice. The environmentally independent diffusion barrier, E_{a0} , is determined by the intercept of the linear fit.

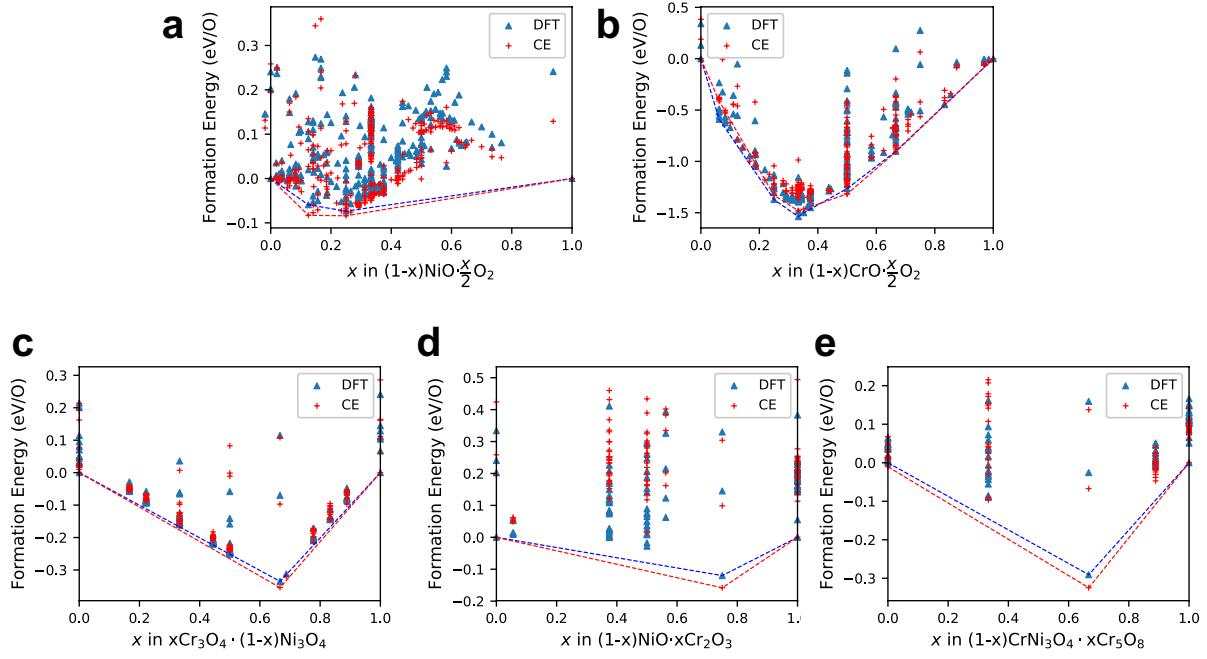


FIG. S15. Energies and convex hulls along five composition lines: (a) $\text{NiO}-\text{O}_2$; (b) $\text{CrO}-\text{O}_2$; (c) $\text{Ni}_3\text{O}_4-\text{Cr}_3\text{O}_4$; (d) $\text{NiO}-\text{Cr}_2\text{O}_3$; (e) $\text{CrNi}_3\text{O}_4-\text{Cr}_5\text{O}_8$.

Figure	Solution	pH (25°C)	pH (90°C)	T (°C)	T (K)	V vs Ag/AgCl	V vs SHE	Deaerate	Time (s)	Analysis
2a	SCW	8.0	8.4	90	363	PD		Yes		CV
2a	pH8- noCl	8.3	8.0	90	363	PD		No		CV
3a, c	pH8- noCl	8.3	8.0	90	363	0.2	0.4	No	60000	AFM, XPS
3a, c	pH8- noCl	8.3	8.0	90	363	0.6	0.8	No	60000	AFM, XPS
3b, c	pH8	8.1	7.5	90	363	0.2	0.4	Yes	60000	AFM, XPS
3b	pH8	8.1	7.5	90	363	0.4	0.6	Yes	60000	AFM
3c	pH8	8.1	7.6	90	363	0.4	0.6	Yes	60000	XPS
4a	pH8	8.1	7.6	90	363	0.2	0.4	Yes	60000	Auger, TEM
4b	pH8	8.1	7.6	90	363	0.4	0.6	Yes	60000	Auger, TEM
5b	pH3- noCl	3.1	3.7	90	363	PD		No		CV
5b	pH3	3.1	3.4	90	363	PD		Yes		CV
5c	pH3- noCl	3.2	3.4	90	363	0.2	0.4	No	60000	XPS
5c	pH3	3.1	2.7	90	363	0.2	0.4	Yes	60000	XPS
6b	SCW	8.0	8.4	30	303	PD		Yes		CV
6b	SCW	8.0	8.4	60	333	PD		Yes		CV
6b	SCW	8.0	8.4	90	363	PD		Yes		CV
7c	pH8	8.0		25	298	0.0	0.2	Yes	300	XAS
7c	pH8	8.0		25	298	0.7	0.9	Yes	300	XAS
7d	pH3	3.0		25	298	0.0	0.2	Yes	300	XAS
7d	pH3	3.0		25	298	0.5	0.7	Yes	300	XAS

TABLE S4. Summary of solution and electrochemical processing parameters for all data shown in the main text

Figure	Solution	pH (25°C)	pH (90°C)	T (°C)	T (K)	V vs Ag/AgCl	V vs SHE	Deaerate	Time (s)	Analysis
S2a-c	pH3	3.1	2.7	90	363	0.2	0.4	Yes	60000	XPS
S2a-d	pH8	8.1	7.5	90	363	0.2	0.4	Yes	60000	XPS
S2a,c	pH8	8.1	7.6	90	363	0.4	0.6	Yes	60000	XPS
S2a,c	pH8	8.1	7.6	90	363	0.7	0.9	Yes	60000	XPS
S2a-d	SCW	8.0	8.1	90	363	PD		Yes	60000	XPS
S3	pH8- noCl	8.3	8.0	90	363	0.2	0.4	No	60000	XAS
S3	pH8- noCl	8.3	8.0	90	363	0.6	0.8	No	60000	XAS
S3	pH3- noCl	3.2	3.4	90	363	0.2	0.4	No	60000	XAS
S4a-d	SCW	8.0	8.1	90	363	PD		Yes		AFM, XPS
S5a	pH8	8.1	7.6	90	363	0.2	0.4	Yes	60000	TEM
S5b	pH8	8.1	7.6	90	363	0.4	0.6	Yes	60000	TEM
S5c	pH8	8.1	7.7	90	363	0.7	0.9	Yes	60000	TEM
S6a	pH8	8.1	7.5	90	363	0.2	0.4	Yes	60000	Auger
S6b	pH8	8.1	7.6	90	363	0.4	0.6	Yes	60000	Auger
S6c	pH8	8.1	7.6	90	363	0.7	0.9	Yes	60000	Auger
S7a	pH3	3.1	2.7	90	363	0.2	0.4	Yes	60000	Auger
S7b	pH3	3.1	2.7	90	363	0.5	0.7	Yes	60000	Auger
S8	pH3	3.1	2.7	90	363	0.2	0.4	Yes	60000	TEM
S8	pH3	3.1	2.9	90	363	0.5	0.7	Yes	60000	TEM
S9	pH3	3		25	298	0.0	0.2	Yes	300	XAS
S9	pH3	3		25	298	0.5	0.7	Yes	300	XAS
S11	pH8- NiCl	8		25	298	0.3	0.5	No	300	XAS
S11	pH8- NiCl	8		25	298	0.5	0.7	No	300	XAS
S11	pH8- NiCl	8		25	298	0.7	0.9	No	300	XAS

TABLE S5. Summary of solution and electrochemical processing parameters for all data shown in the SI

pH	T ₀ (K)	T (K)	E _{Ag/AgCl} (T ₀) (V)	$\Delta V_{\text{thSHE}}^T$ (V)	ΔE_{TLJ} (V)	V _{SHE_298} (T)-V _{meas}
3, 8	298	298	0.199	0.000	0.00	0.20
8	288	303	0.209	0.004	0.01	0.22
8	288	313	0.209	0.013	0.02	0.22
8	288	333	0.209	0.030	0.04	0.22
8	288	363	0.209	0.050	0.07	0.23
3	288	363	0.209	0.050	0.045	0.20
8	298	363	0.199	0.050	0.06	0.21
3	298	363	0.199	0.025	0.00	0.17

TABLE S6. Factors used to correct the voltage scale to SHE at 298 K