

The role of individual nickel surface species in the hydrogen evolution reaction on nickel in alkaline electrolytes

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Supplementary Information

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Supplementary Note 1. Table of values for HER activity on Ni-based catalysts from the literature

Supplementary Table 1. Details of the data normalization used in Fig. 1b and Supplementary Fig. 1.

Refs. #	Catalyst	η [mV] @10 mA cm ⁻²	b [mV]	j_0 [mA cm ⁻²]	ECSA $C_{dl} =$ [mF cm ⁻²]	η_{ECSA} [mV] @10 mA cm ⁻²	$\eta_{ECSA, IR}$ corrected [mV]
1	2nd-Ni/Ni(OH) ₂ /NF-500	53	55		6.1	190	
	1st-Ni/Ni(OH) ₂ /NF-500	116	98		3.8	340	
	c-Ni/Ni(OH) ₂ /NF-500	144	134		2.5	425	
2	3D NiO/NF	70	65		6.8	235	
	NF	243	189		0.9	555	277
3	Ni/NF	178	102		15.3	472	
	A-Ni/NF	187	107		12.2	485	
	C-Ni/NF	198	108		15.2	509	
	AC-Ni/NF (referring to hydroxide form)	30	47		20.8	172	
4	Ni/Ni(OH) ₂ NF	127	140		71.0	624	363
	NF	250	206		0.6	555	322
5	Ni/NiO @ C-1	113	68		24	322	
	Ni/NiO @ C-2	64	55		22	231	
	Ni/NiO @ C-3	137	84		12	370	
	Ni/NiO @ C-2_acid treatment	219	199		47	830	313
	Ni/NiO @ C-2_oxidation	264	249		18	999	373
6	Ni/Ni(OH) ₂ /NiOOH	45	100		0.94	230	
	Ni(OH) ₂ /NiOOH	421	167		0.06	501	
7	Ni/NiO-0s	87	119		325	587	468
	Ni/NiO-3s	25	74		665	261	
	Ni/NiO-10s	47	89		380	428	
	Ni/NiO-3000s	63	93		139	420	
	Ni/NiO-15000s	115	127		65	461	430
8	Ni(OH) ₂ /NF @ 40 V	157	82		2.9	334	
	Ni(OH) ₂ /NF @ 25 V	207	94		1.73	389	
	Ni(OH) ₂ /NF @ 10 V	210	99		1.84	404	
	Ni(OH) ₂ /NF @ 5 V	214	100		1.58	404	
	Ni(OH) ₂ /NF @ 1 V	218	120		1.37	438	
	NF	296	130		2.2	561	460
9	NiO _x /NF	70	68		17.8	271	
	NiO _x /NF-C1	135	159		14.5	590	269
10	Ni/ β -Ni(OH) ₂ NSAs	58	78		168.5	364	
	Ni/ α -Ni(OH) ₂ NSAs	127	101		83.9	493	
11	Ni(111)		115	0.0022	$A_{geo} = 0.063$ cm ⁻²	421	
	Ni(100)		107	0.00092	$A_{geo} = 0.09$ cm ⁻²	432	
	Ni(110)		117	0.0011	$A_{geo} = 0.087$ cm ⁻²	463	
12	Ni/NiO (NF-120)	160	68		0.4	249	
	NF-60	195	77		0.21	274	
	NF-90	176	73		0.31	263	
	NF	288	155		0.125	412	
13	Ni/Ni(OH) ₂ (HZ 1.5)	168	96		1.99	360	
	HZ 0.0	527	71		1.61	662	
	HZ 0.5	390	110		1.80	605	
	HZ 1.0	345	102		1.81	545	
	HZ 2.0	278	103		1.25	463	
	HZ 2.5	242	110		0.45	391	

14	Ni/NiO-250	145	43		3.3	240	
	NiO NSs	251	60		0.9	350	
15	Ni	330 (@5 mA cm ⁻²)	135		Roughness factor (R_f) = 1.9	408	
16	NF	261	94		1.1	425	
17	Ni(poly)	310 (@5 mA cm ⁻²)	144		RF = 1	353	
	Ni/Ni(OH) ₂	235 (@5 mA cm ⁻²)	128		RF = 1	273	
18	Ni/Ni	221	123		8.3	543	
19	Ni/NiO-0.7	401	105		111	794	639
	Ni/NiO-2.7	220	101		115	600	412
	Ni/NiO-3.8	90	41		127	292	
	Ni/NiO-6.1	150	72		124	423	
20	NiO/Ni-240	259	120		108	707	
	NiO/Ni-270	234	111		109	649	
	NiO/Ni-300	194	123		108	653	
	NiO/Ni-350	219	113		109	641	
	Ni	247	110		108	657	
21	β-Ni(OH) ₂	333	230		0.1	494	351
22	Polished Ni rod		115	0.0042	RF = 2.1	351	
	Chemically etched Ni rod		125	0.0047	RF = 3.0	356	
23	NiO @ NF-6	310	231		1.77	760	471
24	Ni	86	68		7.52	261	
	alpha-Ni(OH) ₂	333	127		2.04	588	438
	beta-Ni(OH) ₂	549	450		1.95	1444	551
25	Ni (nanosheets)	354	145		0.066	429	408
	NiO (nanosheets)	372	165		0.062	621	453
	Ni/NiO (nanosheets)	226	135		0.12	422	330
26	Ni(OH) ₂ @ Ni/CC	68	97		2.42	270	
	Ni(OH) ₂ /CC	262	185		5.25	710	542
	Ni/CC	104	184		3.98	527	340
27	Ni @ C-400/Ni foam	110	95		1.38	527	
28	as-deposited 50 nm Ni	263	89		RF = 1.004	263	
	oxidized 50 nm Ni (hydroxide)	220	92		RF = 1.006	220	
	as-deposited 300 nm Ni	256	92		RF = 1.004	256	
	oxidized 300 nm Ni	215	108		RF = 1.011	215	
29	Flame-like Ni(OH) ₂ /NF	56	53		62.3	241	
30	H-Ni/C	167	106		2.75	394	
	H-Ni/NiO/C	87	92		4.89	307	
	H-NiO/C	246	124		1.08	461	
31	β-Ni(OH) ₂ /NF	145	51		30.5	307	
32	Ni(OH) ₂ @Ni/CP	106	88		5.6	321	

Supplementary Note 2. Evaluation of specific activities and IR_u correction of literature data

$$I = -nFAk^\circ(1 - \Theta_{ad}(\Delta G_s^\circ, E))e^{-\alpha F(E-IR_u)/RT} \left(c_{(x=0)} e^{-(\Delta G_i^{\ddagger} + r\Theta_{ad})/RT} \right) \quad (1)$$

In Supplementary Equation 1, where I is the current, n is the number of electrons, F is the Faraday constant, A is the electrochemically active surface area ECSA (geometric surface area, A_{geo} multiplied by the roughness factor, R_f), k° is a unit constant, α is the transfer coefficient, R is the gas constant, T is the temperature, $c_{H_2O(x=0)}$ is the water reactant activity at the electrode surface, $\Delta G_{H_2O}^{\ddagger}$ is the standard free energy of water activated complex, E is the potential applied to the electrode, R_u is the uncompensated resistance, r is a constant describing the rate of change of $\Delta G_{H_2O}^{\ddagger}$ with $\Theta_{ad}(\Delta G_s^\circ, E)$, which is the percentage of the electrode surface that is covered by adsorbed species and is dependent on the free energy of adsorption of these adsorbates ΔG_s° and on the applied potential.

The evaluation of ECSA is not always straightforward. For Ni surfaces, the most common approaches involve determining the charge associated with the anodic peak in the voltammogram (typically at ~ 0.40 V) and evaluation of the double layer capacitance (C_{dl}), either by electrochemical impedance spectroscopy or from current vs. scan rate plot^{4,24,26}.

However, we note that the C_{dl} approach does not include the $(1 - \Theta_{ad}(\Delta G_s^\circ, E))$ term, as it represents the average value of the entire surface in contact with the electrolyte. As such, the C_{dl} gives only an estimation of true ECSA and therefore the normalization process described below does not yield true specific activities ($j_{spec.}$). The situation is further complicated for supported catalysts, where C_{dl} measurement includes the contributions of the support as well.

Accordingly, for the literature-derived data summarized in Supplementary Table 1, which were extracted from previously published studies and used to construct Fig. 1a, we normalized the activities using the C_{dl} values reported in each original publication. The dashed lines in Fig. 1, which represent our own experimental data and serve as a reference for comparison with the published literature values, were therefore derived without including the $(1 - \Theta_{ad}(\Delta G_s^\circ, E))$ term in the normalization. We note that this exclusion applies only to Fig. 1. Throughout the remainder of the manuscript, where we establish the trends that reveal the roles of Ni species in HER, the ECSA values were determined from the charge associated with the anodic peak in the voltammogram.

The normalization procedure applied to literature data is described below. First, ECSA was calculated using Supplementary Equations 2 and 3.

$$R_f = \frac{C_{dl}}{C_s} \quad (2)$$

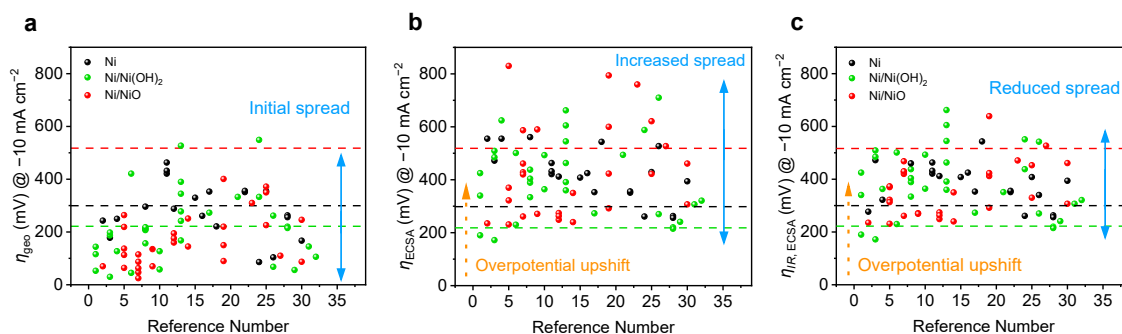
$$ECSA = A_{geo} \times R_f \quad (3)$$

A specific capacitance (C_s) value of $20 \mu F \text{ cm}^{-2}$ was assumed for bare Ni electrode, as commonly reported in the literature^{33–35}.

Next, the normalized activity (j_{ECSA}), i.e., the geometric current (I_{geo}) normalized by ECSA, was calculated using Supplementary Equation 4.

$$j_{\text{ECSA}} = \frac{I_{\text{geo}}}{\text{ECSA}} \quad (4)$$

The hydrogen evolution reaction (HER) activity is most often reported in the literature as overpotential (η_{geo}) required to achieve geometric current density of $-10 \text{ mA cm}^{-2}_{\text{geo}}$. Accordingly, to obtain the ECSA-normalized overpotential values (η_{ECSA}) shown in Fig. 1b, Supplementary Fig. 1 and Supplementary Table 1, we used a normalized current density of $-10 \text{ mA cm}^{-2}_{\text{ECSA}}$.



Supplementary Fig. 1 | Scattered HER activity data for Ni-based catalysts, compiled from numerous published studies. **a**, HER activities plotted as overpotential (η_{geo}) at geometric current density (j_{geo}) of -10 mA cm^{-2} . **b**, HER activities normalized to ECSA. **c**, HER activities normalized to the ECSA and corrected for ohmic overpotential (IR_u drop) to the best of our ability. The blue arrow illustrates the overall spread in HER activity, while the orange arrow indicates the general shift in HER activity upon normalization. Symbols represent literature-reported values for three types of Ni surfaces: metallic Ni^0 (black), NiO/Ni (red), and $\text{Ni(OH)}_2/\text{Ni}$ (green). Multiple data points from individual studies reflect different $\text{NiO}_x\text{H}_y/\text{Ni}$ compositions studied within the same work (see Supplementary References 1-32). Black, red, and green dashed horizontal lines indicate the HER activity values measured in this study: black corresponds to pure metallic Ni, red to the least active NiO/Ni interface, and green to the most active $\text{Ni(OH)}_2/\text{Ni}$ interface.

After normalization, the majority of data points shift to significantly lower activities (i.e., higher overpotentials), as shown in Supplementary Fig. 1b. Strikingly, nearly all of the previously reported highest activities now fall below the intrinsic activity of pure metallic Ni, as measured in this study (black dashed line, Fig. 1). This suggests that the apparent extraordinary activities largely arise from the high surface area of the catalyst rather than their intrinsic performance. Despite normalization, a considerable spread in the data persists.

To address this, we further corrected data points where the ohmic overpotential (IR_u) was clearly undercompensated or not compensated at all, which resulted in a reduction of the true kinetic overpotential (see details in the Supplementary Table 1). This correction noticeably reduced the overall data scatter, as illustrated in Fig. 1c. In several of the referenced papers summarized in Supplementary Table 1, the extended exponential region of the polarization curves was absent; instead, a linear region dominated, strongly indicating incomplete or absent IR_u compensation. To mitigate this, η_{ECSA} at -10 mA cm^{-2} was recalculated from the extracted low-current η values using the Tafel equation (Supplementary Equation 5), yielding $\eta_{\text{ECSA},IR}$ – the overpotential corrected for uncompensated resistance, as shown in Supplementary Table 1.

$$\eta_{\text{ECSA}} = a + b \log j_{\text{ECSA}} \quad (5)$$

Here, b represents the Tafel slope, and a is related to the exchange current density (j_0).

We emphasize that all data used for this correction were taken directly from the respective published studies in Supplementary Table 1, and we cannot account for any underlying inaccuracies in those data that may arise from improper experimental measurement or reporting.

While we could have simply presented the large spread in activity data using only geometric currents (Fig. 1a), we considered it a matter of courtesy and scientific rigor to account for these apparent inconsistencies in the literature data. Importantly, even after applying these careful corrections and normalizations, Fig. 1 and Supplementary Fig. 1 still reveal a substantial spread in HER activity remains across the reported studies.

The remaining data spread in Supplementary Fig. 1c is attributed to the immense complexity of Ni surface chemistry, where species such as metallic Ni, NiH_x , NiO , $\alpha\text{-Ni(OH)}_2$, $\beta\text{-Ni(OH)}_2$, and NiOOH may exist individually or coexist in various combinations.

Together, these data suggest that the HER activity values reported in the literature are often inflated – not only due to poor experimental design and careless handling and analysis of raw data (human error), but also due to a lack of fundamental understanding of the relationship between inherent Ni surface species and HER kinetics in alkaline electrolytes. As will be shown below, this knowledge gap can affect the observed activity by as much as three to four orders of magnitude.

Supplementary Note 3. Preparation protocols and characterization of individual Ni surfaces

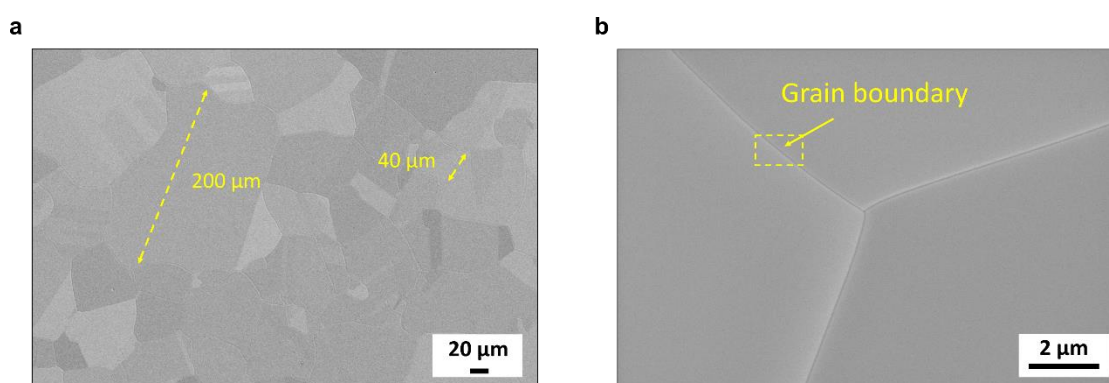
Anyone who has worked with Ni in alkaline electrolytes is familiar with the notorious irreproducibility of its surface, a consequence of the difficulty in stabilizing its surface state. The complexity of Ni surface chemistry, marked by the coexistence of multiple intrinsic species, casts doubt even on seemingly reproducible results.

To establish a meaningful correlation between HER activity and specific Ni species, exact control over the surface composition was essential. To this end, we developed a set of protocols to prepare surfaces dominated by one of the following well-defined Ni states:

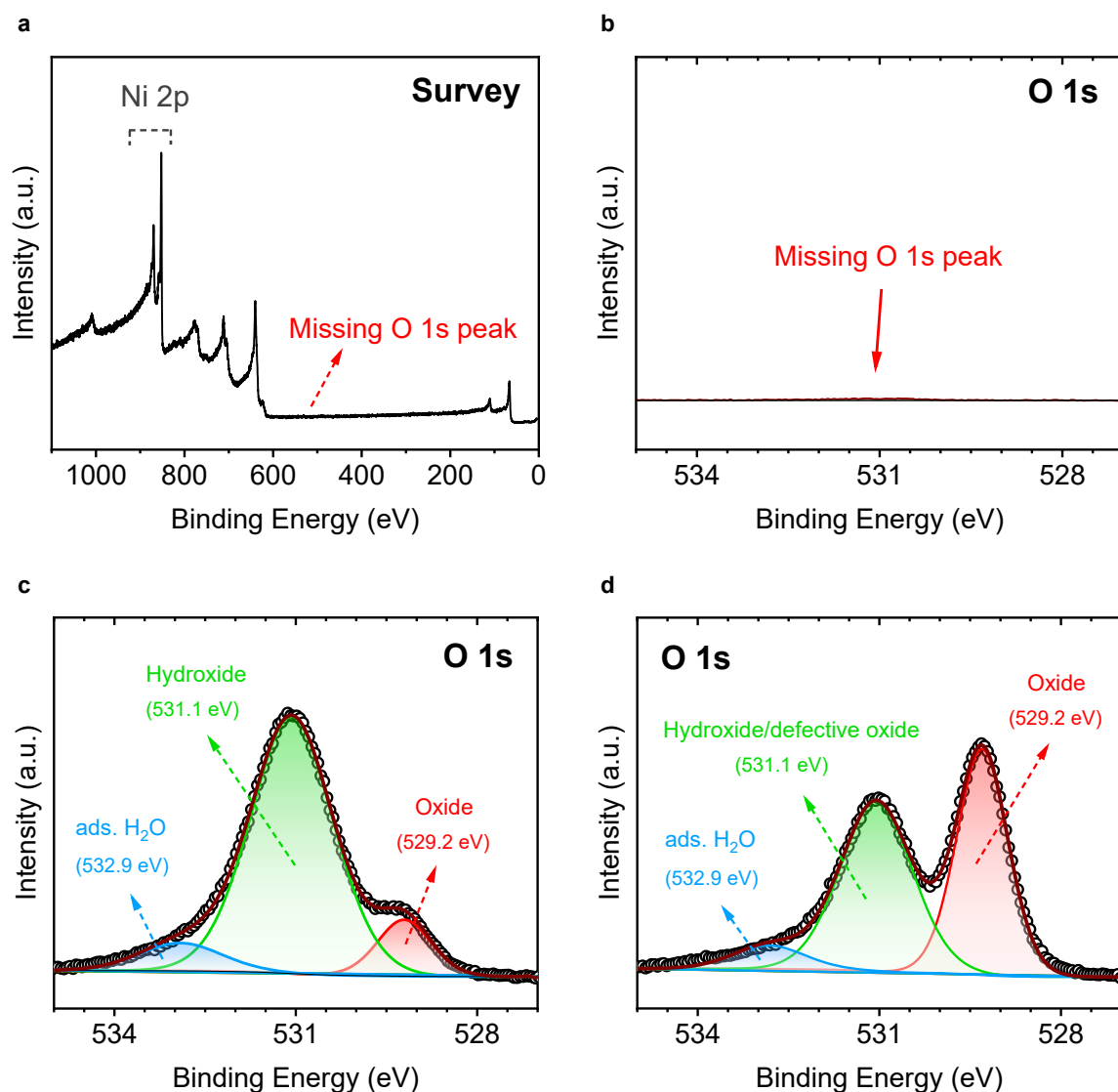
Bare metallic Ni (unmodified surface);
Ni partially modified, predominantly with H_x ;
Ni partially modified, predominantly with $Ni(OH)_2$;
Ni partially modified, predominantly with NiO .

These are denoted as Ni^0 , $Ni_{(H)}$, $Ni_{(OH)}$, and $Ni_{(O)}$, respectively.

To prepare the Ni^0 surface, we employed two distinct approaches. The first involves surface preparation under ultra-high vacuum (UHV) via Ar^+ ion sputtering, followed by a brief annealing step at 600 °C. As shown in the scanning electron microscopy (SEM) image (Supplementary Fig. 2), the annealing produced extended surfaces with large, 10–200 μm -sized grains. Within individual grains, the surface was close to atomically flat, as seen in the atomic force microscopy (AFM) image and the corresponding profile line scan in Fig. 2a. The X-ray photoelectron spectroscopy (XPS) spectrum confirmed that our preparation procedure yielded a surface free of oxygenated species, as indicated by a single prominent Ni $2p_{3/2}$ peak at 852.5 eV, characteristic of metallic Ni (Fig. 2h), and the absence of any significant signal in the O 1s region (Supplementary Fig. 3a,b).



Supplementary Fig. 2 | SEM images of the annealed polycrystalline Ni surface. **a**, Annealing produced an extended surface with large grains ranging from 10 to 200 μm . **b**, Close-up view of selected grain boundaries, showing a surface that appears flat within the resolution of the SEM.



Supplementary Fig. 3 | XPS spectra of different Ni surfaces. a, Survey XPS spectrum for Ni⁰. b-d, Peak deconvolution of high-resolution (HR) XPS O 1s spectra for Ni⁰, Ni(OH)₂, Ni(O), respectively.

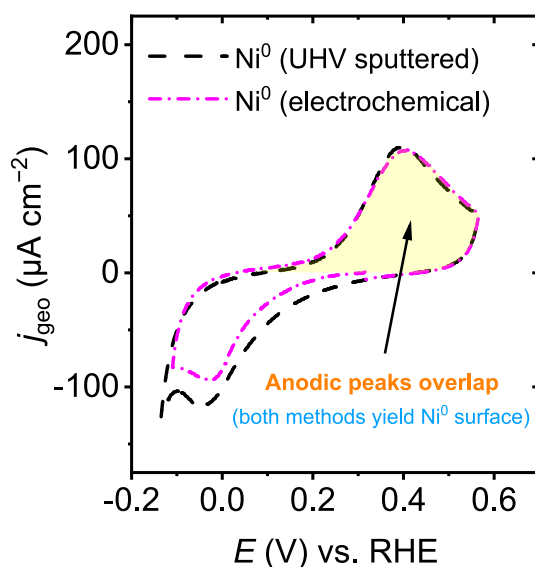
The sample was then transferred from the UHV chamber, under vacuum, to a transfer vessel and subsequently moved to a N₂-filled glovebox. Electrochemical characterization was performed by recording a cyclic voltammogram from 0.00 V to 0.55 V and back to −0.15 V vs. reversible hydrogen electrode (RHE), revealing oxidation and reduction peaks associated with the formation and reduction of Ni(OH)₂, respectively, as described in Supplementary Equation 6 (Fig. 2d).



Alternatively, the Ni⁰ surface can be obtained by inductive heating at 1000 °C in a H₂/Ar atmosphere, followed by transfer through air with a protective droplet of water to shield

the surface from airborne contaminants. The air-formed (hydr)oxide layer is then electrochemically reduced at -0.40 V vs. RHE. To complete the preparation, the subsurface hydride formed during this process is removed by holding the potential at 0.30 V for 20 min – a sufficiently positive value to oxidize unwanted hydride while keeping the co-formed hydroxide within reducible monolayer coverage, thereby minimizing the formation of irreducible $\text{Ni}(\text{OH})_2$. Notably, this step, followed by a potential sweep past -0.15 V, is essential for obtaining a clean, metallic Ni^0 surface (dashed pink, Supplementary Fig. 4). The charge associated with the cathodic peak in the voltammogram, corresponding to $\text{Ni}(\text{OH})_2$ reduction (Supplementary Equation 6), yields a charge density of $355 \mu\text{C cm}^{-2}$, which closely matches the theoretical value of $367 \mu\text{C cm}^{-2}$ corresponding to one monolayer (1 ML) of $\text{Ni}(\text{OH})_2$. This estimate assumes a layered hexagonal structure in which each $\text{Ni}(\text{II})$ layer is sandwiched between two OH^- layers, with a surface density of 1.14×10^{15} ions cm^{-2} , as suggested by Seyeux et al.³⁶. Afterward, the scan direction was reversed toward the anodic side, up to 0.55 V, to characterize the Ni^0 surface.

The reproducibility of the Ni^0 surface prepared by two independent methods was confirmed by the close agreement of their anodic peak features, as shown in Supplementary Fig. 4. However, the differences in the cathodic region were expected, as the two methods involve different starting potentials and the initial direction of the scan.



Supplementary Fig. 4 | Preparation of Ni^0 surface via two methods. In the first, Ni^0 was prepared under UHV by Ar^+ ion sputtering and annealing at 600°C , then transferred under vacuum to a N_2 -filled glovebox. A voltammogram recorded from 0 V to 0.55 V and reverse to -0.15 vs. RHE, showed characteristic $\text{Ni}(\text{OH})_2$ oxidation and reduction peaks (dashed black curve). Alternatively, Ni^0 was obtained by inductive heating at 1000°C in a H_2/Ar atmosphere, followed by air transfer using a protective water droplet. The air-formed (hydr)oxide was reduced at -0.40 V, subsurface hydride removed by holding at 0.30 V for 20 min, followed first by a cathodic sweep to -0.15 V and then anodic sweep to 0.55 V (dashed pink curve). The overlapping anodic peaks indicate that both methods reproducibly yield Ni^0 surfaces.

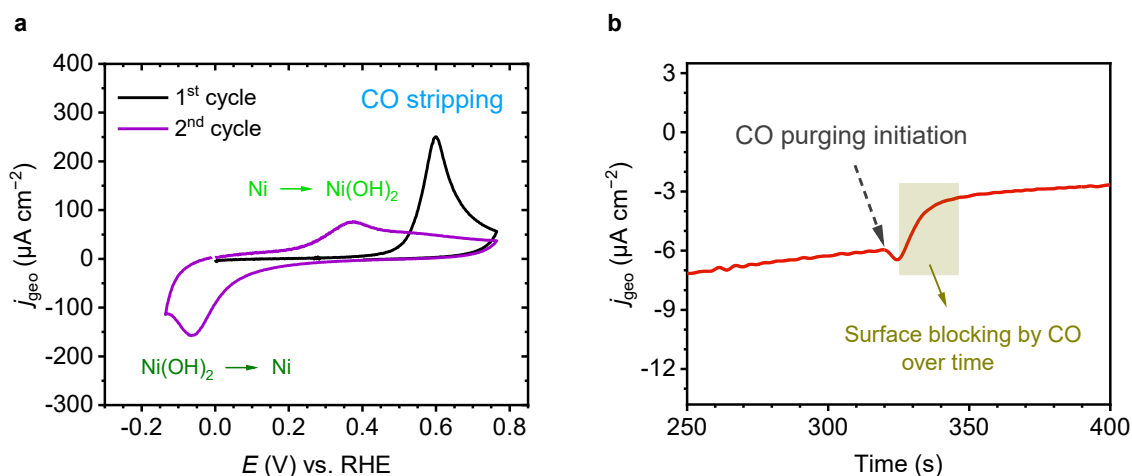
$\text{Ni}_{(\text{H})}$ was prepared by holding the potential of the Ni^0 electrode between -0.05 and -0.40 V vs. RHE. As NiH_x cannot be probed by the XPS, we relied on CV to determine the exact amount present in/on Ni (Supplementary Fig. 15). Comparison of the anodic peaks at 0.40 V, where $\text{Ni}(\text{OH})_2$ forms on Ni^0 (blue dashed line in Fig. 2e, obtained after stripping of

hydride from the Ni surface), as described in Supplementary Equation 6, and coupled formation of $\text{Ni}(\text{OH})_2$ and oxidation of NiH_x on $\text{Ni}_{(\text{H})}$, as described in Supplementary Equations 6 and 7, suggests that 0.29 ML of hydride was formed by holding the electrode at -0.20 V.

To probe the location of hydrogen, we applied a CO displacement method pioneered by the Alicante group, which monitors both the magnitude and polarity of the charge during chronoamperometry as CO adsorbs onto the Ni surface³⁷. The CO adsorption on Ni is well-established in the literature³⁸. In our system, this is further supported by the presence of a clear CO stripping feature in the cyclic voltammogram (Supplementary Fig. 5a). This confirms that CO adsorbs strongly enough to measurably affect the interface. Based on this, we consider CO displacement to be an appropriate qualitative probe for the presence of surface-adsorbed hydrogen.

While H_{ad} desorption produces an electrochemical response, CO adsorption does not. Therefore, a distinct positive current would be expected from H_{ad} desorption during CO displacement, which, notably, was absent in our measurements, indicating no adsorbed hydrogen resides on the surface (Supplementary Fig. 5b).

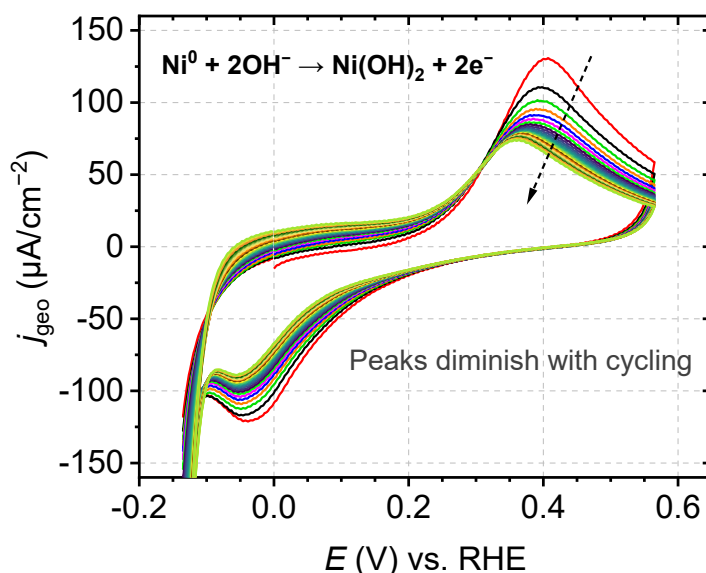
One might perhaps point to a faint transient signal of opposite polarity (Supplementary Fig. 5b). This signal was observed during the physical switch of the gas lines from Ar to CO purging and is attributed to trace amounts of oxygen that entered the system. The minor cathodic transient is therefore explained as an experimental artifact, arising from residual oxygen reduction (ORR).



Supplementary Fig. 5 | CO stripping and CO displacement experiment on Ni surfaces. **a**, CO stripping on a Ni^0 surface. The first cycle shows the absence of the oxidation peak associated with $\text{Ni}(\text{OH})_2$ formation, due to blocking of the surface by adsorbed CO. At more positive potentials, CO is stripped from the surface, thereby exposing Ni sites, as evidenced by the appearance of anodic and cathodic features in the second cycle corresponding to $\text{Ni}(\text{OH})_2$ formation. This behavior indicates that CO adsorbs strongly on metallic Ni and therefore represents a qualitative probe for the presence of surface-adsorbed hydrogen. **b**, CO displacement experiment on a Ni surface modified with H_x . The Ni electrode was first polarized at -0.40 V vs. RHE to make subsurface hydride, then the potential was changed to -0.15 V before introducing CO. The electrolyte was initially purged with Ar, which was then replaced by CO at the time indicated by the dashed black arrow on the graph. The dark yellow band highlights the region where CO progressively blocks the HER. No current transient (spike) associated with H_{ad} desorption was observed, confirming that hydrogen (i.e., hydride) resides beneath the Ni surface.

As noted earlier, exposing the Ni surface to potentials above 0.30 V induces irreversible changes, forming a Ni(OH)₂-modified surface Ni(OH). For example, extending the positive potential limit to 0.55 V results in an anodic peak corresponding to the formation of 1.4 ML of Ni(OH)₂, indicating partial coverage with multilayer hydroxide. This behavior is in good agreement with earlier work by Šimpraga and Conway³⁹, which showed that even at low levels of Ni surface oxidation, hydroxide growth follows Volmer-Weber (VW)-type behavior⁴⁰, with 3D islands forming already at lower coverages, and no uniform monolayer developing. More importantly, this hydroxide is not fully reduced during the cathodic sweep, resulting in a slightly lower cathodic charge compared to the anodic one. Consequently, each successive scan shows diminishing voltammetric peaks (Supplementary Fig. 6).

Fig. 2f displays the 30th scan, where metallic Ni availability is significantly reduced (~30%) relative to Ni⁰. HR XPS Ni 2p_{3/2} spectrum (Fig. 2i) confirms surface composition dominated by metallic Ni and Ni(OH)₂, indicated by peaks at 852.5 eV and 855.9 eV, respectively. O 1s spectrum (Supplementary Fig. 3c) further support this, with a dominant hydroxide peak at 531.1 eV.



Supplementary Fig. 6 | Irreversibility of Ni(OH)₂ species on Ni surface. Thirty potential cycles were performed on the Ni⁰ surface. A gradual decrease in the voltammetric peak intensity was observed with each cycle, reflecting the progressive accumulation of irreducible Ni(OH)₂ species.

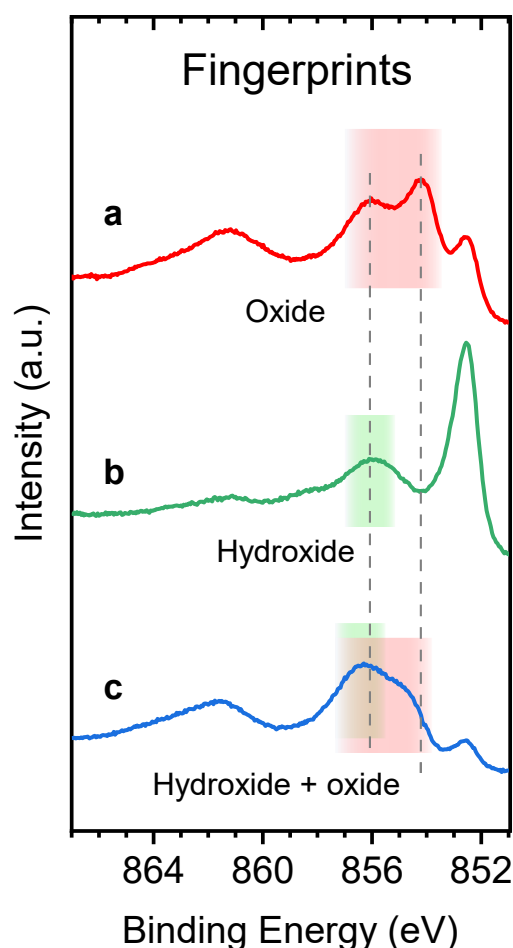
We note that the omission of α - or β -phase designation was intentional. Rather than using structural labels, we classify the species as reversible (reducible) or irreversible (irreducible), which more directly reflects their electrochemical behavior. We are aware that α - or β -phase designations for Ni(OH)₂ are commonly employed in the literature, but such designation is warranted for layered hydroxides (at least two full layers of hydroxide should be present to make a distinction between α - and β -phase). In our study, we deal with partial monolayers, making α/β designations inappropriate.

Finally, the Ni(O) model surface was chemically prepared by thermal oxidation of the Ni⁰ surface at 300 °C in a stream of Ar/O₂ gas. The HR XPS Ni 2p_{3/2} spectrum of Ni(O) displays

an intense metallic Ni peak at 852.5 eV and a distinct fingerprint double-headed peak at 854.0 eV and 855.7 eV, attributed to Ni(II) from oxide species (Fig. 2j).

We note that special care should be taken when drawing conclusions from the XPS data. Three prevalent examples of crude misinterpretation of double-headed feature in the literature^{24,25,27,41–43} can be identified. These include assigning the main peak to metallic Ni and the shoulder to a hydroxide or oxide; attributing the main peak to the oxide and the shoulder to the hydroxide; and interpreting distortions in the relative intensities of the double-headed feature incorrectly, such that a dominant shoulder is taken as evidence for oxide alone despite a substantial contribution from hydroxide species. To avoid potential confusion and guide the reader through the article, Supplementary Fig. 7 provides clear insight into the peak shapes corresponding to specific Ni (hydr)oxide species.

The XPS O 1s spectrum of Ni(O) also shows an intense peak at 529.3 eV, characteristic of oxide species (Supplementary Fig. 3d). Fitting parameters for both Ni 2p_{3/2} and O 1s spectra of Ni(OH) and Ni(O) are listed in Supplementary Tables 2 and 3, following the methodology established by Biesinger and co-workers⁴⁴.



Supplementary Fig. 7 | The XPS spectra exhibit distinct fingerprints for Ni(II) in oxide and hydroxide species. **a**, a double-headed peak with a maximum at 854.0 eV and a shoulder at 855.7 eV, characteristic of Ni(II) in oxide species. **b**, a single peak with a maximum at 855.9 eV, consistent with Ni(II) in hydroxide species. **c**, a double-headed peak with a maximum at more positive binding energy (BE) and a shoulder at lower BE, opposite to the pattern observed for oxide, indicating the prevalence of hydroxide with a significant contribution from oxide species.

Supplementary Table 2. Fitting parameters for HR XPS Ni 2p_{3/2} spectra corresponding to Fig. 2h-j adapted from Biesinger et al.⁴⁴. FWHM denotes the full width at half maximum.

Component	A	B	C	D	E	F	G
Name	metallic Ni¹	metallic Ni²	metallic Ni³	Ni(OH)₂¹	Ni(OH)₂²	Ni(OH)₂³	Ni(OH)₂⁴
Peak position	852.5	856.4	858.8	854.9	856.0	858.0	860.8
Area constraints	A	A × 0.08	A × 0.15	E × 0.16	E	E × 0.07	E × 0.03
FWHM	1.03	2.30	2.30	1.36	2.50	1.40	1.26

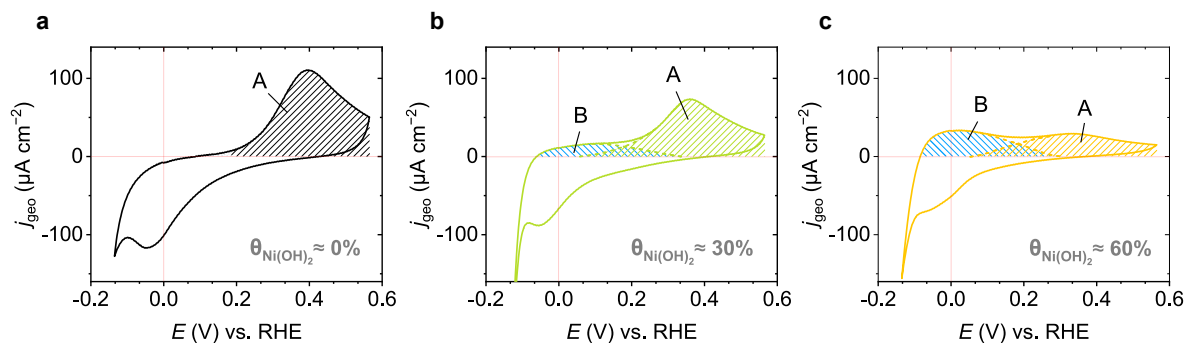
Component	H	I	J	K	L	M	N
Name	Ni(OH)₂⁵	Ni(OH)₂⁶	NiO¹	NiO²	NiO³	NiO⁴	NiO⁵
Peak position	861.5	866.8	854.0	855.7	861.1	864.1	866.7
Area constraints	E × 0.86	E × 0.08	K × 0.32	K	K × 0.77	K × 0.08	K × 0.09
FWHM	4.85	3.20	1.00	3.25	3.76	2.04	2.44

We note that the (hydr)oxide peak positions are slightly shifted to higher binding energies than expected, likely due to differential charging effects⁴⁵. This shift results from the insulating nature of the (hydr)oxide layers relative to the underlying conductive metallic Ni substrate—a well-known, yet often overlooked phenomenon in the surface chemistry literature.

Supplementary Table 3. Fitting parameters for HR XPS O 1s spectra corresponding to Supplementary Fig. 3 adapted from Biesinger et al.⁴⁴.

Component	A	B	C
Name	Oxide	Hydroxide	Water/Organic
Peak position	529.2	531.1	532.9
FWHM	0.95	1.59	B × 1

Supplementary Note 4. ECSA determination



Supplementary Fig. 8 | Cyclic voltammograms illustrating determination of surface coverages (Θ_{ad}). **a**, The hatched area A represents the charge associated with the oxidation of Ni to Ni(OH)_2 and serves as the basis for ECSA determination. **b,c**, The correction term B, increases with hydroxide coverage – being negligible at 0% and progressively larger at higher coverage levels (e.g., 30%, 60%).

The true ECSA of Ni(OH) and Ni(O) was determined by cyclic voltammetry (CV). Here, we show the procedure using Ni(OH) as an example. Quantitatively, the ECSA is given by the product of A and $(1 - \Theta_{ad})$, as described by Supplementary Equation 8:

$$\text{ECSA}_{\text{true}} = A (1 - \Theta_{ad}) \quad (8)$$

where A is the real surface area (A_{geo} multiplied by the R_f), and Θ_{ad} is the surface coverage by adsorbed species. AFM measurements confirm that our electrodes are atomically flat ($R_f = 1$), so A equals the A_{geo} .

The coverage by individual (hydr)oxide surface species (Θ_{ad}) was determined from the charge associated with the anodic peak at approximately 0.40 V (hatched area A in Supplementary Fig. 8), which corresponds to the oxidation of Ni to Ni(OH)_2 per Supplementary Equation 6. We note that, to ensure a fair comparison across all investigated surfaces and their respective coverages, the contribution from the pre-anodic hump, observed at potentials more negative than 0 V vs. RHE and more prominent at higher hydroxide coverages, was excluded from the analysis. This feature, labeled as B (Supplementary Fig. 8b,c), has been attributed in the literature to hydride or hydrogen oxidation (HOR) as a result of prior HER activity^{46,47}. However, the correction term B was not applied for NiO and NiH_x coverages, as these surfaces do not exhibit a significant contribution from this feature. Consequently, NiO coverages were determined in the same manner as shown in Supplementary Fig. 8a—that is, by considering only peak A. Details on hydride coverage determination are provided in Supplementary Note 7. While the relationship between hydroxide coverage and the onset or extent of parasitic processes contributing to this pre-anodic feature may warrant dedicated investigation, it is not essential for elucidating the role of Ni species in HER kinetics on Ni. A detailed discussion of this phenomenon is therefore beyond the scope of the present work.

The Ni^0 surface, exhibiting a charge of $516 \mu\text{C cm}^{-2}$, corresponding to the formation of one monolayer of Ni(OH)_2 on the $\text{Ni}(\text{poly})$ surface^{33,48–50}, was used as the reference, representing 100% of surface Ni atoms being electrochemically accessible (i.e., $\Theta_{\text{Ni(OH)}_2} = 0\%$) (Supplementary Fig. 8a). The deposition of irreducible Ni(OH)_2 on the Ni surface reduces the charge of this anodic peak. The quantitative estimation of Ni(OH)_2 surface coverage was then performed by comparing the voltammograms of partially covered surfaces with that of the Ni^0 reference, with the difference in charge corresponding to $\Theta_{\text{Ni(OH)}_2}$, as defined by Supplementary Equation 9. For example, the Ni(OH) voltammogram (peaks A and B) in Supplementary Fig. 8b shows a total charge of $424 \mu\text{C cm}^{-2}$; after subtracting the correction term B ($53 \mu\text{C cm}^{-2}$), the remaining charge of $371 \mu\text{C cm}^{-2}$ corresponds to 72% electrochemically accessible Ni atoms (i.e., $\Theta_{\text{Ni(OH)}_2} = 28\%$).

$$\Theta_{\text{ad}} = \Theta_{\text{Ni(OH)}_2} = 1 - \left(\frac{q_{\text{Ni(OH)}}}{q_{\text{Ni}}} \right) \quad (9)$$

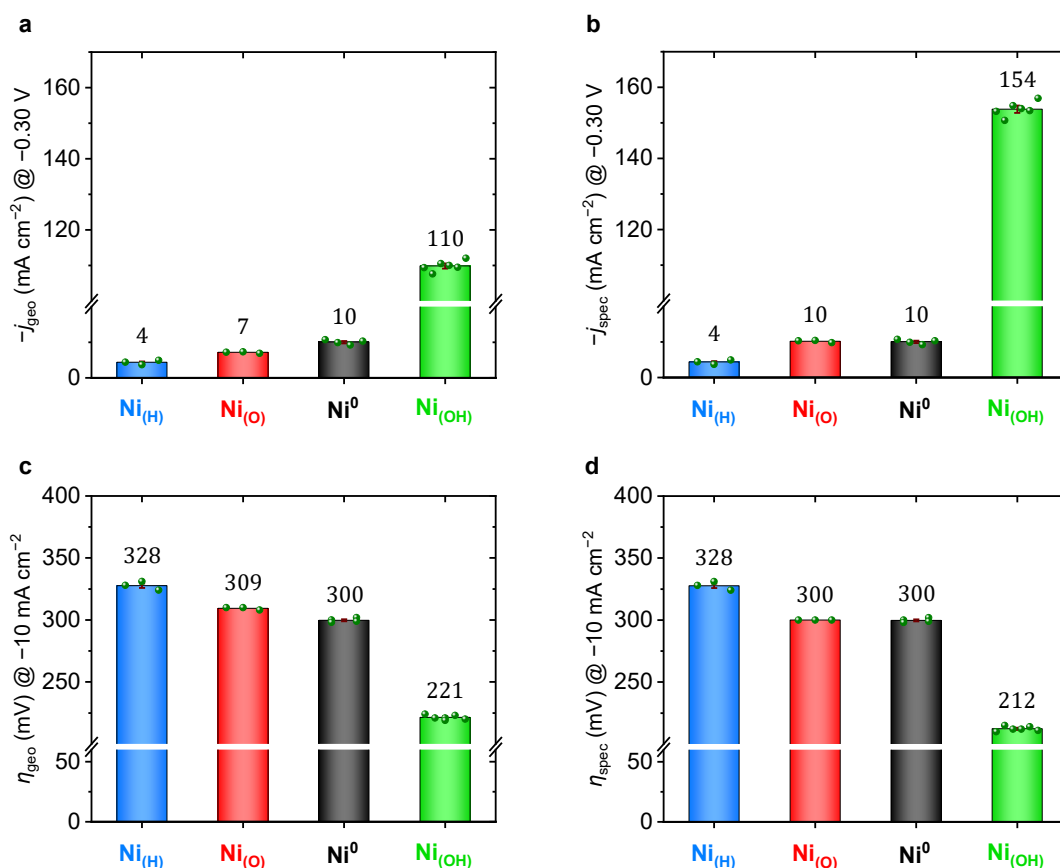
where $q_{\text{Ni(OH)}}$ is the charge density associated with the oxidation of Ni to Ni(OH)_2 on a surface partially covered by irreducible Ni(OH)_2 , and q_{Ni} is the charge density corresponding to the oxidation of Ni to Ni(OH)_2 on an unmodified (bare) Ni surface.

Supplementary Note 5. Specific current density, exchange current density and Tafel slope calculation

In the present work, we highlighted the lack of a standardized protocol for reporting HER activity in the literature. Reported activities, expressed as current densities (j), vary widely and include ECSA-normalized (j_{ECSA} , mA/cm²), geometric (j_{geo} , mA/cm²) or mass-normalized (j_{mass} , mg/cm²) values. To enable meaningful comparisons across different studies and avoid overestimating performance metrics, we strongly recommend reporting true specific current densities (j_{spec}), obtained by normalizing the measured activity to the measured charge density, thereby accounting for both the R_f and the $1 - \Theta_{\text{ad}}$ term, as defined in Supplementary Equation 10.

$$j_{\text{spec}} = j_{\text{geo}} \times \frac{q_{\text{monolayer}}}{q_{\text{measured}}} \quad (10)$$

where j_{geo} is the measured activity (geometric current density), q_{measured} is the measured charge density, and $q_{\text{monolayer}}$ is the charge density of 516 $\mu\text{C cm}^{-2}$. Supplementary Fig. 9 presents bar graphs showing the values of kinetic parameters used to evaluate the HER activity of Ni^0 , $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{OH})}$, and $\text{Ni}_{(\text{O})}$ surfaces.

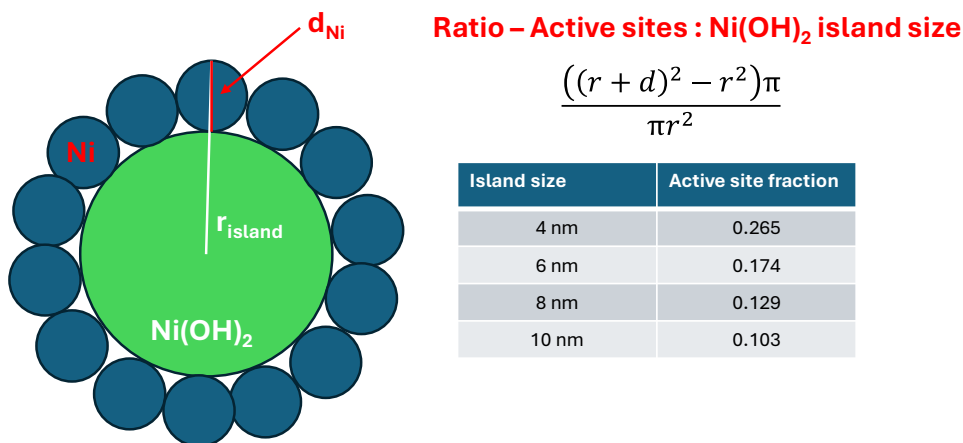


Supplementary Fig. 9 | Kinetic metrics for evaluating the HER activity of different Ni species. **a**, Geometric current densities (j_{geo}) at -0.30 V. **b**, Specific current densities (j_{spec}) at -0.30 V. **c**, Geometric overpotentials (η_{geo}) at -10 mA cm⁻², and **d**, $1 - \Theta_{\text{ad}}$ -normalized overpotentials (η_{spec}) at -10 mA cm⁻². Bar graphs with overlaid data points are derived from the polarization curves in Fig. 3a. Error bars represent mean $\pm$ standard deviation (s.d.). The number of independent experiments/electrode preparations was $n = 3, 3, 4$ and 6 for $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{O})}$, Ni^0 and $\text{Ni}_{(\text{OH})}$, respectively.

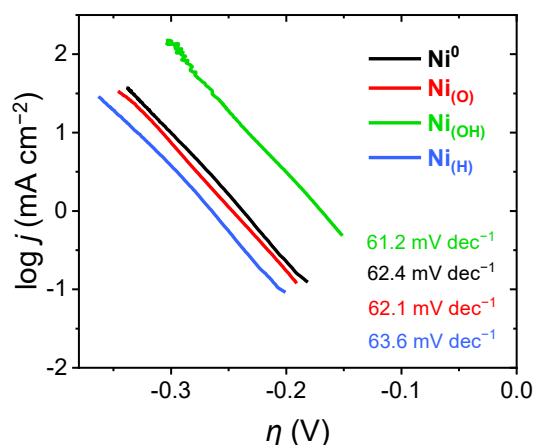
In the above analysis the specific activities of these four individual surfaces are evaluated by normalizing the activity to the number of Ni sites estimated from voltammograms (i.e., ECSA). While such normalization is appropriate for Ni^0 , $\text{Ni}_{(\text{H})}$, and $\text{Ni}_{(\text{O})}$, where the reaction proceeds exclusively on metallic Ni sites, this approach is not directly valid for $\text{Ni}_{(\text{OH})}$ surface. In the latter case, the fastest reaction occurs at Ni metal sites adjacent to $\text{Ni}(\text{OH})_2$, meaning that the number of active sites is significantly overestimated by taking the total metallic surface area as ECSA. We alluded to this on page 8 of the manuscript when discussing the discrepancy between DFT predictions, which indicate ~100-fold higher activity for $\text{Ni}/\text{Ni}(\text{OH})_2$ sites compared to Ni, and the experimentally observed ~15-fold enhancement.

The origin of this discrepancy is consistent with the active surface area being confined to the interface between Ni and $\text{Ni}(\text{OH})_2$ islands. A rough estimation of the interfacial area is shown in Supplementary Fig. 10, and depends on the ratio between the surface Ni atom diameter (~0.25 nm) and the radius of the $\text{Ni}(\text{OH})_2$ islands. For the island size range observed by AFM ($r = 2\text{--}5\text{ nm}$; corresponding to 4–10 nm lateral size, Fig. 2b), we estimate that only 0.10–0.26 of $\Theta_{\text{Ni}(\text{OH})_2}$ is actually electrochemically active. This implies that the reported specific activity for $\text{Ni}(\text{OH})_2$ is underestimated by a factor of ~4–10, corresponding to an intrinsic ~60–150-fold higher activity of $\text{Ni}/\text{Ni}(\text{OH})_2$ interfacial sites relative to metallic Ni sites.

Consequently, when this geometric factor is taken into account, the experimentally derived activity becomes fully consistent with the trends predicted by DFT. This further supports our identification of the $\text{Ni}/\text{Ni}(\text{OH})_2$ interface as the relevant active motif and clarifies the apparent discrepancy between theory and experiment.



Supplementary Fig. 10 | Estimation of the fraction of $\text{Ni}/\text{Ni}(\text{OH})_2$ active sites. Based on the ratio between the surface Ni atom diameter and the radius of the $\text{Ni}(\text{OH})_2$ island, we estimate that only 0.10–0.26 of $\Theta_{\text{Ni}(\text{OH})_2}$ is electrochemically active. This corresponds to a 60–150-fold higher activity of $\text{Ni}/\text{Ni}(\text{OH})_2$ interfacial sites relative to metallic Ni sites.



Supplementary Fig. 11. Tafel slope plot comparing the hydrogen evolution reaction (HER) on four representative benchmark Ni surfaces at matched $\sim 30\%$ coverage.

Supplementary Table 4. Exchange current density values calculated from corresponding Tafel slopes in Supplementary Fig. 11.

Surface	Exchange current density, j_0 (A cm^{-2})	Tafel slope, b (mV dec^{-1})
Ni^0	1.51×10^{-4}	62.4
NiO	1.07×10^{-4}	62.1
Ni(OH)_2	1.60×10^{-3}	61.2
NiH_x	6.46×10^{-5}	63.6

We also report the apparent exchange current density (j_0) and tafel slope (b) values for the four representative benchmark surfaces in Fig. 3a. However, we would caution against interpreting them as universal constants describing HER on Ni, since the present work shows that no single Ni surface state is representative of the full chemistry accessible under alkaline conditions. We also note that classical textbook assignments of HER mechanisms based on idealized Tafel slopes of 30, 40, or 120 mV/dec represent limiting cases that rely on assumptions such as a single distinct rate-determining step, one dominant adsorbate, Langmuir-type coverage behavior, and a chemically homogeneous surface. These assumptions are not generally valid for alkaline HER on Ni, where multiple surface species can coexist and both H- and OH-containing intermediates may contribute to the observed kinetics. For this reason, apparent Tafel slopes and exchange current densities are useful benchmark descriptors, but they cannot be treated as unique mechanistic identifiers in the present system.

Supplementary Note 6. DFT calculations

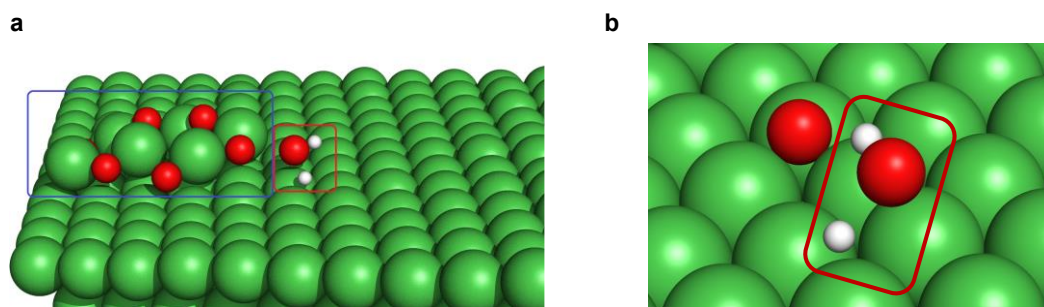
To computationally evaluate the effects of the surface type and co-adsorbed species, H^* , OH^* , and O^* were co-adsorbed on an undecorated Ni(111) surface, as depicted in Fig. 3b and Supplementary Figs. 12 and 13. The feasibility of HER and the properties of different surfaces were studied using several proxy or surrogate quantities. Among them, the dissociation barrier, $E_a^\ddagger$, for the reaction $H_2O^* + * \rightarrow OH^* + H^*$ is most indicative of the reaction kinetics. Furthermore, we computed the adsorption energy of H^* and OH^* as a function of coverage, Bader charges, and work function.

Adsorption. DFT calculations show that H^* readily adsorbs. The adsorption energy of H^* (relative to $\frac{1}{2} H_{2(g)}$) monotonically changes from -0.50 eV to -0.54 eV as the surface coverage increases from 0.00 to 1.00 ML. Surface H^* is highly mobile with a surface diffusion barrier of 0.51 eV. Furthermore, H^* penetration to the subsurface is possible, where the adsorption energies range from $+0.10$ eV to -0.02 eV. This shows that every subsequent H atom penetrates more easily. While these considerations are thermodynamic, kinetics also support them. The barrier for hydrogen migration to the subsurface decreases from 0.75 eV at 0.06 ML to 0.70 eV at 1.00 ML.

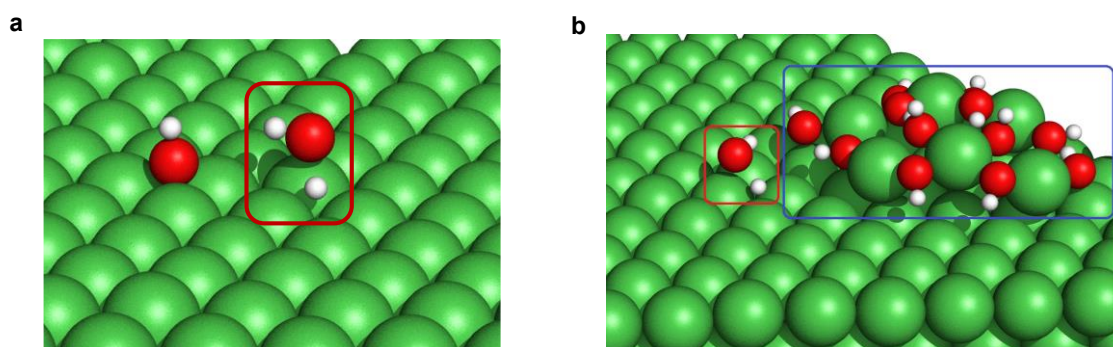
Reaction barriers. We have calculated the reaction energy (ΔE_{rxn}), adsorption energy of a water molecule ($E_{ads(H_2O)}$), and activation barrier for H_2O dissociation ($E_{a(H_2O)}^\ddagger$) on Ni(111) with different co-adsorbed species, as shown in Supplementary Table 5. The co-adsorbed species/moieties that were considered included adsorbed O on Ni ($O@Ni(111)$), Supplementary Fig. 12b), NiO cluster on Ni ($(NiO)_6@Ni(111)$), Supplementary Fig. 12a), adsorbed OH on Ni ($OH@Ni(111)$), Supplementary Fig. 13a), $Ni(OH)_2$ cluster on Ni ($(Ni(OH)_2)_6@Ni(111)$), Supplementary Fig. 13b), $Ni(OH)_2$ full layer on Ni (Supplementary Fig. 14a), Ni adatom on $Ni(OH)_2$ layer on Ni (Supplementary Fig. 14b). For H modified Ni, we considered subsurface H ($H_{sub}@Ni(111)$), surface H ($H_{surf}@Ni(111)$) and both species together ($H_{sub}+H_{surf}@Ni(111)$). We assumed that during HER at high overpotentials, the surface is considerably covered by H_{surf} and that the changes we observe are due to the additional effect of subsurface hydrogen, amounting to 0.04 eV ($E_{a^{H_{sub}+H_{surf}}@Ni(111)}^\ddagger - E_{a^{H_{surf}}@Ni(111)}^\ddagger$), reported in the main text.

Supplementary Table 5. DFT calculated energetics of water dissociation ($H_2O \rightarrow OH + H$). All values are reported in eV.

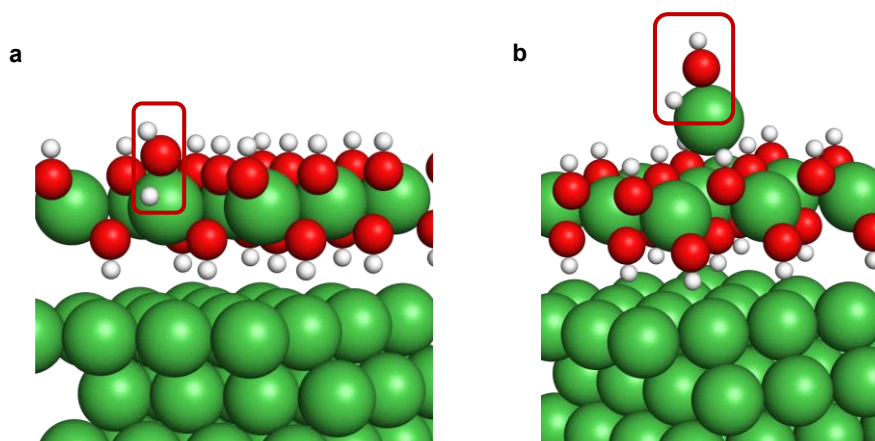
Model	Adsorption energy, $E_{ads(H_2O)}$	Activation energy, $E_{a(H_2O)}^\ddagger$	Reaction energy, ΔE_{rxn}
Ni(111)	-0.43	1.02	+0.07
$H_{sub}@Ni(111)$	-0.46	1.02	+0.09
$H_{surf}@Ni(111)$	-0.34	1.14	+0.41
$H_{sub}+H_{surf}@Ni(111)$	-0.34	1.18	+0.79
$OH@Ni(111)$	-0.37	0.96	-0.01
$O@Ni(111)$	-0.43	1.03	+0.06
$(Ni(OH)_2)_6@Ni(111)$	-0.65	0.89	+0.08
$(NiO)_6@Ni(111)$	-0.53	1.04	+0.15
$Ni(OH)_2$ film on Ni(111)	-0.47	1.64	+1.09



Supplementary Fig. 12 | Structures of transition states for H₂O dissociation on atomistic models, representing active sites for Ni_(O). **a**, at the (NiO)₆@Ni(111)@Ni(111) interface and **b**, on O@Ni(111). Green, red, and white spheres represent Ni, O, and H atoms, respectively. The red frame highlights the dissociating water molecule, while the blue frame indicates the modified Ni surface.

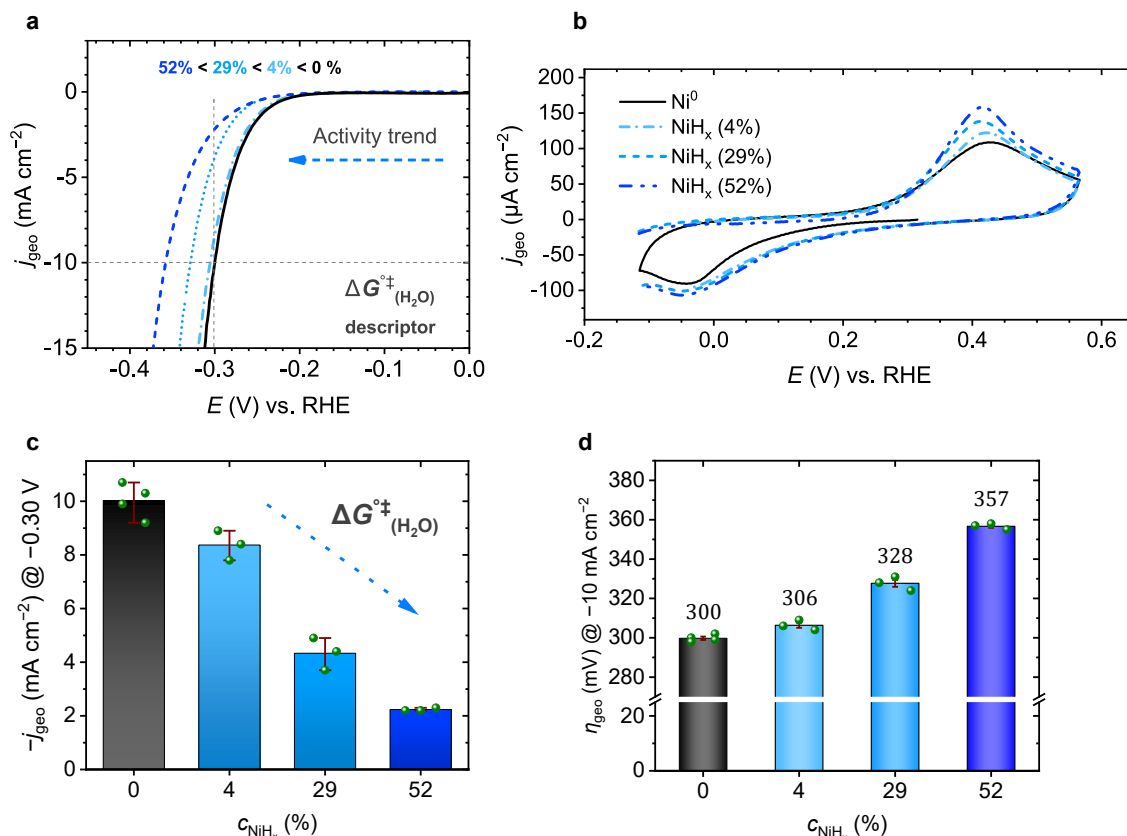


Supplementary Fig. 13 | Structures of transition states for H₂O dissociation on atomistic models, representing active sites for Ni_(OH). **a**, on OH@Ni(111) and **b**, at the (Ni(OH)₂)₆@Ni(111)@Ni(111) interface. Green, red, and white spheres represent Ni, O, and H atoms, respectively. The red frame highlights the dissociating water molecule, while the blue frame indicates the modified Ni surface.



Supplementary Fig. 14 | Structures of transition states for H₂O dissociation on atomistic models, representing active sites for Ni_(OH) involving film structure **a**, directly on the Ni(OH)₂ film, and **b**, on Ni metal atoms located on the Ni(OH)₂ film. Green, red, and white spheres represent Ni, O, and H atoms, respectively. The red frame highlights the dissociating water molecule.

Supplementary Note 7. Effects of surface coverage on HER



Supplementary Fig. 15 | The role of NiH_x in HER on Ni in alkaline electrolytes. **a**, HER polarization curves for NiH_x -modified surfaces. All curves were corrected for IR_u drop. **b**, Cyclic voltammograms for different NiH_x concentrations. **c**, Bar graph with overlaid data points showing HER activity (i.e., j_{geo}), expressed as the current density at -0.30 V. **d**, Bar graph with overlaid data points showing the overpotentials required to reach -10 mA cm^{-2} . Error bars represent mean $\pm$ s.d. The number of independent experiments/electrode preparations was $n = 4, 3, 3$ and 3 for surface coverages of 0, 4, 29 and 52%, respectively.

CV was employed to quantify the amount of NH_x species present in/on Ni (Supplementary Fig. 15b). Different NiH_x concentrations (c_{NiH_x}) were achieved by carefully controlling the electrode surface, as NiH_x is unstable upon potential shifts from the conditions under which it forms. Note that concentrations are used instead of coverage, as we showed in the main text that H resides beneath the Ni surface. The potential was held at various potentials more negative than 0 V vs. RHE for 2 min to define the NiH_x concentration, followed by a CV scan from the respective hold potential to 0.55 V. To obtain subsurface H concentrations of 4%, 29%, and 52%, the electrode potential was held at -0.05 V, -0.20 V, and -0.40 V vs. RHE, respectively.

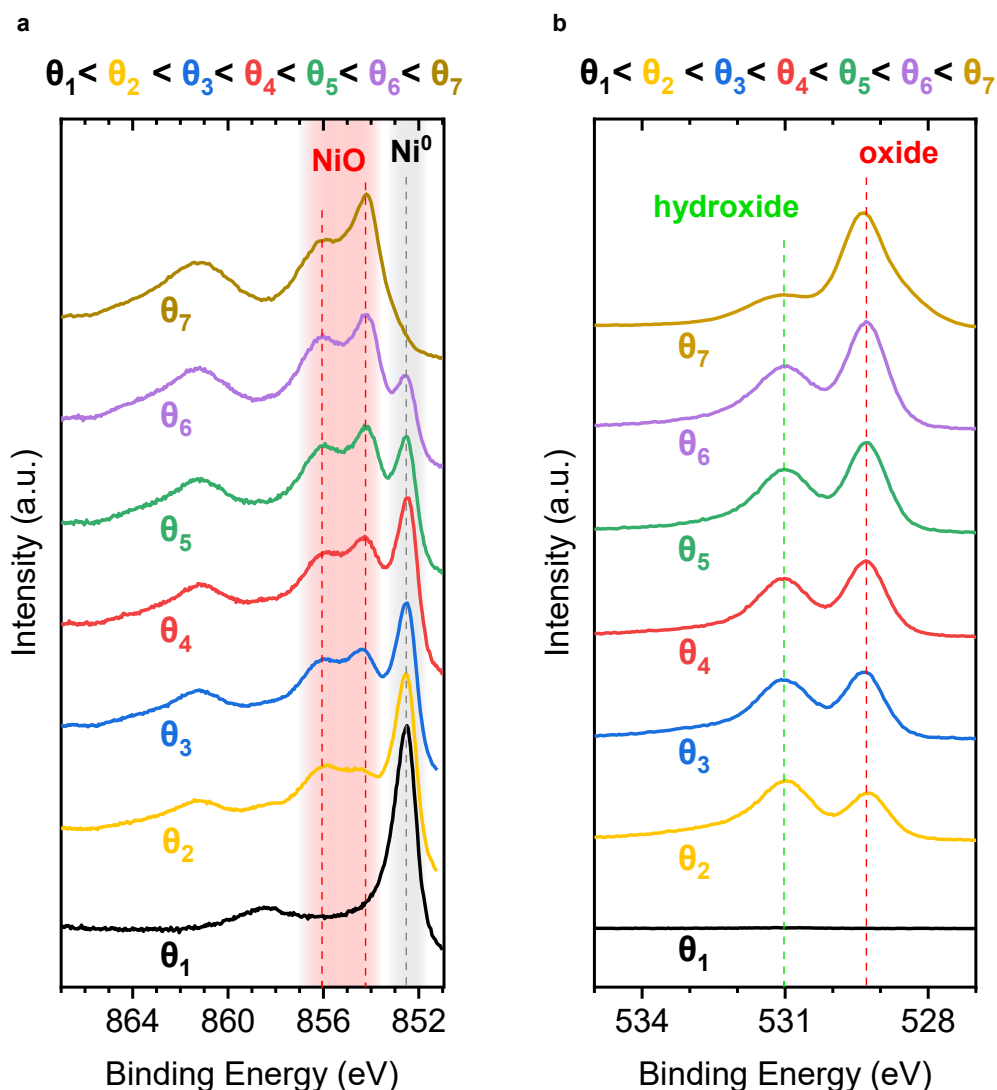
Comparison between the anodic peaks at 0.40 V in the cyclic voltammograms of Ni^0 (solid black line, Supplementary Equation 6) and $\text{Ni}_{(\text{H})}$ (dashed blue line, Supplementary

Equation 6 and 7) reveals an additional charge attributable to the oxidation of subsurface H (Supplementary Fig. 15b). Assuming 1 H atom per Ni surface atom (1 ML coverage), the theoretical charge density for the oxidation of an entire monolayer of H on Ni(poly) surface is typically taken as $258 \mu\text{C cm}^{-2}$ (half of $516 \mu\text{C cm}^{-2}$), reflecting $1e^-$ vs. $2e^-$ processes for subsurface H and Ni oxidation, respectively. Accordingly, the H surface coverage can be determined by dividing the measured extra charge by $258 \mu\text{C cm}^{-2}$.

The Ni^0 surface (solid curve), with a charge of $516 \mu\text{C cm}^{-2}$, was used as the reference, corresponding to 100% of surface Ni atoms being electrochemically accessible (i.e., $\Theta_{\text{ad}} = 0\%$) (Supplementary Fig. 15b). As an example, for the surface with partial hydride coverage, the total charge was $590 \mu\text{C cm}^{-2}$, representing an additional $74 \mu\text{C cm}^{-2}$ relative to the Ni^0 reference. Dividing this extra charge by $258 \mu\text{C cm}^{-2}$ yields 0.29, or 29%, which corresponds to the oxidation of subsurface hydrogen and therefore represents the hydride coverage.

Supplementary Fig. 15a demonstrates that increasing the subsurface H concentration results in a monotonic decrease in HER activity. The extent of the current density reduction at -0.30 V cannot be reasonably attributed to a decrease in the number of available Ni sites (where $(1 - \Theta_{\text{ad}}) = 1$), as would be expected from a classical poisoning (blocking) effect (Supplementary Fig. 15c,d). Since H species reside in the subsurface region, as shown above by CO displacement experiments (Supplementary Fig. 5b) and later supported by DFT calculations (Supplementary Table 5), the observed decline in HER rate is attributed entirely to changes in the activation barrier for water dissociation ($\Delta G_{\text{H}_2\text{O}}^\ddagger$).

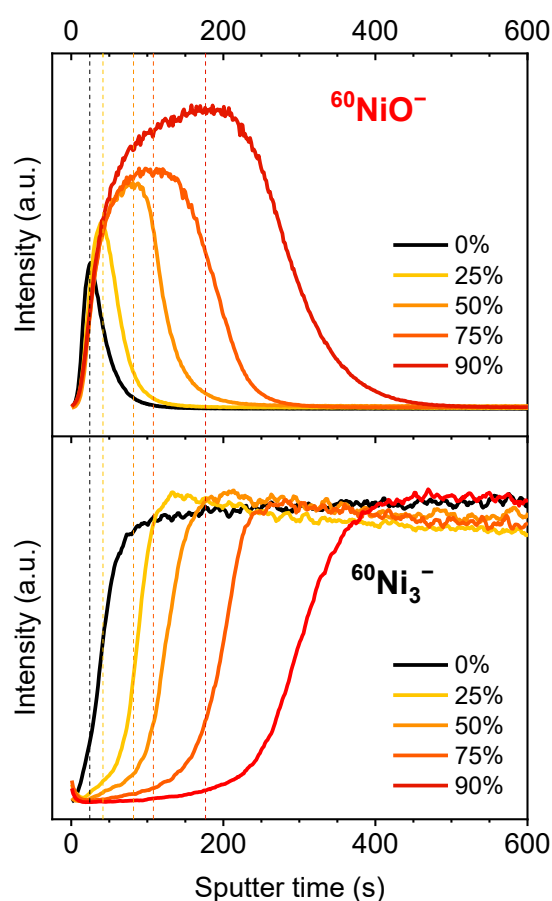
NiO



Supplementary Fig. 16 | HR XPS spectra for varying NiO surface coverages. **a**, Ni 2p_{3/2} spectra: The peak intensity at 852.5 eV indicative of metallic Ni (gray band) decreases with increasing NiO coverage, while the broad double-headed peak (red band) attributed to Ni(II) species, i.e. NiO, becomes more prominent. XPS was not used to quantify Θ_{NiO} , (which was determined via CV), but rather to qualitatively confirm that NiO coverage can be tuned by thermal synthesis. **b**, O 1s spectra: The peak at 529.3 eV indicative of metal oxide increases with the increase in NiO coverage, accompanied by a concomitant decrease in the hydroxide-related signal. Θ_{ad} (with ad = 1–7) indicates a gradual increase in surface coverage from 0–98%.

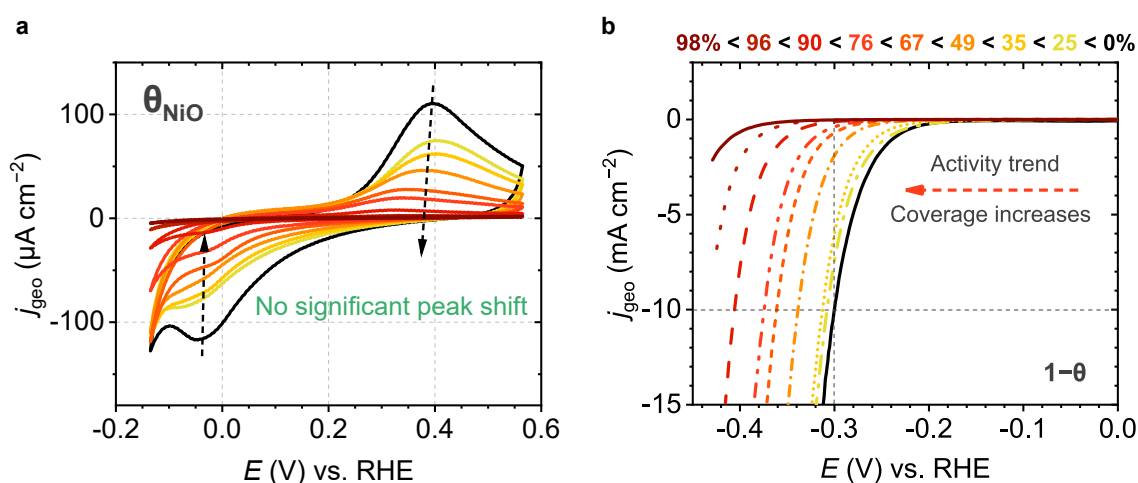
Supplementary Fig. 16a indirectly demonstrates a high degree of surface control that can be achieved by carefully tuning the annealing conditions, such as temperature and duration, in an Ar/O₂ gas mixture. This approach enabled the preparation of a wide range of NiO coverages, characterized by an increasing fingerprint intensity of NiO accompanied by a simultaneous decrease in the signal corresponding to the metallic Ni species.

Purists among us may notice that, for example, at NiO coverage Θ_2 , the surface exhibits minor hydroxide contamination. Such contamination is expected to some degree across all NiO coverages (see hydroxide signal in Supplementary Fig. 16b), but becomes increasingly difficult to discern at first glance in the HR XPS Ni 2p_{3/2} spectra as oxide coverage increases. This is attributed to the transfer of the sample from the annealing apparatus to the XPS chamber. However, we emphasize that this hydroxide contribution is absent during electrochemical measurements, given the extreme susceptibility of the HER to the presence of Ni(OH)₂, which would otherwise accelerate the reaction. Fortunately, no such enhancement was observed; instead, a clear blocking effect was evident, as reflected in the HER activity trend shown in Fig. 4b,c. Nevertheless, it is important to keep in mind that the primary purpose of the ex-situ XPS characterization was to demonstrate that we can control the surface coverage to be dominated by a specific species, in this case, NiO.



Supplementary Fig. 17 | Time-of-flight secondary ion mass spectrometry (ToF-SIMS) negative ion depth profiles for the Ni(O) surface. The intensity of $^{60}\text{NiO}^-$ fragment increases with NiO surface coverage as a function of sputter time (upper panel). This is accompanied by the emergence of $^{60}\text{Ni}_3^-$ fragment representing metallic Ni (lower panel), indicating subsurface composition changes.

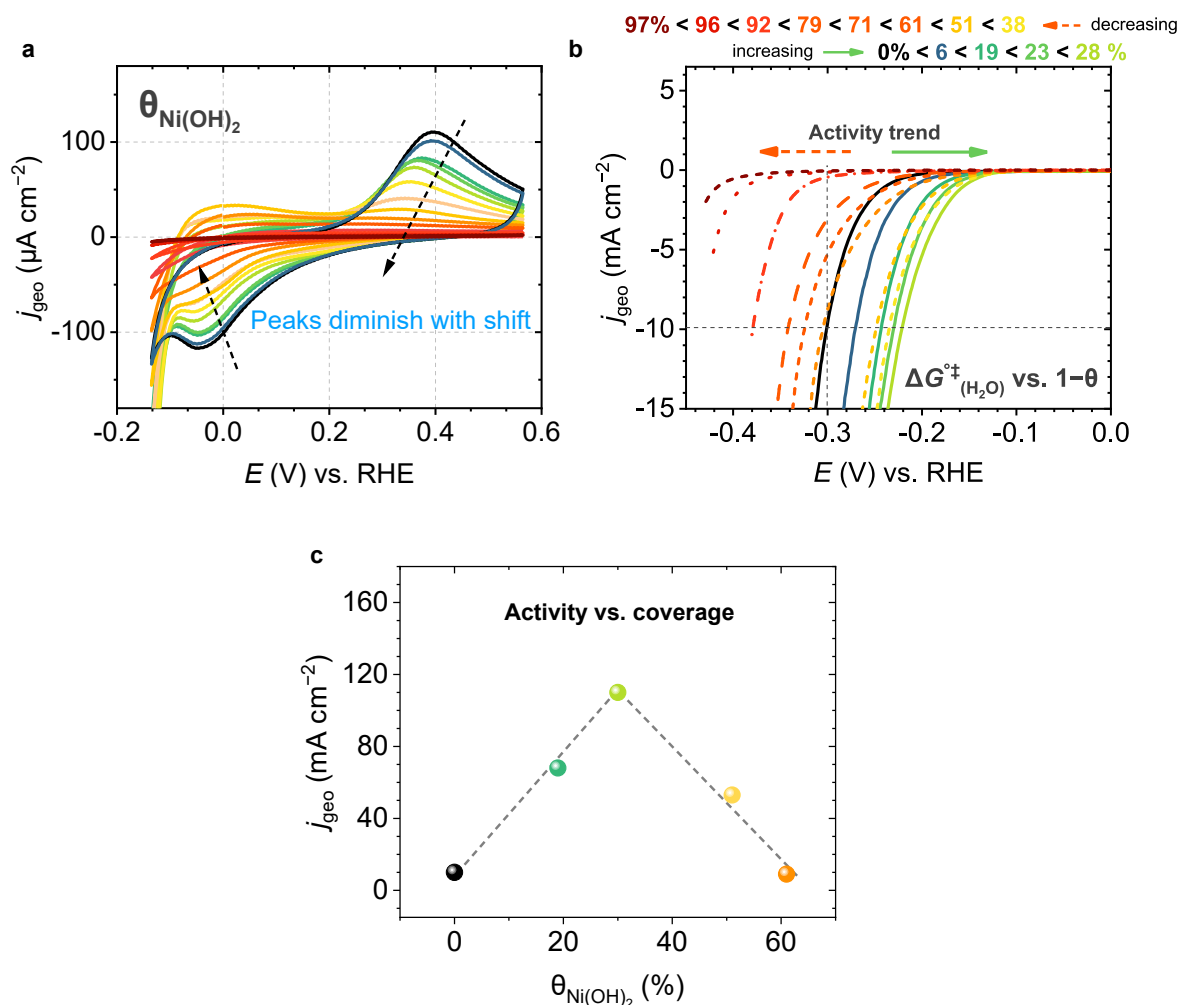
Supplementary Fig. 17 shows the depth profiles that underpin the 3D visualizations presented in Fig. 4c. In the top panel, the increasing intensity and delayed onset (i.e., shift toward longer sputtering times) of the NiO^- signal indicate more abundant oxide formation, manifested as both increased surface coverage (2D growth) and slight thickening of the oxide layer (few-layer 3D growth). Notably, since ToF-SIMS is susceptible to near-surface features, the observed 3D component likely corresponds to sub-nanometer to nanometer-scale oxide structures only a few nanometers thick, rather than bulk-like films. Meanwhile, in the bottom panel (Supplementary Fig. 17), the Ni_3^- signal (metallic Ni) appears later for samples with higher NiO^- intensity, indicating modest increases in oxide coverage. The overlapping region between the Ni^- and NiO^- signals reflects a gradual and laterally heterogeneous Ni/NiO interface, consistent with thin, surface-confined NiO domains rather than a sharp or layered boundary.



Supplementary Fig. 18 | Quantification of the effects of different NiO coverages. **a**, Cyclic voltammograms for all investigated coverages, including the previously omitted data points from Fig. 4a. **b**, HER polarization curves for all investigated coverages, including the data points missing from Fig. 4b. All curves were corrected for IR_u drop.

We challenge the prevailing view that interfacial NiO promotes HER kinetics. To contextualize our findings, we reference a body of literature^{2,5,7,9,12,14,16,19,20,23,25,27,28,30,41–43,51–83} that supports this claim. However, our results clearly show that the reaction rate scales directly with the number of accessible Ni active sites (i.e., coverage), indicating that NiO behaves merely as a spectator species (Supplementary Fig. 18).

$\text{Ni}(\text{OH})_2$



Supplementary Fig. 19 | Quantification of the effects of different $\text{Ni}(\text{OH})_2$ coverages. **a**, Cyclic voltammograms for all investigated coverages, including previously omitted data points from Fig. 5a. **b**, HER activity for all coverages, including previously missing data points from Fig. 5b. All curves were corrected for IR_u drop. **c**, Simplified volcano plot corresponding to the selected data points from Fig. 5c.

In the following discussion, we demonstrate that another type of oxygenated species, interfacial $\text{Ni}(\text{OH})_2$, plays a promotive role.

In Supplementary Fig. 19, we argue that the observed volcano-shaped trend in HER activity (Supplementary Fig. 19c) cannot be explained solely by the $\text{Ni}(\text{OH})_2$ surface coverages ($\Theta_{\text{Ni}(\text{OH})_2}$) derived from cyclic voltammograms (Fig. 5a and Supplementary Fig. 19a). The system is more complex when we consider how different $\Theta_{\text{Ni}(\text{OH})_2}$ values were obtained and consider the actual composition and structure of the surface film.

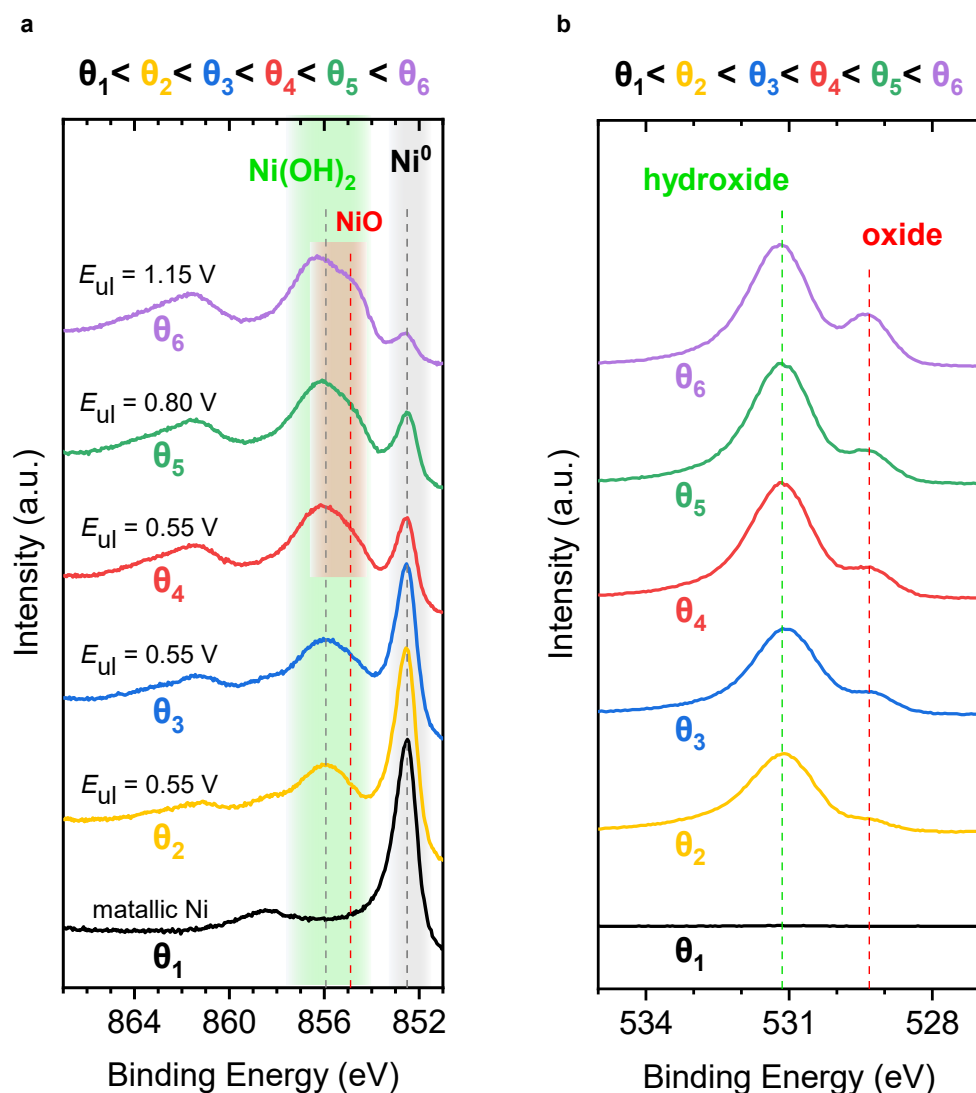
At low surface coverages (0-28%), HER activity increases monotonically. These surfaces were prepared by cycling the potential between -0.15 and 0.55 V, as described in the Experimental section. XPS spectra (Supplementary Fig. 20) show that the surface is composed mainly of $\text{Ni}(\text{OH})_2$ and metallic Ni. After 30 cycles, corresponding to 28% surface coverage,

the highest HER activity is observed. Further cycling within this same potential window does not improve activity; in fact, it begins to decrease. Moreover, increasing the coverage beyond 45% proved experimentally unfeasible using this approach.

To achieve higher Ni(OH)₂ coverages, protocols involving more positive anodic limits (up to 1.15 V) were used, while avoiding the oxidation of Ni(OH)₂ to NiOOH. These potentials are relevant because of direct implications for device operation, as under shutdown conditions the cathode potential drifts toward ~0.8–1.0 V (RHE), driven by reverse currents, leading to Ni oxidation and loss of the metallic Ni active state⁸⁴. Interestingly, beyond ~25% surface coverage, XPS and ToF-SIMS spectra reveal the emergence of NiO alongside Ni(OH)₂, with NiO becoming the dominant species at coverages exceeding 60%.

ToF-SIMS 3D depth profiling shows that NiO resides beneath the Ni(OH)₂, directly contacting the metallic Ni (Fig. 5d and Supplementary Fig. 21). This structural arrangement prevents Ni(OH)₂ from interacting with the metal surface, effectively deactivating the active HER site. Since NiO acts purely as a blocking layer, the overall activity increasingly resembles that of NiO-modified surfaces as coverage increases, despite the continued thickening of the Ni(OH)₂ layer.

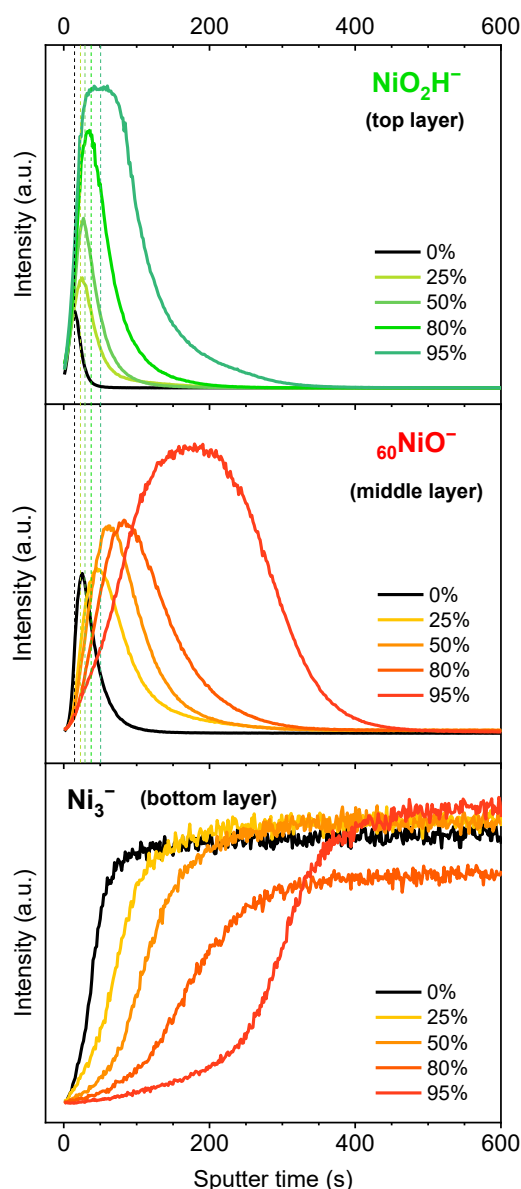
Taken together, these results demonstrate that under well-controlled experimental conditions, HER activity at lower Ni(OH)₂ coverage ($\Theta < 28\%$) is governed primarily by the $\Delta G_{\text{H}_2\text{O}}^\ddagger$. However, once the coverage exceeds ~28%, the activity becomes dominated by $(1 - \Theta_{\text{ad}})$ largely due to the presence of underlying NiO.



Supplementary Fig. 20 | HR XPS spectra for varying Ni(OH)_2 surface coverages. **a**, $\text{Ni } 2p_{3/2}$ spectra: The intensity of the peak indicative of metallic Ni at 852.5 eV (gray band) decreases with increasing Ni(OH)_2 coverage, while the prominent peak indicative of Ni(OH)_2 (green band) becomes more prominent. We emphasize that at higher surface coverages, the contribution of NiO species becomes significant (red dashed lines). **b**, $\text{O } 1s$ spectra: The peak indicative of hydroxide at 531.1 eV increases with the number of potential cycles at the upper anodic limit (E_{ul}) of 0.55 V. Notably, this hydroxide signal remains stable as the E_{ul} increases from 0.55 V to 1.15 V, while the peak representing metal oxide grows, consistent with the trend observed in $\text{Ni } 2p_{3/2}$ spectra. θ_{ad} (with $ad = 1-7$) indicates a gradual increase in surface coverage 0–97%.

Supplementary Fig. 20 presents the XPS spectra for a surface predominantly covered with hydroxide species. The BE of the $\text{Ni}_{(\text{OH})}$ surface shifts slightly to more positive values with increasing Ni(OH)_2 surface coverage. This trend reflects enhanced surface passivation at more positive upper potential limits (E_{ul}), leading to differential charging of the deposits⁸⁵. The Ni(OH)_2 passivation layer forms simultaneously with NiO underlayer, sandwiched between Ni(OH)_2 and metallic Ni. If isolated passive phases (Ni(OH)_2 , NiO) form without intimate

contact with the metallic surface, a higher BE feature would be expected. This behavior is consistent with our ToF-SIMS measurements (Fig. 5c), where 3D images and depth profiles reveal the formation of a progressively thicker (hydr)oxide passive bilayer with increasing surface coverage, in agreement with the findings of Streblow et al⁸⁶. This effect is not as pronounced on the Ni_(O) surface due to the careful control of surface conditions during annealing in an Ar/O₂ atmosphere (Supplementary Fig. 16). To achieve the same Ni(OH)₂ coverage as on NiO, rigorous cycling to more positive potentials is required, where the (hydr)oxide layer thickens, leading to a differential charging effect.



Supplementary Fig. 21 | ToF-SIMS negative ion depth profiles for the Ni(OH)₂ surface. The intensity of NiO₂H⁻ fragment increases with Ni(OH)₂ surface coverage as a function of sputter time (top panel). The intensity of NiO⁻ fragment follows a similar trend (middle panel) but appears with a delay relative to NiO₂H⁻. This is followed by the emergence of the intensity of Ni₃⁻ fragment (bottom panel). Together, these signals suggest a bilayer (hydr)oxide structure, with NiO in contact with metallic Ni and Ni(OH)₂ forming the topmost layer.

Supplementary Fig. 21 shows the depth profiles that underpin the 3D visualizations presented in Fig. 5c. In the top panel, the NiO_2H^- signal, attributed to $\text{Ni}(\text{OH})_2$, intensifies and shifts to longer sputtering times, indicating increased surface coverage and more abundant hydroxide layer. The middle panel shows that for each surface coverage, the NiO^- signal emerges after the NiO_2H^- signal, confirming the moderate thickening of the NiO layer beneath the hydroxide layer. Finally, in the bottom panel, the Ni_3^- signal (metallic Ni) emerges at longer sputtering times, especially for higher (hydr)oxide coverage samples, demonstrating it lies beneath both layers. The consistent rightward shift of all three signals with increasing coverage supports a layered architecture, in which $\text{Ni}(\text{OH})_2$ forms on top of an intermediate NiO layer, which in turn rests on the underlying metallic Ni substrate.

ToF-SIMS and XPS are complementary surface characterization techniques. In this study, ToF-SIMS is particularly valuable for determining submonolayer surface species, making it essential for correlating specific Ni species with HER activity. It provides high surface sensitivity to trace components and excellent depth resolution, which is ideal for analyzing ultra-thin surface layers. In contrast, XPS is more effective for identifying chemical speciation and oxidation states.

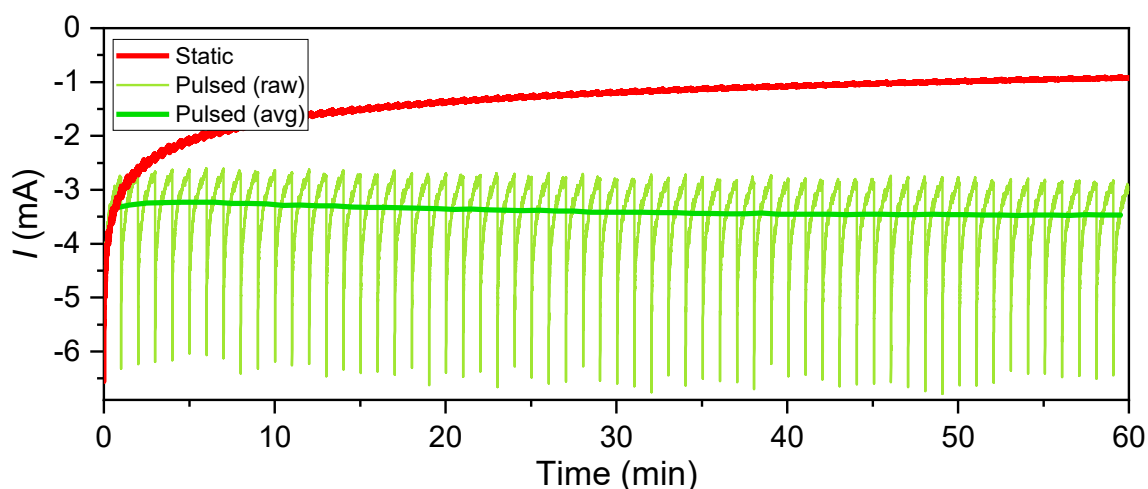
The lateral resolution of ToF-SIMS is typically in the micrometer or sub-micrometer range (down to ~ 30 nm, depending on instrument settings), while the information depth of secondary ions is only 1–2 nm, corresponding to just a few atomic layers. Therefore, ToF-SIMS probes the outermost surface composition rather than the bulk or volumetric composition of the analyzed region.

In our work, we performed sputter profiling with a Cs^+ beam to obtain 3D distribution information of Ni species within the near-surface region. When sputtering metallic or oxide samples with a 250 eV Cs^+ ion beam, the depth resolution in ToF-SIMS is typically around 1 nm or better. Under these conditions, the Bi^+ analysis provides surface coverage information, reflecting the chemical state and spatial distribution of Ni species on the outermost layer (while sputtering), rather than an average volumetric concentration. This approach is well established in the literature, where ToF-SIMS is described as an ultra-surface-sensitive technique capable of combining high-resolution imaging with depth profiling when sputtering is applied separately.

Supplementary Note 8. Stabilization strategy for Ni/Ni(OH)₂ active sites in alkaline electrolysis

Finally, we demonstrate a non-optimized protocol as practical guidance for stabilizing Ni/Ni(OH)₂ active sites on Ni-based catalysts in alkaline water electrolysis (Supplementary Fig. 22). Specifically, a 1 s activation step applied every minute maintains steady activity on the Ni(OH)₂-modified surface, in contrast to the continuously decreasing activity observed for the non-activated system.

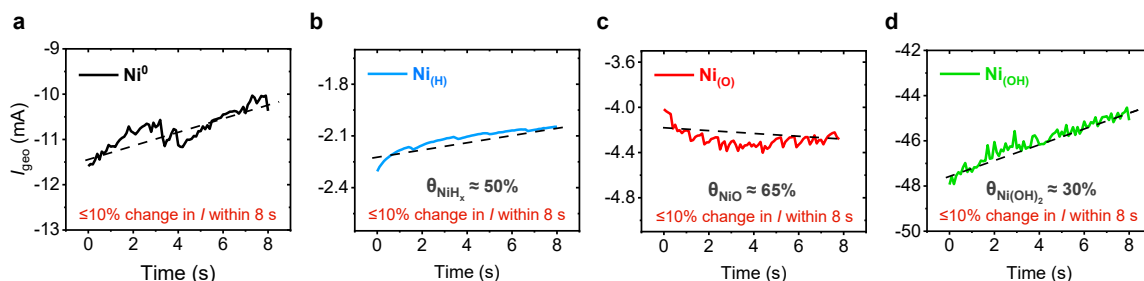
Note that such protocols have recently been utilized in achieving dynamic stability for CO₂ reduction reaction^{87–89}.



Supplementary Fig. 22 | Strategy for stabilizing Ni/Ni(OH)₂ active sites. Normal operation of the Ni/Ni(OH)₂ electrode (red curve) shows a gradual decay in current, attributed to slow removal of beneficial Ni(OH)₂ species and formation of hydride. In contrast, the periodically activated surface (green curves – real and average current), shows no observable current decay over time.

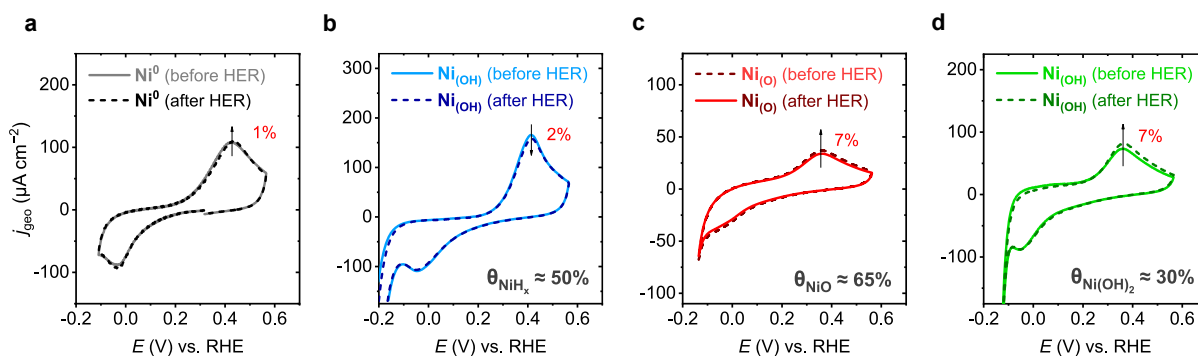
Supplementary Note 9. Stability of representative benchmark Ni surfaces during HER

To gain insight into the stability of four representative benchmark Ni surfaces - Ni^0 , $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{O})}$, and $\text{Ni}_{(\text{OH})}$ - during the HER, we combine detailed electrochemical and surface characterization methods (Supplementary Figs. 23-25).



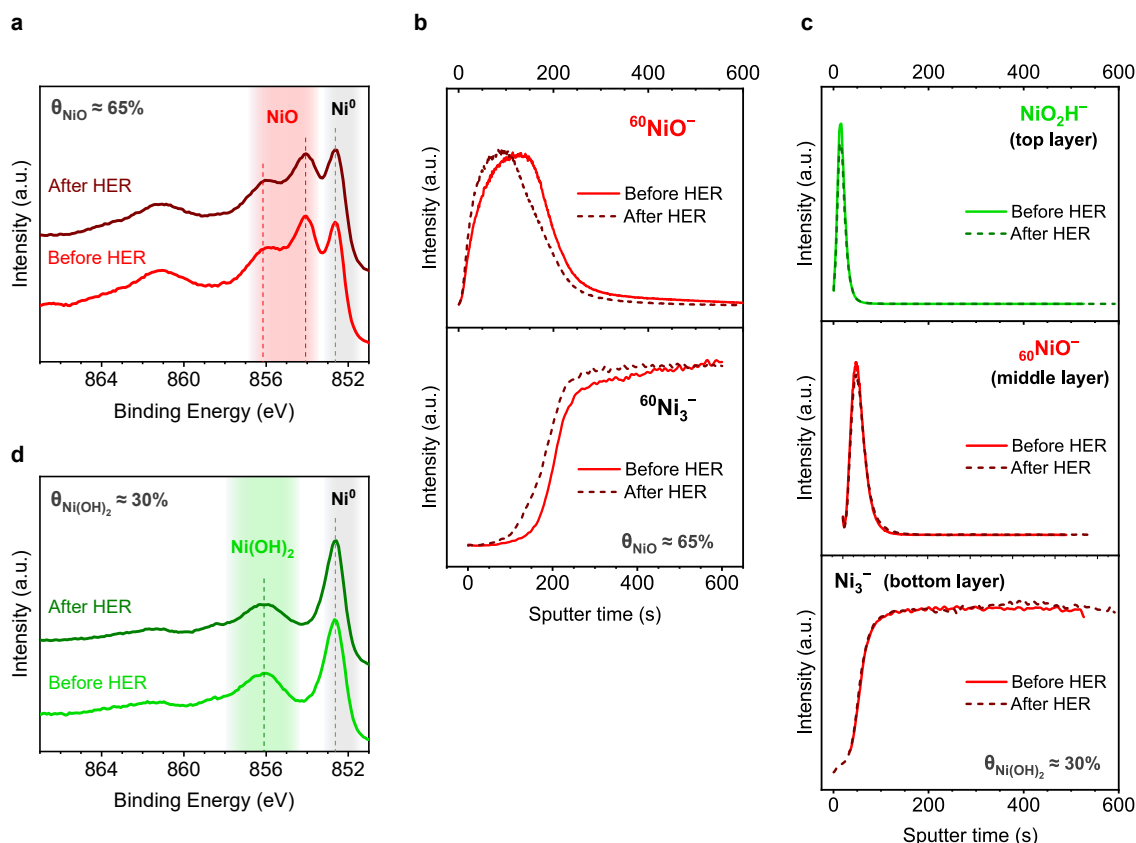
Supplementary Fig. 23 | Stability of four representative benchmark Ni surfaces during the hydrogen evolution reaction (HER). a-d, Chronoamperometric responses of Ni^0 , $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{O})}$, and $\text{Ni}_{(\text{OH})}$ surfaces at -0.40 V (RHE) over an 8-second segment of the polarization scan. All surfaces exhibit a $<10\%$ variation in current (I) over this period, indicating effectively stable currents within the experimental time window.

Electrochemical measurements provide the most direct operando assessment of surface stability. Chronoamperometric measurements (Supplementary Fig. 23) show $<10\%$ change in current over an 8 s period, indicating that the surfaces remain stable under HER conditions. This variation is negligible compared to the orders-of-magnitude differences in activity observed between different surfaces, confirming that our conclusions are not affected by minor restructuring. The 8 s interval was selected to match the duration of the polarization measurements, which were recorded at a relatively high scan rates (50 mV s^{-1}), with each measurement lasting approximately 8 s. The chronoamperometric response was obtained by holding the respective Ni surfaces at the most negative potential of the window (-0.40 V). Consistently, post-measurement cyclic voltammograms (Supplementary Fig. 24) show only minor changes in electrochemical features (e.g., ECSA), further supporting that the surface state remains largely preserved.



Supplementary Fig. 24 | Stability of four representative benchmark Ni surfaces over the experimental timeframe. a-d, Comparison of cyclic voltammetry (CV) curves for Ni^0 , $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{O})}$, and $\text{Ni}_{(\text{OH})}$ surfaces recorded before and after acquisition of the hydrogen evolution reaction (HER) polarization curves. All surfaces exhibit a $<10\%$ variation in charge, determined from integration of the anodic peak current, indicating effectively stable surface coverage within the experimental time window.

In addition, post-measurement XPS and ToF-SIMS analyses (Supplementary Fig. 25) for $\text{Ni}(\text{O})$ and $\text{Ni}(\text{OH})$ surfaces show only minimal changes in surface composition and coverage, indicating that no significant irreversible reconstruction occurs during the HER measurement. While ex situ characterization cannot fully preserve the electrochemically controlled state of the surface, the absence of substantial differences before and after HER testing supports the conclusion that any structural or compositional changes are minor.



Supplementary Fig. 25 | Post-measurement surface characterization of $\text{Ni}(\text{O})$ and $\text{Ni}(\text{OH})$ representative benchmark surfaces recorded before and after acquisition of the hydrogen evolution reaction (HER) polarization curves. a,d, High-resolution XPS Ni 2p_{3/2} spectra for $\text{Ni}(\text{O})$ and $\text{Ni}(\text{OH})$, respectively. **b,c,** ToF-SIMS depth profiles for the $\text{Ni}(\text{O})$ and $\text{Ni}(\text{OH})$, respectively. Both surfaces exhibit only minor changes in surface composition and coverage, indicating no significant irreversible reconstruction during the HER measurement.

For $\text{Ni}(\text{H})$ and Ni^0 surfaces, such analysis is inherently limited. Subsurface hydride species cannot be reliably detected by the employed spectroscopic techniques, while the metallic Ni^0 surface cannot be preserved upon removal from electrochemical potential control and undergoes partial oxidation during transfer. As a result, characterization of the Ni^0 state is experimentally limited to its preparation and probing under potential control and cannot be accessed in a post-measurement (ex situ) configuration. For $\text{Ni}(\text{H})$ and Ni^0 surfaces, we therefore rely on operando electrochemical probes, which likewise show only minor changes during and after the measurement.

Taken together, these results demonstrate that surface reconstruction during the measurement is minimal and does not affect the comparative trends or the conclusions of this work.

Supplementary References

1. Liu, Y. *et al.* Papillae-like morphology of Ni/Ni(OH)₂ hybrid crystals by stepwise electrodeposition for synergistically improved HER. *CrystEngComm* **21**, 3431–3438 (2019).
2. He, B., Kuang, Y., Hou, Z., Zhou, M. & Chen, X. Enhanced electrocatalytic hydrogen evolution activity of nickel foam by low-temperature-oxidation. *Journal of Materials Research* **33**, 213–224 (2018).
3. Lai, W. *et al.* In situ Raman spectroscopic study towards the growth and excellent HER catalysis of Ni/Ni(OH)₂ heterostructure. *International Journal of Hydrogen Energy* **46**, 26861–26872 (2021).
4. Rao, Y., Wang, Y., Ning, H., Li, P. & Wu, M. Hydrotalcite-like Ni(OH)₂ Nanosheets in Situ Grown on Nickel Foam for Overall Water Splitting. *ACS Appl. Mater. Interfaces* **8**, 33601–33607 (2016).
5. Jiang, H. *et al.* Ternary interfacial superstructure enabling extraordinary hydrogen evolution electrocatalysis. *Materials Today* **21**, 602–610 (2018).
6. Rathore, D., Sharma, M. D., Sharma, A., Basu, M. & Pande, S. Aggregates of Ni/Ni(OH)₂/NiOOH Nanoworms on Carbon Cloth for Electrocatalytic Hydrogen Evolution. *Langmuir* **36**, 14019–14030 (2020).
7. Peng, L. *et al.* Nanoporous Ni/NiO catalyst for efficient hydrogen evolution reaction prepared by partial electro-oxidation after dealloying. *Journal of Alloys and Compounds* **911**, 165061 (2022).
8. Saraj, C. S. *et al.* Single-Step and Sustainable Fabrication of Ni(OH)₂/Ni Foam Water Splitting Catalysts via Electric Field Assisted Pulsed Laser Ablation in Liquid. *ChemElectroChem* **8**, 209–217 (2021).
9. Jiang, J. *et al.* Amorphous nickel oxide electrodes with high-current-density electrocatalytic performance for hydrogen evolution. *International Journal of Hydrogen Energy* **51**, 887–894 (2024).

10. Shao, D., Wang, Q., Yao, X., Zhou, Y. & Yu, X.-Y. Phase-engineering of nickel hydroxide in the Ni/Ni(OH)₂ interface for efficient hydrogen evolution and hydrazine-assisted water splitting in seawater. *J. Mater. Chem. A* **10**, 21848–21855 (2022).
11. Varvaris, K. L., Esau, D., Schuett, F. M., Jacob, T. & Jerkiewicz, G. Surface Structure Dependence of Electrochemical Processes at Monocrystalline Nickel Electrodes. Part 1: The Hydrogen Evolution Reaction. *J. Phys. Chem. C* **127**, 14711–14722 (2023).
12. Li, C. *et al.* Acid promoted Ni/NiO monolithic electrode for overall water splitting in alkaline medium. *Sci. China Mater.* **60**, 918–928 (2017).
13. Lim, D. *et al.* Strongly Coupled Ni/Ni(OH)₂ Hybrid Nanocomposites as Highly Active Bifunctional Electrocatalysts for Overall Water Splitting. *ACS Sustainable Chem. Eng.* **8**, 4431–4439 (2020).
14. Yan, X., Tian, L. & Chen, X. Crystalline/amorphous Ni/NiO core/shell nanosheets as highly active electrocatalysts for hydrogen evolution reaction. *Journal of Power Sources* **300**, 336–343 (2015).
15. Sheng, W., Myint, M., Chen, J. G. & Yan, Y. Correlating the hydrogen evolution reaction activity in alkaline electrolytes with the hydrogen binding energy on monometallic surfaces. *Energy Environ. Sci.* **6**, 1509–1512 (2013).
16. Kou, T. *et al.* Carbon doping switching on the hydrogen adsorption activity of NiO for hydrogen evolution reaction. *Nat Commun* **11**, 590 (2020).
17. Danilovic, N. *et al.* Enhancing the Alkaline Hydrogen Evolution Reaction Activity through the Bifunctionality of Ni(OH)₂/Metal Catalysts. *Angewandte Chemie* **124**, 12663–12666 (2012).
18. Wang, P., Wan, L., Lin, Y. & Wang, B. NiFe Hydroxide Supported on Hierarchically Porous Nickel Mesh as a High-Performance Bifunctional Electrocatalyst for Water Splitting at Large Current Density. *ChemSusChem* **12**, 4038–4045 (2019).
19. Zhao, L. *et al.* Steering elementary steps towards efficient alkaline hydrogen evolution via size-dependent Ni/NiO nanoscale heterosurfaces. *National Science Review* **7**, 27–36 (2020).
20. Peng, L. *et al.* Chimney effect of the interface in metal oxide/metal composite catalysts on the hydrogen evolution reaction. *Applied Catalysis B: Environmental* **245**, 122–129 (2019).

21. Balčiūnaitė, A. *et al.* Steps towards highly-efficient water splitting and oxygen reduction using nanostructured β -Ni(OH)₂. *RSC Adv.* **12**, 10020–10028 (2022).
22. Grdeń, M. & Jerkiewicz, G. Influence of Surface Treatment on the Kinetics of the Hydrogen Evolution Reaction on Bulk and Porous Nickel Materials. *Electrocatalysis* **10**, 173–183 (2019).
23. Zheng, J. *et al.* Homologous NiO//Ni₂P nanoarrays grown on nickel foams: a well matched electrode pair with high stability in overall water splitting. *Nanoscale* **9**, 4409–4418 (2017).
24. Xue, S., Liang, Y., Hou, S., Zhang, Y. & Jiang, H. Alpha-Nickel Hydroxide Coating of Metallic Nickel for Enhanced Alkaline Hydrogen Evolution. *ChemSusChem* **15**, e202201072 (2022).
25. Faid, A. Y., Barnett, A. O., Seland, F. & Sunde, S. Ni/NiO nanosheets for alkaline hydrogen evolution reaction: In situ electrochemical-Raman study. *Electrochimica Acta* **361**, 137040 (2020).
26. Xing, Z., Gan, L., Wang, J. & Yang, X. Experimental and theoretical insights into sustained water splitting with an electrodeposited nanoporous nickel hydroxide@nickel film as an electrocatalyst. *J. Mater. Chem. A* **5**, 7744–7748 (2017).
27. Xi, W. *et al.* Dual-valence nickel nanosheets covered with thin carbon as bifunctional electrocatalysts for full water splitting. *J. Mater. Chem. A* **4**, 7297–7304 (2016).
28. Neumüller, D. *et al.* Hydrogen Evolution Reaction on Ultra-Smooth Sputtered Nanocrystalline Ni Thin Films in Alkaline Media—From Intrinsic Activity to the Effects of Surface Oxidation. *Nanomaterials* **13**, 2085 (2023).
29. Zhou, Y. *et al.* Flame-like Ni(OH)₂ strongly promotes the dissociation of water and can be used to produce an excellent hybrid electrocatalyst for the hydrogen evolution reaction in alkaline media. *Electrochemistry Communications* **91**, 66–70 (2018).
30. Do, H. H. *et al.* Hollow Ni/NiO/C composite derived from metal-organic frameworks as a high-efficiency electrocatalyst for the hydrogen evolution reaction. *Nano Convergence* **10**, 6 (2023).

31. Yang, J.-H. *et al.* Morphology-controllable nanocrystal β -Ni(OH)₂/NF designed by hydrothermal etching method as high-efficiency electrocatalyst for overall water splitting. *Journal of Electroanalytical Chemistry* **882**, 115035 (2021).
32. Lu, S. *et al.* Electrodeposited porous spherical Ni(OH)₂@Ni on carbon paper for high-efficiency hydrogen evolution. *International Journal of Hydrogen Energy* **46**, 1540–1547 (2021).
33. Machado, S. A. S. & Avaca, L. A. The hydrogen evolution reaction on nickel surfaces stabilized by H-absorption. *Electrochimica Acta* **39**, 1385–1391 (1994).
34. Lasia, A. & Rami, A. Kinetics of hydrogen evolution on nickel electrodes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **294**, 123–141 (1990).
35. Trasatti, S. & Petrii, O. A. Real surface area measurements in electrochemistry. *Pure and Applied Chemistry* **63**, 711–734 (1991).
36. Seyeux, A., Maurice, V., Klein, L. H. & Marcus, P. In Situ STM Study of the Effect of Chloride on Passive Film on Nickel in Alkaline Solution. *J. Electrochem. Soc.* **153**, B453 (2006).
37. Clavilier, J. *et al.* Study of the charge displacement at constant potential during CO adsorption on Pt(110) and Pt(111) electrodes in contact with a perchloric acid solution. *Journal of Electroanalytical Chemistry* **330**, 489–497 (1992).
38. Wang, K., Chottiner, G. S. & Scherson, D. A. Electrochemical oxidation of nickel(111)c(4.times.2)-carbon monoxide in alkaline electrolytes. *J. Phys. Chem.* **96**, 6742–6744 (1992).
39. Šimpraga, R. & Conway, B. E. Realization of monolayer levels of surface oxidation of nickel by anodization at low temperatures. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **280**, 341–357 (1990).
40. Campbell, C. T. Bimetallic Surface Chemistry. *Annu. Rev. Phys. Chem.* **41**, 775–837 (1990).
41. Gong, M. *et al.* Nanoscale nickel oxide/nickel heterostructures for active hydrogen evolution electrocatalysis. *Nat Commun* **5**, 4695 (2014).

42. Li, X. *et al.* Sequential Electrodeposition of Bifunctional Catalytically Active Structures in MoO₃/Ni–NiO Composite Electrocatalysts for Selective Hydrogen and Oxygen Evolution. *Advanced Materials* **32**, 2003414 (2020).
43. Lu, K. *et al.* Li_xNiO/Ni Heterostructure with Strong Basic Lattice Oxygen Enables Electrocatalytic Hydrogen Evolution with Pt-like Activity. *J. Am. Chem. Soc.* **142**, 12613–12619 (2020).
44. Biesinger, M. C., Payne, B. P., Lau, L. W. M., Gerson, A. & Smart, R. St. C. X-ray photoelectron spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide systems. *Surface and Interface Analysis* **41**, 324–332 (2009).
45. Maibach, J., Lindgren, F., Eriksson, H., Edström, K. & Hahlin, M. Electric Potential Gradient at the Buried Interface between Lithium-Ion Battery Electrodes and the SEI Observed Using Photoelectron Spectroscopy. *J. Phys. Chem. Lett.* **7**, 1775–1780 (2016).
46. Pshenichnikov, A. G. Electrocatalytic properties of nickel and nickel-based alloys. *Materials Chemistry and Physics* **22**, 121–148 (1989).
47. Floner, D., Lamy, C. & Leger, J.-M. Electrocatalytic oxidation of hydrogen on polycrystal and single-crystal nickel electrodes. *Surface Science* **234**, 87–97 (1990).
48. Obradović, M. D. & Gojković, S. Lj. Challenges in determining the electrochemically active surface area of Ni-oxides in the oxygen evolution reaction. *Journal of Electroanalytical Chemistry* **918**, 116479 (2022).
49. Alsabet, M., Grden, M. & Jerkiewicz, G. Electrochemical Growth of Surface Oxides on Nickel. Part 1: Formation of α -Ni(OH)₂ in Relation to the Polarization Potential, Polarization Time, and Temperature. *Electrocatal* **2**, 317–330 (2011).
50. Beden, B., Floner, D., Léger, J. M. & Lamy, C. A voltammetric study of the formation on hydroxides and oxyhydroxides on nickel single crystal electrodes in contact with an alkaline solution. *Surface Science* **162**, 822–829 (1985).
51. Jo, S. *et al.* High-Performance Nickel–Bismuth Oxide Electrocatalysts Applicable to Both the HER and OER in Alkaline Water Electrolysis. *ACS Appl. Mater. Interfaces* **17**, 11946–11955 (2025).

52. Koshy, S. S., Rath, J. & Kiani, A. Laser fabricated binder-free Ni/NiO nanostructured electrodes for enhanced hydrogen evolution. *International Journal of Electrochemical Science* **20**, 101004 (2025).
53. Mondal, A., Paul, A., Srivastava, D. N. & Panda, A. B. NiO hollow microspheres as efficient bifunctional electrocatalysts for Overall Water-Splitting. *International Journal of Hydrogen Energy* **43**, 21665–21674 (2018).
54. Kong, Q. *et al.* Hydrothermal Synthesis of Nanoporous NiO Rods Self-Supported on Ni Foam as Efficient Electrocatalysts for Hydrogen Evolution Reaction. *JOM* **71**, 621–625 (2019).
55. Kenney, M. J. *et al.* An electrodeposition approach to metal/metal oxide heterostructures for active hydrogen evolution catalysts in near-neutral electrolytes. *Nano Res.* **12**, 1431–1435 (2019).
56. Dong, Y., Dang, J., Wang, W., Yin, S. & Wang, Y. First-Principles Determination of Active Sites of Ni Metal-Based Electrocatalysts for Hydrogen Evolution Reaction. *ACS Appl. Mater. Interfaces* **10**, 39624–39630 (2018).
57. Kamal, K. M. *et al.* Precise design and construction of NiO-Ni heterostructures for active hydrogen evolution photocatalysis. *Applied Catalysis O: Open* **194**, 206997 (2024).
58. Xie, K. *et al.* Ni/NiO hybrid nanostructure supported on biomass carbon for visible-light photocatalytic hydrogen evolution. *J Mater Sci* **56**, 12775–12788 (2021).
59. Han, H., Park, S., Jang, D. & Kim, W. B. N-doped carbon nanoweb-supported Ni/NiO heterostructure as hybrid catalysts for hydrogen evolution reaction in an alkaline phase. *Journal of Alloys and Compounds* **853**, 157338 (2021).
60. Wang, J. *et al.* Reaction-driven transformation of Ni/NiO hybrid structure into Ni single atoms. *Materials Today Energy* **17**, 100436 (2020).
61. Yan, Y., Ma, Q., Cui, F., Zhang, J. & Cui, T. Carbon onions coated Ni/NiO nanoparticles as catalysts for alkaline hydrogen evolution reaction. *Electrochimica Acta* **430**, 141090 (2022).

62. Huang, J. *et al.* Boosting Hydrogen Transfer during Volmer Reaction at Oxides/Metal Nanocomposites for Efficient Alkaline Hydrogen Evolution. *ACS Energy Lett.* **4**, 3002–3010 (2019).
63. Chen, F. *et al.* Ultrastable and highly efficient hydrogen evolution by heterogeneous NiO/Ni catalysts under industrial electrolysis conditions. *Inorg. Chem. Front.* **11**, 425–435 (2024).
64. Navarro-Pardo, F. *et al.* Nickel oxide/nickel nanohybrids for oxygen and hydrogen evolution in alkaline media. *Electrochimica Acta* **506**, 145002 (2024).
65. Li, C. *et al.* Accelerating water dissociation at carbon supported nanoscale Ni/NiO heterojunction electrocatalysts for high-efficiency alkaline hydrogen evolution. *Nano Res.* **16**, 4742–4750 (2023).
66. Poimenidis, I. A., Lykaki, M., Moustazis, S., Loukakos, P. & Konsolakis, M. One-step solvothermal growth of NiO nanoparticles on nickel foam as a highly efficient electrocatalyst for hydrogen evolution reaction. *Materials Chemistry and Physics* **305**, 128007 (2023).
67. Zhang, T. *et al.* Engineering oxygen vacancy on NiO nanorod arrays for alkaline hydrogen evolution. *Nano Energy* **43**, 103–109 (2018).
68. Liu, Y. *et al.* Nickel/Nickel Oxide-Nitrogen Self-Doped Carbon Nanosheets for Electrocatalytic Oxygen and Hydrogen Evolution Reactions. *ACS Appl. Nano Mater.* **5**, 2953–2961 (2022).
69. Oshchepkov, A. G., Bonnefont, A. & Savinova, E. R. On the Influence of the Extent of Oxidation on the Kinetics of the Hydrogen Electrode Reactions on Polycrystalline Nickel. *Electrocatalysis* **11**, 133–142 (2020).
70. Xu, Y.-F., Gao, M.-R., Zheng, Y.-R., Jiang, J. & Yu, S.-H. Nickel/Nickel(II) Oxide Nanoparticles Anchored onto Cobalt(IV) Diselenide Nanobelts for the Electrochemical Production of Hydrogen. *Angewandte Chemie* **125**, 8708–8712 (2013).
71. Foster, M. E., Kendrick, I., Mukerjee, S. & Jones, R. Role of Graphene on Ni/NiO for the Hydrogen Evolution Reaction. *J. Phys. Chem. C* **126**, 16158–16163 (2022).

72. Chen, H. *et al.* In situ surface reconstruction synthesis of a nickel oxide/nickel heterostructural film for efficient hydrogen evolution reaction. *Chem. Commun.* **56**, 10529–10532 (2020).
73. Bates, M. K., Jia, Q., Ramaswamy, N., Allen, R. J. & Mukerjee, S. Composite Ni/NiO-Cr₂O₃ Catalyst for Alkaline Hydrogen Evolution Reaction. *J. Phys. Chem. C* **119**, 5467–5477 (2015).
74. Thiruvengadam, D., Nithiasri, R., Davidrichetson, A., Santhosh Kumar, K. & Jayabharathi, J. Unleashing Potential of BNiO-300 as a Superior Electrocatalyst for Overall Water Splitting. *Energy Fuels* **39**, 2799–2811 (2025).
75. Oshchepkov, A. G. *et al.* Exploring the Influence of the Nickel Oxide Species on the Kinetics of Hydrogen Electrode Reactions in Alkaline Media. *Top Catal* **59**, 1319–1331 (2016).
76. Liu, X., Wang, X., Yuan, X., Dong, W. & Huang, F. Rational composition and structural design of in situ grown nickel-based electrocatalysts for efficient water electrolysis. *J. Mater. Chem. A* **4**, 167–172 (2015).
77. Zhou, F. & Tao, G. Structure Sensitivity in Hydrogen Adsorption on Ni/NiO Interfaces for the Hydrogen Evolution Reaction. *J. Phys. Chem. C* **127**, 23180–23188 (2023).
78. Wang, J. *et al.* Dominating Role of NiO on the Interface of Ni/NiO for Enhanced Hydrogen Evolution Reaction. *ACS Appl. Mater. Interfaces* **9**, 7139–7147 (2017).
79. Wang, L.-L. *et al.* Tailoring Lewis Acidity of Metal Oxides on Nickel to Boost Electrocatalytic Hydrogen Evolution in Neutral Electrolyte. *J. Am. Chem. Soc.* **147**, 7555–7563 (2025).
80. Gong, M. *et al.* Blending Cr₂O₃ into a NiO–Ni Electrocatalyst for Sustained Water Splitting. *Angewandte Chemie International Edition* **54**, 11989–11993 (2015).
81. Zhang, Z., Liu, S., Xiao, F. & Wang, S. Facile Synthesis of Heterostructured Nickel/Nickel Oxide Wrapped Carbon Fiber: Flexible Bifunctional Gas-Evolving Electrode for Highly Efficient Overall Water Splitting. *ACS Sustainable Chem. Eng.* **5**, 529–536 (2017).
82. Lovell, E. C., Lu, X., Zhang, Q., Scott, J. & Amal, R. From passivation to activation – tunable nickel/nickel oxide for hydrogen evolution electrocatalysis. *Chem. Commun.* **56**, 1709–1712 (2020).

83. Zhang, G., Li, G. & Wang, X. Surface Modification of Carbon Nitride Polymers by Core–Shell Nickel/Nickel Oxide Cocatalysts for Hydrogen Evolution Photocatalysis. *ChemCatChem* **7**, 2864–2870 (2015).
84. Abdel Haleem, A. *et al.* Effects of operation and shutdown parameters and electrode materials on the reverse current phenomenon in alkaline water analyzers. *Journal of Power Sources* **535**, 231454 (2022).
85. Connell, J. G. *et al.* Tuning the Reversibility of Mg Anodes via Controlled Surface Passivation by H₂O/Cl[–] in Organic Electrolytes. *Chem. Mater.* **28**, 8268–8277 (2016).
86. Hoppe, H.-W. & Strehblow, H.-H. XPS and UPS examinations of the formation of passive layers on Ni in 1 M sodium hydroxide and 0.5 M sulphuric acid. *Surface and Interface Analysis* **14**, 121–131 (1989).
87. Kimura, K. W. *et al.* Controlled Selectivity of CO₂ Reduction on Copper by Pulsing the Electrochemical Potential. *ChemSusChem* **11**, 1781–1786 (2018).
88. Jännsch, Y. *et al.* Pulsed potential electrochemical CO₂ reduction for enhanced stability and catalyst reactivation of copper electrodes. *Electrochemistry Communications* **121**, 106861 (2020).
89. Steering the structure and selectivity of CO₂ electroreduction catalysts by potential pulses | Nature Catalysis. <https://www.nature.com/articles/s41929-022-00760-z>.