

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

Corresponding Author: Dr Dusan Strmcnik

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The role of surface species of catalysts in the hydrogen evolution reaction (HER) under alkaline conditions remains a key challenge for sustainable hydrogen production. Many works focusing on interfacial species effects toward alkaline HER have been reported, but conclusion have not reached a consensus as yet. This topic is meaningful and the finding in this work maybe interesting. However, the theoretical models, experiments and theories used in this work are too simplified and the analyses and discussion cannot sufficiently support the conclusion in this work. It should be carefully to discuss hetero catalysis via electrochemical processes, since it is very complicated and many factors such as specific absorption, ionic effects and solvent effects in electric doubled layer at electrochemical interfaces can affect kinetics and thermodynamics of HER synergically. Many confusions come out after reading this paper and it is far away from deep revealing mechanisms of alkaline HER based on current analyses in the manuscript. Therefore, I do not recommend this work for publication on Nature Catalysis. Detailed comments are provided as below:

1. For CV test to verify prepared Ni species of NiH_x, the author claims the extra charge has been attributed to the oxidation of Ni hydrides formed at negative potentials as shown in Fig. 2e. I don't agree with this statement. Two electrochemical reactions (Reaction 1 and 2 in manuscript) with different valence of Ni must have different standard electrode potentials, which means the peaks in CV must be different, no matter it is an unstable diffusion-controlled kinetic process or pseudo capacitor process. This is basic electrochemistry principle. The extra charge is not attributed to reaction of oxidation of Ni hydrides according to the reaction 2. The author should reconsider and analyze the CV data.

2. Many works demonstrates that potential of zero charge (PZC) has important effects on kinetics of HER (J. Am. Chem. Soc. 2025, 147(17):14122-30; J. Am. Chem. Soc. 2024, 146(11): 7305-12; Nature, 2021, 600(7887): 81-5; J. Catal., 2021, 398: 161-70.), and changing species on Ni surface might shifting the PZC, which is a crucially important parameter to determine kinetics of alkaline HER. The influence from PZC differences should be considered while revealing effects of species on HER. However, PZC effects is not discussed in this work.

3. I noticed solution effects in also neglected in this work. Generally, solutions have critical impacts such as specific absorption in inner Helmholtz plane, chemical bonding between solvent and surface Ni species and intermediates during HER at outer Helmholtz plane, which should be considered while studying mechanisms for electrochemical catalysis.

4. Orientation of interfacial water molecules and distance between them and surface is also a determining factor to role the kinetics of alkaline HER. Therefore, different Ni species on surface can modify orientation of interfacial water molecules and the distance? Please verify it.

5. It is known to us alkaline cations in electrolytes can tune processes of electrochemical reduction reactions like CO₂ reduction, HER through several mechanism including stabilization intermediates, regulating electric field strength in EDL, and some works reported that alkaline cations can also poison active sites. So, I am wondering that if Ni species can change alkaline distribution in EDL. Please refer to Ref. (J. Am. Chem. Soc., 2019, 141(7): 3232-9; Nat. Catal., 2022, 5(10): 923-33; J. Am. Chem. Soc., 2024, 146(4): 2426-34; Nat. Catal., 2025, 8(1): 79-91; Nat. Catal., 2024, 7(9): 1000-9; Nat. Catal., 2023, 5(4), 268-276.)

6. For DFT calculations in this work, there are also many questions to be addressed. Applied potentials will change electronic structures and surficial states of Ni catalysts. Thus, why the author still uses the pristine DFT calculations without applied potentials at 0 K? Constant-potential-DFT (CP-DFT), GCE-DFT, CIP-DFT calculations are widely developed and applied for studies of electrochemical reactions, please refer to Ref. (J. Am. Chem. Soc., 2023, 145(26): 14267-75; Chem. Rev., 2024, 124(14): 8620-56; npj Computational Materials, 2024, 10(1), 5; J. Am. Chem. Soc., 2021, 143(25): 9423-8; J. Am. Chem. Soc., 2023, 145(46): 25352-6.).

7. Apparently, Ni alloys and oxides have special magnetic structures. This means magnetic structures will influence electronic structures and electrochemical behaviors of catalysts. Therefore, Heisenberg exchange or super-exchange parameters in Ni and NiO, Ni(OH)₂ are missed but should be calculated and analyzed while analyzing electronic structures and catalytic performance.

8. For 3d transition metal-based oxides or hydroxides, there is complicated interaction between different electrons of 3d orbitals. For geometric optimization processes, simple DFT used in this work is not accurate enough to describe the interactions. Even though single-pass calculations with the HSE06 functional were performed on the revised PBE-optimized geometries, d-bands interactions also should be precisely treated in geometric optimization. Complete Active Space Self-Consistent Field (CASSCF) method, at least DFT + Hubbard U method should be employed. Please redo the DFT calculations.

9. For theoretical DFT calculation model, I noticed that OH, O atoms are placed on the top of surface of Ni, while H are set in body of Ni FCC structures, why? It is more stable than that H on surface of Ni. The author carried out a simple CO displacement experiment and claimed that no current associated with Had desorption can verify hydrogen beneath the Ni surface (Fig. S5). It should be kept in mind that CO replacement and Had desorption occur simultaneously, and it is impossible to detect additional current for Had desorption even H adsorbed on surface of Ni. This experiments essentially fail to rule out H on surface of NiH_x. The author should provide more proper and accurate experiments and give convincing reasons for choosing this special model.

10. When using HSE06 potentials with hybridization of PBE and Hartree Fock potentials in a certain proportion, the parameters such as HFSCREEN and AEXX are missed in this work. All important parameters should be offered to make sure researchers can reproduce your experiments or simulations.

11. It is reported by lots of previous works that during alkaline HER proton transfer occurs through hydrogen-bonding system rather than direct water dissociation on surfaces of catalysts. This is mainly because energy barrier for solvent reconstruction through hydrogen-bonding system is lower than direct water dissociation according to Marcus Electron Transfer Theory. How does authors make sure and validate that proton transfer process come from water dissociation rather than hydrogen-bonding system? please refer to Ref. (Nat. Commun. 2024, 15(1): 7179; Nat. Catal., 2022, 5(10): 900 11; J. Am. Chem. Soc., 2023, 145(22): 12051 8; Nat. Commun., 2025, 16: 6459.)

12. Tafel slop and exchange current densities are generally used to analyze mechanism and reaction pathway in alkaline HER rather than LSV curves and overpotentials. Please compare the Tafel slop and exchange current densities for different catalysts with various Ni-based species and then fitting kinetic equations such as Butler-Volmer equation.

13. In general, many defects commonly exist such as vacancies, twined boundaries, stacking defaults, which can modify electronic structure and intrinsic catalytic activity. So, high resolution TEM, atomic-resolution STEM, XAS techniques should be adopted to characterize prepared Ni catalysts to determine atomical and precise structures. Please see Ref. (ACS Catal., 2024, 14(5):2917 23; Nat. Mater., 2025, 24(3): 424 32; Nat. Nanotechnol., 2021, 16(12):1371 7.)

14. In fact, there is dynamic changes during interaction of electrolytes and surfaces during HER under different applied potentials. How to make sure all states are keeps the initial deliberately produced states under HER processes? The prepared Ni-based species is thermodynamically stable? Please calculated the surface Pourbaix diagram and discuss it.

15. During HER, transition-metal Ni or Ni compounds, especially at boundary with unsaturated coordination, are also easy to be oxidized to high valent state such as NiO and Ni(OH)₂ (please see Ref. Nat. Commun. 2024, 15(1): 5336; Int. J. Hydrogen Energ., 2021, 46(53): 26861 72.). In this case, pure Ni cannot keep initial states and all conclusion based on this condition might be incorrect in this work. In-situ surface enhanced spectrum techniques such as FT-IR, surface-enhanced Raman spectroscopy (SERS) should be used to detect surface evolution during HER.

16. Fig. 3d show a specific energy landscape of water dissociation. Nevertheless, I notice that only energy barriers and Gibbs free energies for H₂O dissociation are calculated. How do you draw the energy landscape only based on energy barriers and Gibbs free energies? I suggest the author should conduct meta-dynamic calculation from AIMD to remake it. This current Figure in the manuscript is misleading and might not correct.

17. Similarly, how to search the transition states and calculated the energy barriers toward H₂O dissociation? By CI-NEB, Dimer or other methods? It is of importance for validation and accuracy of results but missed in the manuscript.

18. For H₂O dissociation energy, lower energy barrier for H₂O dissociation generally means strong OH* adsorption energy on surface. Strong OH* binding means difficulty for desorption of OH* off surface, which will also block subsequent H₂O dissociation processes and hinders the whole HER process. This work does not consider the OH* liberation processes as one of whole processes during alkaline HER. please see Ref. (Nat. Catal. 2022, 5(5): 374-81; J. Am. Chem. Soc. 2020, 143(3): 1399-408; J. Am. Chem. Soc. 2024, 146(7): 4883-91.)

19. For XPS fitting, there is a smaller blue peak in Fig. 2j, which is not labeled in the Figure or related caption. Furthermore, the peak is totally covered by red peak of NiO, and center of the peak is very close to that of NiO (red peak). How to fit the XPS data and deconvoluted into two peaks. Please check it and treat data of XPS carefully.

20. As for electrochemical catalysis processes, only surface monolayer can participate in electrochemical reactions. How to determine surface coverage of Ni species by ToF-SIMS? The resolution of ToF-SIMS is in micrometers and the percentage detected by ToF-SIMS is more likely to be average volumetric content rather than surface coverage. Inner content and surface content might be different and average volumetric content cannot represent the status of surface.

Reviewer #2

(Remarks to the Author)

This manuscript investigates the role of Ni surface species in the hydrogen evolution reaction (HER). The authors seek to disentangle the catalytic contributions of different surface states of Ni, and they attempt to control surface coverage by tuning potential and reaction time. Through systematic variation, they correlate surface composition with HER activity. The study provides useful experimental insights and could serve as a reference for future work on Ni-based HER catalysts. That said, the physical analysis is largely restricted to initial, pristine-state conditions. It is unclear whether the reported electrochemical activity reflects freshly prepared surfaces or reconstructed ones in repeated CVs without post-mortem analysis. Since electrocatalysts inevitably restructure under operating conditions, the transient behavior is as critical as the initial activity. Also, the manuscript requires additional experimental validation and clearer mechanistic support. As a result, the conclusions, while intriguing, are not sufficiently substantiated for publication in a broad high-impact journal.

1. In Figure 1b, the use of double-layer capacitance as a universal proxy for ECSA is problematic. The specific capacitance (C_s) differs for different Ni surface states, so normalization may be biased. For example, outer-sphere redox probes would provide a more reliable measure of conducting surface area, independent of double-layer artifacts.
2. In meta-analysis and iR compensation, iR corrections were applied by “manually extending” Tafel regions, which is subjective. Extrapolated overpotentials may also reflect background reactions, not solely HER. The conclusions drawn from Figure 1 thus rest on uncertain adjustments. A more rigorous, standardized iR treatment is necessary.
3. Resistance values for each measurement are not reported. Electrode size should be minimized to reduce iR artifacts; the use of ultramicroelectrodes would be especially informative. Electrochemical impedance spectroscopy (EIS) should be provided to quantify ohmic and kinetic resistances.
4. It is not clearly stated if Figures 2d–e correspond to the 30th CV cycle as in 2f. Ex-situ XPS or ToF-SIMS should be used to verify whether controlled coverage is retained after cycling. Since pristine Ni, hydride, and oxide terminations are unlikely to persist under alkaline HER, possible reconstruction must be considered.
5. Potentials between -0.05 and -0.4 V vs. RHE generate Ni(H) species, but no current–time data are shown. Because HER occurs in this range, in situ monitoring of current decay would directly demonstrate whether increasing Ni–H coverage suppresses HER. Given the sensitivity of catalyst–electrolyte interfaces to ex-situ handling, such data are critical.
6. The $\sim 100\times$ rate enhancement inferred from DFT assumes (i) the Volmer step is always rate-determining and (ii) prefactors are similar for Ni and Ni(OH) $_2$ /Ni. Neither assumption is experimentally tested. Arrhenius plots or isotope effects would provide the necessary kinetic validation.
7. Peak B is attributed to Ni(OH) coverage, but it closely resembles a hydrogen desorption feature, suggesting Ni–Had. A clearer mechanistic assignment, with corresponding reaction equations, is required.
8. Reporting exchange current densities extracted under kinetic control would offer a more quantitative benchmark for intrinsic activity than overpotential comparisons alone.
9. The claim that H readily penetrates into subsurface sites requires stronger justification. Why vertical migration is preferred over lateral diffusion and recombination should be mechanistically explained, supported by experiment or simulation.
10. The method for calculating coverage is not sufficiently described. The rationale based solely on electronic modification of Ni 0 is too narrow; hydroxide and oxide species also alter the electronic structure. A more comprehensive discussion of how each species affects Ni states and HER activity is needed.
11. The DFT calculations employ a Ni(111) model, yet the experiments use polycrystalline Ni. Extension of the results to other facets should be justified. Water dissociation on NiO should also include oxygen-bonded Ni sites, not only adjacent metallic Ni.
12. The synthesized Ni(OH) $_2$ phase should be identified more clearly as α or β , since these phases differ significantly in stability and conductivity.
13. The monotonic decline in HER with NiO coverage (Figs. 4c, 5c–d) suggests NiO is not a simple spectator but actively blocks metallic Ni sites. The text should reflect this interpretation.
14. The separation of Ni(OH) $_2$ coverage effects from HER performance is unconvincing, since NiO appears already at $\sim 25\%$ coverage (Fig. 5d). Strategies to decouple Ni(OH) $_2$ and NiO contributions should be described, and comparisons with bulk Ni(OH) $_2$ would be valuable.
15. If Ni(OH) $_2$ accelerates water dissociation, formation of Ni(H) species is inevitable. Could Ni-based catalyst degradation be linked to Ni(H) accumulation? A deeper discussion of this mechanism would strengthen the interpretation.

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The manuscript presents a systematic investigation into the influence of nickel hydrides, oxides, and hydroxides on the

Hydrogen Evolution Reaction (HER) in alkaline media. The authors' primary motivation—to resolve the significant data scatter in literature through ultra-controlled surface preparation and potential-controlled immersion—is technically sound and addresses a relevant challenge in electrocatalysis. However, the conceptual advancement of the work is less clear. The roles identified (Ni-hydroxide as a promoter, Ni-hydride as an inhibitor, and Ni-oxide as a spectator) are largely established and accepted qualitative notions within the field.

The authors argue that their specific protocol allows for "well-controlled" surfaces. While this methodological rigor is commendable, the authors stop short of utilizing this control to provide the quantitative kinetic benchmarks that the community requires to resolve the very "scatter" the authors highlight. By their own admission in the rebuttal, the authors suggest that these quantitative derivations are "beyond the scope." This leaves the manuscript in a paradoxical position: it claims superior control but offers only qualitative trends.

The authors demonstrate that their "sweet spot" for activity (approximately 28% hydroxide coverage) is kinetically transient and subject to degradation via hydride accumulation. While the "first shot" measurement is useful for isolating active sites, the lack of quantitative kinetic values or a strategy for stabilizing these sites limits the paper's impact. Without these data, the work serves as a confirmation of existing theories rather than a platform for new catalyst design.

The identification of the "volcano" relationship for Ni-OH and the detrimental role of Ni-H are, at this stage, well-trodden concepts. The provided ToF-SIMS and XPS data are excellent supporting clues, but they reinforce existing mechanisms rather than introducing a new paradigm or a significantly higher level of quantitative precision that can be generalized across different Ni-based systems.

In its current form, the manuscript lacks the breakthrough quantitative insight or mechanistic novelty expected for a full research article in a specialized, high-impact journal. The study is a well-executed case study that provides a refined experimental verification of common claims. Therefore, the reviewer suggests the paper is more suitable as a short letter or Communication in a more specialized journal.

Reviewer #3

(Remarks to the Author)

The reviewer has carefully read this revised manuscript, as well as the comments from other reviewers. I expect the work to be interesting for and inspiring new research into the design of Ni-based alkaline HER electrocatalysts. The main issue lies in the fact that certain species may not be stable during the HER testing, implying that the observed results do not fully correspond to the initial structures. Therefore, the authors need to further strengthen their analysis in this aspect. The comments below should be addressed before I can recommend publication in Nature Catalysis.

1. Due to the short catalysts lifetime, error bars in Fig3c, 4c, 5c, S9 and S13 need to be provided.
2. The authors obtained activity data very carefully and also demonstrated small performance variation during Chronoamperometric test. Nevertheless, the resulting data might still represent measurements taken after catalyst reconstruction. The electrode structure after 8 seconds of testing should be characterized, including surface phase composition, coverage, and related features.
3. All polarization curves presented in this study correspond to the first scan of each surface, recorded at a relatively high scan rates (50 mV s⁻¹). This is an effective method to avoid the impact of interface changes on performance. However, during the initial cycle test, the reconstruction of the surface electric double layer may introduce uncertainties to the polarization curve.
4. The interfaces of Ni and loaded species may key active sites for HER (Science, 2011, 334, 1256-1260). Normalizing by interfacial quantities may provide more comprehensive evidence.
5. The text comparing the HER performance in Fig. 4b should be 98 % < 96 < 90 < 76 < 49 < 25 < 0%.

Reviewer #4

(Remarks to the Author)

The article by Dzevad K. Kozlica et al. addresses, in a quite elegant way, how different oxo-hydroxo species on the surface of Nickel, as well as subsurface hydrogen or hydride formation, influence the onset potential and activity during alkaline HER.

The authors argue that thermally induced NiO essentially blocks active sites, thereby reducing HER activity; the formation of hydride changes the electronic structure, inhibiting HER; in contrast, electrochemically induced oxohydroxo species enhance HER activity by interacting with and altering the water solvent network, facilitating water dissociation.

To demonstrate the presence of different Ni surface species, XPS and ToF-SIMS were used to evaluate the chemical nature and oxidation state of adsorbed species, and their distribution at different depths (with ToF-SIMS). Surface coverage is carefully tuned during both thermal and electrochemical treatments, as verified and quantified by measuring changes in

integrated charge in blank cyclic voltammograms of the prepared surfaces.

The cyclic voltammogram response looks clean, supporting control of experimental conditions. The initial Ni(0) benchmarking surface is also carefully prepared, yielding a relatively flat surface with clear grain boundaries. This detail is relevant because the growth or distribution of new surface species is likely dependent on substrate structure, and rough structures may result in uncontrolled coverage. Looking at the voltammetric profiles and surface images, there is strong control over surface conditioning and preparation, resulting in well-defined interfaces.

From the reported blank cyclic voltammograms, it is clear that the observed effects in HER are not related to changes in electroactive surface area but instead to changes in surface structure, composition, and adsorbate distribution.

The effect of coverage of NiO and Ni(OH)₂ or NiOOH (electrochemical) is systematically addressed and reported, demonstrating that NiO only have a site-blocking effect, whereas HER on electrochemically-induced Ni(OH)₂-Ni(0) follows a volcano relationship with coverage, i.e. low amount of Ni(OH)₂ affects water solvent structure, but a high coverage block active surface sites. A similar effect and a potential shift at lower Ni(OH)₂ coverages have been observed for Pt surfaces modified with Ni(OH)₂.

Even though identifying the exact nature of surface species and site structure under reaction conditions may require future studies combining operando surface characterisation and in situ spectroscopy, the insights and messages of this article are important. In particular, I highlight three points: 1) The lack of normalisation of catalytic activity by the electroactive surface area is a problem that persists in the field of electrocatalysis, not only for Ni but also for other surfaces, and it is nice to highlight that and encourage others to measure active areas. 2) Surface pretreatment and conditioning have a tremendous impact on the catalytic properties of the surface, and therefore, working with well-defined surfaces is rather important to rationalise effects in catalysis. 3) Adsorbates of different natures affect catalysis by affecting the site structure or the electrolyte structure, as shown for Ni. These effects can be tuned by tuning the coverages of species. Quantification of surface coverage can be done by careful, systematic recording of blank cyclic voltammograms.

Based on the abovementioned reasons, I recommend this article for Nature Catalysis (with minor comments to assess), and I believe that this work will not only be of interest to those who need guidelines and descriptors to optimise their Ni-based catalyst, but will also encourage others to perform studies on well-prepared surfaces and use the cyclic voltammetry technique to address electrified interfaces.

Comments:

1) I am not sure if the CO displacement technique is a valuable technique to evaluate Ni hydrides (Figure S5). The CO-displacement technique is used on Pt, Ir, Pd... i.e. on surfaces where CO adsorbs strongly. CO-displacement would not work, for example, on copper, because the adsorption of CO is too weak in this metal. My impression is that CO does nothing or is a spectator, and the negative current is just HER or hydride formation. If there was CO on the surface, there should be a CO stripping peak in the CV, or a change in the CV. Reconsider the utility of this experiment in this situation.

2) The voltammetric behaviour in Fig 2b, showing an increased anodic peak after holding the electrode at -0.4 V, is similar to that reported in other metals, which also form a hydride phase, for example, Cu. For Cu, spectroscopic evidence of hydride formation is observed. Maybe referring to other metal examples can reinforce the assumption of hydride in Ni, even though the article does not provide direct speciation measurements, which are challenging. 10.1021/acs.jpcclett.1c03131.

3) The shift toward lower onset potential with Ni(OH)₂ coverages up to 40% has also been observed on Pt(111). Over 40%, site-blocking effects predominate. Consider whether this simile is useful for reinforcing the discussion. 10.1021/acsami.8b15003

4) I understand that the objective of this work is not to address the stability of the prepared interfaces but just to evaluate how the coverage of different adsorbates influences the onset potential and HER activity on Ni electrodes. Nevertheless, I think it is valuable to show the blank cyclic voltammograms (CVs) after the HER cyclic voltammograms in Figure 3a (30% coverage of individual species) to ensure that blank CVs do not change dramatically, indicating electrolyte contamination or other factors to consider. This is a common practice when evaluating the catalytic performance of, e.g. metal single crystals, particularly in alkaline media or 0.1 M KOH, which sometimes contain traces of impurities.

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

My concerns have been adequately addressed through the inclusion of new data and analyses. The authors have significantly strengthened the study by conducting post-measurement XPS and ToF-SIMS analyses. This study systematically distinguishes the mechanistic roles of Ni, NiH_x, NiO, and Ni(OH)₂ surface states in the HER. By demonstrating that the active species comprises interfacial metallic Ni adjacent to Ni(OH)₂, rather than the hydroxide film itself. It also clarifies that NiO functions as a spectator while NiH_x inhibition is predominantly electronic in origin. I recommend publication of this revised version in Nature Catalysis.

Reviewer #4

(Remarks to the Author)

The authors have adequately addressed my questions and those of other reviewers and have improved the discussion and clarity in the new version. In particular, I highlight the quality of the experiments presented in this work and the new additions, such as blank CVs before and after HER electrocatalysis, which show relatively good stability, and a CO-stripping CV that demonstrates the presence of metallic Ni and suggests that adsorbed hydrogen exists like subsurface hydrogen. I suggest the present manuscript for publication.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Response to Reviewers

Reviewer #1

The role of surface species of catalysts in the hydrogen evolution reaction (HER) under alkaline conditions remains a key challenge for sustainable hydrogen production. Many works focusing on interfacial species effects toward alkaline HER have been reported, but conclusion have not reached a consensus as yet. This topic is meaningful and the finding in this work maybe interesting. However, the theoretical models, experiments and theories used in this work are too simplified and the analyses and discussion cannot sufficiently support the conclusion in this work. It should be carefully to discuss hetero catalysis via electrochemical processes, since it is very complicated and many factors such as specific absorption, ionic effects and solvent effects in electric doubled layer at electrochemical interfaces can affect kinetics and thermodynamics of HER synergically. Many confusions come out after reading this paper and it is far away from deep revealing mechanisms of alkaline HER based on current analyses in the manuscript.

We thank the reviewer for taking the time to evaluate our manuscript. However, based on the reviewer's summary of the insights derived from this work, it would appear that the reviewer might have missed the focus of the manuscript, as stated in the title: "*The role of individual nickel surface species in the hydrogen evolution reaction on nickel in alkaline electrolytes.*" The intention of this study was not to provide a rigorous kinetic analysis of the HER or a detailed discussion of its reaction mechanism (in fact, the word mechanism is only mentioned once in the entire manuscript and SI). Rather, our goal was to elucidate the roles of individual Ni species in HER on Ni by establishing clear activity trends on carefully prepared Ni surfaces – something that is clearly the cause of the significant data spread and controversy in the literature. To underline these issues, we have included more than 60 references in the main manuscript and the Supplementary Information (SI) —not to meet a citation quota, but because they genuinely reflect the current state-of-the-art in HER on Ni.

Instead, the reviewer has cited approximately 30 references in the comments that extend beyond the scope of this work. We suggest that our work is evaluated based on its rationale and what is included, not on what is not, as no single paper can (or should) aim to describe a field as broad as HER.

1. For CV test to verify prepared Ni species of NiH_x, the author claims the extra charge has been attributed to the oxidation of Ni hydrides formed at negative potentials as shown in Fig. 2e. I don't agree with this statement. Two electrochemical reactions (Reaction 1 and 2 in manuscript) with different valence of Ni must have different standard electrode potentials, which means the peaks in CV must be different, no matter it is an unstable diffusion-controlled kinetic process or pseudo capacitor process. This is basic electrochemistry principle. The extra charge is not attributed to reaction of oxidation of

Ni hydrides according to the reaction 2. The author should reconsider and analyze the CV data.

We strongly but respectfully disagree with the reviewer's comment. The criticism is incorrect on several grounds, as clarified in the detailed response below:

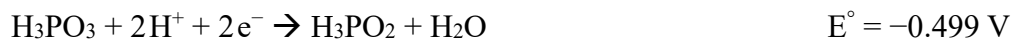
1. The overlap between Ni oxidation and hydride oxidation has been thoroughly discussed in the literature with the consensus that the extra charge comes from NiH_x. Corresponding references have been provided in our manuscript [including Machado et al., *Electrochimica acta*, **39**, 1385-1391, (1994); Hall et al. *Journal of The Electrochemical Society*, **160** F235-F243 (2013), and others]
2. The position of a voltammetric peak does not depend merely on the standard potential of the electrochemical process, but also on the kinetics of the process, which can shift the peak substantially (hence the general possibility of peak overlap).
3. Even the reviewer's notion that two electrochemical reactions involving same elements with different valence must have different standard electrode potentials does not carry much merit as there are plenty of such examples in electrochemistry with closely spaced standard electrode potentials:



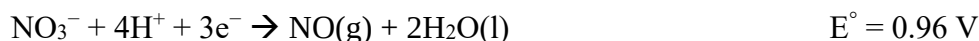
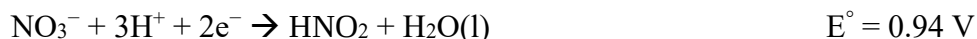
$$\Delta E^\circ = 0 \text{ mV}$$



$$\Delta E^\circ = 6 \text{ mV}$$



$$\Delta E^\circ = 9 \text{ mV}$$



$$\Delta E^\circ = 20 \text{ mV}$$

4. Finally, the most likely reason for observing the overlap of the two reactions is that they share a common reactive species. The oxidation of NiH_x very likely proceeds through

the reaction with adsorbed OH_{ad} which is also the precursor for the oxidation of Ni^0 (Equation 1 and 2 in the manuscript).

2. Many works demonstrates that potential of zero charge (PZC) has important effects on kinetics of HER (J. Am. Chem. Soc. 2025, 147(17):14122-30; J. Am. Chem. Soc. 2024, 146(11): 7305-12; Nature, 2021, 600(7887): 81-5; J. Catal., 2021, 398: 161-70.), and changing species on Ni surface might shifting the PZC, which is a crucially important parameter to determine kinetics of alkaline HER. The influence from PZC differences should be considered while revealing effects of species on HER. However, PZC effects is not discussed in this work.

3. I noticed solution effects in also neglected in this work. Generally, solutions have critical impacts such as specific absorption in inner Helmholtz plane, chemical bonding between solvent and surface Ni species and intermediates during HER at outer Helmholtz plane, which should be considered while studying mechanisms for electrochemical catalysis.

4. Orientation of interfacial water molecules and distance between them and surface is also a determining factor to role the kinetics of alkaline HER. Therefore, different Ni species on surface can modify orientation of interfacial water molecules and the distance? Please verify it.

As summarized above, in this manuscript we are concerned with *what* is the role of individual Ni surface species, not *how* they achieve the observed effect. The latter is admittedly an important question, which was assumed and adopted from our previous extensive work on the HER problematics in alkaline electrolytes, which proposes the water dissociation as the rate determining step [see Strmcnik et al., *Nature chemistry* 5, 300-306, (2013); Strmcnik et al., *Nano Energy* 29, 29-36, (2016), Subbaraman et al., *Science* 334 (6060), 1256-1260., (2011); Subbaraman et al., *Nature materials*, 11(6), pp.550-557, (2012) and others]. Therefore, the reviewer's comments (2, 3, and 4) touch upon an ongoing and fundamental debate within the electrocatalysis community concerning the true factors governing HER kinetics.

A recent *Nature Catalysis* Perspective by Sebastián-Pascual et al. (2025, pp. 1–14) summarizes three main schools of thought that attempt to rationalize the impact of electrolyte–adsorbate–surface interactions on reaction kinetics, each based on distinct mechanistic descriptors. The first emphasizes that the binding energy of key adsorbed intermediates (such as H^* and OH^*) dictates the reaction kinetics. The second highlights the role of charge and electric fields near the electric double layer, shaped by the PZC, in stabilizing the polar adsorbates and governing proton transfer. The third focuses on energy barriers arising from the restructuring of the water solvation spheres of both electrolyte and reactants.

We believe that this discussion should be carried out within the published scientific literature. Although our group has played a substantial role in the first school of thought [Stamenkovic et al., 2017. *Nature materials*, 16(1), pp.57-69.; Strmcnik et al., *Nature Chemistry* 1(6), 466–472, (2009); Subbaraman et al., *Science* 334 (6060), 1256-1260, (2011); Subbaraman et al., *Nature materials*, 11(6), pp.550-557, (2012); Strmcnik et al., *Nature chemistry* 5, 300-306, (2013);

Strmcnik et al., Nano Energy 29, 29-36, (2016), etc.], we don't think this manuscript is the avenue to discuss or defend it as it deals with a different topic and is, most importantly, based on observed trends. Thus, regardless of the school of thought, the results, observed trends in activity, and conclusions presented in this manuscript remain entirely unaffected. In essence, the much needed discussion on the three schools of thought is only possible if a body of published data exists, which this manuscript contributes to significantly.

5. It is known to us alkaline cations in electrolytes can tune processes of electrochemical reduction reactions like CO₂ reduction, HER through several mechanism including stabilization intermediates, regulating electric field strength in EDL, and some works reported that alkaline cations can also poison active sites. So, I am wondering that if Ni species can change alkaline distribution in EDL. Please refer to Ref. (J. Am. Chem. Soc., 2019, 141(7): 3232-9; Nat. Catal., 2022, 5(10): 923-33; J. Am. Chem. Soc., 2024, 146(4): 2426-34; Nat. Catal., 2025, 8(1): 79-91; Nat. Catal., 2024, 7(9): 1000-9; Nat. Catal., 2023, 5(4), 268-276.)

We thank the reviewer for his-her comment. The cation effect is also known to us as we have introduced it to the field in 2009 as *non-covalent interactions* [Strmcnik *et al.*, *Nature Chemistry* 1(6), 466–472, (2009)]. The recent references the reviewer lists actually build upon our previous work and might give a false impression regarding the history of this effect and the current state-of-the-art.

We would like to reiterate that this study was to identify the distinct *roles* of individual species, naturally present on the inherently complex Ni surface, and quantify their effects through surface coverage-HER activity correlations. The observed trends can be well explained purely through water dissociation energetics, so we see no reason to invoke the potential contributions of other effects. In fact, simpler models are often preferred in explaining trends, as much more complex models can obscure the fundamental relations.

While possible that cations would be involved in the transition state, this was not the focus here, and neither cation nature nor concentration was varied. This topic may be addressed as a part of our future work but would obfuscate the message of the present manuscript.

6. For DFT calculations in this work, there are also many questions to be addressed. Applied potentials will change electronic structures and surficial states of Ni catalysts. Thus, why the author still uses the pristine DFT calculations without applied potentials at 0 K? Constant-potential-DFT (CP-DFT), GCE-DFT, CIP-DFT calculations are widely developed and applied for studies of electrochemical reactions, please refer to Ref. (J. Am. Chem. Soc., 2023, 145(26): 14267-75; Chem. Rev., 2024, 124(14): 8620-56; npj Computational Materials, 2024, 10(1), 5; J. Am. Chem. Soc., 2021, 143(25): 9423-8; J. Am. Chem. Soc., 2023, 145(46): 25352-6.).

The reviewer suggests three different approaches to model water dissociation on Ni, which are all quite different and have different advantages and disadvantages. As it is often in modelling, no single *best model* exists. We have employed constant-charge DFT calculations because our goal was not to determine exact values—which would require a highly complex set of calculations and merit a dedicated technical paper in a specialized journal—but rather to analyze trends that are evident when comparing different surface motifs relatively. The relative performance of trends is not expected to change when moving from DFT to constant-potential DFT (CP-DFT), as the two approaches are thermodynamically equivalent in large unit cells [Kastlunger *et al.*, *ChemPhysChem*, 25(10), p.e202300950, (2024)].

7. Apparently, Ni alloys and oxides have special magnetic structures. This means magnetic structures will influence electronic structures and electrochemical behaviors of catalysts. Therefore, Heisenberg exchange or super-exchange parameters in Ni and NiO, Ni(OH)₂ are missed but should be calculated and analyzed while analyzing electronic structures and catalytic performance.

The DFT calculations were performed on pristine Ni(111) and various decorated Ni(111) surfaces, which are fundamentally ferromagnetic, not on pure NiO or Ni(OH)₂, which are correlated insulating materials. For our structures, the ferromagnetic structure is well described by spin-polarized calculations, as performed. Correlated bulk oxide phases might require including Heisenberg exchange to obtain very precise electronic structure due to long-range ordering and correlation effect, which could dominate the electronic structure. To obtain the magnetic ground state of various Ni(111)-derived structures, and evaluate adsorptions and activation energies, this is not relevant and would not provide additional information.

8. For 3d transition metal-based oxides or hydroxides, there is complicated interaction between different electrons of 3d orbitals. For geometric optimization processes, simple DFT used in this work is not accurate enough to describe the interactions. Even though single-pass calculations with the HSE06 functional were performed on the revised PBE-optimized geometries, d-bands interactions also should be precisely treated in geometric optimization. Complete Active Space Self-Consistent Field (CASSCF) method, at least DFT + Hubbard U method should be employed. Please redo the DFT calculations.

In our tests, a *revised* PBE with the Hubbard correction (DFT+U) was found to have a negligible effect on the geometries of reactants, products and transition states, with H adsorption displacements of less than 0.005 Å when compared to plain GGA calculations. For energy calculations and electronic structures, this is not relevant, as a highly accurate and computationally costly hybrid functional (HSE06) was employed, as noted by the reviewer. Magnetic moments were accounted for as part of the spin-polarized calculation, as dictated by the electronic structure of nickel.

CASSCF is typically applied to multireference systems, which periodic metallic slabs are generally not. In nickel systems, the main caveat is correctly capturing the effects of *d* electrons,

which is remedied using the hybrid functional HSE06 (or even doing cheap DFT+U with an appropriate value of U).

9. For theoretical DFT calculation model, I noticed that OH, O atoms are placed on the top of surface of Ni, while H are set in body of Ni FCC structures, why? It is more stable than that H on surface of Ni. The author carried out a simple CO displacement experiment and claimed that no current associated with H_{ad} desorption can verify hydrogen beneath the Ni surface (Fig. S5). It should be kept in mind that CO replacement and H_{ad} desorption occur simultaneously, and it is impossible to detect additional current for H_{ad} desorption even H adsorbed on surface of Ni. This experiments essentially fail to rule out H on surface of NiHx. The author should provide more proper and accurate experiments and give convincing reasons for choosing this special model.

DFT part:

All species (OH, O and H) were evaluated on all available surface sites (hcc, fcc, top and bridge). In all cases, the fcc site was found to be the most stable and was therefore used in the calculations. H_2O , in contrast, preferentially sits atop atoms, as clearly illustrated in Figure S11a. If the reviewer is referring to Fig 3, note that it depicts the transition state. Since this is an early transition state—structurally closer to the reactants (H_2O) than to the products—OH is positioned near the top of the atom. This is not a stable structure, but rather a saddle point.

CO displacement:

We utilized the well-established CO displacement method, which relies on monitoring both the magnitude and polarity of the charge obtained from chronoamperometric measurements during the adsorption of CO onto the metal surface. We are unsure whether the reviewer's comment was intended to question the validity of this method as a means of identifying H_{ad} on metal surfaces. Indeed, CO adsorption and H_{ad} desorption occur simultaneously during the experiment—but this simultaneity is precisely the basis of the method, pioneered by Alicante group [Clavilier et al., *Journal of Electroanalytical Chemistry*, 330(1-2), pp.489-497, (1992).].

While H_{ad} desorption produces an electrochemical response, CO adsorption does not, so a distinct positive current would be expected from H_{ad} desorption during CO displacement, which, notably, was absent in our measurements.

We have modified this section for clarity in the *Supplementary Information*, where the changes are highlighted in yellow.

10. When using HSE06 potentials with hybridization of PBE and Hartree Fock potentials in a certain proportion, the parameters such as HFSCREEN and AEXX are missed in this work. All important parameters should be offered to make sure researchers can reproduce your experiments or simulations.

HSE06 is defined by HFSCREEN = 0.2 and AEEXX = 0.25; any other value would imply a different functional, not HSE06. This info has been added to Methods section.

11. It is reported by lots of previous works that during alkaline HER proton transfer occurs through hydrogen-bonding system rather than direct water dissociation on surfaces of catalysts. This is mainly because energy barrier for solvent reconstruction through hydrogen-bonding system is lower than direct water dissociation according to Marcus Electron Transfer Theory. How does authors make sure and validate that proton transfer process come from water dissociation rather than hydrogen-bonding system? please refer to Ref. (Nat. Commun. 2024, 15(1): 7179; Nat. Catal., 2022, 5(10): 900-11; J. Am. Chem. Soc., 2023, 145(22): 12051-8; Nat. Commun., 2025, 16: 6459.)

Please refer to our answers to questions 2-5.

12. Tafel slop and exchange current densities are generally used to analyze mechanism and reaction pathway in alkaline HER rather than LSV curves and overpotentials. Please compare the Tafel slop and exchange current densities for different catalysts with various Ni-based species and then fitting kinetic equations such as Bulter-Volmer equation.

We would like to reiterate that neither the mechanism nor reaction pathway were analyzed in this work. We emphasize that a rigorous kinetic analysis of the HER, including a detailed discussion of its reaction mechanism, lies beyond the scope of this manuscript and warrants a dedicated study, which is already in the works. Our primary objective here was to establish clear activity trends to elucidate the roles of individual Ni species in the HER on Ni. No additional information on the role of these species would be gained by fitting the Butler-Volmer equation.

13. In general, many defects commonly exist such as vacancies, twined boundaries, stacking defaults, which can modify electronic structure and intrinsic catalytic activity. So, high resolution TEM, atomic-resolution STEM, XAS techniques should be adopted to characterize prepared Ni catalysts to determine atomical and precise structures. Please see Ref. (ACS Catal., 2024, 14(5):2917-23; Nat. Mater., 2025, 24(3): 424-32; Nat. Nanotechnol., 2021, 16(12):1371-7.)

We are again confused by the reviewer's comment as neither TEM, STEM nor XAS can be used to analyze the samples prepared in our study.

14. In fact, there is dynamic changes during interaction of electrolytes and surfaces during HER under different applied potentials. How to make sure all states are keeps the initial deliberately produced states under HER processes? The prepared Ni-based

species is thermodynamically stable? Please calculate the surface Pourbaix diagram and discuss it.

Electrochemistry, or electrocatalysis, of course requires favorable thermodynamics as a necessary condition, but this is by no means a sufficient condition. Fuel cells and water electrolyzers do not operate at 1.23 V; instead, kinetics plays a decisive important role in electrochemistry. Pourbaix diagrams are measures of thermodynamics and are of very limited use in kinetic studies, as they cannot determine the stability of kinetically determined species and phases, as is the case for $\text{Ni}(\text{OH})_2$, NiO , etc.

Nevertheless, the reviewer raises an important point in questioning the stability of the prepared surfaces during the HER. The problem with Ni surfaces is, namely, that there is hardly a potential window where one can achieve long-term stability. This is actually one of the breakthroughs in this manuscript: we have succeeded in preparing 4 surfaces with isolated chemistries that were stable in the timeframe of the experiment. All polarization curves presented in this study correspond to the first scan of each surface, recorded at a relatively high scan rates (50 mV s^{-1}), with each measurement taking approximately 8 seconds in total. Herein, we provide the data on how much the activity (current) changes by holding these surfaces at the most negative end of the potential window, i.e., @ -0.4 V (Figure R1). As can be seen, the electrocatalytic properties experience only minor changes: the current decreases by $\sim 10\%$, corresponding to a minor change ($\sim 10\%$) in the surface catalytic properties, indicating that the surface remains largely intact during the measurement. In practice, this change is even smaller, because the chronoamperometry is recorded for 8 s at -0.4 V , whereas in the LSV measurement the surface spends only a fraction of a second at this extreme potential. Based on these considerations, we are confident that the experimental results, observed activity trends, and conclusions presented in this manuscript remain entirely valid and meaningful.

We would be pleased to include a clarification on this point in the Supplementary Information upon reviewer's request.

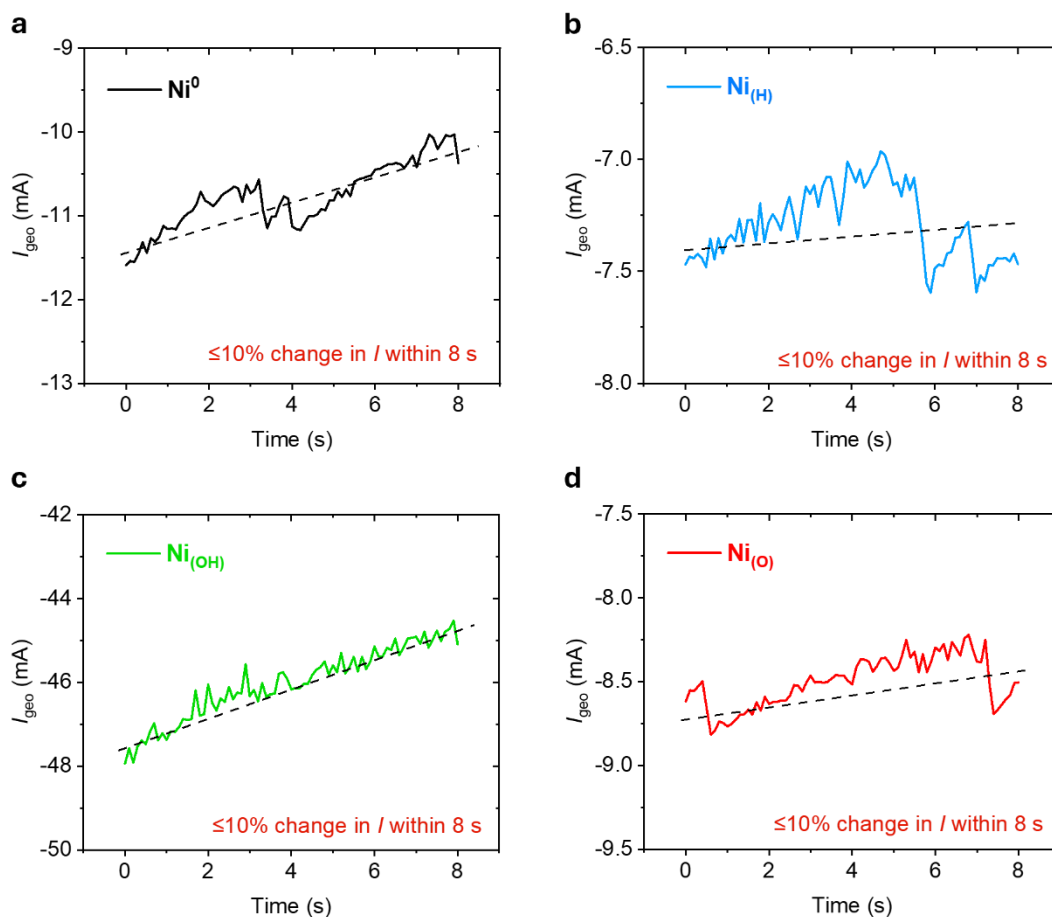


Figure R1. Stability of the prepared surfaces during HER. a-d, Chronoamperometric response of Ni^0 , $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{OH})}$ and $\text{Ni}_{(\text{O})}$ surfaces at -0.40 V over an 8-second segment of the polarization scan. All surfaces, show a $\leq 10\%$ change in current (I), over this period, indicating that the currents are effectively stable within the experimental timeframe.

15. During HER, transition-metal Ni or Ni compounds, especially at boundary with unsaturated coordination, are also easy to be oxidized to high valent state such as NiO and Ni(OH)₂ (please see Ref. Nat. Commun. 2024, 15(1): 5336; Int. J. Hydrogen Energ., 2021, 46(53): 26861-72.). In this case, pure Ni cannot keep initial states and all conclusion based on this condition might be incorrect in this work. In-situ surface enhanced spectrum techniques such as FT-IR, surface-enhanced Raman spectroscopy (SERS) should be used to detect surface evolution during HER.

We have partially already addressed this question in our answer to comment #14 above:

1. During the timeframe of our experiments, the individual surfaces undergo only minute changes.
2. In this study, we were not interested in the long-term evolution of the Ni surface chemistry as it does not benefit the investigation of the role of individual Ni species.

Moreover, while $\text{Ni}(\text{OH})_2$ or NiO are kinetically relatively stable under HER conditions, their formation below their reversible potentials, as suggested by the reviewer, cannot be substantiated experimentally or conceptually.

In fact, a lot of the references the reviewer is referring to suffer from such discrepancies and contribute to the large spread of data in Figure 1 of our manuscript (to list just a few sources of discrepancies: inadequate potential control during electrode immersion, poor choice in counter electrode, improper ECSA estimation, misinterpretation of XPS data, etc.)

In fact, such studies only underscore the motivation behind our work—to uncover the true origins of these inconsistencies and to elucidate the distinct roles of individual Ni species in the HER.

16. Fig. 3d show a specific energy landscape of water dissociation. Nevertheless, I notice that only energy barriers and Gibbs free energies for H_2O dissociation are calculated. How do you draw the energy landscape only based on energy barriers and Gibbs free energies? I suggest the author should conduct meta-dynamic calculation from AIMD to remake it. This current Figure in the manuscript is misleading and might not correct.

As explicitly stated in the text and Figure caption of Figure 3, we are showing a schematic of the activation barriers, not a full energy landscape, which would fit to a full mechanistic study, which is not discussed in this manuscript. The only calculated values are the activation Gibbs free energies of water dissociation, represented by the height of the saddle for individual reaction.

17. Similarly, how to search the transition states and calculated the energy barriers toward H_2O dissociation? By CI-NEB, Dimer or other methods? It is of importance for validation and accuracy of results but missed in the manuscript.

As described in the methods section of the manuscript, the transition states (and consequently the barriers) are calculated using the dimer method with a force convergence threshold of $0.01 \text{ eV}/\text{\AA}$, which is very strict as most works settle for $0.01\text{-}0.05 \text{ eV}/\text{\AA}$. The transition states were validated using vibrational analysis, which revealed exactly one imaginary frequency, corresponding to the reaction path, which is clearly stated in the manuscript.

For sake of completeness, we can provide more details here. In principle, any method of determining transition states is sufficient provided it arrives at the optimized transition state, as confirmed by vibrational analysis. Practically, our workflow includes a non-CI NEB for a rough approximation (up to $0.1 \text{ eV}/\text{\AA}$), which takes 30-50 ionic cycles. This yields a good approximate structure, which we use as the initial guess for the dimer method to optimize it fully. This approach is an order of magnitude faster than running CI-NEB.

18. For H₂O dissociation energy, lower energy barrier for H₂O dissociation generally means strong OH* adsorption energy on surface. Strong OH* binding means difficulty for desorption of OH* off surface, which will also block subsequent H₂O dissociation processes and hinders the whole HER process. This work does not consider the OH* liberation processes as one of whole processes during alkaline HER. please see Ref. (Nat. Catal. 2022, 5(5): 374-81; J. Am. Chem. Soc. 2020, 143(3): 1399-408; J. Am. Chem. Soc. 2024, 146(7): 4883-91.)

Upon electron transfer, OH* becomes OH⁻, so it is this species that is getting desorbed, and at negatively charged surface should not constitute a major hindrance to the overall reaction. The OH* species would not be desorbing during the HER.

19. For XPS fitting, there is a smaller blue peak in Fig. 2j, which is not labeled in the Figure or related caption. Furthermore, the peak is totally covered by red peak of NiO, and center of the peak is very close to that of NiO (red peak). How to fit the XPS data and deconvoluted into two peaks. Please check it and treat data of XPS carefully.

The smaller peak in green, not blue, corresponds to Ni(OH)₂, in accordance with the color scheme used throughout the manuscript, and arises from air exposure during transfer to the XPS chamber. We have added this label to the *caption* of Fig. 2 (highlighted in yellow).

The green peak is overlapped by the red peak solely for aesthetic reasons, to emphasize the overall predominance of the red peak (attributed to NiO), but it remains clearly visible. This is already discussed in Note S7 in Supplementary Information.

We appreciate the reviewer's concern regarding the proximity of the green and red deconvoluted peaks in Fig. 2j. However, there is nothing problematic with this deconvolution procedure. Ni, as a transition metal, exhibits a complex XPS spectrum, comprising multiple peaks for each species potentially present on the surface—including metallic Ni (3 peaks), Ni(OH)₂ (6 peaks), and NiO (5 peaks)—that may partially or fully overlap. Our XPS data were fitted following state-of-the-art deconvolution procedures established by Payne and Biesinger [Biesinger et al., 2009, *Surface and Interface Analysis*, 41(4), pp.324-332. (1928 citations); Biesinger et al., 2011. *Applied Surface Science*, 257(7), pp.2717-2730. (9458 citations)], whose XPS expertise on Ni and related elements is widely recognized in the fields of electrocatalysis, battery and corrosion. We kindly encourage the reviewer to consult Table S2 in the Supplementary Information for the detailed fitting parameters, as well as the related XPS references.

20. As for electrochemical catalysis processes, only surface monolayer can participate in electrochemical reactions. How to determine surface coverage of Ni species by ToF-SIMS? The resolution of ToF-SIMS is in micrometers and the percentage detected by ToF-SIMS is more likely to be average volumetric content rather than surface coverage. Inner content and surface content might be different and average volumetric content cannot represent the status of surface.

This is a common misunderstanding of ToF-SIMS depth sensitivity. While the lateral resolution of ToF-SIMS is typically in the micrometer or sub-micrometer range (down to 30 nm, depending on the ToF-SIMS settings), the information depth of secondary ions is only 1–2 nm, corresponding to just a few atomic layers. Therefore, ToF-SIMS does not measure volumetric composition, but rather the outermost surface 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 lower. Consequently, the Bi^+ analysis provides surface coverage information, reflecting the chemical state and spatial distribution of Ni species on the outermost layer (while sputtering), not an average volumetric concentration. This principle is well established in the literature [e.g., Vickerman & Briggs, ToF-SIMS: Surface Analysis by Mass Spectrometry, 2nd Ed., 2013], 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.

We have added an additional clarification in the *Supplementary Information* (highlighted in yellow).

Rebuttal to Reviewer #2

This manuscript investigates the role of Ni surface species in the hydrogen evolution reaction (HER). The authors seek to disentangle the catalytic contributions of different surface states of Ni, and they attempt to control surface coverage by tuning potential and reaction time. Through systematic variation, they correlate surface composition with HER activity. The study provides useful experimental insights and could serve as a reference for future work on Ni-based HER catalysts. That said, the physical analysis is largely restricted to initial, pristine-state conditions. It is unclear whether the reported electrochemical activity reflects freshly prepared surfaces or reconstructed ones in repeated CVs without post-mortem analysis. Since electrocatalysts inevitably restructure under operating conditions, the transient behavior is as critical as the initial activity. Also, the manuscript requires additional experimental validation and clearer mechanistic support. As a result, the conclusions, while intriguing, are not sufficiently substantiated for publication in a broad high-impact journal.

We thank the reviewer for taking the time to evaluate our manuscript. As clearly stated in the title: "*The role of individual nickel surface species in the hydrogen evolution reaction on nickel in alkaline electrolytes*", the purpose of this study revolves around the role of nickel species in the HER, not around the mechanism of HER on Ni. We are interested in the *what*, not the *how*. To effectively capture the role of these species, a specific condition had to be met, i.e., that the

initial state of the surface does not significantly change in properties during the electrochemical analysis. As thoroughly described in the response to question #14 from reviewer 1, these conditions were met in our study. While transient conditions and restructuring of the catalyst are very relevant for the stability of the catalysts in general, they are not relevant for the identification of the roles of the species presented in our study.

One of the nuisances in working with Ni-based catalysts is that they can simultaneously form multiple native surface species depending on the potential when in contact with an alkaline electrolyte. To elucidate the individual roles of these species in HER, it was therefore essential to develop specific protocols/methods that enabled the preparation of four distinct well-defined Ni surfaces, each predominantly terminated by a single species: Ni^0 , NiH_x , NiO and Ni(OH)_2 . This approach allowed us, for the first time, to obtain highly reproducible data—overcoming the longstanding challenge associated with the dynamic nature of nickel’s solid-electrolyte interface. Such a rigorous level of control was crucial for establishing both qualitative and quantitative correlations between the individual Ni species and HER kinetics. Finally, our results strongly suggest that the widespread data in literature stems NOT from the experimental noise, but from the fundamental fact that Ni surfaces are chemically heterogeneous, and often not well-controlled. The electrochemical behavior of Ni is governed by the dynamic interplay of surface and subsurface NiO , Ni(OH)_2 , and NiH_x species, whose coverage, distribution, and identity critically influence HER kinetics.

We have carefully addressed all individual comments by the reviewer below and we feel none of them raise enough concern to preclude our manuscript from being published in Nature Catalysis.

1. In Figure 1b, the use of double-layer capacitance as a universal proxy for ECSA is problematic. The specific capacitance (C_s) differs for different Ni surface states, so normalization may be biased. For example, outer-sphere redox probes would provide a more reliable measure of conducting surface area, independent of double-layer artifacts.

We fully agree with the reviewer’s critique that in Figure 1b, the use of double-layer capacitance (C_{dl}) as a proxy for the electrochemically active surface area (ECSA) is problematic. In fact, this is precisely what we stated in our detailed discussion in Note S2 of the Supplementary Information. We would like to bring the reviewer’s attention to that the HER activity data presented in Figures 1a,b and Figures S1a-c originate exclusively from previously published studies by other groups (hereafter referred to as “literature data”) and do not represent an analysis of data obtained from our own experiments.

Generally, “the literature lacks a standardized protocol for reporting HER activity, such as expressing specific activities (currents normalized to ECSA)”, as we highlighted in the *Analysis of the literature data* section of the Results and Discussion. It would simply be unfair to represent the widely scattered HER activity data for Ni-based catalyst reported in the literature solely as geometric currents (Figure 1a), since all reported samples possess different effective surface areas (i.e., their roughness factors differ). Therefore, as a gesture of good will, we

normalized geometric currents to the surface area to provide as fair conditions as possible for representing the spread in HER activity (Figure 1b). Also, it should be emphasized that all ECSA values used for current normalization in Figure 1b were taken directly from the respective published studies (details provided in Table S1) and were not determined in our experiments. Finally, although we agree with the reviewer regarding the rather uncertain nature of using C_{dl} to estimate ECSA, these values were used exactly as reported in the original publications. Consequently, they cannot be modified, even though we acknowledge that their accuracy may be affected by significant experimental errors. This is one of the key takeaways of our manuscript.

In contrast, the ECSA values used in our study were obtained by integrating the charge under the anodic peak in the Ni voltammograms.

We provided additional clarification of this comment in the "*Note S2. Evaluation of specific activities and IR correction*" section in the Supplementary Information (highlighted in yellow).

2. In meta-analysis and iR compensation, iR corrections were applied by “manually extending” Tafel regions, which is subjective. Extrapolated overpotentials may also reflect background reactions, not solely HER. The conclusions drawn from Figure 1 thus rest on uncertain adjustments. A more rigorous, standardized iR treatment is necessary.

As stated in the previous comment, the data provided are taken from the literature and we cannot ascertain whether or not they have been measured properly, i.e., if there were background reactions occurring simultaneously, that is due to improperly executed experiments not due to the problems in our analysis. In general, assuming that the reaction mechanism does not change, extending the linear portion of the Tafel slope to higher current values should not be in itself problematic.

In several of the referenced papers in the manuscript, the expected exponential region of the polarization curves was absent, and instead a linear region dominated—strongly indicating incomplete or absent *IR* compensation. To minimize this effect, we manually adjusted the uncompensated *IR* drop within the smallest reasonable margin of error, by extending the linear portion of the reported Tafel plots to the higher current range.

Note that the adjustment of the uncompensated resistance only “increased” the reported catalytic activities and reduce the overall spread in the data. While we could have simply shown the large spread in activity data using only the geometric currents (Figure 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, Figures 1 and S1 clearly demonstrate that a substantial spread in HER activity remains across the reported studies.

We provided additional clarification of this comment in the "Note S2. Evaluation of specific activities and IR correction" section in the Supplementary Information (highlighted in yellow).

3. Resistance values for each measurement are not reported. Electrode size should be minimized to reduce iR artifacts; the use of ultramicroelectrodes would be especially informative. Electrochemical impedance spectroscopy (EIS) should be provided to quantify ohmic and kinetic resistances.

Our study used 6 mm Ni disk samples. As explained in the "Electrochemical measurements" in the Methods section of our manuscript, the EIS was used to measure the ohmic resistances that were used for IR compensation – 85% during the measurement (i.e., *in-situ*), and 15% in the post-processing. It would not be possible to apply microelectrodes in our study.

4. It is not clearly stated if Figures 2d–e correspond to the 30th CV cycle as in 2f. Ex-situ XPS or ToF-SIMS should be used to verify whether controlled coverage is retained after cycling. Since pristine Ni, hydride, and oxide terminations are unlikely to persist under alkaline HER, possible reconstruction must be considered.

The voltammograms shown in Fig. 2d, 2e, and 2g correspond to the 1st cycle recorded immediately after applying the specific surface-preparation protocol used to generate each surface. The only exception is the Ni(OH)₂ surface in Fig. 2f, which required 30 cycles as part of the actual protocol needed to form a surface partially covered by irreducible Ni(OH)₂ (see "Preparation of surfaces with individually isolated Ni species" in the Methods section). Thus, for Fig. 2f, the 30th cycle defines the prepared surface in the same way that the 1st cycle defines the surfaces shown in Fig. 2d, 2e, and 2g. It would not be meaningful to discuss the roles of individual Ni species if also the surfaces shown in Figures 2d, 2e, and 2g corresponded to the 30th cycle, as they would no longer represent the species of interest. The central aim of this work is to decouple the roles of individual Ni species in HER kinetics.

As emphasized throughout the paper, the Ni surface is highly dynamic, and it is extremely difficult to maintain a single surface termination under alkaline conditions. Thus, it was essential to control the dominance of each species precisely. We kindly ask the reviewer to note the critical surface control step described in the Experimental section: in each experiment, the electrode was immersed in the electrolyte under potential control at 0.0 V versus RHE, thereby preventing exposure to the open-circuit potential (OCP) at approximately 0.5 V upon immersion—which would otherwise lead to surface contamination through the growth of an irreducible fraction of Ni(OH)₂. Continued cycling between –0.4 and 0.55 V leads to the gradual accumulation of irreducible Ni(OH)₂ species (see Figure S6), which would contaminate other model species such as Ni⁰, NiH_x, and NiO.

If, however, the reviewer's concern refers to whether the controlled coverage is preserved *after* the HER regime, please see our detailed answer to a similar question by reviewer 1 (answer #14).

We provided additional clarification of this comment in *Methods* section in the manuscript (highlighted in yellow).

5. Potentials between -0.05 and -0.4 V vs. RHE generate Ni(H) species, but no current–time data are shown. Because HER occurs in this range, in situ monitoring of current decay would directly demonstrate whether increasing Ni–H coverage suppresses HER. Given the sensitivity of catalyst–electrolyte interfaces to ex-situ handling, such data are critical.

We agree with the reviewer that *in situ* monitoring of current decay would directly demonstrate whether increasing Ni–H coverage suppresses HER. To address this, we provide the chronoamperometric curve below, recorded at potential of -0.4 V, which clearly shows a gradual decrease in activity over time due to the buildup of subsurface hydrogen (hydride species).

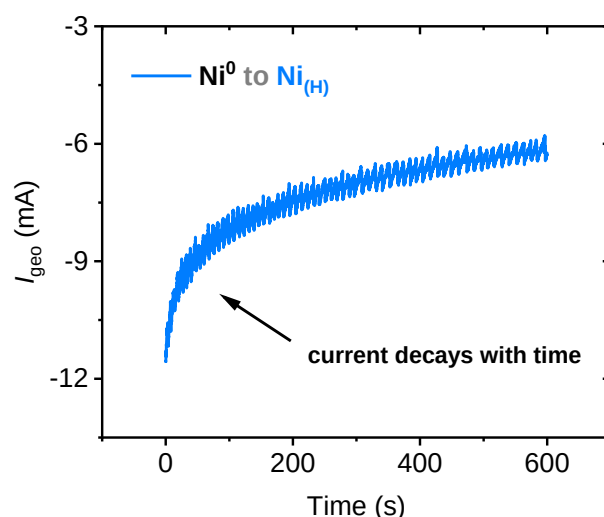


Figure R2. In situ monitoring of current decay driven by NiH_x formation. Chronoamperometry was conducted at -0.4 V for 10 minutes revealing a time-dependent decrease in current associated with the formation of NiH_x species on the Ni surface.

Note, however, that NiH_x is prepared and electrochemically characterized in-situ. As stated in the text, NiH_x characterization is not possible spectroscopically.

6. The $\sim 100\times$ rate enhancement inferred from DFT assumes (i) the Volmer step is always rate-determining and (ii) prefactors are similar for Ni and $\text{Ni(OH)}_2/\text{Ni}$. Neither assumption is experimentally tested. Arrhenius plots or isotope effects would provide the necessary kinetic validation.

The $\sim 100\times$ rate enhancement claim is simply a consequence of the measured Tafel slopes for both surfaces (60 mV/decade) and the calculated difference in the barrier for the rate determining step (0.130 eV).

7. Peak B is attributed to Ni(OH) coverage, but it closely resembles a hydrogen desorption feature, suggesting Ni–Had. A clearer mechanistic assignment, with corresponding reaction equations, is required.

We would like to stress that peak B in Figure S8 was excluded from the integration of the voltammograms on hydroxide covered surfaces as clearly stated in note S4: “*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 (Fig. S8b,c), has been attributed in the literature to hydride or hydrogen oxidation (HOR) as a result of prior HER activity.*”, in agreement with reviewer’s observation.

8. Reporting exchange current densities extracted under kinetic control would offer a more quantitative benchmark for intrinsic activity than overpotential comparisons alone.

We thank the reviewer for the suggestion. We believe the most informative way of presenting the catalysts activity is by showing the entire polarization curve, which we do for all our samples. Moreover, the most common approach in electrocatalysis to report catalytic activities is either by overpotential η at specified current density or as current density at specified overpotential. To give relevance to our data in respect to the literature, we have also utilized this approach rather than reporting the exchange current densities.

9. The claim that H readily penetrates into subsurface sites requires stronger justification. Why vertical migration is preferred over lateral diffusion and recombination should be mechanistically explained, supported by experiment or simulation.

1. The existence of NiH_x on Ni has been reported and commonly accepted. Corresponding references have been provided in our manuscript [including Machado et al., *Electrochimica acta*, **39**, 1385-1391, (1994); Hall et al. *Journal of The Electrochemical Society*, **160** F235-F243 (2013), and others].
2. We do not make any claims that suggest vertical migration is preferred over lateral diffusion.
3. Instead, based on DFT data we argue that vertical migration is *possible* but not more likely than surface adsorption or lateral diffusion. The energy of surface adsorption is roughly –0.5 eV and a diffusion barrier is 0.51 eV. The energy of subsurface adsorption is from +0.10 to –0.02 eV, which is only slightly thermodynamically favorable. This means, however, that the interaction becomes more favorable as more hydrogen is adsorbed in the subsurface. The barrier for the subsurface migration is roughly 0.7 eV, which is higher than for surface diffusion.

We have changed the wording of “*readily*” or “*easily*” to indicate that the penetration of H into the subsurface is *possible*.

10. The method for calculating coverage is not sufficiently described. The rationale based solely on electronic modification of Ni⁰ is too narrow; hydroxide and oxide species also alter the electronic structure. A more comprehensive discussion of how each species affects Ni states and HER activity is needed.

1. A detailed explanation for ECSA determination/surface coverage calculation was provided in the Supplementary Information (Note S4). We provide additional clarification in the Supplementary Information for improved understanding.

We added the following text in Note S4 (highlighted in yellow):

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 Fig. S8), which corresponds to the oxidation of Ni to Ni(OH)₂ per Equation S6.

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. Therefore, NiO coverages were determined in the same manner as shown in Figure S8a—that is, by considering only peak A. Details on the determination of hydride coverage are provided in Note S7.

The Ni⁰ surface, exhibiting 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., $\Theta_{\text{Ni(OH)}_2} = 0\%$) (Fig. S8a). 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 Ni⁰ reference, with the difference in charge corresponding to $\Theta_{\text{Ni(OH)}_2}$, as defined by Equation S9. For example, the Ni(OH)₂ voltammogram (peaks A and B) in Fig. S8b 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., $\Theta_{\text{Ni(OH)}_2} = 28\%$).

We added the following text in Note S7 (highlighted in yellow):

The Ni⁰ 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., $\Theta_{\text{ad}} = 0\%$) (Figure S13b). 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 Ni⁰ 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.

2. We would be happy to provide additional computational data on the electronic structure changes brought about by these species, such as density of states (DOS), differential charge density or integrated Bader charges upon the reviewer's request.

11. The DFT calculations employ a Ni(111) model, yet the experiments use polycrystalline Ni. Extension of the results to other facets should be justified. Water dissociation on NiO should also include oxygen-bonded Ni sites, not only adjacent metallic Ni.

We chose to work with Ni(poly) for practical reasons – so we could employ many samples in parallel in our extensive study. However, based on the properties of Ni(111) compared to Ni(poly) (see voltammograms in Figure R3 below), these two surfaces are very similar, likely due to the predominance of Ni(111) facet in our Ni(poly). Both surfaces exhibit cyclic voltammograms of comparable shape and features, indicating that, from an experimental standpoint, they are expected to show similar trends. The voltametric profile of Ni(111) is well-known in the literature to closely resemble that of Ni(poly) [Floner *et al.*, 1990. *Surface science*, 234(1-2), pp.87-97.].

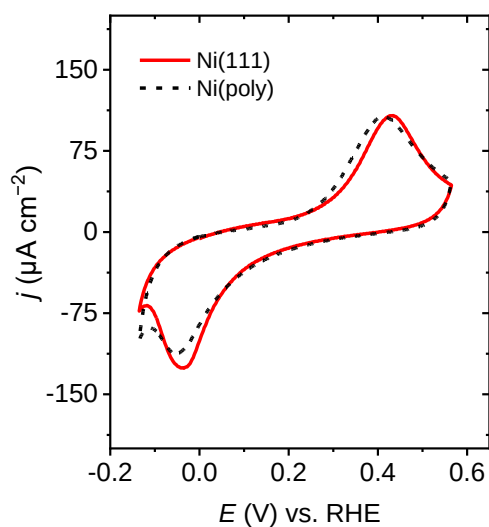


Figure R3. Representative cyclic voltammograms of metallic Ni for Ni(111) and Ni(poly) surfaces. Both voltammograms display similar features, likely reflecting the predominance of the Ni(111) facet in the polycrystalline sample.

DFT calculations require choosing a crystalline model for several reasons. Most importantly, the number of atoms in a periodic cell is limited by the available computational power, necessitating at least a medium-range order. A polycrystalline proxy would therefore introduce

ordering-related artefacts and would be non-reproducible. Furthermore, it would be difficult to argue that a true global minimum was found. Hence, a crystalline surface must be selected. A Ni(111) surface was chosen as the most stable and commonly studied surface, which – as justified above – is very similar to the actual experimental sample.

12. The synthesized Ni(OH)₂ phase should be identified more clearly as α or β , since these phases differ significantly in stability and conductivity.

We thank the reviewer for pointing that out. This omission of α - or β -phase designation was intentional, as we opted to use electrochemically more meaningful terms such as *reversible (reducible)* and *irreversible (irreducible)* species instead of structural designations.

We are aware that α - or β -phase designations for Ni(OH)₂ are commonly used across 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 case we are dealing with partial monolayers, so we feel such designation is not warranted.

We added this clarification in the Supplementary Information (highlighted in yellow).

13. The monotonic decline in HER with NiO coverage (Figs. 4c, 5c–d) suggests NiO is not a simple spectator but actively blocks metallic Ni sites. The text should reflect this interpretation.

In electrocatalysis literature, spectator and blocking species are synonymous. (Strmcnik et al., Nature Chemistry **1** (2009) 466–472; Stamenkovic et al., Science **315** (2007) 493–497; Rodriguez et al., Nature Chemistry **4** (2012) 177–182), which is how we also use this term.

14. The separation of Ni(OH)₂ coverage effects from HER performance is unconvincing, since NiO appears already at ~25% coverage (Fig. 5d). Strategies to decouple Ni(OH)₂ and NiO contributions should be described, and comparisons with bulk Ni(OH)₂ would be valuable.

NiO and Ni(OH)₂ contributions are decoupled by preparing Ni_(O) surface, with exclusive contribution from NiO. As can be seen in Figure 4, NiO has no beneficial effect on HER electrocatalysis. Since we already know the effect of NiO, it is quite straightforward to determine the effect of Ni(OH)₂ on Ni_(OH) surface (Figure 5).

It is true that some NiO is already present on Ni_(OH) surface, even at lower coverages, as pointed out by the reviewer. In fact, it is actually impossible to prepare higher coverages of Ni(OH)₂ without partial transformation to NiO. This can also be shown computationally, where increasingly high concentrations of OH first induce crowding out and ultimately conversion to NiO and H₂O (see Figure R4 below).

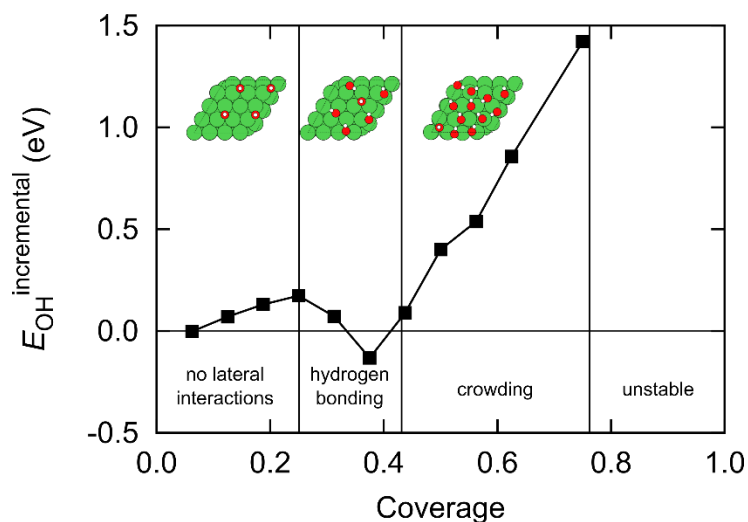


Figure R4. Differential adsorption energy for one additional OH* species on Ni(111) as a function of surface coverage, reported relative to $H_2O(g) - \frac{1}{2} H_2(g)$. The adsorption energies of OH* on Ni(111) were calculated as a function of surface coverage, which is reported relative to $H_2O(g) - \frac{1}{2} H_2(g)$. At low coverages, there are limited lateral interactions, and the differential adsorption energy is trending slightly upwards (unfavorable). At higher coverages, crowding out was observed, and the differential adsorption energy becomes very unfavorable, eventually leading to OH* breakdown (into surface O* and desorbed H_2O , according to equation $2OH^* \rightarrow O^* + H_2O$).

However, the initial predominance by $Ni(OH)_2$ at low coverages, where HER activity is high, and the latter dominance of NiO at high coverages, where HER activity is low again, confirm the same conclusion that $Ni(OH)_2$ is the promotor for HER, when adjacent to metal Ni sites (Figure 5).

15. If $Ni(OH)_2$ accelerates water dissociation, formation of $Ni(H)$ species is inevitable. Could Ni-based catalyst degradation be linked to $Ni(H)$ accumulation? A deeper discussion of this mechanism would strengthen the interpretation.

At the same current density, the rate of HER and hence the formation of H_{ad} is the same regardless of the Ni surface.

In our study and this response, we clearly demonstrated the detrimental effect of NiH_x on the HER performance in the initial stages and over time. In a parallel study, we are investigating the effect of individual species on the removal of NiH_x species and its link to long-term performance, but this is not within the scope of this study.

To conclude, we acknowledge that the fundamental mechanisms of degradation of catalytic materials in the Ni field are generally poorly understood and merit dedicated investigation; however, regardless of the degradation mechanism, the results, observed trends, and conclusions of this manuscript remain unaffected.

Response to Reviewers

We thank the reviewers for the time and effort invested into evaluating our manuscript. Our detailed answers to the raised questions are summarized below.

Reviewer #2:

1) The manuscript presents a systematic investigation into the influence of nickel hydrides, oxides, and hydroxides on the Hydrogen Evolution Reaction (HER) in alkaline media. The authors' primary motivation—to resolve the significant data scatter in literature through ultra-controlled surface preparation and potential-controlled immersion—is technically sound and addresses a relevant challenge in electrocatalysis. However, the conceptual advancement of the work is less clear. The roles identified (Ni-hydroxide as a promoter, Ni-hydride as an inhibitor, and Ni-oxide as a spectator) are largely established and accepted qualitative notions within the field.

We respectfully disagree that the roles of the individual Ni species are already well-established or broadly accepted in the literature.

A central motivation for this study was the absence of a unified picture of HER on Ni. As shown in Fig. 1 and Table S1, the literature exhibits a very broad scatter in reported HER activities, even after normalization and correction procedures. Moreover, the conflicting interpretations regarding the roles of NiO, Ni(OH)₂, NiH_x, and related surface species are discussed throughout the manuscript and SI, where it becomes clear that the field contains mutually inconsistent assignments for essentially every major Ni surface species.

In our view, these two problems - the large spread in reported HER activity and the contradictory mechanistic interpretations - have the same root cause: **insufficient control over the chemical state of the Ni surface**. Because multiple species such as metallic Ni, NiH_x, NiO and Ni(OH)₂ can form and coexist under alkaline conditions, nominally similar “Ni” catalysts can in fact probe very different surface chemistries. As a result, both the measured activity and its interpretation can vary substantially from study to study. This is also the framework adopted in the manuscript, where the remaining spread in the normalized literature data is explicitly attributed to the complexity and poor control of Ni surface chemistry.

The conceptual advance of our work is therefore not simply to restate that hydroxide can be beneficial or hydride can be detrimental. Rather, it is to **resolve these ambiguities by establishing well-defined Ni surface states and determining the role of each species under controlled conditions**. In particular, we show that:

- **NiO acts as a spectator/blocking species rather than a promoter**. This directly challenges a substantial body of literature (we provided almost 50 references in the SI) that

assigns a promoting role to NiO. This includes highly cited and influential prior studies that have been interpreted as evidence for a promoting NiO/Ni synergy. Our results lead us to a different conclusion and suggest that such effects may, at least in some cases, reflect insufficient surface-state control and/or misinterpretation of ex-situ characterization.

In our measurements, the HER rate clearly scales with the number of accessible Ni sites, indicating that NiO primarily reduces site availability rather than enhancing intrinsic activity.

- **The active motif is the interfacial metallic Ni adjacent to Ni(OH)₂.** Our combined experimental and theoretical analysis supports a mechanism in which water dissociation is facilitated at metallic Ni sites in the vicinity of Ni(OH)₂, in contrast to interpretations that assign the active role directly to the hydroxide film.
- **The descending branch of the apparent Ni(OH)₂ volcano originates from growth of an intervening NiO layer at high hydroxide coverage,** rather than from Ni(OH)₂ alone.
- **NiH_x deactivates HER through inhibition/electronic effects rather than simple site blocking.**

We therefore believe that the main novelty of the manuscript is that it provides a systematic, surface-controlled framework that explains both why the literature has remained so scattered and why so many conflicting mechanistic claims have emerged. More broadly, the study assigns distinct roles to the major Ni surface species, identifies the relevant interfacial active-site motif, and provides guidance for improving Ni-based HER catalysts in alkaline media.

In addition, we believe that the present work provides an important **benchmarking framework for evaluating Ni-based HER catalysts**. By mapping the activity across well-defined Ni surface states and coverages, the study establishes the range of intrinsic activities that can be expected from Ni under alkaline conditions. This is particularly relevant in light of the wide spread of reported performances in the literature and provides a physically grounded reference against which newly reported “improved” Ni catalysts can be assessed. (A sentence has been added to the last paragraph of the manuscript to emphasize this point, page 13, highlighted in yellow)

2) **The authors argue that their specific protocol allows for "well-controlled" surfaces. While this methodological rigor is commendable, the authors stop short of utilizing this control to provide the quantitative kinetic benchmarks that the community requires to resolve the very "scatter" the authors highlight. By their own admission in the rebuttal, the authors suggest that these quantitative derivations are "beyond the scope." This leaves the manuscript in a paradoxical position: it claims superior control but offers only qualitative trends.**

The authors demonstrate that their "sweet spot" for activity (approximately 28% hydroxide coverage) is kinetically transient and subject to degradation via hydride accumulation. While the "first shot" measurement is useful for isolating active sites, the lack of quantitative kinetic values or a strategy for stabilizing these sites limits the paper's impact. Without these

data, the work serves as a confirmation of existing theories rather than a platform for new catalyst design.

We agree that quantitative kinetic benchmarks are useful. However, we suggest that the broad scatter in reported Ni HER kinetics is not primarily a consequence of missing benchmark values, but rather a consequence of the multidimensional surface-state space accessible to Ni under alkaline conditions. In practice, nominally similar Ni electrodes can differ substantially in the identity, coexistence, and coverage of species such as Ni, NiH_x, NiO, and Ni(OH)₂. Each such surface state can, in principle, exhibit its own apparent exchange current density and Tafel slope. In this sense, the scatter in the literature is not an anomaly that can be removed simply by adding a small set of benchmark values; rather, it reflects the fact that different studies have sampled different regions of the Ni surface-state space.

A central goal of our work was therefore to explain the origin of this scatter by isolating and benchmarking well-defined regions of the Ni surface-state space under controlled conditions. Within the controlled set of measurements shown in Fig. 3, where the surfaces are compared at matched ~30% coverage, the apparent Tafel slopes are similar and close to ~60 mV/dec. This internal consistency is important because it shows that, within the constraints of our benchmark comparison, the major differences in HER activity arise primarily from changes in active-site availability and transition-state energetics rather than from a large change in the apparent kinetic regime.

To address the reviewer's request directly, in Figure R1 and Table R1, we report the apparent exchange current density (j_0) and Tafel slope (b) values for the four representative benchmark surfaces in Fig. 3a (These have also been added to the SI, note S5). We believe these values are useful descriptors for the controlled surface states examined here. At the same time, we would caution against interpreting them as universal constants for "Ni-HER," 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.

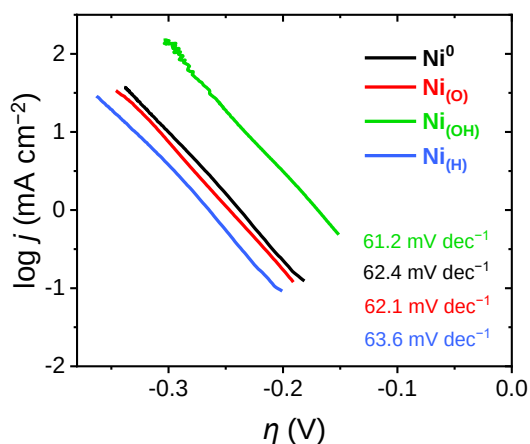
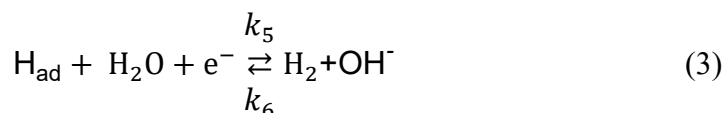


Figure R1. Tafel plots comparing the hydrogen evolution reaction (HER) on four representative Ni benchmark surfaces at matched ~30% coverage.

Table R1. Exchange current density values calculated from corresponding Tafel slopes in Fig. R1.

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

In principle, a full microkinetic analysis could be used to explore such a system in greater detail; however, achieving a unique mechanistic description for a surface-state space of this complexity is highly underdetermined. The conventional HER mechanism consists of three distinct steps: Volmer, Heyrovsky, and Tafel. In addition to these conventional 3-step scheme (see, for example, the seminal review paper on HER impedance by Lasia: *International Journal of Hydrogen Energy*, **44**, 2019, pp. 19484-19518), we include an additional step in line with recent literature (e.g. *Nat Commun* **14**, 5289 (2023), *Chem. Commun.* **60**, 9829 (2024).) and our own interpretation in the case of Nickel-based catalyst (see Eq.(1) below):





Each step in scheme (1-4) is described by two rate constants (forward and backward), totaling eight. Adding the two transfer coefficients for the Volmer and Heyrovsky electrochemical steps (Eqs. (2) and (3)), along with the density of active sites, results in a baseline of eleven free parameters. Importantly, these eleven parameters assume a completely homogeneous surface. In the case of a non-uniform surface, the number of free parameters increases substantially, as the rate constants and active site densities will depend heavily on specific surface features, such as structural defects or chemical modifications. Conversely, even the most sensitive electrochemical methods—such as impedance spectroscopy—can typically extract a maximum of only 7 to 8 reliable model parameters, and this is only achievable if performed systematically across a range of controlled conditions (variable potential, reactant concentration, pH, etc.) with near-ideal measurements (minimal scatter, highly extended frequency range). Consequently, it remains essentially impossible at present to uniquely determine the exact mechanism for a catalyst as complex as Ni, since multiple different parameter sets can mathematically reproduce the same apparent kinetic behavior. More specifically, in terms of the measured Tafel slope, this spatial complexity inevitably yields an averaged, non-ideal value; because the foundational kinetic parameters fluctuate across a heterogeneous surface rather than maintaining unique, uniform values, the resulting slope cannot be strictly mapped to a single textbook mechanism (in principle, any slope value can be expected under such non-uniform conditions). We therefore consider a rigorous microkinetic inversion to be beyond the scope of the present manuscript. The aim of this work is instead to establish the controlled experimental framework upon which such analyses can be meaningfully built. A dedicated microkinetic treatment of this system is currently the subject of ongoing work and will be reported separately.

Regarding the reviewer's concern that the optimum Ni(OH)₂-modified state is transient and lacks a stabilization strategy, we note that the manuscript already provides such guidance in the conclusion of the manuscript. Specifically, we propose avoiding cathodic excursions below −0.10 V to minimize hydride formation, limiting anodic excursions above 0.50 V to suppress NiO growth, and periodically activating the surface at ~0.5 V to restore the beneficial Ni(OH)₂ coverage. We now further support this point experimentally by adding Figure R2 (also included in the SI as Fig. S22 / Note 8), which demonstrates that periodic brief activation can maintain a stable HER response on the Ni/ Ni(OH)₂ surface.

In Figure R2, we demonstrate a non-optimized protocol for stabilization of Ni/Ni(OH)₂ active sites, where a 1s activation step every minute preserves a steady activity on the Ni(OH)₂-modified surface, compared to a continuously decreasing activity on the non-activated one.

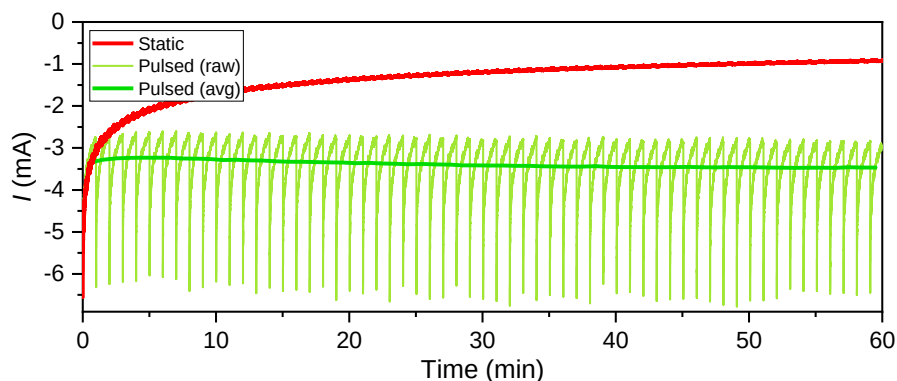


Figure R2. Strategy for stabilizing Ni/Ni(OH)₂ active sites. Normal operation of the Ni/Ni(OH)₂ electrode (red curve) shows a gradual decay in current, attributed to slow removal of beneficial Ni(OH)₂ species and formation of hydride. In contrast, the periodically activated surface (green curves – real and average current), shows no observable current decay over time.

Note that such protocols have recently been utilized in achieving dynamic stability for CO₂ reduction reaction [K. W. Kimura, et al., *ChemSusChem*, 11, 1781 (2018).; Jännisch, Y. et al., *Electrochemistry Communications*, 121, p.106861 (2020).; Timoshenko, J. et al., *Nature catalysis*, 5(4), pp.259-267. (2022)].

We have included Figure R2 also in the supplementary information (SI), and refer the reader to it in the main text: “Specifically, we propose avoiding cathodic excursions below -0.10 V (to minimize hydride formation), limiting anodic excursions above 0.50 V (which promote NiO growth), and periodically activating the surface at $\sim 0.5\text{ V}$ to restore beneficial Ni(OH)₂ coverage (Figure S22, Note S8).

3) The identification of the "volcano" relationship for Ni-OH and the detrimental role of Ni-H are, at this stage, well-trodden concepts. The provided ToF-SIMS and XPS data are excellent supporting clues, but they reinforce existing mechanisms rather than introducing a new paradigm or a significantly higher level of quantitative precision that can be generalized across different Ni-based systems.

We respectfully disagree that the present work merely confirms accepted views. The novelty of the manuscript is not the isolated observation that Ni(OH)₂ may enhance HER or that NiH_x may be detrimental, but rather the resolution of **why and under which surface-state conditions** these trends arise.

As discussed in our responses to Comments 1 and 2, a central conclusion of this work is that the broad scatter and contradictory interpretations in the Ni HER literature originate from insufficient control over the multidimensional Ni surface-state space. The present study addresses this directly by isolating and benchmarking well-defined Ni, NiH_x, NiO, and Ni(OH)₂-modified surfaces under

controlled conditions. Within this framework, the manuscript goes beyond prior qualitative descriptions in several important ways:

- it distinguishes the **beneficial low-coverage Ni(OH)₂ regime** from the **high-coverage regime where HER declines because an intervening NiO layer disrupts the active Ni/Ni(OH)₂ interface**;
- it shows that the relevant active motif is **interfacial metallic Ni adjacent to Ni(OH)₂**, rather than the hydroxide film itself;
- it demonstrates that **NiO is not a promoter**, but a spectator/blocking species that reduces the number of accessible metallic Ni sites without enhancing their intrinsic activity; and
- it distinguishes **NiH_x inhibition** from simple site blocking by showing that its effect is predominantly electronic/subsurface in origin.

We therefore believe that the manuscript provides a meaningful increase in mechanistic precision and a general framework for understanding why nominally similar Ni-based catalysts can exhibit widely different HER activities depending on the identity, coexistence, and coverage of native surface species.

4) In its current form, the manuscript lacks the breakthrough quantitative insight or mechanistic novelty expected for a full research article in a specialized, high-impact journal. The study is a well-executed case study that provides a refined experimental verification of common claims. Therefore, the reviewer suggests the paper is more suitable as a short letter or Communication in a more specialized journal.

We respectfully disagree with this assessment.

The contribution of the present work is not a single isolated observation, but the resolution of a long-standing and unusually complex problem in Ni HER electrocatalysis. As discussed above, the literature exhibits both a broad scatter in reported activities and mutually inconsistent mechanistic interpretations, which we attribute to insufficient control over the chemical state of Ni surfaces. The present study addresses this issue directly by establishing and benchmarking well-defined regions of the Ni surface-state space. In our view, the key quantitative contribution of the manuscript is not the reporting of a single exceptional activity value, but the establishment of a surface-coverage/activity framework that explains the origin of the broad and long-standing scatter in the Ni HER literature.

Within this framework, the manuscript provides a consistent and experimentally validated description of how Ni, NiH_x, NiO, and Ni(OH)₂ influence HER activity, and explains why nominally similar Ni-based catalysts can exhibit widely different performance depending on the identity, coexistence, and coverage of surface species.

Importantly, this is achieved through an integrated approach that combines:

- controlled preparation of model Ni surfaces with defined surface states,
- electrochemical benchmarking using both geometric and specific normalization,
- surface characterization,
- and DFT calculations linking activity trends to changes in water-dissociation barriers and interfacial structure.

In addition, the manuscript provides practical guidance for stabilizing the beneficial Ni/ Ni(OH)₂ interfacial state under operating conditions, which is now further supported by new experimental evidence.

Taken together, we believe that the scope and depth of the study go beyond a case-specific validation and instead establish a general, surface-controlled framework for understanding and improving Ni-based HER catalysts in alkaline media. We therefore consider the manuscript to be well suited for publication as a full research article.

Reviewer #3:

The reviewer has carefully read this revised manuscript, as well as the comments from other reviewers. I expect the work to be interesting for and inspiring new research into the design of Ni-based alkaline HER electrocatalysts. The main issue lies in the fact that certain species may not be stable during the HER testing, implying that the observed results do not fully correspond to the initial structures. Therefore, the authors need to further strengthen their analysis in this aspect. The comments below should be addressed before I can recommend publication in Nature Catalysis.

We sincerely thank the reviewer for taking the time to evaluate not only our revised manuscript, but also for carefully reading and considering the comments from the other reviewers and our responses to them.

We understand the reviewer's primary concern regarding the stability of Ni species during HER testing, as this represents a critical aspect of the overall study. A detailed response to these points is provided below.

1. Due to the short catalysts lifetime, error bars in Fig3c, 4c, 5c, S9 and S13 need to be provided.

The error bars summarizing the most relevant polarization curves from Figures 3a, 4a, 5a and S9 were already presented in Figure 6b. At the reviewer's request, we have now extended this representation and added error bars to all bar graphs.

2. The authors obtained activity data very carefully and also demonstrated small performance variation during Chronoamperometric test. Nevertheless, the resulting data might still represent measurements taken after catalyst reconstruction. The electrode structure after 8 seconds of testing should be characterized, including surface phase composition, coverage, and related features.

Our study was designed to probe well-defined surface states under controlled conditions, and the HER polarization curves were recorded as the **first LSV immediately after completion of the preparation protocol for each individual surface state, with potential control maintained throughout**. This minimized the time available for surface reconstruction prior to measurement.

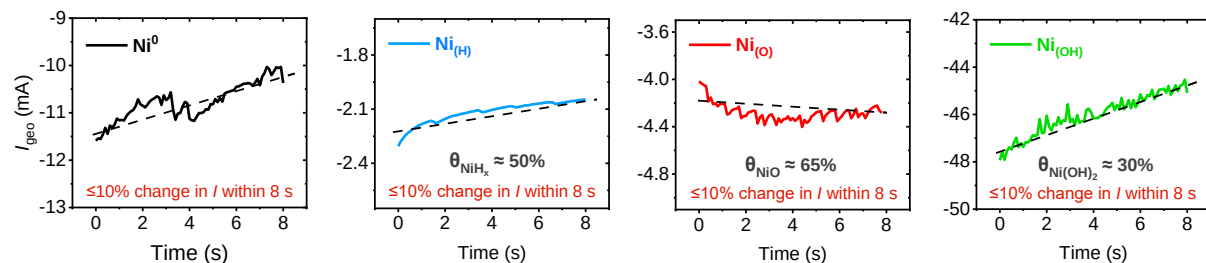


Figure R3. Stability of four representative benchmark Ni surfaces during the hydrogen evolution reaction (HER). **a-d**, Chronoamperometric responses of Ni^0 , $\text{Ni}_{(\text{H})}$, $\text{Ni}_{(\text{O})}$, and $\text{Ni}_{(\text{OH})}$ surfaces at -0.4 V (RHE) over an 8-second segment of the polarization 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 (Figure R3) show **$<10\%$ change in current over an 8-second 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. Consistently, post-measurement cyclic voltammograms (Figure R4) show only minor changes in electrochemical features (e.g., ECSA), further supporting that the surface state remains largely preserved.

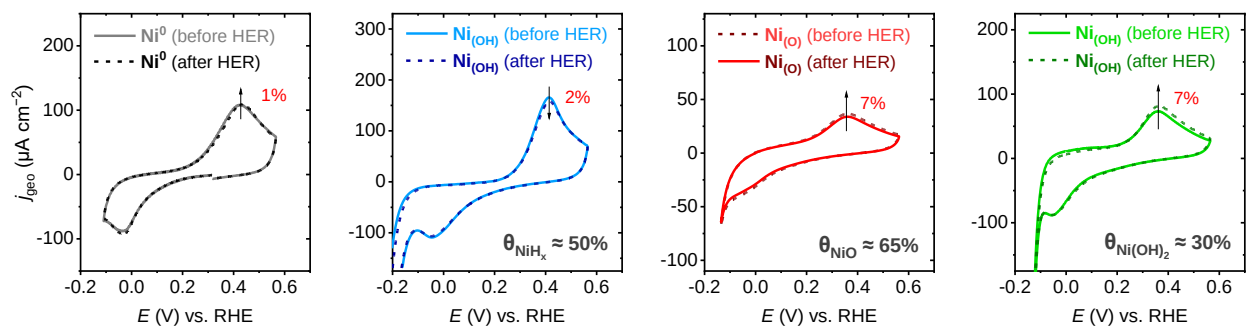


Figure R4. Stability of four representative benchmark Ni surfaces over the experimental timeframe. a-d, Comparison of cyclic voltammetry (CV) curves for Ni^0 , $\text{Ni}(\text{H})$, $\text{Ni}(\text{O})$, and $\text{Ni}(\text{OH})$ surfaces recorded before and after acquisition of the hydrogen evolution 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.

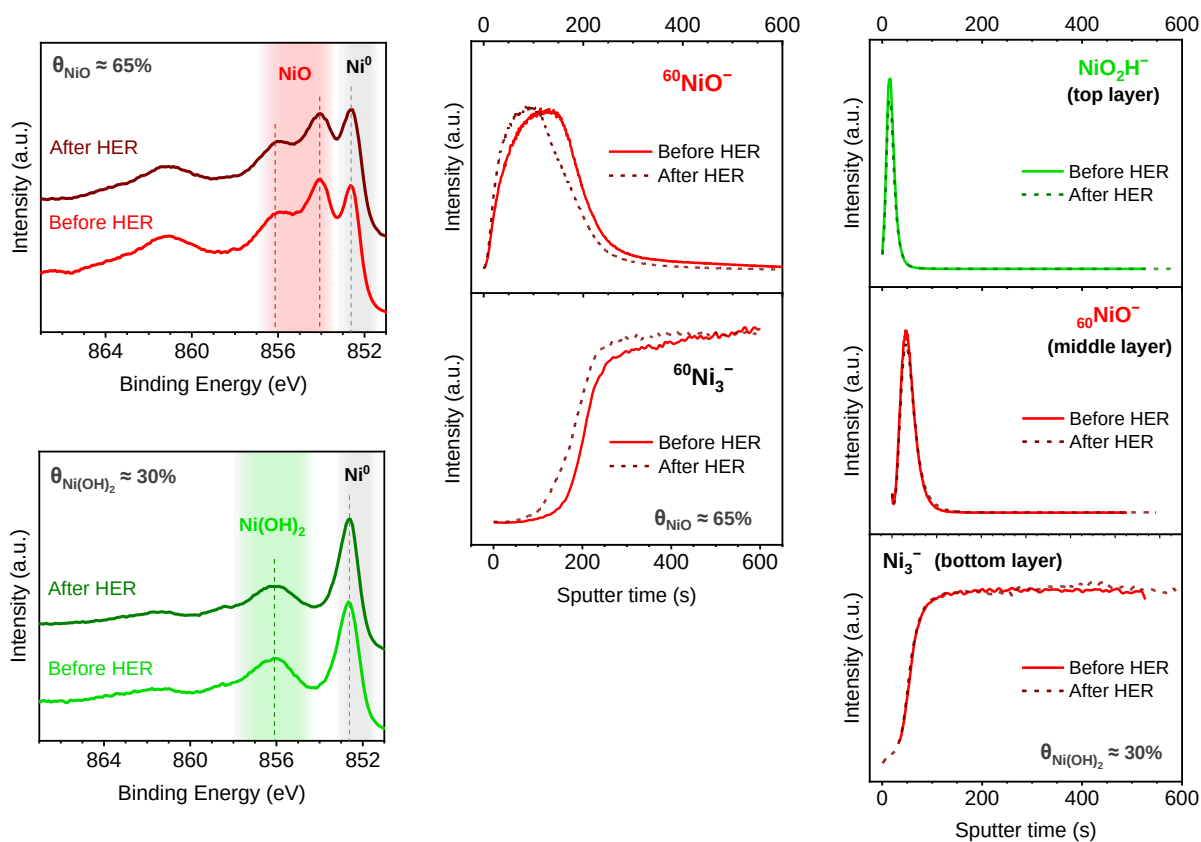


Figure R5. Post-measurement surface characterization of Ni_(O) and Ni_(OH) representative benchmark surfaces recorded before and after acquisition of the hydrogen evolution reaction (HER) polarization curves. **a,d**, High-resolution XPS Ni 2p_{3/2} spectra for Ni_(O) and Ni_(OH), respectively. **b,c**, ToF-SIMS depth profiles for the Ni_(O) and Ni_(OH), respectively. Both surfaces exhibit only minor changes in surface composition and coverage, indicating no significant irreversible reconstruction during the HER measurement.

In addition, post-measurement XPS and ToF-SIMS analyses (Figures R5) for Ni_(O) and Ni_(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.

For Ni_(H) and Ni⁰ surfaces, such analysis is inherently limited. Subsurface hydride species cannot be reliably detected by the employed spectroscopic techniques, while the metallic Ni⁰ surface cannot be preserved upon removal from electrochemical potential control and undergoes partial oxidation during transfer. As a result, characterization of the Ni⁰ state is experimentally limited to its preparation and probing under potential control and cannot be accessed in a post-measurement (ex situ) configuration. For Ni_(H) and Ni⁰ 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.**

(The above analysis has been added to the SI as Note S9)

3. All polarization curves presented in this study correspond to the first scan of each surface, recorded at a relatively high scan rates (50 mV s⁻¹). This is an effective method to avoid the impact of interface changes on performance. However, during the initial cycle test, the reconstruction of the surface electric double layer may introduce uncertainties to the polarization curve.

We thank the reviewer for this point. We interpret the comment as referring either to (i) capacitive/pseudocapacitive contributions during the first scan, or (ii) possible restructuring of the interfacial double layer, such as reorientation of water molecules or redistribution of cations.

If the concern is related to capacitive and pseudocapacitive currents that run in parallel with the Faradaic HER current, we note that at 50 mV/s these contributions are on the order of ~1–100 $\mu\text{A}/\text{cm}^2$. Such currents may affect the response at low overpotentials (from 0 to -0.2 V), where Ni surfaces still exhibit significant currents connected with the reduction of “reversible” Ni(OH)₂, but they are negligible in the potential range used for our analysis (from -0.2 V to -0.3 V).

If the concern is instead related to restructuring of the interfacial double layer, for example through rearrangement of water molecules or cations, we note that exploratory control experiments in which KOH was replaced by LiOH did not produce changes indicative of significant cation contribution to the surface-to-surface differences reported here. The consistent trends observed across the benchmark surfaces, together with the correlation to active-site availability and DFT-calculated reaction barriers, indicate that the dominant contributions in our system are captured within this framework.

4. The interfaces of Ni and loaded species may key active sites for HER (Science, 2011, 334, 1256-1260). Normalizing by interfacial quantities may provide more comprehensive evidence.

The reviewer makes a valid point. Our manuscript provides the specific activities of individual surfaces, where Ni available sites based on voltammograms are used to calculate the ECSA. Such normalization is relevant for Ni^0 , $\text{Ni}(\text{H})$ and $\text{Ni}(\text{O})$, where the reaction proceeds exclusively on metallic Ni sites. However, on $\text{Ni}(\text{OH})_2$, the fastest reaction proceeds on the Ni metal sites adjacent to $\text{Ni}(\text{OH})_2$, making the number of active sites significantly smaller. This makes the utilized normalization somewhat inconsistent. In fairness, however, we alluded to this on page 8 of the manuscript, when explaining the discrepancy between DFT that predicts 100-fold higher activity on $\text{Ni}/\text{Ni}(\text{OH})_2$ sites compared to Ni, vs. the experimentally measured 15-fold activation. The reason is exactly what the reviewer pointed out. The active surface area is only on the interface between Ni and $\text{Ni}(\text{OH})_2$ islands. A quick approximation of the “interfacial surface area” is shown in Figure R6. It depends on the ratio between the surface Ni atom diameter (~ 0.25 nm) and the radius of the $\text{Ni}(\text{OH})_2$ island. For the approximate size range of islands observed with the AFM ($r = 2\text{-}5$ nm corresponding to island diameters $4\text{-}10$ nm), we estimate that only $0.10\text{-}0.26$ of the $\theta_{\text{Ni}(\text{OH})_2}$ is actually involved in electrocatalysis. This means that the current specific activity for $\text{Ni}(\text{OH})_2$, reported in the paper, is underestimated by $\sim 4\text{-}10$ times, corresponding to $60\text{-}150$ -fold higher activity on $\text{Ni}/\text{Ni}(\text{OH})_2$ sites compared to metallic Ni sites.

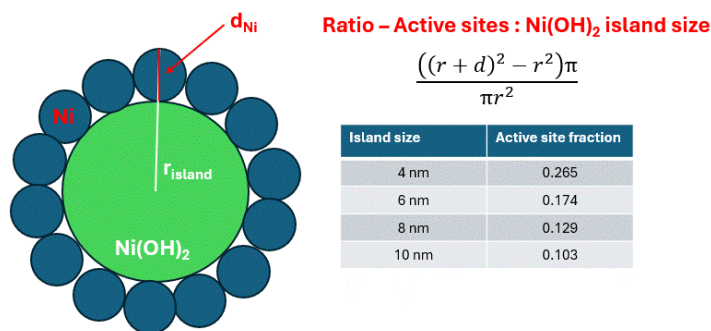


Figure R6. Estimation of the fraction of $\text{Ni}/\text{Ni}(\text{OH})_2$ active sites. Based on the ratio between the surface Ni atom diameter and the radius of the $\text{Ni}(\text{OH})_2$ island, we estimate that only $0.10\text{-}0.26$ of $\theta_{\text{Ni}(\text{OH})_2}$ is electrochemically active. This corresponds to a $60\text{-}150$ -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 Ni/Ni(OH)₂ interface as the relevant active motif and clarifies the apparent discrepancy between theory and experiment.

We have added a sentence to the manuscript on page 8 providing more clarity on this apparent discrepancy. (the detailed explanation has been added the SI, Note S5)

5. The text comparing the HER performance in Fig. 4b should be 98 % < 96 < 90 < 76 < 49 < 25 < 0%.

We thank the reviewer for drawing our attention to the typo in the arrow direction indicating the activity trend in Figure 4b. This has now been corrected, and the same adjustment has been applied to Figures 5b, S18b, and S19b.

Reviewer #4:

The article by Dzevad K. Kozlica et al. addresses, in a quite elegant way, how different oxo-hydroxo species on the surface of Nickel, as well as subsurface hydrogen or hydride formation, influence the onset potential and activity during alkaline HER.

The authors argue that thermally induced NiO essentially blocks active sites, thereby reducing HER activity; the formation of hydride changes the electronic structure, inhibiting HER; in contrast, electrochemically induced oxohydroxo species enhance HER activity by interacting with and altering the water solvent network, facilitating water dissociation.

To demonstrate the presence of different Ni surface species, XPS and ToF-SIMS were used to evaluate the chemical nature and oxidation state of adsorbed species, and their distribution at different depths (with ToF-SIMS). Surface coverage is carefully tuned during both thermal and electrochemical treatments, as verified and quantified by measuring changes in integrated charge in blank cyclic voltammograms of the prepared surfaces.

The cyclic voltammogram response looks clean, supporting control of experimental conditions. The initial Ni(0) benchmarking surface is also carefully prepared, yielding a relatively flat surface with clear grain boundaries. This detail is relevant because the growth or distribution of new surface species is likely dependent on substrate structure, and rough structures may result in uncontrolled coverage. Looking at the voltammetric profiles and

surface images, there is strong control over surface conditioning and preparation, resulting in well-defined interfaces.

From the reported blank cyclic voltammograms, it is clear that the observed effects in HER are not related to changes in electroactive surface area but instead to changes in surface structure, composition, and adsorbate distribution.

The effect of coverage of NiO and Ni(OH)₂ or NiOOH (electrochemical) is systematically addressed and reported, demonstrating that NiO only have a site-blocking effect, whereas HER on electrochemically-induced Ni(OH)₂-Ni(0) follows a volcano relationship with coverage, i.e. low amount of Ni(OH)₂ affects water solvent structure, but a high coverage block active surface sites. A similar effect and a potential shift at lower Ni(OH)₂ coverages have been observed for Pt surfaces modified with Ni(OH)₂.

Even though identifying the exact nature of surface species and site structure under reaction conditions may require future studies combining operando surface characterisation and in situ spectroscopy, the insights and messages of this article are important. In particular, I highlight three points: 1) The lack of normalisation of catalytic activity by the electroactive surface area is a problem that persists in the field of electrocatalysis, not only for Ni but also for other surfaces, and it is nice to highlight that and encourage others to measure active areas. 2) Surface pretreatment and conditioning have a tremendous impact on the catalytic properties of the surface, and therefore, working with well-defined surfaces is rather important to rationalise effects in catalysis. 3) Adsorbates of different natures affect catalysis by affecting the site structure or the electrolyte structure, as shown for Ni. These effects can be tuned by tuning the coverages of species. Quantification of surface coverage can be done by careful, systematic recording of blank cyclic voltammograms.

Based on the abovementioned reasons, I recommend this article for Nature Catalysis (with minor comments to assess), and I believe that this work will not only be of interest to those who need guidelines and descriptors to optimise their Ni-based catalyst, but will also encourage others to perform studies on well-prepared surfaces and use the cyclic voltammetry technique to address electrified interfaces.

We thank the reviewer for their time in evaluating our work and for highlighting its significance in such a detailed manner. Below, we provide responses to the comments.

1) I am not sure if the CO displacement technique is a valuable technique to evaluate Ni hydrides (Figure S5). The CO-displacement technique is used on Pt, Ir, Pd... i.e. on surfaces where CO adsorbs strongly. CO-displacement would not work, for example, on copper, because the adsorption of CO is too weak in this metal. My impression is that CO does nothing or is a spectator, and the negative current is just HER or hydride formation. If there

was CO on the surface, there should be a CO stripping peak in the CV, or a change in the CV. Reconsider the utility of this experiment in this situation.

We agree that the utility of the CO-displacement technique depends on whether CO adsorbs sufficiently strongly on the investigated surface under the relevant conditions.

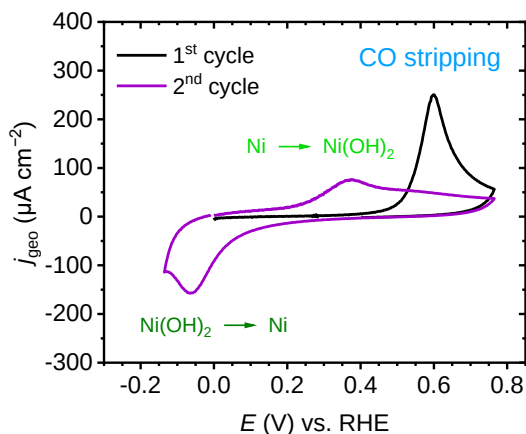


Figure R7. CO stripping on a Ni⁰ surface. The first cycle shows the absence of the oxidation peak associated with Ni(OH)₂ formation, due to blocking of the surface by adsorbed CO. At more positive potentials, CO is stripped from the surface, thereby exposing Ni sites, as evidenced by the appearance of anodic and cathodic features in the second cycle corresponding to Ni(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.

In the case of Ni, CO adsorption is well established in the literature [e.g., *J. Phys. Chem.*, **97** (1993)], and in our system this is further supported by the presence of a clear CO stripping feature in the cyclic voltammogram (Figure R7). 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. If significant H_{ad} were present on the surface, its displacement during CO adsorption would be expected to produce a distinct positive current contribution. We do not observe such a response in Figure S5. Instead, the signal is consistent with progressive suppression of HER as CO blocks the surface.

We therefore conclude that the hydrogen species formed under our conditions are not predominantly present as surface-adsorbed hydrogen. While the CO-displacement experiment alone does not determine the exact location of hydrogen with complete certainty, in combination with the voltammetric behavior and the literature on Ni hydride formation, it supports our assignment of hydrogen residing predominantly beneath the surface.

(We have added the additional explanation and figure to SI, note S3)

2) The voltammetric behaviour in Fig 2b, showing an increased anodic peak after holding the electrode at -0.4 V, is similar to that reported in other metals, which also form a hydride phase, for example, Cu. For Cu, spectroscopic evidence of hydride formation is observed. Maybe referring to other metal examples can reinforce the assumption of hydride in Ni, even though the article does not provide direct speciation measurements, which are challenging. 10.1021/acs.jpcclett.1c03131.

We thank the reviewer for the valuable suggestion. We added the citation in the discussion part of the manuscript (page 5, highlighted in yellow).

3) The shift toward lower onset potential with Ni(OH)₂ coverages up to 40% has also been observed on Pt(111). Over 40%, site-blocking effects predominate. Consider whether this simile is useful for reinforcing the discussion. 10.1021/acsami.8b15003

We found this reference valuable for strengthening the discussion and have therefore added it to the manuscript (page 12, highlighted in yellow).

4) I understand that the objective of this work is not to address the stability of the prepared interfaces but just to evaluate how the coverage of different adsorbates influences the onset potential and HER activity on Ni electrodes. Nevertheless, I think it is valuable to show the blank cyclic voltammograms (CVs) after the HER cyclic voltammograms in Figure 3a (30% coverage of individual species) to ensure that blank CVs do not change dramatically, indicating electrolyte contamination or other factors to consider. This is a common practice when evaluating the catalytic performance of, e.g. metal single crystals, particularly in alkaline media or 0.1 M KOH, which sometimes contain traces of impurities.

The answer to this question is provided in detail in our response to the second comment from Reviewer 3. Briefly, we showed that the cyclic voltammograms change negligibly, by up to ~7%.