



Combining ToF-SIMS and Multivariate Analysis to Resolve Active Sites on Ni-Based HER Catalysts

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Abstract: Unambiguous identification of active sites in heterogeneous catalysis remains a major challenge, particularly for materials with ultrathin, chemically mixed surface layers. Here, we demonstrate a generalizable approach that combines time-of-flight secondary ion mass spectrometry (ToF-SIMS) with multivariate statistical analysis (principal component analysis [PCA] and multivariate curve resolution [MCR]) to resolve catalytically relevant motifs at the nanoscale. Using Ni electrodes as a model system, PCA distinguished hydroxide-enriched domains from oxide- and metal-rich regions, while MCR decomposed depth profiles and 3D images into hydroxide, oxide, and metallic layers with nanometer resolution. A unique secondary-ion fragment, NiO_3H_3^- (m/z 108.94), emerged as a marker of hydroxide-rich environments and correlated with hydrogen evolution reaction (HER) activity across a series of Ni electrodes. Complementary density functional theory (DFT) calculations revealed that $\text{Ni}(\text{OH})_2$ clusters adjacent to metallic Ni offer the most favorable water dissociation energetics, establishing the structural origin of the marker. While illustrated here for Ni-based HER, this workflow provides a broadly applicable framework to isolate and rank near-surface patterns that govern catalytic activity, thereby extending ToF-SIMS from a qualitative probe to a predictive tool for active site identification.

Introduction

Understanding the identity and structure of active sites on catalyst surfaces remains one of the central challenges in heterogeneous catalysis. The concept of active sites, specific atomic ensembles that govern catalytic activity and selectivity, was first postulated by Taylor in 1925.^[1] Despite a century of progress, these sites remain difficult to isolate and characterize, particularly in complex, real-world materials. Exact identification of these sites is essential for rational

catalyst design and optimization, especially as the field moves toward more earth-abundant, chemically diverse alternatives to noble metals.

The standard strategy for uncovering active sites combines synthesizing model or shape-controlled catalysts with defined surface terminations, detailed surface characterization, and theoretical modeling, most often via density functional theory (DFT).^[2–9] Techniques such as surface x-ray diffraction (SXRD), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, x-ray absorption spectroscopy (XAS), and scanning probe microscopy (SPM) or scanning transmission electron microscopy (STEM) have been instrumental in resolving structural and chemical properties of well-defined catalysts.^[10–16] This strategy has proven highly effective in noble metal systems like Pt-based catalysts, where clean, well-controlled surfaces can be reproducibly prepared and easily interpreted.

However, this framework becomes increasingly limited when applied to more chemically complex materials. Ni-based catalysts, for example, represent an important class of earth-abundant materials used in electrocatalytic hydrogen evolution (HER) and oxygen evolution reactions (OER), but their surface composition is often a dynamic mixture of pristine metallic Ni, Ni oxides, Ni hydroxides (α - and β - $\text{Ni}(\text{OH})_2$), Ni hydrides, and Ni oxyhydroxides (e.g., α -/ γ - NiOOH). These phases can coexist at ultrathin surface coverages, often below a monolayer, making both their identification and spatial resolution extraordinarily difficult.

Such complexity poses significant challenges for conventional surface analysis techniques, which may lack the surface sensitivity, chemical specificity, or depth resolution

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needed to detect and differentiate these overlapping species, especially when they exist in mixed or partial monolayer configurations.^[17–19] Invaluable spectroscopic methods such as XPS, UPS, Raman, and XAS typically integrate signals over depths much greater than the ultrathin interfacial regions that often govern catalytic behavior. XPS and UPS achieve surface sensitivity on the order of a few nanometers,^[20] while Raman and XAS probe hundreds of nanometers or more.^[21,22] These penetration depths lead to averaging of bulk and surface contributions, obscuring chemical gradients confined to only a few atomic layers. On the other hand, scanning probe electrochemical methods respond exclusively to surface electrochemical properties. Scanning electrochemical microscopy (SECM) maps spatial variations in electrochemical reactivity via faradaic tip currents, whereas scanning ion conductance microscopy (SICM) provides non-contact topography (and local ion-transport/charge-related contrast) via ionic conductance. While both enable (quasi-)operando measurements in electrolyte, their lateral resolution is in the 100 nm–10 μ m range and neither technique intrinsically provides molecular-level speciation of surface components.^[23–25] In contrast, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has a low penetration depth, excellent mass resolution, and controllable sputter-depth profiling, while also providing chemical information about surface species and their matrix, making it exceptionally suited for detecting ultrathin layers and buried or gradient interfaces.

Despite these advantages, ToF-SIMS remains strikingly underutilized in electrocatalysis, particularly in efforts to identify surface species or active sites. Instead, techniques like XPS, (S)TEM, and XAS remain the default choices for surface and oxidation state analyses. The underuse of ToF-SIMS stems not from technical shortcomings, but from challenges in data interpretation: the technique generates rich and complex fragmentation patterns, where chemically similar secondary ions (fragments) can be generated from different parent species and different chemical environments, depending on local bonding, sputter conditions, and matrix effects. As a result, ToF-SIMS has typically been applied in a limited or qualitative capacity, rather than as a quantitative tool for active site identification.

To address these limitations, herein, a methodology is presented that couples ToF-SIMS with multivariate statistical tools, that is, principal component analysis (PCA) and multivariate curve resolution (MCR), to resolve and interpret complex chemical environments on catalytic surfaces. Applying PCA allows patterns and compositional differences to be revealed, separating signals that may otherwise be indistinguishable. MCR further enhances this by decomposing spectral data into MCR factors, enabling the identification and localization of distinct layers.^[26–35]

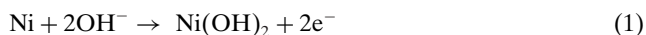
We applied this approach to our recently developed, well-defined model system comprising Ni surfaces with varying degrees of hydroxide and oxide modification—materials representative of real HER electrodes in alkaline electrolytes.^[36] These surfaces feature nanoscale mixtures of Ni(OH)₂ and NiO, phases that are notoriously difficult to distinguish and quantify using conventional surface techniques. By combining ToF-SIMS with PCA and MCR, we resolved chemically

distinct layers, extracted indicative secondary ions, and identified a unique marker associated with highly active Ni(OH)₂-modified Ni domains.

Beyond the specific case of Ni HER catalysts, this work establishes a generalizable framework for applying ToF-SIMS in electrocatalysis. The approach not only provides depth-resolved tracking of surface species and discrimination between active and inert domains, but also transforms ToF-SIMS from a largely qualitative probe into a robust, predictive tool for identifying catalytic motifs in complex materials. Such systematic application of ToF-SIMS coupled with multivariate analysis opens a new pathway toward rational catalyst design based on direct identification of active-site chemistry.

Results and Discussion

Five different Ni samples with controlled surface compositions were prepared (i.e., Ni(OH)₂^{28%}, Ni(OH)₂^{6%}, Ni_{AP}, Ni(O)₂^{49%}, and Ni(O)₂^{90%}; for details see Section *Sample Preparation* in Supporting Information, SI) to investigate the relationship between surface chemistry and HER activity. These surfaces were synthesized using optimized procedures to achieve exact coverages of Ni-based species on Ni substrate (as explained in^[36]). The coverage by individual oxygenated Ni surface species (Θ_{ad}) was deduced from the charge under the anodic peak at 0.40 V in the cyclic voltammograms shown in Figure 1a, corresponding to the oxidation of metallic Ni per Equation 1. The fraction of Ni metallic sites corresponds to (1 – Θ_{ad}).



The Ni_{AP} surface, exhibiting a charge of 516 $\mu\text{C}/\text{cm}^2$, was used as a reference, corresponding to 100% of surface Ni atoms being electrochemically accessible (i.e., $\Theta_{\text{ad}} = 0$). The coverage by NiO or Ni(OH)₂ species on the other four surfaces was then evaluated by comparing the cyclic voltammograms to the reference cyclic voltammogram of Ni_{AP}, with the difference in the charge corresponding to Θ_{ad} .^[36]

The initial chemical composition of individual surfaces was inferred from Ni 2p_{3/2} XPS spectra in Figure 1b. The Ni(OH)₂-modified surfaces showed dominant features at 852.5 eV and 856.0 eV, typical for metallic Ni and Ni(OH)₂, respectively.^[37] The Ni(O)₂ surfaces displayed the distinctive peaks at 854.2 eV and 855.9 eV, both attributed to NiO,^[37] in addition to the metallic Ni signal at 852.5 eV. Lastly, the XPS spectrum of Ni_{AP} shows a prominent metallic Ni signal, with a spectral feature from (hydr)oxide contribution due to air exposure during transfer.

These chemically distinct surfaces exhibited markedly different HER activities, with the explicit roles of individual Ni surface species discussed in detail in our recent study.^[36] As shown in Figures 1c–e, the catalytic activity followed the trend: Ni(OH)₂^{28%} > Ni(OH)₂^{6%} > Ni_{AP} > Ni(O)₂^{49%} > Ni(O)₂^{90%}, with the most active surface Ni(OH)₂^{28%} approximately three orders of magnitude more active than the least active Ni(O)₂^{90%}. This significant variation in HER performance,

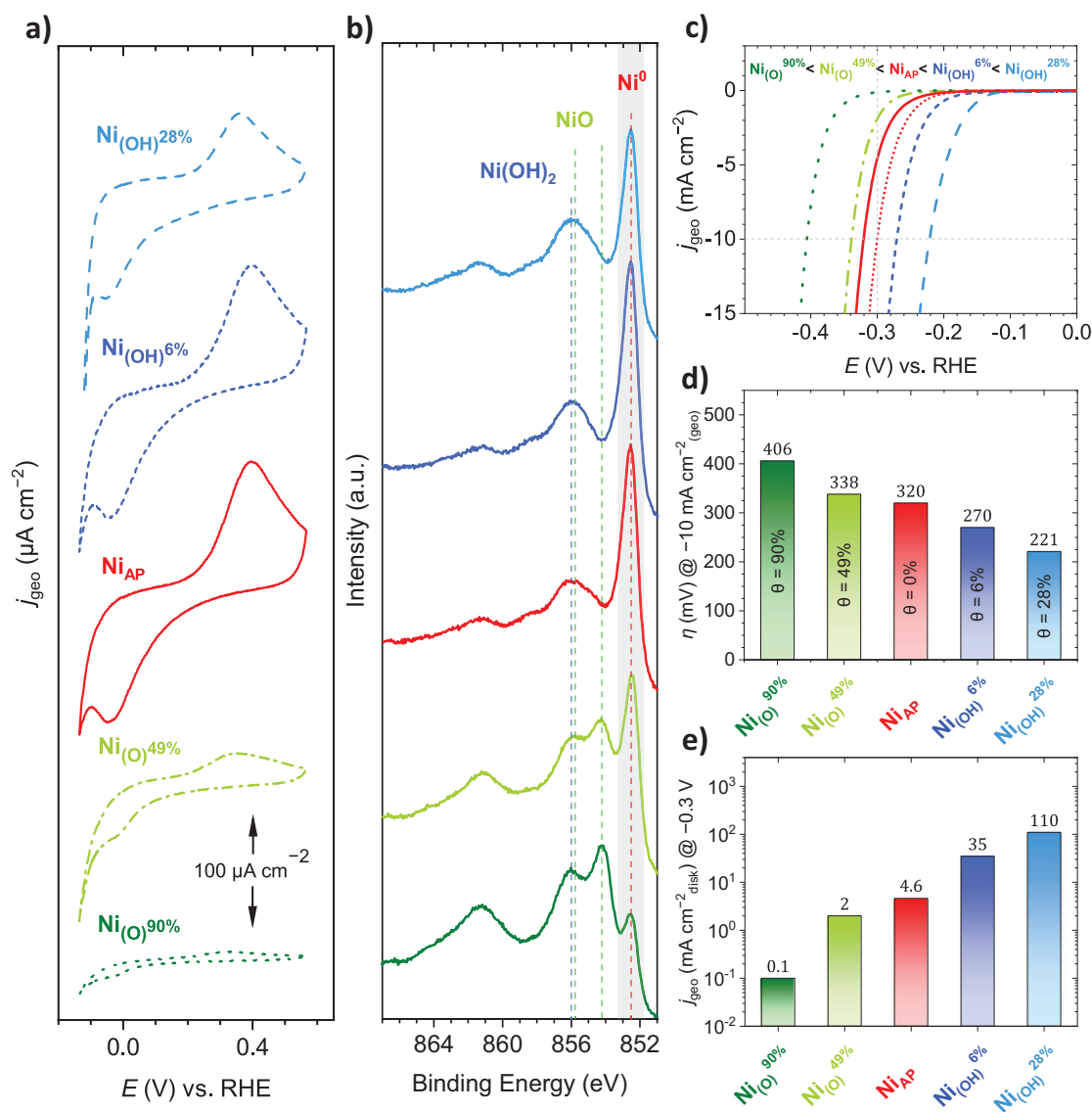


Figure 1. a,c,d,e) Electrochemical and b) XPS characterization of five different Ni surfaces: $\text{Ni(OH)}_2^{28\%}$, $\text{Ni(OH)}_2^{6\%}$, NiAP , $\text{Ni(O)}^{49\%}$, and $\text{Ni(O)}^{90\%}$; a) Cyclic voltammograms measured in 0.1 M KOH at a sweep rate of 50 mV s^{-1} and 3600 rpm. E denotes the electrode potential referenced to the reversible hydrogen electrode (RHE); b) $\text{Ni } 2p_{3/2}$ XPS spectra; c) HER polarization curves; d) HER activities—overpotential (η) at geometric current density of 10 mA cm^{-2} ; e) HER activities—geometric current density (j_{geo}) at -0.30 V versus RHE. All polarization curves were corrected for IR drop (100% compensation), where I stands for current and R for resistance.

arising from subtle changes in surface composition of these five well-defined surfaces, thus served as an ideal testbed for evaluating how surface chemical composition influences HER activity, and for identifying robust spectroscopic markers that correlate with reactivity. However, as discussed below, XPS and cyclic voltammetry (CV) techniques fall short in providing unambiguous chemical information that can explain the observed catalytic trends.

Although the CV is vital for characterizing electrochemical behavior, it provides no direct information on chemical composition. This limitation is evident in Figure 1a, where there is a clear disconnect between the trend in the features observed in cyclic voltammograms and the HER activity trend depicted in Figures 1c–e. Namely, HER activity increases as the anodic peak for the Ni(OH)_2 surfaces decreases at higher

surface coverage, whereas for the Ni(O) surfaces, the HER activity decreases with increasing coverage as the anodic peak decreases. This lack of correlation between voltametric features and HER activity highlights the need for surface-sensitive techniques capable of directly probing chemical identity. The most employed analytical tool for this purpose is XPS, but it suffers from key drawbacks when applied to Ni-based or similar complex systems. In particular, the $\text{Ni } 2p_{3/2}$ region shows substantial overlap between NiO and Ni(OH)_2 peaks,^[38–41] making confident chemical assignment challenging. Moreover, as illustrated in Figure 1b, even minor spectral differences correspond to substantial differences in HER activity, underscoring how difficult it is to derive definitive mechanistic insights from XPS alone. The situation is further complicated by the layered nature of these surfaces.

Thin Ni hydroxide films may obscure underlying Ni oxide layers, limiting the surface sensitivity of XPS. Additionally, for the analysis of alloys, XPS and Auger peaks overlap, such as those for Ni 2p_{3/2} and the Mn L₃VV Auger transition, which pose problems in multi-element systems.^[42]

In contrast, ToF-SIMS offers significantly enhanced surface sensitivity and depth resolution, particularly when operated with a low-energy Cs⁺ sputter source (250 eV). Unlike O₂⁺ sources, Cs⁺ sputtering does not introduce oxidative artifacts. In negative polarity, Ni oxides and hydroxides preferentially yield distinct secondary ions (e.g., NiO[−], Ni₂O₃[−], NiOH[−], NiO₂H[−]), facilitating compositional analysis of the outermost atomic layers. ToF-SIMS can produce parent ions; however, in the present case, it produces and detects secondary ions that are significantly influenced by the local atomic environments: the formed secondary ions are influenced by the local bonding geometry, chemical composition, and immediate matrix from which they are ejected. This makes them highly susceptible to subtle variations in surface structure, but also difficult to interpret without additional context. Importantly, because these secondary ions encode information about their local chemical surroundings, they can potentially serve as indirect fingerprints of the catalytic microenvironments, offering a route to identifying active site motifs based on their fragmentation signatures—provided that the spectral complexity can be effectively resolved.

Despite its strengths, the interpretation of ToF-SIMS spectra is inherently challenging. Many secondary ions, such as NiO[−] and NiO₂[−], have been reported for both NiO and Ni(OH)₂ phases,^[39,42–47] owing to shared fragmentation pathways. Moreover, as reported by Mazenc et al.,^[47] due to surface hydroxylation effects, signals like NiOH[−], NiOH₂[−], NiO₂H[−], and NiO₂H₂[−] may also arise from both NiO and Ni(OH)₂ phases (for the summary of reported ToF-SIMS signals for Ni, Ni hydroxide, and Ni oxide, see Table S1 in SI). This overlap limits the unambiguous assignment of individual secondary ions to specific surface phases and complicates efforts to track catalytically relevant species.

To overcome these challenges, PCA and MCR were applied to ToF-SIMS datasets. These data-driven methods enabled the deconvolution of complex spectra, isolating statistically significant variations associated with chemically distinct species. By correlating multivariate signal patterns with known reference materials and experimental trends, this approach provided a robust framework for the identification of Ni surface phases.

Differentiation between Ni_(OH), Ni_{AP}, and Ni_(O) Surface Species Using ToF-SIMS and PCA/MCR

To resolve the subtle but catalytically critical differences in surface chemistry between Ni_(OH), Ni_{AP}, and Ni_(O) surfaces, ToF-SIMS was employed in combination with PCA and MCR. These multivariate statistical tools help distill complex spectral data by uncovering hidden patterns: PCA reduces dimensionality of the dataset to highlight key differences between samples, while MCR separates mixed signals into distinct, chemically meaningful components. While conven-

tional analytical techniques struggle with overlapping spectral features and limited surface sensitivity and exactness to assign chemical species, the approach presented herein enables direct, chemically specific interrogation of surface and sub-surface layers, down to fractions of a monolayer, that can significantly affect HER activity.

Ni_(OH)^{28%}, Ni_(O)^{49%}, and Ni_{AP} surfaces were selected as representative samples for multivariate analysis because they exemplify the three distinct protocols used to prepare the broader set of Ni-based catalysts examined in this study. These samples served as anchors for classifying and interpreting the full range of surface chemistries encountered.

Detailed PCA processing and explanation for the differentiation between Ni_(OH), Ni_(O), and Ni_{AP} surfaces are presented in Note S1 in SI. PCA was applied to composite ToF-SIMS spectra constructed from cumulative depth profiles signals at different sputter time intervals (from 0–50 s to 0–900 s). These composite ToF-SIMS spectra capture the evolving surface composition as sputtering progresses, from the outermost layers to the bulk. This stepwise profiling was crucial for distinguishing between Ni_(OH)^{28%} and Ni_(O)^{49%}/Ni_{AP} surfaces.

As presented on the PCA score plots for a single principal component (PC) (Figure 2a–g), PCA consistently yielded a distinct PC (PC 1), exhibiting a strong positive correlation with Ni_(OH)^{28%} (PCA scores for Ni_(OH)^{28%} are represented as blue bars) across all depths. In contrast, Ni_{AP} (red bars) and Ni_(O)^{49%} (green bars) exhibited a negative correlation with PC 1 (Figure 2a–g). The PC 1 versus PC 2 and PC 1 versus PC 5 PCA score plots (Figure 2h–v) showed clustering of PCA scores, representing replicate Ni_(OH)^{28%} samples with 95% confidence ellipses that do not overlap with those for Ni_(O)^{49%} and Ni_{AP}. These results demonstrate that such an approach can differentiate Ni_(OH)^{28%} from Ni_(O)^{49%} and Ni_{AP} solely based on the surface layer compositions. Moreover, MCR processing of the same composite ToF-SIMS spectra that were used for PCA resulted in one distinct MCR factor for Ni_(OH)^{28%}, with more intense MCR scores compared to Ni_(O)^{49%} and Ni_{AP} (Figure S2 in SI).

Despite successful differentiation of Ni_(OH)^{28%}, PCA revealed some overlapping of clusters for Ni_{AP} and Ni_(O)^{49%}, indicating similarities between surface chemistries. This likely reflects the formation of a native NiO layer on Ni_{AP}, even under inert transfer conditions, due to the inherent thermodynamic instability of metallic Ni in ambient environments encountered during sample transfer.

Furthermore, as explained in Note S2 in SI, segmenting the data into the middle section sputter time intervals (i.e., 50–100 s, 150–200 s, 200–250 s, and 150–250 s), Ni_(OH)^{28%} can be distinguished at shallow-to-moderate sputter depths, whereas at deeper regions, PC 1 and the first MCR factor are associated with the Ni_(O)^{49%} analyte (Figures S3–S5). The PCA and MCR loadings further reveal that PCs/MCR factors that differentiate Ni_(OH)^{28%} from the other two analytes exhibit hydroxide-rich signals, while PCs/MCR factors that differentiate Ni_(O)^{49%} are dominated by oxide-rich signals (Note S3 in SI emphasizing signals with the most intense PCA and MCR loadings in Tables S2–S5).

As explained above and in Notes S1–S3, PCA and MCR provided differentiation of Ni_(OH)^{28%} (or, to some extent,

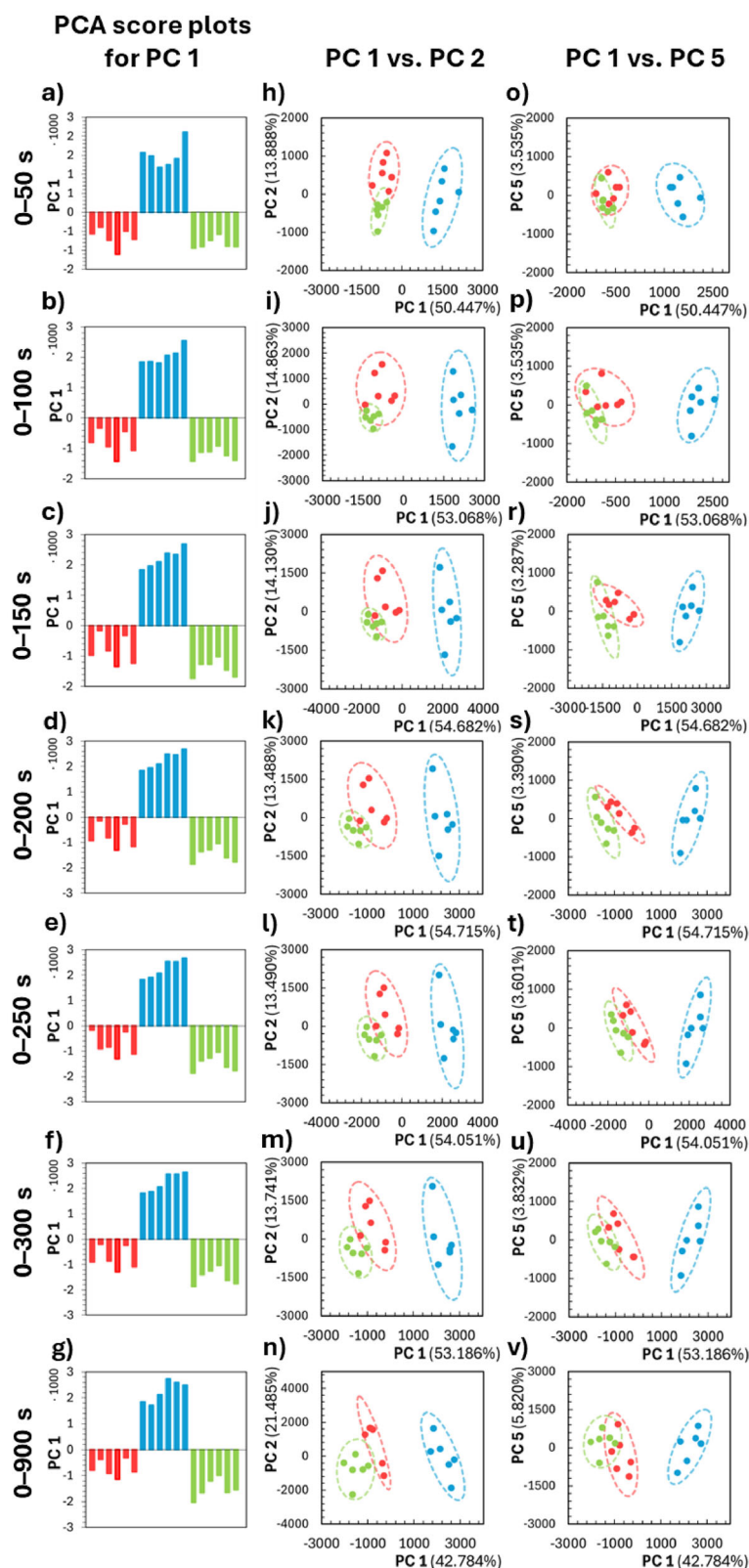


Figure 2. a–v) PCA score plots illustrating the differentiation of $\text{Ni}(\text{OH})^{28\%}$ (blue), $\text{Ni}(\text{O})^{49\%}$ (green), and Ni_{AP} (red) derived based on composite ToF-SIMS spectra collected at different sputter time intervals. Plots display the results of PCA processing of composite ToF-SIMS spectra from sputter time intervals of a,h,o) 0–50 s, b,i,p) 0–100 s, c,j,r) 0–150 s, d,k,s) 0–200 s, e,l,t) 0–250 s, f,m,u) 0–300 s, and g,n,v) 0–900 s. The h–n) PC 1 versus PC 2 and o–v) PC 5 versus PC 1 score plots show clustering with 95% confidence ellipses of $\text{Ni}(\text{OH})^{28\%}$ (blue), distinguishing from $\text{Ni}(\text{O})^{49\%}$ (green) and Ni_{AP} (red).

in deeper layers also $\text{Ni}_{(\text{O})}^{49\%}$) from the remaining analytes based on overall surface composition. To resolve the distribution of chemical signals and capture the spatial evolution of surface species, MCR was applied to the ToF-SIMS depth profiles and 3D ToF-SIMS imaging datasets (0–900 s sputter time interval). Under the employed sputtering conditions, depth profiles were limited to the first few nanometers. Since the electrocatalytic properties are determined by first few atomic layers, the relevant information is expected to be contained in the first part of the depth profile. ToF-SIMS possesses the depth resolution of a few angstroms (corresponding to a monolayer-to-submonolayer regime), so it allows us to distinguish even atomically thick individual phases from each other, as demonstrated below.

The selection of four factors for MCR processing reflects the layered structure of Ni surfaces subjected to electrochemical or atmospheric conditions. For $\text{Ni}_{(\text{OH})}^{28\%}$, the four MCR factors correspond to distinct layers that develop during the formation of oxides and hydroxides as:

1. 1st layer (i.e., the outermost layer), which consists of adventitious carbonaceous species, originating from environmental exposure,
2. 2nd layer beneath the contamination layer, corresponding to the catalytically active Ni hydroxide layer, which plays a crucial role in electrochemical reactions,
3. 3rd layer, corresponding to the Ni oxide sublayer, which forms beneath Ni hydroxide through progressive oxidation, and
4. 4th layer that corresponds to bulk Ni, detected at greater depths, where the sputtering process reveals the Ni substrate.

A similar MCR four-factor model was applied to $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} to account for the comparable layered structures observed across different analytes. For these analytes, the MCR factor associated with 2nd layer correlates with Ni oxide (however, this layer also contains Ni-O-H species, as shown in Table S5) as the dominant phase, while the third MCR factor reflects deeper oxide regions or transitional Ni oxide species. This uniform application of four MCR factors across all samples ensures consistent analysis and facilitates direct comparison of $\text{Ni}_{(\text{OH})}^{28\%}$ with $\text{Ni}_{(\text{O})}^{49\%}$, and Ni_{AP} .

Figure 3a–c displays the MCR processing of ToF-SIMS depth profiles, illustrating how the contribution of each chemical layer (MCR factor) changes during sputtering. It shows that the three analytes (Ni surfaces) differ in (i) the sputter-time intervals over which the MCR factors are present, reflecting the apparent thickness of the respective layers; (ii) the degree of overlap between MCR factors, indicating the persistence and simultaneous presence of multiple layers; and (iii) the shape and decay behavior of MCR factors, which reflects the rate at which the layers diminish with depth. For $\text{Ni}_{(\text{OH})}^{28\%}$ (Figure 3a), MCR factors for the 2nd and 3rd layers indicate an extended and gradual transition from hydroxide to oxide before reaching metallic Ni, consistent with a structured hydroxide-oxide-metal interface. MCR factors for the 1st and 2nd layers decay within the first ~50 s, and the MCR factor for the bulk reaches a steady state by ~70 s, indicating a relatively thin oxidized overlayer. $\text{Ni}_{(\text{O})}^{49\%}$ (Figure 3b) exhibits a delayed bulk plateau (~100–

120 s), while the oxide-related MCR factor for the 3rd layer extends deeper and persists until ~150 s. For $\text{Ni}_{(\text{O})}^{49\%}$, the oxide-related 3rd layer is therefore thicker, and a more gradual oxide-to-metal transition is observed. In contrast, Ni_{AP} (Figure 3c), compared to $\text{Ni}_{(\text{O})}^{49\%}$, exhibits a more rapid decrease of oxide-related MCR factor for the 3rd layer, due to a very thin native oxide film. Accordingly, the bulk plateau is reached earlier (~70–80 s) than in $\text{Ni}_{(\text{O})}^{49\%}$.

To capture spatial inhomogeneity, the MCR processing was also applied to 3D ToF-SIMS images (Figure 3d–s). This provided a volumetric perspective of each layer's distribution and confirmed the MCR factors separation across the imaged volume.

The MCR results provided a chemically resolved, depth-dependent presentation of the three representative analyte surfaces and showed that the highly active $\text{Ni}_{(\text{OH})}^{28\%}$ surface is chemically and compositionally different than $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} . This layered decomposition was essential for isolating species correlated with catalytic performance and laid the foundation for identifying characteristic and unique markers presented in Section *Correlating NiO_3H_3^- Intensity with HER Activity: From Signal to Active Site*.

Following MCR processing, characteristic signals were identified for the 2nd and 3rd layers—those layers are the most relevant to catalytic performance. If an MCR loading for a signal had high intensity for one MCR factor, but had negligible (or zero) intensity for all other MCR factors, that signal was considered characteristic. In this analysis, only characteristic signals observed in all six replicate ToF-SIMS measurements were retained. The characteristic signals are summarized in Table 1 (for 3D ToF-SIMS images analysis) and Table S6 in SI (for depth profile analysis), offering a robust set of layer-specific markers for $\text{Ni}_{(\text{OH})}^{28\%}$, Ni_{AP} , and $\text{Ni}_{(\text{O})}^{49\%}$.

Among the characteristic signals in Tables 1 and S6, the signal NiO_3H_3^- (m/z 108.94) emerged as a particularly notable one, as it appeared exclusively in the 2nd layer of the $\text{Ni}_{(\text{OH})}^{28\%}$ analyte. As shown in Figure S6a,d, the MCR loading of this signal exhibits high intensity for the MCR factor for the 2nd layer in $\text{Ni}_{(\text{OH})}^{28\%}$, with negligible or no contribution to other MCR factors. In contrast, for $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} (Figures S6b–f), the NiO_3H_3^- signal was not found to be characteristic for the 2nd layer. This absence strongly supports the designation of NiO_3H_3^- as a unique marker of the MCR factor for the 2nd layer (i.e., the hydroxide-rich layer) of $\text{Ni}_{(\text{OH})}^{28\%}$, thereby distinguishing it from the oxide-dominated compositions of $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} . For a more detailed explanation of characteristic and unique signal determination, see Note S4 in SI.

It has to be pointed out that NiO_3H_3^- signal was also detected (but was not characteristic signal), albeit at lower intensity, in the near-surface regions of $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} . However, its greater intensity, persistence into deeper layers, and direct association with the hydroxide-rich region in $\text{Ni}_{(\text{OH})}^{28\%}$ differentiate it from the other analytes. This is further supported by ToF-SIMS depth profiles (Figures 4a–d) and 3D ToF-SIMS images (Figures 4e–g), where NiO_3H_3^- displays a broader and more gradual depth distribution in $\text{Ni}_{(\text{OH})}^{28\%}$, indicating a greater extent of species producing

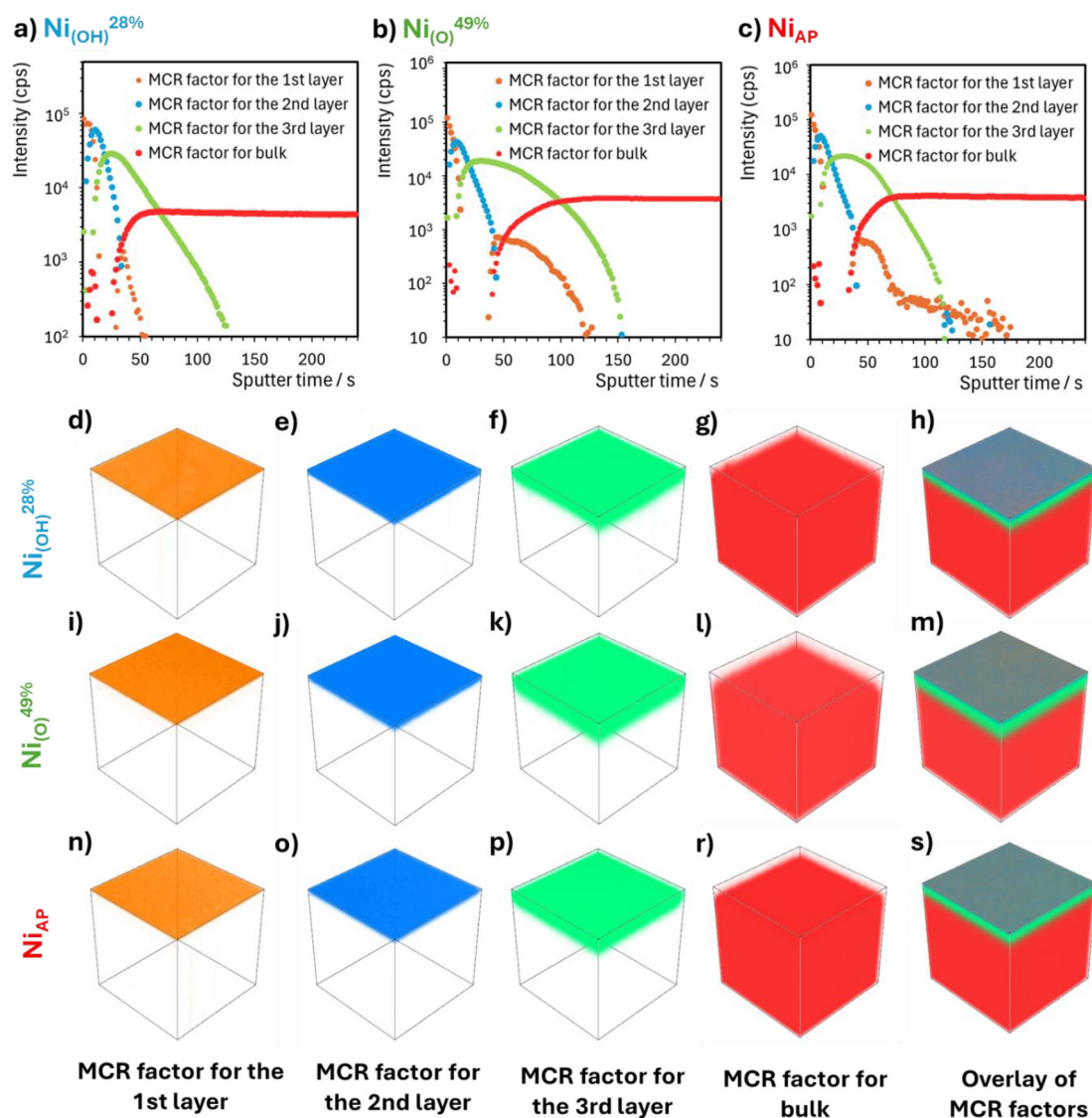


Figure 3. a–c) The determined MCR factors after MCR processing of ToF-SIMS depth profiles for a) $\text{Ni}_{(\text{OH})}^{28\%}$, b) $\text{Ni}_{(\text{O})}^{49\%}$, and c) Ni_{AP} . d–s) The MCR factors after MCR processing of 3D ToF-SIMS images (sputter time interval 0–900 s) for d–h) $\text{Ni}_{(\text{OH})}^{28\%}$, i–m) $\text{Ni}_{(\text{O})}^{49\%}$, and n–s) Ni_{AP} . For every analyte, the data are shown for one measurement.

NiO_3H_3^- secondary ion in direct contact with underlying metallic Ni (see intercept of NiO_3H_3^- and Ni_2^- signal intensities in Figure 4a,b corresponding to the Ni hydroxide and Ni metal abundance, respectively) compared to $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} . This property is also visible in ToF-SIMS depth profiles normalized to Cs^+ and Ni_2^- signals intensities (Figure S7).

Based on these findings, the signal for NiO_3H_3^- was subsequently employed as the selected interval for spatial scaling in PCA processing. As shown in the PCA score plots (Figure 4h,i) for PC 1 and PC 1 versus PC 2 (sputter time interval 0–900 s), the PCA scores for $\text{Ni}_{(\text{OH})}^{28\%}$ are clearly separated from the PCA scores of the remaining analytes, clustered close to zero intensity. This demonstrates that spatial scaling based on NiO_3H_3^- directly confirms the relation of this signal with the $\text{Ni}_{(\text{OH})}^{28\%}$, thereby functionally distinguishing it from the $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} analytes. The explicit connection of this signal to the hydroxide-rich 2nd layer of

$\text{Ni}_{(\text{OH})}^{28\%}$ is further confirmed by incorporating NiO_3H_3^- for spatial scaling in PCA processing of data collected across different sputter time intervals (Figure S8a–e), where consistent separation of $\text{Ni}_{(\text{OH})}^{28\%}$ analyte from $\text{Ni}_{(\text{O})}^{49\%}$ and Ni_{AP} was observed for the sputter time intervals that cover the hydroxide-associated shallow depths.

Correlating NiO_3H_3^- Intensity With HER Activity: from Signal to Active Site

Having established NiO_3H_3^- as a distinguishing feature of the $\text{Ni}_{(\text{OH})}^{28\%}$ surface, its intensity was next sought to be correlated with the catalytic performance of the full set of Ni surfaces. To this end, two additional samples, $\text{Ni}_{(\text{OH})}^{6\%}$ and $\text{Ni}_{(\text{O})}^{90\%}$, originally introduced in Figure 1 but not included

Table 1: Characteristic signals with MCR loadings that contribute most significantly to MCR factors for the 2nd and 3rd layer. The analysis was made after MCR processing (6 replicates) of the 3D ToF-SIMS images (these images correspond to depth profiles for the sputter time interval of 0–900 s).

Analyte	Characteristic signals		
	$\text{Ni(OH)}^{28\%}$	$\text{Ni(O)}^{49\%}$	NiAP
2nd layer	93.94 ($^{60}\text{NiO}_2\text{H}_2^-$)	164.86 ($\text{Ni}_2\text{O}_3\text{H}^-$)	93.94 ($^{60}\text{NiO}_2\text{H}_2^-$)
	95.93 ($^{62}\text{NiO}_2\text{H}_2^-$)	166.86 ($^{60}\text{NiNiO}_3\text{H}^-$)	94.93 ($^{62}\text{NiO}_2\text{H}_2^-$)
	164.86 ($\text{Ni}_2\text{O}_3\text{H}^-$)	168.85 ($^{60}\text{Ni}_2\text{O}_3\text{H}^-$)	95.93 ($^{62}\text{NiO}_2\text{H}_2^-$)
	108.94 (NiO_3H_3^-)		168.85 ($^{60}\text{Ni}_2\text{O}_3\text{H}^-$)
	166.86 ($^{60}\text{NiNiO}_3\text{H}^-$)		
3rd layer	75.93 ($^{60}\text{NiO}^-$)	75.93 ($^{60}\text{NiO}^-$)	75.93 ($^{60}\text{NiO}^-$)
	77.92 ($^{62}\text{NiO}^-$)	77.92 ($^{62}\text{NiO}^-$)	77.92 ($^{62}\text{NiO}^-$)
	79.92 ($^{64}\text{NiO}^-$)	79.92 ($^{64}\text{NiO}^-$)	79.92 ($^{64}\text{NiO}^-$)
	93.92 ($^{62}\text{NiOO}^-$)	91.92 ($^{60}\text{NiOO}^-$)	91.92 ($^{60}\text{NiOO}^-$)
	147.86 (Ni_2O_2^-)	93.92 ($^{62}\text{NiOO}^-$)	93.92 ($^{62}\text{NiOO}^-$)
	149.86 ($^{60}\text{NiNiO}_2^-$)	95.92 ($^{64}\text{NiOO}^-$)	95.92 ($^{64}\text{NiOO}^-$)
	151.85 ($^{60}\text{Ni}_2\text{O}_2^-$)	147.86 (Ni_2O_2^-)	147.86 (Ni_2O_2^-)
	205.80 (Ni_3O_2^-)	149.86 ($^{60}\text{NiNiO}_2^-$)	149.86 ($^{60}\text{NiNiO}_2^-$)
	207.79 ($^{60}\text{NiNi}_2\text{O}_2^-$)	151.85 ($^{60}\text{Ni}_2\text{O}_2^-$)	151.85 ($^{60}\text{Ni}_2\text{O}_2^-$)
		163.86 (Ni_2O_3^-)	163.86 (Ni_2O_3^-)
		167.85 ($^{60}\text{Ni}_2\text{O}_3^-$)	167.85 ($^{60}\text{Ni}_2\text{O}_3^-$)
		205.80 (Ni_3O_2^-)	205.80 (Ni_3O_2^-)
		207.79 ($^{60}\text{NiNi}_2\text{O}_2^-$)	207.79 ($^{60}\text{NiNi}_2\text{O}_2^-$)

in the PCA and MCR analysis, were analyzed to demonstrate the robustness of the presented procedure.

Figure 5a–c shows the NiO_3H_3^- signal intensity from composite ToF-SIMS spectra (0–900 s sputter time interval) across all five analyte surfaces. While the signal is present for every sample, it is significantly more intense for $\text{Ni(OH)}^{28\%}$, with a general trend in agreement with HER activity: $\text{Ni(OH)}^{28\%} > \text{Ni(OH)}^{6\%} > \text{NiAP} > \text{Ni(O)}^{49\%} > \text{Ni(O)}^{90\%}$.

This trend suggests that the presence and intensity of NiO_3H_3^- reflect key features of the catalytically active environment. However, while the signal serves as a strong qualitative marker, the intensity does not have a linear correlation with j_{geo} (Figure 1e) and thus cannot provide a quantitative measure of HER activity as presented in Figure 5f. The calculated current density ($j_{\text{calc 1}}$) was obtained for every analyte by multiplying the NiO_3H_3^- intensity (taken at the sputter time where the intensity of the NiO_3H_3^- signal was the most intense in the ToF-SIMS depth profiles) by the normalization conversion constant K_1 (Equation 2). As shown in Figure 5f and summarized in Table S7, the $j_{\text{calc 1}}$ spans only one order of magnitude across all samples—insufficient to fully account for the three-order-of-magnitude difference in catalytic activity (as given in Figure 1c–e). This implies that NiO_3H_3^- intensity is a necessary, but not the only requirement for high HER activity on Ni surfaces.

$$j_{\text{calc 1}} = K_1 \times \text{Intensity}_{[\text{NiO}_3\text{H}_3^-]} \quad (2)$$

Moreover, the NiO_3H_3^- signal should not be interpreted as a direct representation of Ni(OH)_2 surface species. Secondary ions (fragments) reflect local atomic environments, shaped by bonding geometry, chemical composition, and the immediate matrix from which they are ejected. Nevertheless, the consistent association of NiO_3H_3^- with highly active surfaces indicates that OH-rich environments near Ni atoms play a critical role in HER catalysis.

To probe the structural origin of the NiO_3H_3^- fragment and its link to HER activity, three plausible OH-rich surface configurations were considered: (i) adsorbed OH on Ni(111) ($\text{OH}_{\text{ad}}@ \text{Ni}$, Figure S9a), (ii) a full monolayer of Ni(OH)_2 on Ni(111) ($(\text{Ni(OH)}_2)_{\text{full}}@ \text{Ni}$, Figure S9b), and (iii) a six formula unit Ni(OH)_2 cluster on Ni(111) ($(\text{Ni(OH)}_2)_6@ \text{Ni}$, Figure S9c). To assess which of these configurations can account for the experimental observations, DFT calculations were performed (details available in Note S5 in SI) to evaluate their thermodynamic stability and the activation barrier for water dissociation, a key kinetic descriptor of HER performance (Table S8).

1. Ni(111) surface with a high OH coverage ($\text{OH}_{\text{ad}}@ \text{Ni}$)—At low OH coverage, the water dissociation barrier decreased slightly (0.96 eV versus 1.02 eV for bare Ni). However, DFT analysis of OH adsorption energetics (Figure S10) shows that coverages above ~ 0.4 monolayer (ML) become progressively thermodynamically unstable due to crowding as the coverage increases. At even higher coverages (above 0.8 ML), the model surface tends to decompose into O^* and H_2O (Equation S1), making this configuration highly unlikely. This is further confirmed experimentally, where the high activity is observed at relatively low coverages ($\theta \approx 0.3$).

2. Continuous Ni(OH)_2 overlayer on Ni(111) ($(\text{Ni(OH)}_2)_{\text{full}}@ \text{Ni}$)—A full nickel hydroxide film proved to be thermodynamically stable, but it also showed a significantly higher H_2O dissociation barrier (1.64 eV), 0.64 eV above bare Ni, making this configuration catalytically inactive.

3. Ni(OH)_2 cluster supported on Ni(111) ($(\text{Ni(OH)}_2)_6@ \text{Ni}$)—This mixed configuration provided the best match with experiment. A localized $(\text{Ni(OH)}_2)_6$ cluster adjacent to exposed metallic Ni sites exhibited a lower dissociation barrier (0.89 eV), 0.12 eV below pristine Ni(111), pointing to a synergistic effect between hydroxide domains and metallic Ni. This makes the structural origin of the NiO_3H_3^- fragment and the

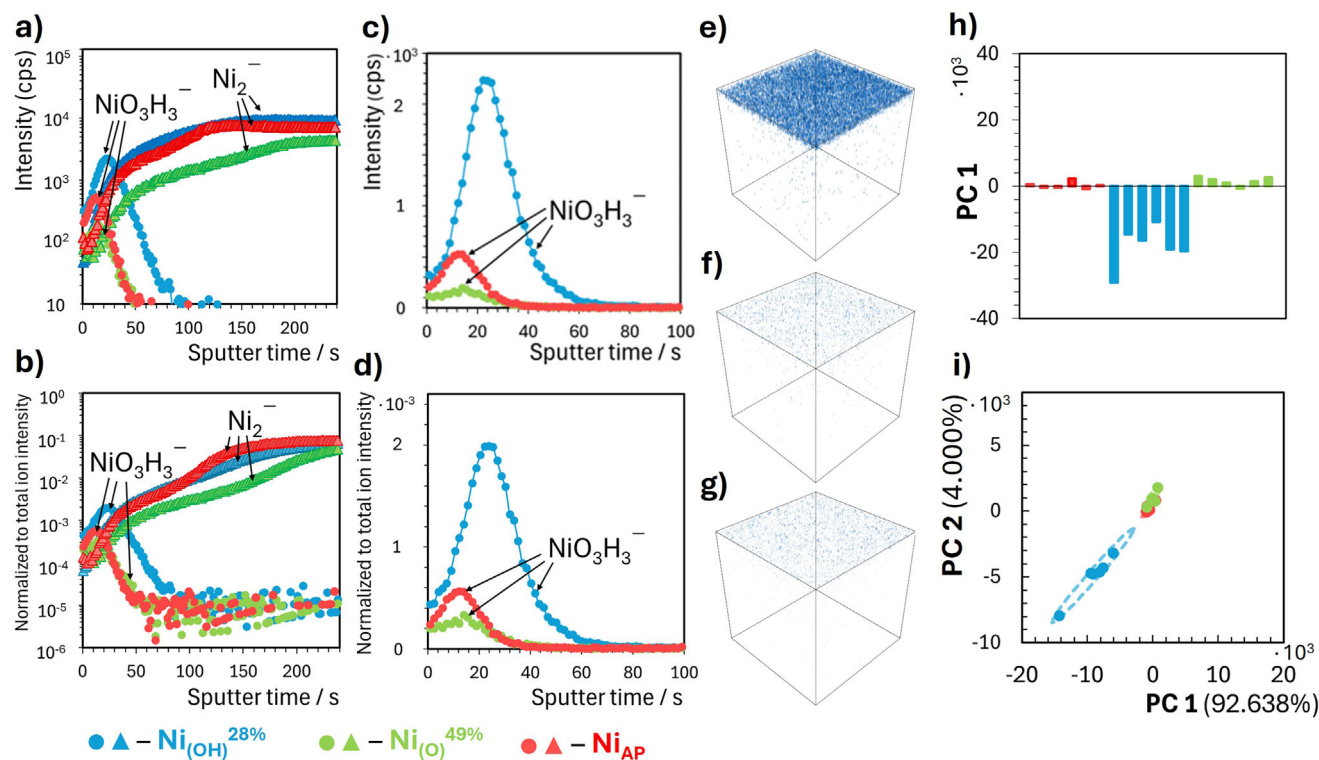


Figure 4. The comparison between ToF-SIMS depth profiles of a,b) NiO_3H_3^- and Ni_2^- signals on a logarithmic scale, and c,d) NiO_3H_3^- signal on a linear scale for $\text{Ni(OH)}_2^{28\%}$ (blue lines), $\text{Ni(O)}^{49\%}$ (green lines), and NiAP (red lines); The ToF-SIMS depth profiles are presented as a,c) signal intensity, b,d) signal intensity normalized to total ion intensity. 3D ToF-SIMS images showing the spatial distribution of NiO_3H_3^- signal for e) $\text{Ni(OH)}_2^{28\%}$, f) $\text{Ni(O)}^{49\%}$, and g) NiAP ; PCA score plots for h) PC1 and i) PC1 versus PC2 using targeted spatial scaling based on the identified unique NiO_3H_3^- signal.

experimentally observed catalytic enhancement the most plausible.

Figure S10 shows that OH^* adsorption energies on Ni(111) become increasingly unfavorable above ~ 0.38 ML, indicating that high, uniform hydroxyl coverages of pristine Ni(111) are thermodynamically disfavored; this supports interfacial motifs rather than fully hydroxylated terraces as the active configuration. A full coverage with Ni(OH)_2 as opposed to simply adsorbed OH , is thermodynamically allowed due to a larger unit cell, effectively making the number of OH groups per Ni(111) site lower, but is catalytically inactive.

Taken together, these DFT results indicate that the most active sites are not uniformly hydroxylated or oxidized surfaces, but rather interfacial regions where hydroxide of Ni(OH)_2 moieties are directly adjacent to metallic Ni atoms. Such bifunctional mechanism has previously been established for other systems (e.g., bimetallic Pt catalysts, hydroxide-modified Pt catalysts, etc.), where the active sites arise from the cooperative action of metallic and hydroxide species.^[48–50] This scenario aligns with NiO_3H_3^- serving as an indirect marker of such local environments.

To reflect this structural insight in the experimental correlation, Equation 2 was refined by incorporating the intensity of Ni_2^- representing metallic Ni , into the descriptor, resulting in the corrected calculated current density ($j_{\text{calc}2}$) as shown in Equation 3. The intensity of Ni_2^- was acquired

at the sputter time where the NiO_3H_3^- signal exhibited the maximum intensities in the ToF-SIMS depth profiles measured for each analyte.

$$j_{\text{calc}2} = K_2 \times \text{Intensity}[\text{NiO}_3\text{H}_3^-] \times \text{Intensity}[\text{Ni}_2^-] \quad (3)$$

As shown in Figure 5g, this combined descriptor provides a substantially better match to the observed HER activity trend in Figure 1d,e across the five samples than NiO_3H_3^- intensity alone. This confirms that both Ni(OH)_2 and Ni metal must coexist to form catalytically competent active sites, and that their co-localization at the nanoscale is key to high electrocatalytic performance. The match between experimental and calculated points is in good agreement, with the only remaining discrepancy for the $\text{Ni(O)}^{90\%}$, where the established descriptor fails to capture catalytic behavior, indicating that an additional, yet unidentified factor governs its activity. Uncovering this factor will be an important direction for future studies, as it may reveal new mechanistic insights and further validate the robustness of the presented approach.

Conclusion

This study establishes time-of-flight secondary ion mass spectrometry (ToF-SIMS) in combination with multivariate statistical analysis as a powerful approach for resolving catalytically

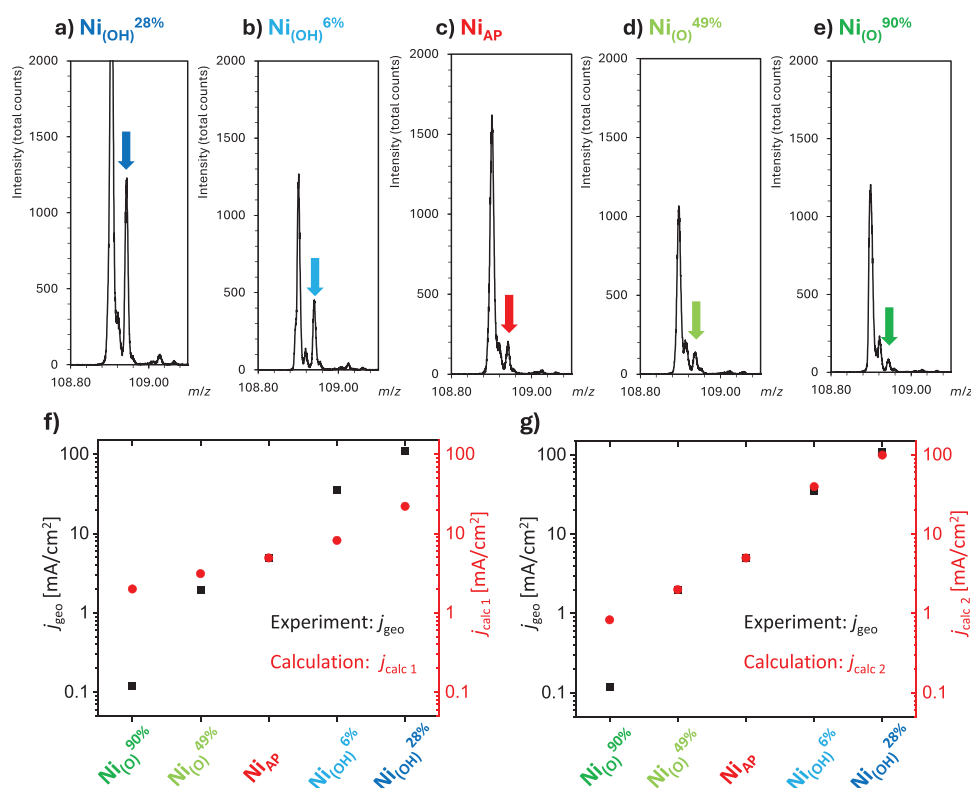


Figure 5. ToF-SIMS spectra (detailed view) showing the intensities of NiO_3H_3^- signal (position marked with arrow) for a) $\text{Ni}(\text{OH})_2$ 28%, b) $\text{Ni}(\text{OH})_2$ 6%, c) Ni_{AP} , d) $\text{Ni}(\text{O})_2$ 49%, and e) $\text{Ni}(\text{O})_2$ 90%, f, g) the comparison of j_{geo} with the calculated values f) $j_{\text{calc 1}}$ and g) $j_{\text{calc 2}}$.

active surface species in complex materials. The method overcomes key limitations of conventional techniques, which often lack the detection limit, chemical exactness, and depth resolution to distinguish ultrathin, multicomponent surface layers. By coupling ToF-SIMS with principal component analysis (PCA) and multivariate curve resolution (MCR), the rich fragmentation patterns distinctive of this technique can be systematically deconvoluted, allowing direct identification of chemically distinct motifs that govern catalytic activity. This framework enables both the characterization of active sites and the classification of unknown surfaces based on their chemical fingerprints. To demonstrate the utility of this approach, it was applied to Ni-based catalysts. In this prototypical but chemically complex system, multiple oxide and hydroxide species coexist at sub-monolayer coverages, strongly influencing hydrogen evolution reaction (HER) activity.

Ni surfaces modified with varying hydroxide and oxide coverages were model systems. A central finding of this work is the determination of NiO_3H_3^- as a unique and reproducible marker associated with the high catalytic activity of Ni surfaces for HER.

While the correlation between NiO_3H_3^- intensity and HER activity across five model surfaces established a strong qualitative link between surface chemistry and catalytic performance, its combination with the metallic Ni_2^- signal also captured quantitative trends in HER activity. Density functional theory (DFT) calculations supported this observation, identifying complex partially hydroxylated surfaces,

consisting of $\text{Ni}(\text{OH})_2$ adjacent to metallic Ni sites, rather than simple OH adsorption, as the most catalytically favorable configuration for water dissociation in alkaline media.

This integrated ToF-SIMS/PCA/MCR methodology provides a robust and chemically understanding route for identifying active sites on catalytic surfaces. Overcoming the limitations of traditional surface analysis methods in distinguishing closely related species delivers both a diagnostic tool and a predictive framework for catalyst optimization. These insights contribute to a deeper understanding of structure–activity relationships and open new pathways for the rational design of efficient electrocatalysts. For Ni HER catalysts, based on the established HER activity trends, the key design guidelines are governed by both the nature of the surface species and their coverages. While NiO should be completely avoided, as it behaves purely as a blocking species, the most active catalyst configuration requires an optimal $\text{Ni}(\text{OH})_2/\text{Ni}$ interfacial structure, which can be achieved by careful electrode preparation and potential control in electrolyzer operation.

Supporting Information

The authors have cited additional references within the Supporting Information.^[51–57] Supporting Information includes Figures S1–S10 and Tables S1–S8, as well as a detailed description of the materials and methods, and additional data interpretation in Notes S1–S2.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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