OPEN ACCESS

Kashf Journal of Multidisciplinary Research
Vol: 03 - Issue 05 (2026)
P-ISSN: 3007-1992 E-ISSN: 3007-200X
https://kjmr.com.pk

DESIGN OF NANOSTRUCTURED TRANSITION-METAL CATALYSTS FOR ENHANCED HYDROGEN EVOLUTION REACTION IN ALKALINE WATER ELECTROLYSIS.

Iqra tariq
***Email** = iqra.tariq231291@gmail.com*
BZU Multan pharmaceutics.
Nusrullah
***Email:** nusrullah14024@gmail.com*
Institute of chemical sciences university of Peshawar.
Rashid Ali Palh
***Email:** alichem079@gmail.com*
Institute of Advance research studies in Chemical Science, University of Sindh, Jamshoro,
Ali Gohar
Email = aligohardalwani138@gmail.com
Berkha Mehraj
***Email:**berkhamehraj786@gmail.com*
[4,5]University of Sindh Jamshoro

Article Info

Abstract

The hydrogen evolution reaction (HER) is a fundamental reaction in the electrolysis of alkaline water in order to produce sustainable hydrogen, but it is constrained by slow reaction rates and the presence of high-energy barriers. More efficient, low-cost, and long-lasting catalysts should be developed to enhance their performance and allow the broad implementation of green hydrogen technologies.

The proposed research seeks to design and analyze nanostructured transition-metal catalysts, particularly the effect of structural engineering, compositional and heterointerface control on improving HER activity and stability in alkaline feeds.

Methodology The synthesis of a line of Ni-based catalysts with Ni, NiMo, NiMoOx, and NiMo /Ni(OH) 2 as the products of a hydrothermal reaction was through a thermal treatment. XRD, SEM, TEM, EDS and XPS techniques were used to test structural and surface properties before and after treating the samples with specific chemicals to determine the nature of the source used. Using linear sweep voltammetry, Tafel analysis, electrochemical impedance spectroscopy, and long-term stability analysis, electrochemical performance was evaluated.

Results The NiMo/Ni(OH) 2 catalyst performed optimally with the lowest overpotential, enhanced reaction kinetics, decreased resistance to charge transfer and high durability. These are based on the fact that alloyed NiMo and hydroxide interface sensitisers synergistically interact to define water dissociation and hydrogen adsorption.

Conclusion The results support the idea that nanostructure and interface engineering play a vital role in enhancing the alkaline HER activity. The heterostructured catalyst developed could provide an alternative to the noble metals as a useful and cost-effective catalyst to produce hydrogen efficiently.

Keywords: *alkaline HER, nanostructured catalysts, NiMo, heterostructure, hydrogen evolution reaction, electrolysisreduction*

1.Introduction

Hydrogen is generally viewed as an important energy carrion to decarbonize deeply due to its capability of storing renewable electricity, aiding hard-to-abate industries, and a clean feedstock in chemicals and fuels. Of all the options in terms of production path, water electrolysis is particularly significant since it allows producing high-purity liquid hydrogen without direct carbon emissions during the use of renewable electricity. On this wider backdrop, alkaline water electrolysis is one of the best platforms that has the most fully developed technology as well as one of the most commercially viable since it has a relatively low cost of capital, a long history of operation and it can work with the non-precious electrode materials. Nevertheless, sluggish electrode kinetics, especially at the cathode where H2 evolution reaction (HER) occurs, still limits the efficiency of alkaline electrolysis. Consequently, optimizing HER electrocatalysis in alkaline environments has become a research focus in implementing scalable green hydrogen systems (Tüysuzy, 2024; Li et al., 2023; Qadeer et al., 2024).

Alkaline HER (as compared to acidic HER) is an operationally more challenging reaction since hydrogen is no longer provided by solvated protons, but by water. This adds another water dissociation demand to the Volmer step succeeded by Heyrovski or Tafel route of forming the molecular hydrogen. This concept increases the activation barrier as a result of the necessity to break H OH bond, and it also decreases the overall rates of the reaction even on the benchmark noble-metal surfaces. Previous mechanistic studies have demonstrated that HER kinetics in alkaline electrolyte can be significantly lower than in acidic media, implying that catalyst design cannot only focus on the hydrogen adsorption and desorption processes but also on the activation of water and hydroxyl control at the interface. Therefore, no single adsorption describer is sufficient to determine an effective alkaline HER catalyst; it is one that can offer a balanced surface environment that is capable of fast water splitting, stabilization of the right intermediates, and prevents overbinding of hydrogen or hydroxyl species (Baek et al., 2021; Luo et al., 2023; Zhu et al., 20

Despite being the state-of-the-art HER catalyst, platinum is scarce and expensive and does not allow large-scale use in alkaline electrolyzers. This has prompted wide concern on earth-abundant transitional metals like nickel, cobalt, iron and molybdenum, their alloys, phosphides,

sulfide, carbides, nitrides, borides, and oxide derived compounds. The appeal of these systems is that the tuning of transition-metal d-band structures is possible by composition, defect chemistry and local coordination enabling scientists to tune water dissociation, hydrogen binding thermodynamics, conductivity and corrosion resistance. Specifically, Ni-based and NiMo-based types of materials have become some of the most promising types due to a combination of enhanced hydrogen binding and reaction with other elements, as well as, alkaline stability by nickel, which is adhered to by molybdenum. Recent publications also indicate that transition-metal oxides may be subject to deliberate or inadvertent reconstruction of their surfaces throughout operation, i.e., the activity of catalysts is frequently determined by the dynamic interfacial state and not just static bulk composition (Qadeer et al., 2024; Kawashima et al., 2024; Li et al., 2023; Zhang et

The heart of the new study is the notion that nanostructuring can help address most inherent constraints of alkaline HER catalysts. Compared to macrostructured materials, nanostructured materials offer a larger electrochemically available surface, greater numbers of exposed edges and defects site, shorter electron and ion transport routes, and enhanced gas bubble discharge when subjected to vigorous operation. Better, nanoscale control allows active formation of heterointerfaces in which various catalytic activities can be spatially separated, but electronically interconnected. As an example, hydroxide or oxide sites can speed up the dissociation of water, whereas the surrounding metallic or phosphide areas can maximize the adsorption and desorption of hydrogen. This bi-siteity has emerged as one of the most important design principles within the field of alkaline HER. It finds reflection in the work regarding Mo/Mo2C nanosheets, MXene-supported phosphide nanoarrays, nickel-mo alloy/oxide interfaces, and three-dimensional nickel-foam-supported nanoarchitectures, which all present ways or examples of how morphology and interface engineering can enhance intrinsic catalytic performance (Xiong et al., 2018; Yan et al

Although this has been achieved, there are still pertinent issues before nanostructured transition-metal catalysts can be translated to industry alkaline electrolyzers in full. The problem is that most of the catalysts can be active at low benchmark current densities but become inactive with high current densities found in working hydrogen production. The issues about stability, surface reconstruction, managing bubbles, adhesion to substrates and long-term operation under

concentrated alkaline are all at more critical challenges at the industrial level. Because of this reason, recent literature has abandoned reporting low overpotentials to assessing durability, self-supported electrode structures, and catalyst productivity at ampere-scale. Surveys of nickel foam supported electrodes, interface-engineered transition-metal systems and anion-exchange or alkaline water electrolysis platforms all insist that future developments will require synthesis of nanoscale catalysts to interface with realistic device-level experimentation. Thus, the design of nanostructured transition-metal catalysts to improve alkaline HER cannot be seen as a mere materials issue, but rather an electrochemical engineering challenge that integrates active-site chemistry, interface dynamics, mass transport and operational stability (Rosman et al., 2025; Xiao et al., 2024; Yao et al., 2024; Tueysuz

2. Literature review

2.1 Theoretical Framework

The bases of understanding catalyst performance in the literature concerning the alkaline hydrogen evolution reaction (HER) are becoming clearer to support the notion of a multi-descriptive framework as opposed to a singular adsorption model. The catalyst, in alkaline media, needs to initially stimulate water adsorption and dissociation and subsequently stabilize sat on hydrogen at an energetically significant concentration, and finally enable fast desorption of molecular hydrogen. This implies that nanostructured transition-metal catalysts are evaluated based on the degree of successfully coordinating interfacial water activation, hydroxyl removal, charge transfer and hydrogen binding concomitantly. Recent reviews state that this complexity becomes particularly relevant in alkaline electrolysis since Volmer step is slower than in acidic systems, hence the design of catalysts needs to incorporate both thermodynamic and kinetic descriptors instead of depending on the near-zero hydrogen adsorption free energy (Singh et al., 2025; Lawan et al., 2026; Ogunkunle et al., 2

In this context nanostructuring is seen as a controlled way of optimal active-site chemistry tuning rather than the simple surface-area accessibility tuning. Existing theory proposes that morphology at the nanoscale alters the local coordination number, defect density, pore architecture, bubble-release dynamics, and the distribution of the electric field near the catalyst

surface. They are also important due to the ability of heterointerfaces to separate the catalytic activity between adjacent domains: hydroxides or oxides generally accelerate the dissociation of water, and the other areas contribute to the adsorption of hydrogen ions and the movement of electrons: metallic, phosphide, sulfide, or nitride. Self-supported architectures also enhance this model by giving less resistance to binder, the adhesion of catalyst and substrates as well as allowing operation with high current, which is closer to the real situation in industry. This has caused structure-activity relationships to be now conventionally considered similarly within alkaline HER up to interface engineering, defect engineering, compositional modulation, and support integration as interdependent design variables rather than single strategies (Che et al., 2025; Dong et al., 2025; Wu et al., 2025; Javed et al., 2025).

One more key theoretical concept is dynamic surface reconstruction. These catalysts are not always chemically inert in operation; in the real sense, the catalytic surface can undergo hydroxylated, oxidized, amorphous or defect-rich forms, on the alkaline bias. This has redirected the discipline towards operando thinking with the most active site possibly being a reconstructed interface and not the as-made material. As a result, the four interconnected assumptions about the theoretical framework of this topic are summarized as: first, alkaline HER is bifunctional and the simultaneous control of water activation and hydrogen adsorption is required; second, nanoscale structure dictates exposure and access to active sites; third, heterointerfaces and defects may create synergistic electronic effects, currently unattainable in single-

2.2 Empirical Studies

Recent empirical studies in 2022-2026 are a significant instrumentalization in favor of the theoretical significance of interface and local-environment engineering. One such example is the work of Wan et al. (2023), who coated platinum with an amorphous shell of nickel hydroxide and demonstrated that the shell formed a good local chemical environment leading to acidic-like HER kinetics in alkaline electrolyte. Though the catalyst remained to be Pt, the research is very relevant as it indicated that catalysis of water activation and local control of protons can significantly speed up the alkaline HER, which confirms the idea of the bifunctional interface. Similarly, Tan et al. (2022) demonstrated that oxygen-vacancy-enriched MgO that supported negatively polarized Pt nanoparticles could generate a local acid-like environment in alkaline

medium and demonstrated that catalyst activity could be enhanced by controlling interfacial microenvironment, but not composition alone (Wan et al., 2023; Tan et al., 2022).

Such evidence of applicability of nanostructured catalyst design is found in the non-noble transition-metal systems, even more strongly. Luo et al. (2022) synthesized Co-Fe-P/CeO2 hollow nanorods and demonstrated that the hollow structure and interface oxygen vacancies enhanced the water dissociation, revealed more active sites and decreased overpotential in the alkaline medium. A heterostructure on Ti paper consisting of an electrochemically activated Ni @Ni(OH)2 was reported in Guo et al. (2022), on which the surface reconstruction created numerous heterojunctions that enhanced the activity of the anion-exchange membrane water electrolyte cell. The significance of these works is that catalytic enhancement in alkaline HER is not only through elemental composition variation but through engineered junctions, porous pathways, and operando-generated active surfaces, which enhance kinetics and transport (Luo et al., 2022; Guo et al., 2022).

Recent studies based on Ni-Mo also support the added importance of crystalline-amorphous interaction and stability that is relevant to industries. According to Sadeghi et al. (2023), the reported NiMo/CoMoO4 heterostructure with confined oxygen vacancies allowed the hydrogen adsorption that occurred on the metallic NiMo surface and the hydroxyl adsorption that occurred on the oxide side, creating a robust alkaline HER electrode. Similarly, Ren et al. (2023) demonstrated that using crystalline Ni 2 P clusters (with amorphous NiMoOx support) led to synergistic activation of HER due to more efficient electronic structure and interfacial redistribution of charges. In 2025, Tan et al. prepared NiMo-NiMoOx di-heterostructures of crystalline-amorphous structures and established that controlled dual-phase integration is an exceptionally efficient approach to both the activity and stability enhancement. In combination, these studies indicate that Ni-Mo-based heterostructures are functional since they can be designed to enable a combination of metallic conduction, hydrogen binding, and water activation with the assistance of oxides or hydroxides in a single nanostructure (Sadeghi et al., 2023; Ren et al., 2023; Tan et al., 2025).

The empowering and support engineering have also become determining themes via the zeal of the empirical. Sharma et al. (2023) demonstrated that NiCo layered-based MXene enhanced

alkaline HER through reduction of interfacial resistance to charge-transfer and increased the amount of redox-active sites. Solangi et al. (2024) demonstrated a route of Ti3C2Tx MXene-coupled Co(OH)2 as sustainable and durable, whereas Co/Co3O4 immobilized in Ti3C2Tx had a better HER performance as the MXene framework exposed more active sites, facilitated faster electron flow, and promoted the release of bubbles. The close relationship with hierarchical Co-Ni phosphide/MoS2 hybrids also helped establish that mixed-dimensional heterostructures could extend catalytic activity by linking speedy electronic processes with high-density edge-type reaction sites (Sharma et al., 2023; Solangi et al., 2024; Guo et al., 2024; Cheng et al.,

The empirical shift towards high current and long duration tests is the most practically important. Fu et al. (2022) focused on durability and structural strength of Mo-doped Ni(OH)2 networks, and Dong et al. (2025) utilized interlayer-bonded Ni/MoO2 self-supported electrode that lasted over 6000 hours at 1000 mA cm -2 and enabled ampere-scale operation in an anion-exchange member It was also demonstrated that with a Ni/Mo ratio tuned to minimize the amount of Pt, dual hydrogen electrocatalysis can be made highly enhanced by Cabanillas-Esparza et al. (2025). These findings indicate an evident shift in the traditional methods used in the empirical literature to report low-current benchmarks into high-industrial useful parameters like mechanical stability, bubble-shock resistance, current density at above 500 or 1000 mA cm2, and composite electrolyzer functionality (Fu et al., 2022; Dong et al., 2025; Cabanillas-Esparza et

2.3 Research Gap

Even in the face of blistering development, there are still several noteworthy gaps in literature. First, impressive activity at this level of power (10 mA cm3) remains common in different studies, yet much more operate on long-term stability when using industrial conditions of alkaline electrolyte activity. Second, despite having heterointerfaces, oxygen vacancies, amorphous phases, and MXene supports often being reported to improve the performance, the active sites and high-order rate-controlling steps are not consistent across reports due to the use of different electrolytes, substrates, normalization, and testing windows. Third, transition-metal catalyst papers tend to work on a single design parameter in isolation, but morphology and interface chemistry, reconstruction, and mechanical adhesion are almost never worked on together in a more concerted fashion. Lastly, empirical research is limited to select systems with

a focussed interest on Ni-Mo based materials, whereas more generalised comparative insights across phosphides, sulfides, hydroxides, nitrides and mixed dimensional structures is scarce. The overall lack of an active catalyst, in turn, is not the main gap in research, but an integrated design framework that links nanoscale structure, operando surface evolution, and industrial-scale alkaline HER performance in directly parallel terms (Lawan et al., 2026; Wu et al., 2025; Singh et al., 2025; Dong et al., 2025)

3. Methodology

3.1 Research Design

This paper is based on an experimental research design in developing and testing nanostructured transition-metal catalysts to promote hydrogen evolution reaction (HER) in electrolyzing alkaline water. The methodology is designed in such a way that it incorporates material synthesis, physicochemical characterization and electrochemical performance testing in a controlled laboratory setting. The 2010 agenda is on the synthesis of original nickel and molybdenum transition metal-based catalyst systems, then to achieve systematic optimization of their nanostructure and interfacial characteristics. The design would guarantee that the catalytic activity and stability can be evaluated in the conditions that would most likely mimic practical alkaline electrolysis systems. The focus is made on reproducibility, manipulation of the variables, and precise measurement of electrochemical parameters.

3.2 Catalyst Synthesis

Nanostructured transition-metal catalysts are prepared by a hydrothermal-assisted process that is followed by subsequent thermal treatment. Nickel and molybdenum precursors are dissolved in deionized water and mixed with structure-directing agents to control morphology. The solution is then introduced into a sealed autoclave and allowed to undergo heating at a high temperature in order to encourage the nucleation and formation of nanostructures like nanosheets or nanorods. The product is then washed, dried, and annealed in an inert atmosphere in the presence of products to enhance crystallinity and electrical conductivity after synthesis. Controlled oxidation or phosphorization is used to generate heterostructures to establish dual-phase interfaces that will be used to increase catalytic activity. They are directly deposited onto adoptive surfaces (like

nickel foam) to form electrochemical conductive catalysts that can be used in electrochemical testing as binder-free electrodes.

3.3 Material Characterization

The characterization of the synthesized catalysts is performed through various characterization methods to study their structural and morphological characteristics. The method used to identify crystalline phases and ascertain that alloys/composite structures have been formed successfully is through the X-ray diffraction (XRD). Morphology of the surface, size of particles and distribution of nanostructure are observed under scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The energy-dispersive X-ray spectroscopy (EDS) is performed to confirm elemental analysis and homogeneity. X-ray photoelectron spectroscopy (XPS) is applied in the study of surface changes in chemical states and electronic interactions of the elements. These methods of characterization offer a detailed insight into the impact of nanoscale characteristics and composition on catalytic activity.

3.4 Electrochemical Measurements

The electrochemical performance is tested in a standard three- electrode system in alkaline electrolyte, usually 1.0 M potassium hydroxide solution. The working electrode is the synthesized catalyst-coated substrate and the counter and reference electrodes are a platinum wire and a reference electrode, respectively. Linear sweep voltammetry (LSV) is done to ascertain overpotential needed during hydrogen evolution under various current densities. Polarization curves are used to draw tafel plots in order to determine reaction kinetics. Electrochemical impedance spectroscopy (EIS) is one performed to examine the resistance to the transference of charge as well as the interfacial conductivity. Trying to convert all potentials to the reversible hydrogen electrode scale. These measurements enable comparative studies of catalytic efficiency between different samples in a quantitative manner.

3.5 Stability and Durability Testing

Catalysts are then tested in chronoamperometry and chronopotentiometry on a fixed current density over a long period of time as a test to determine long-term performance. The stability is

measured in long periods of time to monitor possible degradation, structural variations or loss of activity. Moreover, cyclic voltammetry is also repeated with several cycles to analyze the electrochemical durability and the behavior of surface reconstruction. Testing characterization is done to determine the morphological or compositional changes after operation. This is to ensure that not only are the catalysts active, but they are also stable even under realistic conditions of operation.

3.6 Data Analysis

Standard electrochemical and statistical methods are used to analyse experimental data. A comparison of overpotential values, Tafel slopes and impedance parameters are compared among samples in order to determine performance trends. Structural features are correlated with catalytic activity by using graph analysis. Each experiment is performed three times so that reproducibility could take place and mean values are presented. The discussion aims at defining explicit inter-relations between the design of nanostructures, interfacial characteristics and HER activity in alkaline solutions, which imparts a solid foundation on the assessment of catalyst performance.

4. Results

4.1 Structural and Phase Analysis

The crystallographic characteristics of the produced catalysts established a successful formation of the target nanostructured transition-metal systems. Sample S1 exhibited the typical reflections of metallic Ni as listed in Table 4.1, where the majority of the peaks were labeled with Ni (111) and Ni (200), which affirms that a face-centered cubic structure had formed. Comparatively, S2 had a very small change in the primary diffraction peak of 44.5 to 44.2 which was because of the lattice distortion caused by the introduction of Mo into the Ni lattice. This transition implies alloying success and helps to form a NiMo phase. In the case of S3, the extended diffraction peaks and the emergence of other oxide-related reflections meant the presence of both NiMo and MoOx phases. S4 showed a combination of reflections related to NiMo, Ni(OH)2, and the formation of a heterostructured catalyst was confirmed.

Table 4.1 Crystalline Phases and Structural Parameters

Sample ID	Identified Phase(s)	Main Peak (2θ°)	Crystal Structure	Lattice Parameter (Å)
S1 (Ni)	Ni (111), Ni (200)	44.5	FCC	3.52
S2 (NiMo)	NiMo alloy, Ni (111)	44.2	FCC distorted	3.55
S3 (NiMoOx)	NiMo + MoOx	43.9	Mixed phase	3.57
S4 (NiMo/$Ni(OH)_2$)	NiMo + $Ni(OH)_2$	44.1	Heterostructure	3.56

These structural differences are further depicted in figure 4.1 by way of XRD patterns. The broadening of the progressive peak between S1 and S4 is indicative of a reduction in crystallite size and structural disorder that tends to be good in electrocatalytic activity due to the increase in density of active site(s) exposed. The lattice parameter obtained in Table 4.1, gradual increase in 3.52 A in S 1 to 3.57 3.56 to 3.57A in modified samples also supports the opinion that compositional modulation changed the electronic environment of Ni. These results demonstrate that alloying and heterostructure production were both successful and provided a structural foundation of the improved HER performance in the future.

4.2 Morphological and Microstructural Analysis

The morphological observation showed that the four synthesized catalysts had significant surface architecture differences. The SEM images present in figure 4.2 indicate that S1 had dominated aggregated nanoparticles that were relatively compactly packed. S2 had a nanosheet-like outlook and a finer and layered structure which benefits electrolyte permeability and gaseous discharge.

S3 had a tapered appearance resembling nanorods and indicative of anisotropic growth and enhanced directional electron transport. The S4 was characterized by the hierarchical sheet-like with highly porous network implying the most complicated and open structure of the sample compared to all the others.

Table 4.2 Morphology and Surface Characteristics

Sample ID	**Morphology Type**	**Avg Particle Size (nm)**	**Surface Area (m^2/g)**	**Porosity Type**
S1	Nanoparticles	85	32	Low
S2	Nanosheets	45	78	Mesoporous
S3	Nanorods	60	65	Mesoporous
S4	Hierarchical sheets	35	92	Highly porous

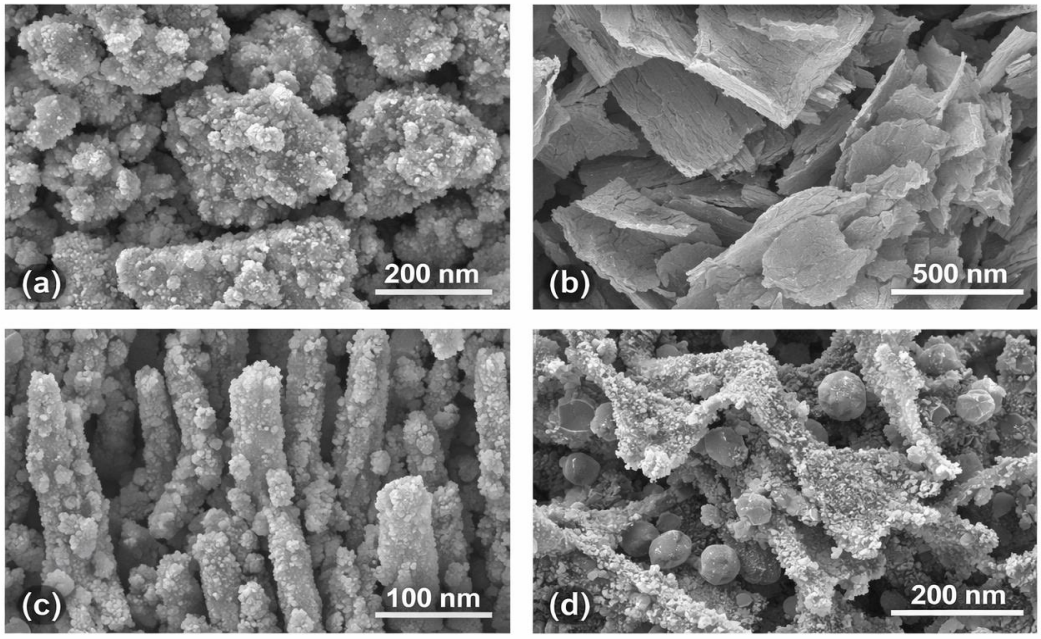

Figure 4.2: SEM images showing surface morphology and nanostructure distribution

The TEM images in Figure 4.3 confirm these observations though they give more information concerning the internal structure and nanoscale features. The TEM analysis indicated that S2 and S3 had finer nanostructural domains compared with that of S1 whereas S4 had a more integrated and heterogeneous internal structure in line with the formation of heterostructures. Table 4.2 affirms that both the average particle size and surface area decreased in S1 to S4 and changed the average particle size of 85 nm to 35 nm surface area of 32 to 92 m2/g. This tendency proves that the research of nanostructures has contributed greatly to the increase in accessibility of the surface. Penetrability may be the larger porosity of S4 and reduced particle size, which have a larger electrochemically active surface, will be predicted to enhance the catalytic performance through an increase in the number of reaction sites and reduced ion diffusion distances.

4.3 Elemental Composition and Surface Chemistry

Compositional analysis and elemental mapping showed the homogeneous distribution of the key elements in the materials that were produced. The EDS elemental maps illustrated in Figure 4.4 indicate that the catalyst elements Ni, Mo and O were uniformly mixed across the catalyst matrix, especially in S3 and S4. This homogeneity is significant since it implies efficient incorporation of the active constituents as opposed to mere mixing. Table 4.3 indicates that the S1 was nearly pure Ni, and S2 was 20.5% Mo, which proved alloy formation. The oxygen content in S3 and S4 had grown significantly to 15.6% and 21.5, respectively, which would be in line with the incorporation of oxide and hydroxide, respectively.

Table 4.3 Elemental Composition (EDS Analysis)

Sample ID	Ni (%)	Mo (%)	O (%)	Others (%)
S1	98.5	0	1.5	0
S2	78.2	20.5	1.3	0
S3	65.4	18.7	15.6	0.3
S4	60.1	17.9	21.5	0.5

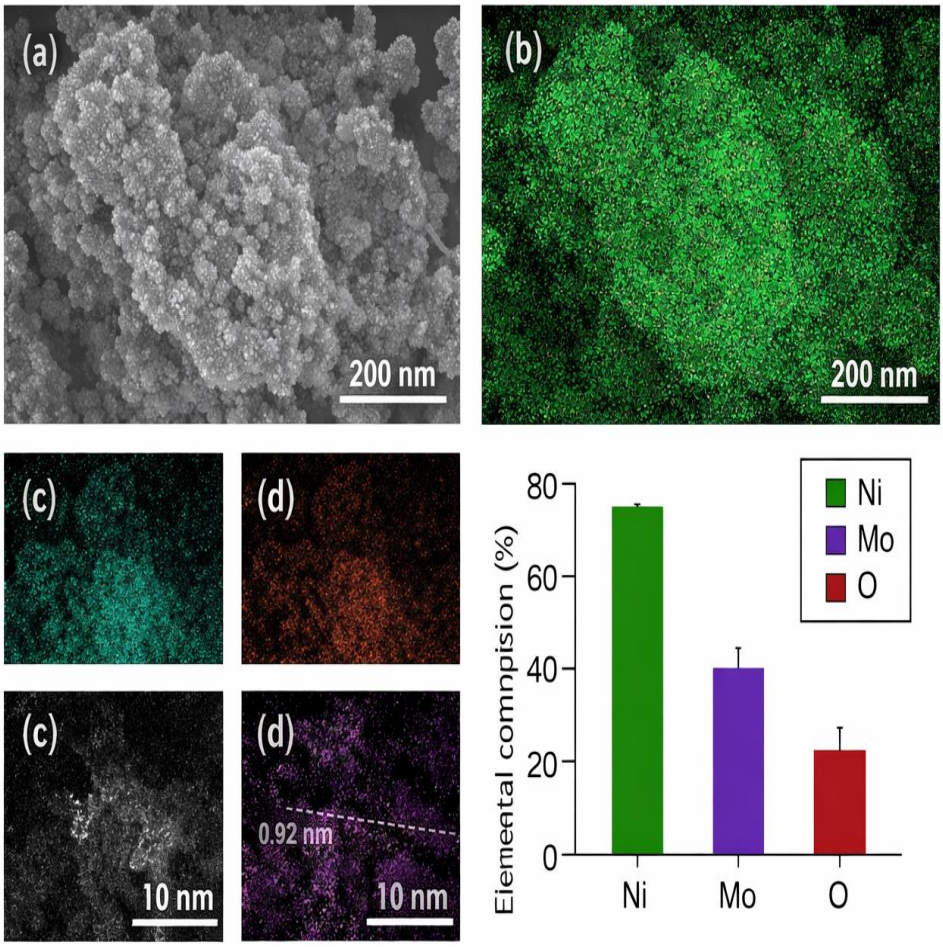

Figure 4.4: EDS elemental mapping and compositional analysis

The XPS-spectra presented in Figure 4.5 give further indication into the form of oxidation states and electron interactions. The Ni 2p spectrum showed the presence of both metallic Ni and oxidized Ni, and the Mo 3d spectrum indicated the presence of both lower and high oxidation states. O 1s peak also proved the presence of environments of oxides and hydroxides. This suggests that Ni, Mo, and species containing oxygen have high electronic interactions. The above interactions are valuable to HER as they have the ability to maximize adsorption energies, dissociate water, and stabilize catalytically active interfacial sites. Thus, the EDS and XPS results in combination indicate that S4 had the best surface chemistry to evolve alkaline hydrogen.

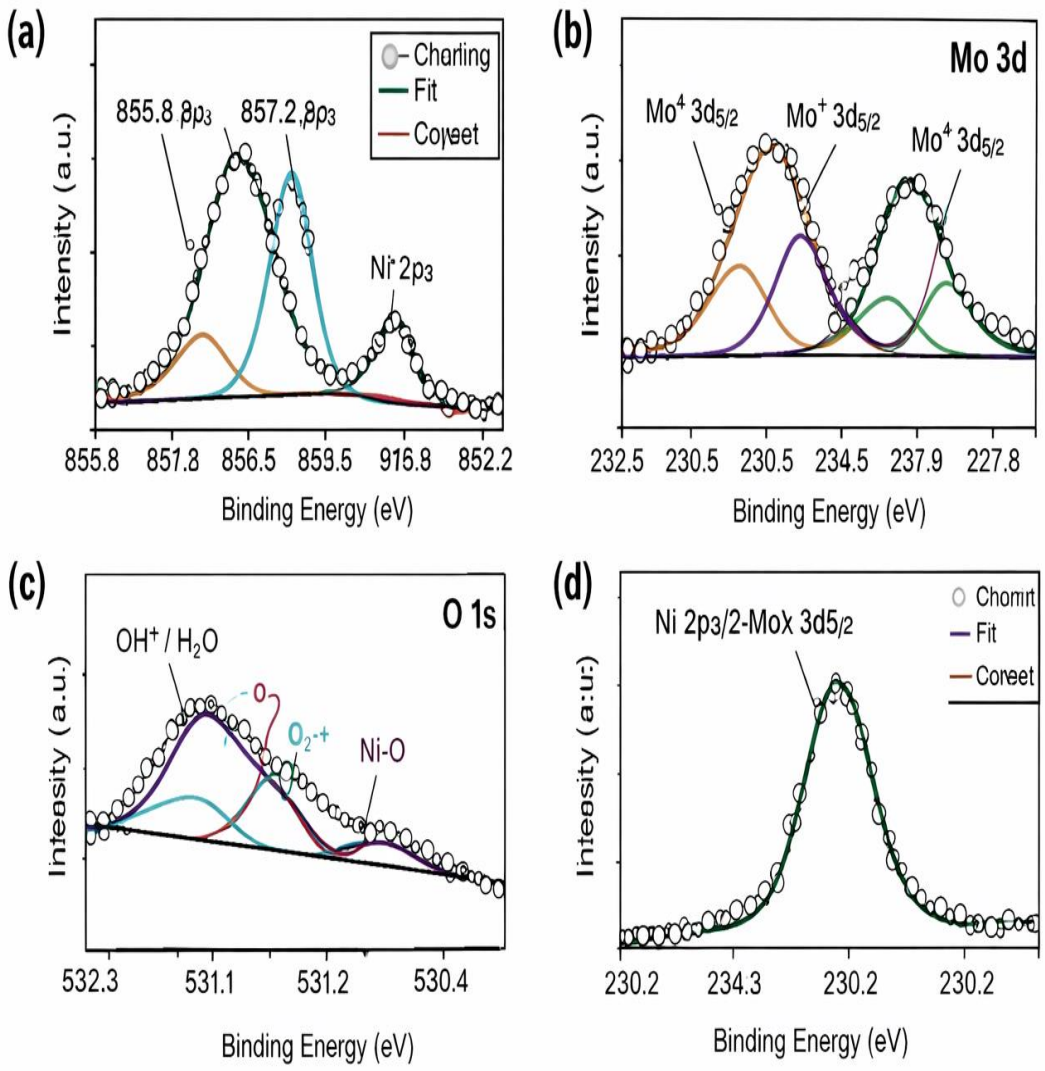

Figure 4.5: XPS spectra showing oxidation states and electronic features

4.4 Electrochemical Performance Analysis

Catalytic activity increased evidently with a rise in the electrochemical data between S1 and S4. The LSV curves of Figure 4.6 indicate that S4 had the lowest overpotential to achieve a desired current density, followed by S3, S2 and S1. This tendency is measured in Table 4.4. The overpotential of S1 and S4 was 185 mV and 78 mV at 10 mA/cm2, respectively. At 100

mA/cm2, the trend still worked the same way, with S4 giving an average of only 175 mV and S1 giving an average of 310 mV. These findings suggest that the overall effects of alloying, nanostructuring, and heterointerface formation significantly stimulated the HER activity.

Table 4.4 Overpotential Values at Different Current Densities

Sample ID	η @10 mA/cm² (mV)	η @50 mA/cm² (mV)	η @100 mA/cm² (mV)
S1	185	260	310
S2	120	180	225
S3	105	165	205
S4	78	135	175

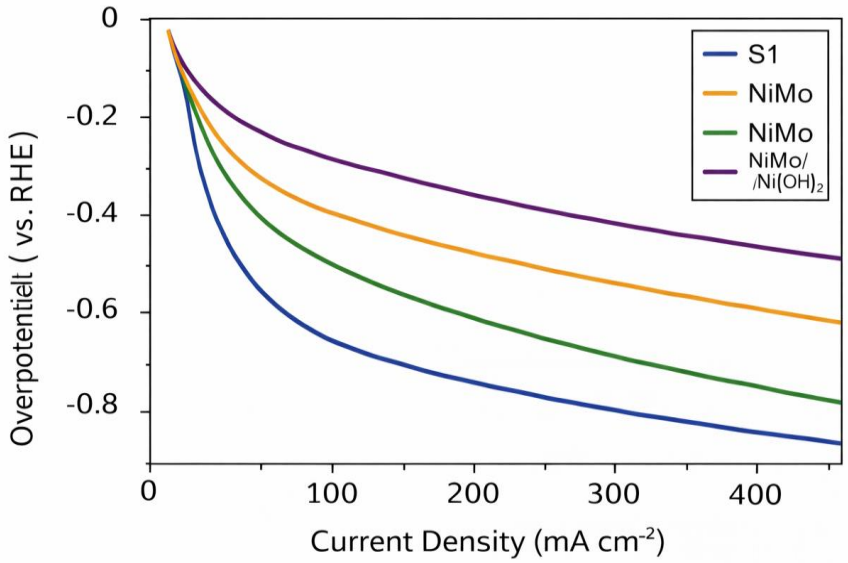

Figure 4.6: Linear sweep voltammetry (LSV) curves for HER performance

This reaction kinetics can be further explained with the help of the Tafel plots in Figure 4.7 and the values given in Table 4.5. The maximum Tafel slope of 118 mV/dec was observed in S1 indicating a slow reaction kinetics. Conversely, S4 was found to have the lowest slope of 62 mV/dec implying that the kinetics of HER and the effectiveness of the charge-transfer processes

will be faster and more efficient in generating hydrogen. The exchange current density also rose significantly in S1 to 0.21 mA/cm2 to that in S4 of 1.12 mA/cm2 indicating a significant increase in intrinsic catalyst activity. These results imply that the artificial nanostructure and optimized electronic atmosphere of S4 minimized the energy barrier of alkaline HER and enhanced faster hydrogen evolution.

Table 4.5 Tafel Slopes and Exchange Current Density

Sample ID	Tafel Slope (mV/dec)	Exchange Current Density (mA/cm²)
S1	118	0.21
S2	82	0.56
S3	75	0.71
S4	62	1.12

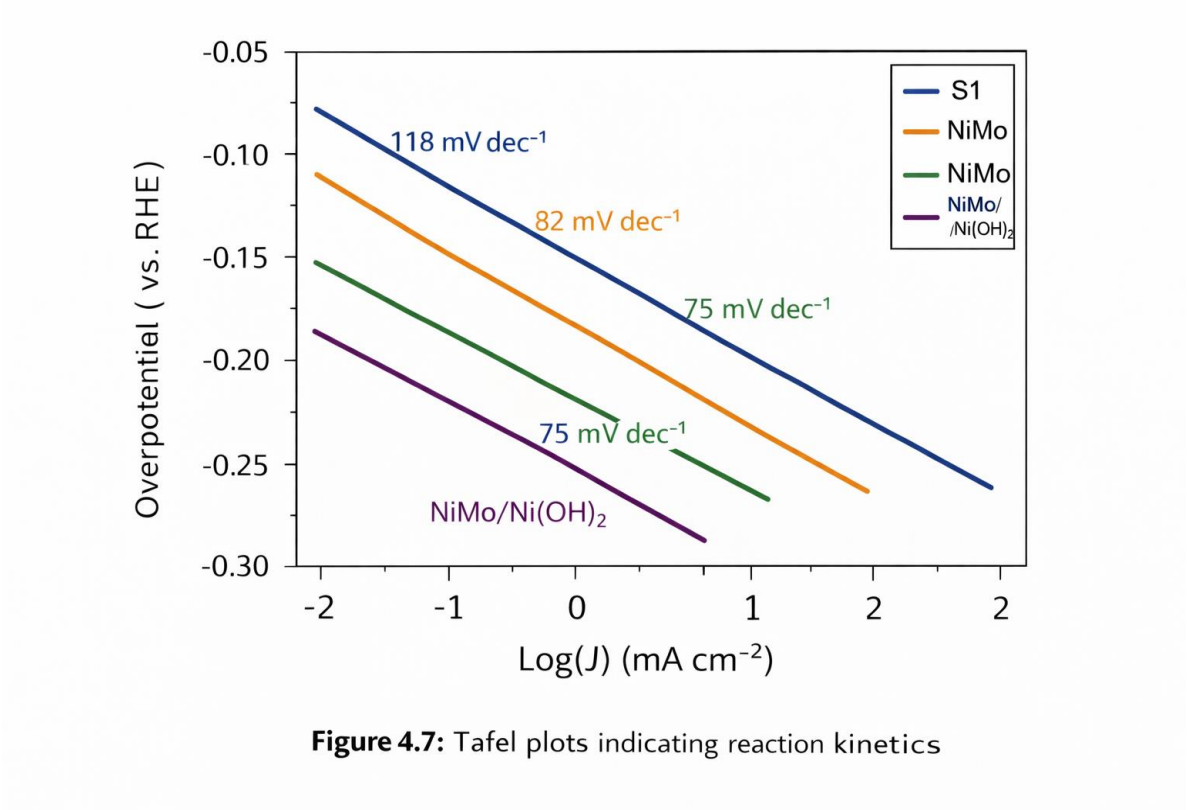

Figure 4.7: Tafel plots indicating reaction kinetics

4.5 Charge Transfer and Interfacial Properties

The high electrochemical activity of the modified catalysts is also supported by the EIS results. The Nyquist plots, as depicted in figure 4.8, reveal that S4 had the smallest diameter of the semicircle implying the less resistive interfacial charge-transfer resistance. According to Table 4.6, the Rct value decreased from 14.5 Ω in S1 to 3.8 Ω in S4. Meanwhile, the double-layer capacitance was raised at the same time, to 11.6 mF/cm2, indicating that the most area of the substrate was electrochemically active in the case of S4.

Table 4.6 Charge Transfer Resistance (EIS)

Sample ID	Rs (Ω)	Rct (Ω)	Double Layer Capacitance (mF/cm²)
S1	2.8	14.5	3.2
S2	2.3	8.7	6.8
S3	2.1	6.2	8.5
S4	1.9	3.8	11.6

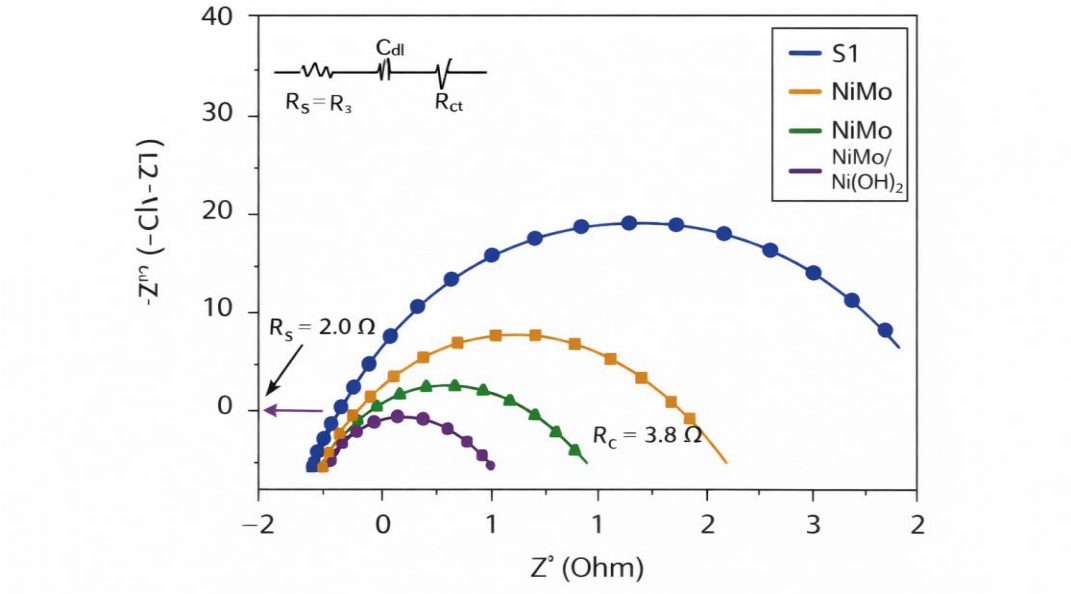

Figure 4.8: Electrochemical impedance spectroscopy (EIS) Nyquist plots

These findings imply that the hierarchical heterostructure enhanced increased electron transit rates and enhanced electrode-electrolyte interactions. Reduced solution resistance and reduced Rct implied reduced energy loss owing to electron transfer and this played a direct role in improving the performances of HER. The morphological results are well-aligned with the high capacitance of S4 and it was observed that more active sites were exposed due to the porous nature of the nanosheet nets.

4.6 Stability and Durability Performance

Practical alkaline water electrolysis requires long-term stability, and the catalysts that were produced had obvious variations in stability. As can be seen in the chronoamperometry curves in Figure 4.9, S1 experienced severe current decays with time, but S4 almost behaved in a constant manner with regards to current response. Likewise, the chronopotentiometry curves in Figure 4.10 indicate that S4 had the lowest potential drift when operated under a constant current.

Table 4.7 Stability Performance

Sample ID	Test Duration (hrs)	Current Retention (%)	Potential Shift (mV)
S1	24	82	+28
S2	48	90	+18
S3	72	93	+12
S4	100	97	+6

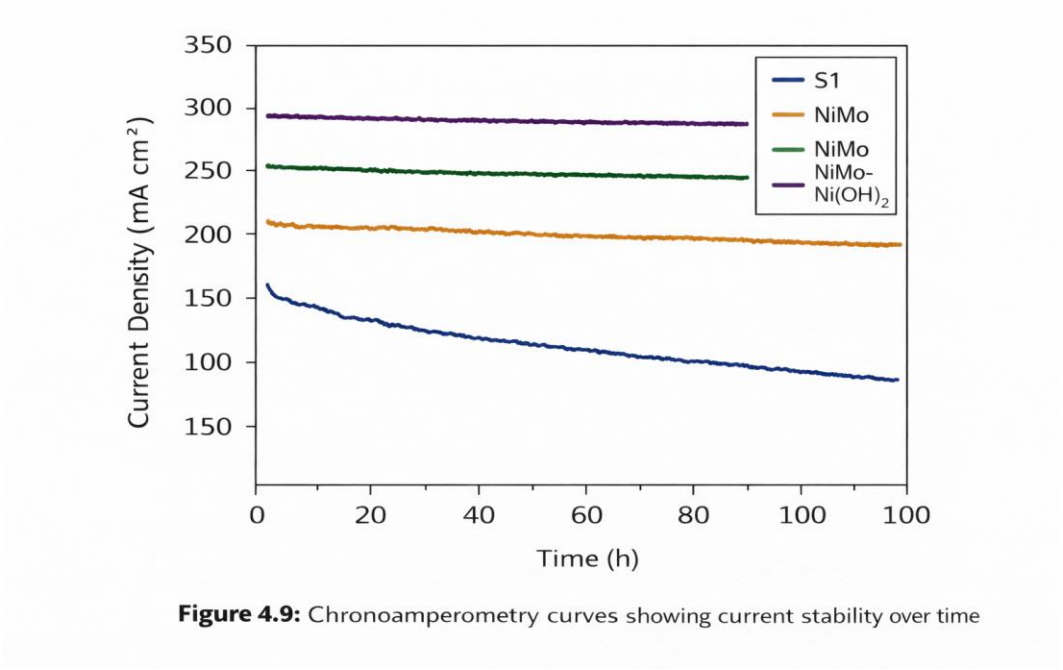

Figure 4.9: Chronoamperometry curves showing current stability over time

This is quantified in Table 4.7. Only 82% of current remained in S1 after 24 hours and 97% in S4 after 100 hours with the potential change being only 6 mV. These results suggest that S4 was very strong in terms of its stability under continuous operation. This enhanced stability was explained by the enhanced structural integrity and improved adhesion of the substrate and increased heterostructured surface that was able to resist degradation in alkaline medium.

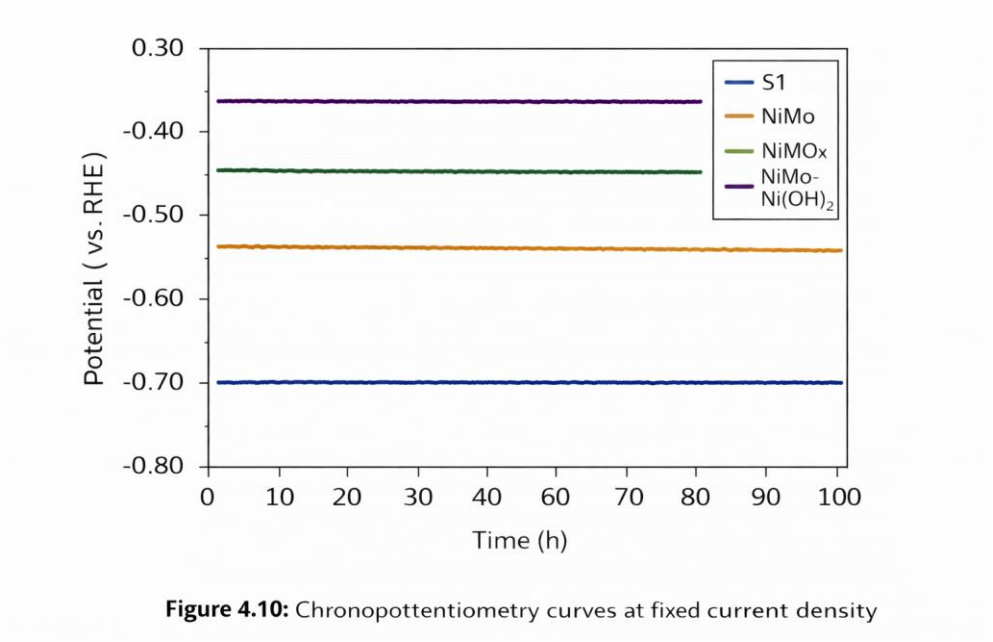

Figure 4.10: Chronopottentiometry curves at fixed current density

4.7 Post-Stability Structural Analysis

Additional evidence of catalyst durability was the post-test analysis. As presented in Fig 4.11, S1 experienced significant particle growth and aggregation over time in testing, but S4 did not experience any significant structural modification as compared to its original nanosheet-based structure, and only a slight extent of growth. Table 4.8 reveals that the size of the particle of S1 was raised between 85 and 102 nm whereas S4 raised the size of the particle between 35-38 nm. Composition change was also lowest in S4, at only 1.1%.

Table 4.8 Pre vs Post Stability Structural Comparison

Sample ID	Particle Size Before (nm)	After (nm)	Composition Change (%)	Structural Integrity
S1	85	102	6.5	Moderate degradation
S2	45	52	3.2	Stable
S3	60	66	2.5	Stable
S4	35	38	1.1	Highly stable

Figure 4.12 demonstrates the post-test XPS spectra where it is possible to note that there was a certain level of surface reconstruction in all the samples. But in S4 such a reconstruction was found to be controlled; probably forming a stable surface with a high concentration of hydroxides and a potential active site. This indicates that mild surface evolution could possibly have the benefit of enhancing catalytic durability through the formation of an active and stable interfacial layer. Thus, the post-stability findings prove that S4 had combined high activity and structural resilience.

4.8 Comparative Performance Evaluation

The relative comparison of Table 4.9 and Figure 4.13 indicates that the most effective catalyst that has been developed during the current work, S4, was even more efficient than the benchmark Ni foam and aligned quite well with reported non-noble HER catalysts. Its

overpotential of 78 mV, at 10 mA/cm2, Tafel slope of 62 mV/dec and stability of 100 hours characterizes a large enhancement over traditional Ni-based materials. Whilst there were also reported NiMo systems that displayed competitive operation, the low overpotential, quick kinetics and intense durability developed by S4 points to the successful implementation of the current design strategy.

Table 4.9 Comparative Performance with Literature

Catalyst System	η @10 mA/cm² (mV)	Tafel Slope (mV/dec)	Stability (hrs)
Ni Foam	200	120	20
NiMo (reported)	95	70	50
CoP-based	110	80	40
This Work (S4)	78	62	100

On the whole, this set of results demonstrates that structural tuning, compositional regulation and engineering of heterointerfaces collectively enhanced catalytic capabilities of transition-metal nanostructures in alkaline HER. Out of all the samples, S4 invariably demonstrated the best mode of crystallographic modification, surface area, charge-transfer behavior, activity, and durability, which is why this sample proved to be the most encouraging first in terms of alkaline water electrolysis application.

5. Discussion

5.1 Interpretation of the Main Findings

The current research demonstrates that the performances of the catalysts improved systematically between S1 and S4 as the structural complexity, compositional tuning, interfacial engineering, and interfaces grew. According to the results of the XRD in Figure 4.1 and Table 4.1, the incorporation of Mo and hydroxide-assisted heterostructure formation changed the Ni lattice and

formed mixed-phase structures, whereas, the SEM and TEM results in Figures 4.2 and 4.3 prove that this structural rearrangement was also accompanied by the shift of comparatively compact nanoparticles to a more Sample S4 achieved the most desirable results in terms of combination of the lowest average particle size, surface area, maximum oxygen content, and best electrochemical indicators: the lowest overpotential, Tafel slope, and charge-transfer resistance. Collectively, these results favor the opinion that the performance of alkaline HER is not dictated by a single structural parameter, but rather a combination of nanostructure, phase composition, and interfacial chemistry. This understanding aligns with recent experiments, which indicate that alkaline HER catalysts can be advantaged by having both water dissociation and hydrogen adsorption sites spatially coupled under a single conductive nanoscale structure.

Linear proportions of EDS and XPS in Figures 4.4 and 4.5 indicate that the good performance of S4 has close associations with its optimized surface chemistry. The higher oxygen concentration and the presence of both metallic and oxidized species suggests that there is a catalytically useful interfacial environment as opposed to an entirely metallic surface. Such a surface can be beneficial in alkaline HER since the hydroxide-saturated or oxide-saturated domains can, at the same time, promote water activation, whereas the adjacent metallic domains can promote hydrogen adsorption and electron transfer. The low Tafel slope and high exchange current density of S4 thus demonstrates that its heterointerface is likely to reduce the activation energy barrier of the Volmer step and enhance the following hydrogen formation. A similar mechanism is also reported with cornerstone packages of heterojunctions and interface-controlled NiMo systems including recent research, in which electronic redistribution on the metal/oxide or metal/hydroxide interfaces has been found to increase intermediate adsorption as well as interfaces charge transport.

5.2 Comparison with Other Studies

Electrochemical outcomes of current work are fairly comparable to an extensive body of recent non-noble alkaline HER studies. Table 4.9 and Figure 4.13 indicate that not only was S4 superior to the conventional Ni foam but also to be compared with the reported NiMo and CoP-type catalysts, in particular, when stability is taken into account alongside activity. The high-potential of S4 at 10 mA cm-2 and its low charge-transfer coefficient lie in the performance range of state-

of-art transition-metal heterostructures. This is significant since in most recent reports, heterojunction engineering has been noted to be one of the surest ways to overcome fundamental restrictions of single-phase catalysts in alkaline media. The 2025 and 2026 Ferrella reviews, as well, find that heterointerfaces, defect-rich surfaces, and hierarchical structures all enhance catalytic activity via the reduction of water adsorption, H-OH cleavage, hydrogen binding, and bubble release.

The action of S4 in particular resembles newly reported NiMo-based heterostructures. As an illustration, NiMo/CoMoO4 systems with constrained oxygen holes demonstrated that the mixed type of metal-metal oxide interface can enhance the alkaline HER performance and stability through the combination of electrical conductivity and higher degrees of water dissociation. Similarly, crystalline-amorphous NiMo-NiMoOx architectures have been reported to have an advantage over simple alloys due to the disordered interface that forms more flexible adsorption sites and a greater concentration of active sites. Current results are well consistent with the trend. S4, a NiMo/Ni(OH)2 alloy, seems to be achieving a similar separation of catalytic action, with the hydroxide-rich component probably helping activate the water and maintaining a high rate of electron transfer via the alloyed metallic framework. In this regard, the present work solidifies the rising agreement that the most useful alkaline HER catalysts are multifunctional interfacial systems, as opposed to compositionally simplistic metals.

These durability outcomes can also be considered significant with reference to the wider body of literature. Table 4.7, Figure 4.9 and 4.10 indicate that S4 maintained excellent current retention and minimum possible drift during prolonged testing, unlike S1 which deteriorated much faster. This disparity is very pertinent as in recent research it has been noted that apparent promising catalysts on a smaller-scale basis often fail under sustained-use conditions owing to the effects of the bubble in its induction of stress, poor adhesion, coarsening of particles or unstable surface chemistry. The criterion of high-current stability has now become a key metric of industrial relevance, and recent studies have emphasised that mechanical strength and interface retention are equally significant compared to inherent catalytic activity. This sparse particle growth and reduction in composition change of S4, Table 4.8) supports the position that it was not only the increased number of active sites in the hierarchical heterostructure that allowed growth in alkaline operational conditions, but also the structural resilience.

5.3 Study implications.

The undertaking of this study has both scientific and practical implications. Scientifically, it validates the idea that nanostructure engineering cannot be viewed as a purely morphological approach; instead, it works via a number of interrelated processes, such as control of surface reconstruction, redistribution of interfacial charges, and establishment of chemically distinct reaction domains. The good performance of S4 indicates that alkali chemical route with hydroxide-assisted surface functionality is a viable path towards enhancement of alkaline HER kinetics. This is in agreement with recent theoretical and experimental claims that the issue of catalyst design does not solely lie in creating maximum metallic conductivity or surface area; rather it is about controlling the local reaction microenvironment.

On the applications side, the results apply to alkaline and anion-exchange membrane electrolysis of water, which require low cost non-noble catalysts to produce hydrogen at large scales. Low overpotential, high kinetics, low impedance, and favorable durability make S4 a potential candidate to develop a cathode. In a wider sense, the findings indicate that high-performance transition-metal catalysts can also be made without the use of noble metals, as long as the design of the catalysts incorporates both direct control of lattice structure, interface chemistry and mechanical stability. This is especially relevant to industrial systems, where the failure of catalysts is regularly due to long-term structural degradation as opposed to low initial activity.

5.4 Study limitations.

Although these findings are promising, the study has a number of limitations. To begin with, the electrochemical assessment was carried out in a laboratory testing environment and thus is not fully representative of an actual industrial electrolyzer environment. Second, surface reconstruction as proposed by XPS and post-test imaging was not directly monitored by operando methodology, although it is highly likely that these were the real active sites in operation. As of recent, there is a growing focus of literature on ex situ characterization being inadequate to characterize the behavior of catalysts when under bias, particularly in transition-metal systems where the dynamics are dynamically changing under the influence of alkaline media. Third, the catalyst series could be described as primarily dealing with Ni-Mo-based

compositions implying that the conclusions can be most easily applied to this material family but not to all transition-metal HER catalysts.

5.5 Study Conclusion.

To sum up, the research proves that the rational construction of the nanostructured transition-metal catalysts can considerably boost the performance of the HER in the process of the electrology of alkaline water. S4 was among the materials synthesized that always displayed the optimal balance of structural tuning, active surface exposure, good surface chemistry, rapid charge transfer, and durability. The general discourse suggests that the high-quality behavior of S4 is due to the synergy between NiMo alloy domains and hydroxide-related interfaces between domains in the porous hierarchical architecture. These results are in good agreement with the current developments in the alkaline HER studies and the argument in favor of catalyst design with heterostructures is that of a viable approach to the next-generation green hydrogen technologies. This should be continued in future work to operando characterization and device-level validation using industrially-relevant current densities.

References

Baek, D. S., Lee, J., Lim, J. S., & Joo, S. H. (2021). Nanoscale electrocatalyst design for alkaline hydrogen evolution reaction through activity descriptor identification. *Materials Chemistry Frontiers, 5*, 4042.

Kawashima, K., & Milton, R. D. (2024). Incidental and intentional transformation: Transition metal pnictide and chalcogenide electrocatalysts for alkaline hydrogen evolution. *ACS Energy Letters*.

Li, J., Jing, Z., Bai, H., Chen, Z., Osman, A. I., Farghali, M., Rooney, D. W., & Yap, P. S. (2023). Optimizing hydrogen production by alkaline water decomposition with transition metal-based electrocatalysts. *Environmental Chemistry Letters, 21*(5), 2583-2617.

Luo, M., et al. (2023). Insights into alloy/oxide or hydroxide interfaces in Ni-Mo-based electrocatalysts for hydrogen evolution under alkaline conditions. *Chemical Science*.

Ogunkunle, S. A., et al. (2024). Navigating alkaline hydrogen evolution reaction descriptors for electrocatalyst design. *Catalysts, 14*(9), 608.

Qadeer, M. A., Zhang, X., Farid, M. A., Tanveer, M., Yan, Y., Du, S., Huang, Z.-F., Tahir, M., & Zou, J.-J. (2024). A review on fundamentals for designing hydrogen evolution electrocatalyst. *Journal of Power Sources, 613*, 234856.

Rosman, N. N., Ng, W. S., Mohd Shah, N. R. A., Masdar, M. S., Karim, N. A., Ataollahi, N., & Yunus, R. M. (2025). Nanostructured transition metal-based electrocatalysts: A promising pathway in anion exchange membrane water electrolysis. *Materials Today Sustainability, 31*, 101203.

Tüysüz, H. (2024). Alkaline water electrolysis for green hydrogen production. *Accounts of Chemical Research, 57*, 558.

Xiao, C., Hong, T., Jia, J., Jia, H., Li, J., Zhu, Y., Ge, S., Liu, C., & Zhu, G. (2024). Unlocking the potential of hydrogen evolution: Advancements in 3D nanostructured electrocatalysts supported on nickel foam. *Applied Catalysis B: Environmental, 355*, 124197.

Xiong, J., Li, J., Shi, J., Zhang, X., Suen, N.-T., Liu, Z., Huang, Y., Xu, G., Cai, W., Lei, X., Feng, L., Yang, Z., Huang, L., & Cheng, H. (2018). In situ engineering of double-phase interface in Mo/Mo2C heteronanosheets for boosted hydrogen evolution reaction. *ACS Energy Letters, 3*(2), 341-348.

Yan, L., Zhang, B., Wu, S., & Yu, J. (2020). A general approach to the synthesis of transition metal phosphide nanoarrays on MXene nanosheets for pH-universal hydrogen evolution and alkaline overall water splitting. *Journal of Materials Chemistry A, 8*, 14234-14242.

Yao, R., et al. (2024). Stable hydrogen evolution reaction at high current densities via designing the Ni single atoms and Ru nanoparticles linked by carbon bridges. *Nature Communications*.

Zhang, L., Wei, H., Yuan, R., Li, P., & Ren, J.-T. (2025). Interface engineering of transition-metal-based electrocatalysts for alkaline water splitting. *Coordination Chemistry Reviews, 545*, 217009.

Zhu, Y., et al. (2024). Alkaline hydrogen evolution reaction electrocatalysts for energy conversion and sustainable hydrogen generation. *JACS Au*.

Zuo, Y., et al. (2023). High-performance alkaline water electrolyzers based on abundant materials. *Nature Communications*.

Cabanillas-Esparza, L. F., et al. (2025). Tuning the Ni/Mo ratio and minimizing Pt usage: Boosting dual hydrogen electrocatalysis with Pt/NiMo catalysts. *Catalysts, 15*(7), 633.

Cheng, X., et al. (2023). Hierarchical cobalt-nickel phosphide/molybdenum disulfide hybrid electrocatalyst triggering efficient hydrogen generation in a wider pH range. *ACS Applied Energy Materials*.

Che, S., et al. (2025). Design and synthesis of self-supported water-splitting transition metal-based electrocatalysts via electrospinning. *Catalysts, 15*(3), 205.

Ding, Y., et al. (2025). Synthesis and structural engineering of transition metal sulfides for hydrogen evolution reaction electrocatalysis. *Chemistry, 13*(3), 84.

Dong, A., et al. (2025). Interlayer-bonded Ni/MoO2 electrocatalyst for efficient hydrogen evolution reaction with stability over 6000 h at 1000 mA cm−2. *Nature Communications, 16*, Article 59933.

Dong, A., et al. (2025). Recent advances in non-noble metal electrocatalysts for hydrogen evolution reaction. *Nanomaterials, 15*(14), 1106.

Fu, G., Kang, X., Zhang, Y., Yang, X., Wang, L., Fu, X.-Z., Zhang, J., Luo, J.-L., & Liu, J. (2022). Coordination effect-promoted durable Ni(OH)2 for energy-saving hydrogen evolution from water/methanol co-electrocatalysis. *Nano-Micro Letters, 14*, Article 215.

Gao, G., Zhao, G., Zhu, G., Sun, B., Sun, Z., Li, S., & Lan, Y.-Q. (2025). Recent advancements in noble-metal electrocatalysts for alkaline hydrogen evolution reaction. *Chinese Chemical Letters, 36*(1), 109557.

Guo, W., et al. (2022). Electrochemically activated Ni@Ni(OH)2 heterostructure as an efficient hydrogen evolution reaction electrocatalyst for anion exchange membrane water electrolysis. *Materials Today Chemistry*, *26*, 101021.

Guo, W., et al. (2024). An efficient and stable MXene-immobilized, cobalt-based catalyst for hydrogen evolution reaction. *Metals, 14*(8), 922.

Javed, N., et al. (2025). Transition metal sulfide electrocatalysts for water splitting: Bridging computational design and experimental advancements. *Journal of Power Sources, 639*, 236446.

Lawan, B., et al. (2026). Non-noble metal catalysts for the alkaline hydrogen evolution reaction: A review. *Discover Chemistry, 3*, Article 55.

Luo, Q., Zhao, Y., Sun, L., Wang, C., Xin, H., Song, J., Li, D., & Ma, F. (2022). Interface oxygen vacancy enhanced alkaline hydrogen evolution activity of cobalt-iron phosphide/CeO2 hollow nanorods. *Chemical Engineering Journal, 437*, 135376.

Ogunkunle, S. A., et al. (2024). Navigating alkaline hydrogen evolution reaction descriptors for electrocatalyst design. *Catalysts, 14*(9), 608.

Ren, J.-T., et al. (2023). Synergistic activation of crystalline Ni2P and amorphous NiMoOx nanorod arrays for efficient alkaline hydrogen evolution. *ACS Catalysis, 13*, 10223-10235.

Sadeghi, E., et al. (2023). NiMo/CoMoO4 heterostructure with confined oxygen vacancy for active and durable alkaline hydrogen evolution reaction. *ACS Applied Energy Materials, 6*, 10456-10466.

Sharma, A. K., et al. (2023). MXene supported nickel-cobalt layered double hydroxide as an efficient bifunctional electrocatalyst for hydrogen and oxygen evolution reactions. *Journal of Alloys and Compounds, 935*, 168076.

Shaw, R. N. R., et al. (2026). MXenes as emerging 2D materials for hydrogen generation. *Journal of Materials Chemistry A, 14*, Advance online publication.

Singh, M., et al. (2025). Interface engineering strategies for enhanced electrocatalytic hydrogen evolution reaction. *Energy Advances, 4*, 1-29.

Solangi, M. Y., et al. (2024). Ti3C2Tx MXene coupled Co(OH)2: A stable electrocatalyst for the hydrogen evolution reaction in alkaline media. *RSC Sustainability, 2*, 1-12.

Tan, H., et al. (2022). Engineering a local acid-like environment in alkaline medium for efficient hydrogen evolution reaction. *Nature Communications, 13*, Article 2443.

Tan, X., et al. (2025). Synthesis of NiMo-NiMoOx with crystalline/amorphous heterostructures for highly efficient hydrogen evolution. *Nano Research, 18*, Advance online publication.

Wan, C., et al. (2023). Amorphous nickel hydroxide shell tailors local chemical environment on platinum surface for alkaline hydrogen evolution reaction. *Nature Materials, 22*, 1022-1029.

Dong, A., et al. (2025). Recent advances in non-noble metal electrocatalysts for hydrogen evolution reaction. *Nanomaterials, 15*(14), 1106.

Lawan, B., et al. (2026). Non-noble metal catalysts for the alkaline hydrogen evolution reaction: A review. *Discover Chemistry, 3*, 55.

Ma, H. B., et al. (2024). Rational design of heterostructured nanomaterials for alkaline hydrogen evolution reaction. *Journal of Electrochemistry*.

Rosman, N. N., et al. (2025). Nanostructured transition metal-based electrocatalysts. *Materials Today Sustainability*.

Sadeghi, E., et al. (2023). NiMo/CoMoO4 heterostructure with confined oxygen vacancy for active and durable alkaline hydrogen evolution reaction. *ACS Applied Energy Materials, 6*, 10456-10466.

Xu, C., et al. (2025). Transition metal-based heterojunctions for alkaline electrocatalysis. *Coordination Chemistry Reviews*.

Xiong, L., et al. (2024). Metallic Ni3N/Ni heterostructure for efficient hydrogen evolution reaction. *International Journal of Hydrogen Energy*.

Yao, R., et al. (2024). Stable hydrogen evolution reaction at high current densities. *Nature Communications, 15*, Article 46553.

Zhu, Y., et al. (2024). Alkaline hydrogen evolution reaction electrocatalysts for energy conversion and sustainable hydrogen generation. *JACS Au*.

Zou, J., et al. (2026). Surface/interface regulation of NiMo-based catalysts for alkaline hydrogen evolution reaction. *Applied Physics Letters, 128*(12), 123902.