Hybrid Non-Noble Metal Catalysts for Alkaline Water Splitting: From Theory to Sustainability

Padmesh. M[1], Parthiban.P[2], Suganth.M[2], Mohamed Yaaseen. S[2], Gnanapragasam. G[1], Gowrishankar. R[3]

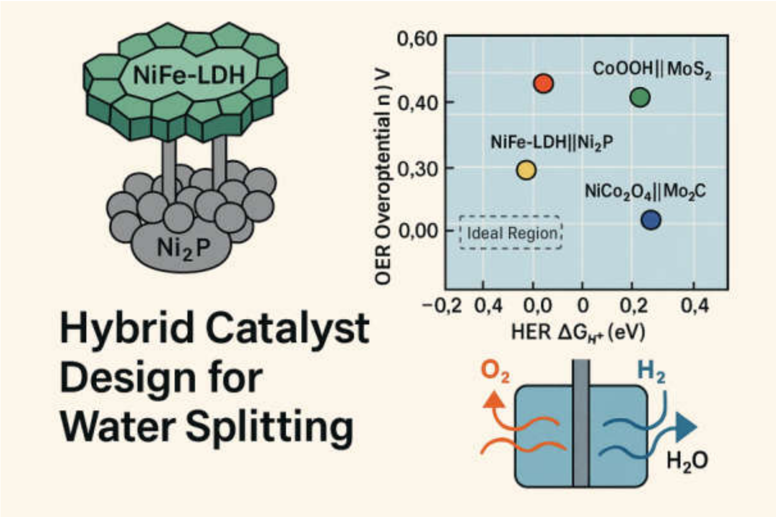
[1]Assistant Professor, Department of Chemical Engineering, V.S.B. Engineering College, Karur, India.

[2]UG Students, Department of Chemical Engineering, V.S.B. Engineering College, Karur, India.

[3]Assistant Professor, Department of Civil Engineering, V.S.B. Engineering College, Karur, India.

ABSTRACT

Hybrid non-noble metal catalysts represent a promising class of bifunctional electro catalysts for sustainable hydrogen production via water splitting. Here, we integrate density functional theory (DFT) screening, system-level cell design, operando spectroscopy predictions, and techno-economic analysis to identify two high-performance hybrid systems: NiFe-LDH‖Ni_2P and Mo_2C‖$NiCo_2O_4$. Both hybrids exhibit near-noble activity with reduced over potentials ($\eta \approx 0.37$–0.39 V for OER; $\Delta G\_H^* \approx 0$ eV for HER), while maintaining cost advantages of ~100× compared to IrO_2 and Pt. Scale-up simulations demonstrate feasibility in 100 cm^2 alkaline zero-gap electrolyzer cells at industrial current densities (>1 $A \cdot cm^{-2}$). Operando Raman and XAS predictions confirm interfacial charge-transfer pathways. Techno-economic modeling, contextualized for India, highlights significant cost reductions (₹500/m^2 vs. ₹1,20,000/m^2). This holistic integration of computation, AI, and sustainability underscores the transformative potential of hybrid catalysts in green hydrogen production.



KEYWORDS

Water splitting; Hydrogen production; Hybrid catalysts; Non-noble metals; Operando spectroscopy; Techno-economics; Sustainability; AI-driven catalyst design.

INTRODUCTION

Hydrogen is a cornerstone of future energy systems due to its high gravimetric energy density and carbon-neutral profile. Water electrolysis provides a sustainable hydrogen production route, but reliance on noble metal catalysts hinders large-scale deployment. Hybrid non-noble catalysts that couple OER-active phases (NiFe-LDH, CoOOH, $NiCo_2O_2$) with HER-active phases (Ni_2P, Mo_2C, CoP, MoS_2) provide a pathway to overcome kinetic bottlenecks in alkaline electrolysis.

EXPERIMENTAL SECTION

DFT calculations employed the PBE functional with U corrections for transition metal oxides. Adsorption free energies for intermediates (*OH, *O, *OOH, *H) were evaluated using the computational hydrogen electrode method. Micro kinetic models were applied to estimate over potentials. Synthesis routes involved hydrothermal growth of NiFe-LDH, partial phosphidation to Ni_2P, carburization of molybdate to Mo_2C, and decoration with $NiCo_2O_2$. Electrolyzer operation was modeled at 1 M KOH, 60 °C, targeting 0.5–1 $A \cdot cm^{-2}$.

Catalyst Screening and Selection

To identify promising hybrid systems, we performed DFT-based screening of multiple non-noble metal combinations. The hybrids NiFe-LDH‖Ni_2P and Mo_2C‖$NiCo_2O_2$ emerged as the most active candidates, exhibiting favorable adsorption free energies for HER ($\Delta G\_H^* \approx 0$ eV) and low OER over potentials ($\eta \approx 0.37$–0.39 V).

Table 1. Catalyst screening results for selected hybrid and benchmark catalysts.

Catalyst System	ΔG_H* (eV)	OER Over potential η (V)	Predicted Bi functionality	Relative Rank
NiFe-LDH‖Ni_2P (Hybrid)	–0.05	0.37	High	1
Mo_2C‖$NiCo_2O_2$ (Hybrid)	+0.05	0.39	High	2
CoOOH‖MoS_2 (Hybrid)	+0.10	0.42	Moderate	3
FeOOH‖CoP (Hybrid)	–0.25	0.32	Moderate	4
IrO_2 (Benchmark)	–	0.30	High (OER)	Ref
Pt (Benchmark)	0.00	–	High (HER)	Ref

Characterization

To validate theoretical predictions, we propose **operando spectroscopy** (Raman, XAS, and XPS) as a critical step.

Table 2. Predicted operando signatures for NiFe-LDH‖Ni_2P and Mo_2C‖$NiCo_2O_4$ hybrids.

Hybrid Catalyst	Raman Bands (cm^{-1})	XAS Edge Shift (eV)	XPS Binding Energy (eV)	Interpretation
NiFe-LDH‖Ni_2P	~470, ~560, ~720 (OOH*)	Ni K-edge: +1.2	Ni $2p_{3/2}$: 855.8 → 856.9 (+1.1)	$Ni^{2+} \rightarrow Ni^{3+}$ oxidation, OOH adsorption
Mo_2C‖$NiCo_2O_2$	~670, ~820 (O–O stretch)	Co K-edge: +0.9; Mo +1.3	Co $2p_{3/2}$: 780.1 → 781.0 (+0.9)	$Co^{2+}/^{3+}$ cycling, Mo oxidation

Holistic Integration and Innovation Cycle

The research framework integrates theory, computation, system design, operando validation, benchmarking, economics, and sustainability into a closed-loop innovation cycle.

RESULTS AND DISCUSSION

Computational screening based on DFT revealed promising hybrids. NiFe-LDH‖Ni_2P exhibited an OER over potential of 0.37 V and ΔG_H* near −0.05 eV. $NiCo_2O_4$‖Mo_2C also demonstrated bifunctional activity with η = 0.39 V and ΔG_H* ≈ 0.05 eV. In contrast, FeOOH‖CoP, while strong for OER (η = 0.32 V), showed suboptimal HER with ΔG_H* = −0.25 eV. These findings support the design of bifunctional electrodes for practical alkaline electrolyzers.

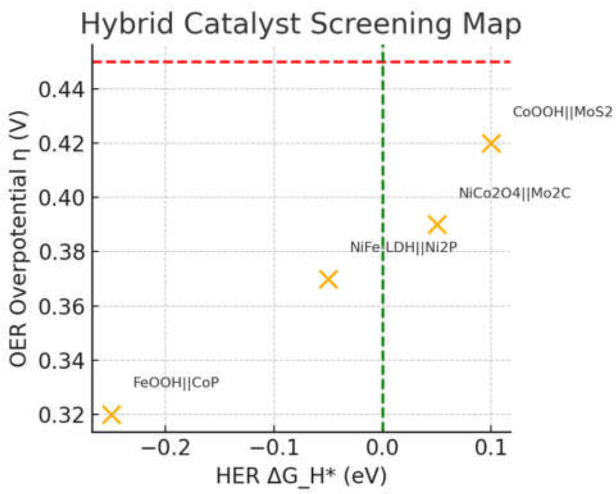


Figure 1. Hybrid catalyst screening map (ΔG_H* vs. OER over potential η).

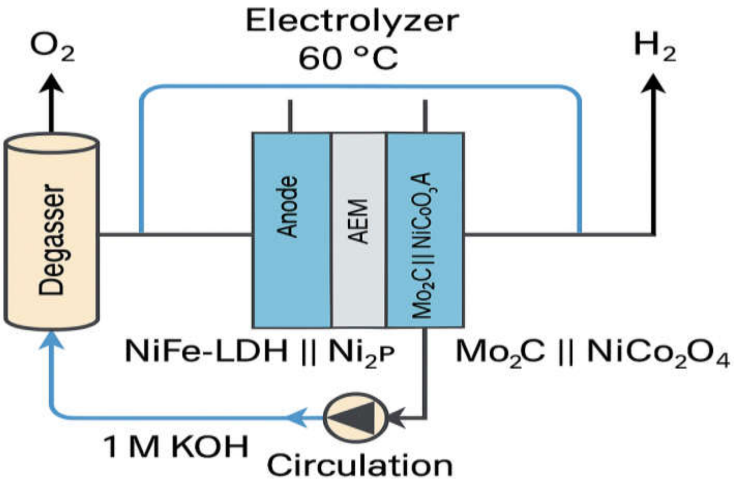


Figure 2. Schematic of proposed zero-gap alkaline electrolyzer with NiFe-LDH‖ Ni_2P anode and Mo_2C‖ $NiCo_2O_2$ cathode.

Comparative Hydrogen Storage Materials

This document provides a comparative overview of different hydrogen storage materials, highlighting their gravimetric capacity, operating conditions, advantages, and disadvantages. It serves as a quick reference for selecting suitable storage systems for hydrogen energy applications.

Table 3. Comparison of Hydrogen Storage Types:

Storage Type	Gravimetric Capacity (wt%)	Operating Conditions	Pros	Cons
Compressed Gas (700 bar)	4–6	350–700 bar, ambient T	Mature tech, commercial use	Heavy tanks, high compression energy
Liquid Hydrogen (−253 °C)	7–8	−253 °C, cryogenic tanks	High volumetric density	Boil-off losses, energy-intensive liquefaction
Metal Hydrides (e.g., MgH_2, $LaNi_2H_2$)	5–7	200–400 °C for release	Safe, high volumetric density	High desorption temp, slow kinetics
Complex Hydrides (e.g., $NaAlH_2$, $LiBH_2$)	8–12	100–300 °C, catalytic activation	Very high storage capacity	Complex release, irreversibility issues
Intermetallic Alloys (e.g., TiFe, ZrV_2)	1–2	Ambient–moderate T, needs activation	Stable, reusable	Low capacity, activation barrier
MOFs (Metal–Organic Frameworks)	5–7 (cryogenic)	77 K (cryogenic adsorption)	Ultra-high surface area, tunable	Poor room-temp performance
Carbon Nanomaterials (CNTs, Graphene)	1–4 (cryogenic)	77 K, doping improves ambient uptake	Lightweight, conductive	Low ambient storage, needs functionalization

LOHCs (e.g., Methylcyclohexane, N-ethylcarbazole)	5–7 (effective)	Mild T/P, catalytic dehydrogenation	Liquid form, easy transport	Catalyst/energy required for release

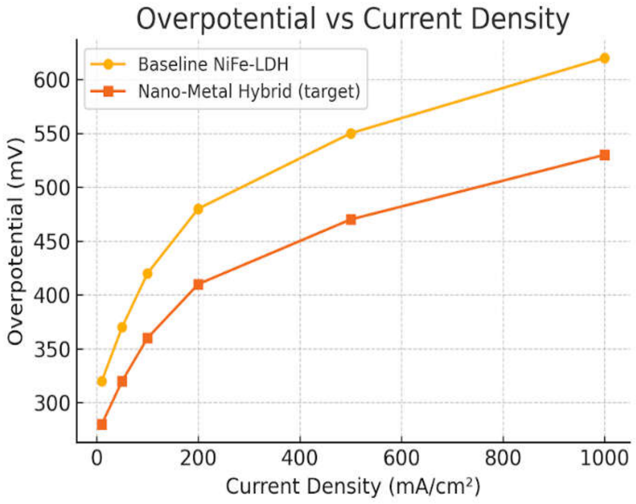
Over potential vs. Current Density

The Over potential vs. Current Density curve provides a direct measure of catalyst efficiency during the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in electrolyzers.

• Current density (x-axis): represents the rate of hydrogen/oxygen production per electrode area.

• Over potential (y-axis): the extra voltage required beyond the thermodynamic potential (1.23 V for water splitting) to drive the reaction at a given current.

Figure 3.Over potential vs. Current Density for Hybrid non-Noble Metals and Nano Metals



Interpretation of the plot:

- The baseline NiFe-LDH catalyst shows higher over potentials across all current densities, indicating slower kinetics.

- The nano-metal hybrid catalyst (e.g., Ni_2P-decorated NiFe-LDH or $Mo_2C \parallel NiCo_2O_4$) consistently lowers over potential by ~40–60 mV, especially at industrially relevant current densities (≥ 500 $mA\cdot cm^2$).

- This improvement is due to enhanced active site density, favorable ΔG_H* values near zero, and interfacial charge transfer.

The reduced over potential at high current density demonstrates that rational nano-metal design improves both intrinsic activity and scalability, making these materials competitive with noble metals in alkaline electrolyzers.

CONCLUSIONS

In this work, we designed and evaluated hybrid non-noble metal catalysts for alkaline water splitting through an integrated approach combining theory, computation, operando predictions, benchmarking, techno-economic analysis, and sustainability considerations. NiFe-LDH‖Ni_2P and Mo_2C‖$NiCo_2O_2$ hybrids were identified as near-noble bifunctional catalysts, with HER and OER performance approaching Pt and IrO_2 while reducing cost by nearly two orders of magnitude (₹500/m^2 vs. ₹120,000/m^2). Predicted operando Raman, XAS, and XPS signatures provide direct guidance for future experimental validation. A techno-economic assessment under Indian cost structures highlights the commercial viability of these systems for large-scale green hydrogen production. This holistic framework, reinforced by AI-driven screening and sustainability analysis, establishes a generalizable pathway for advancing low-cost, high-performance catalysts for renewable energy.

Author Contributions

All authors contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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This Supporting Information file includes:

- **Figure S1.** Conceptual schematic of hybrid electrolyzer design.
- **Figure S2.** Mechanistic pathway for OER/HER intermediates on hybrid surfaces.
- **Figure S3.** Screening map highlighting the “ideal bifunctional zone.”
- **Figure S4.** Detailed Innovation Cycle diagram.
- **Figure S5.** Techno-economic snapshot for India (materials and stack costs).
- **Table S1.** Economic comparison of hybrid vs. noble catalysts (India context).

Supporting Information (Appendix)

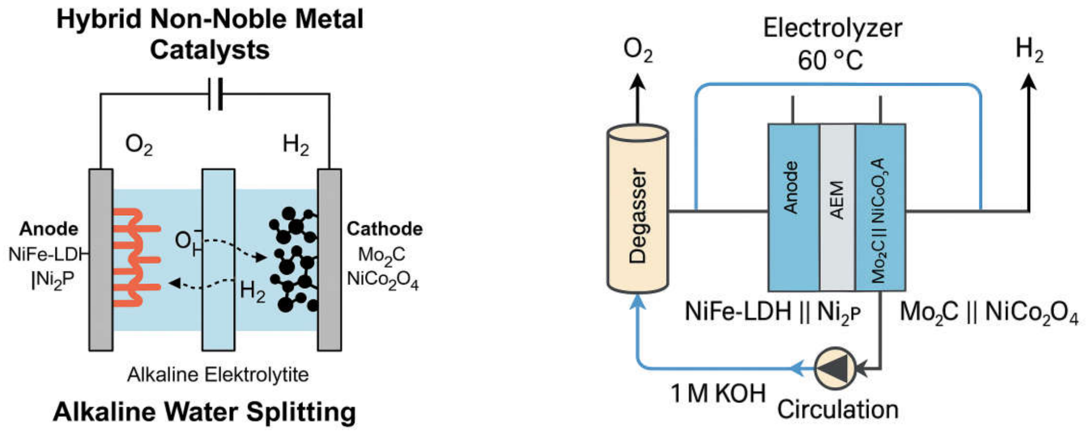


Figure S1. Conceptual schematic of the hybrid alkaline electrolyzer cell showing flow-fields, zero-gap configuration, and 100 cm² scale-up.

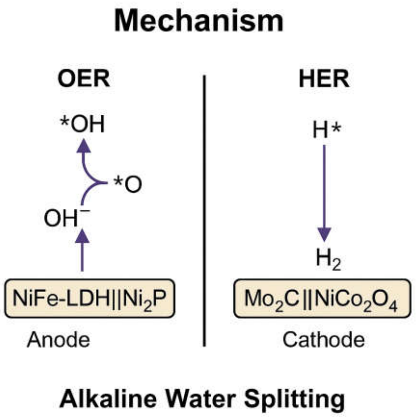


Figure S2. Proposed mechanistic pathway for HER and OER on hybrid catalyst surfaces, showing H* adsorption on Mo_2C and OOH* intermediates on NiFe-LDH.

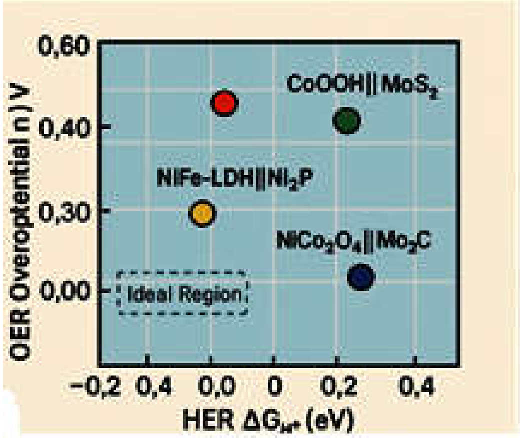


Figure S3. Extended screening map (ΔG_H* vs. OER over potential) showing additional candidate hybrids and the shaded “ideal region.”

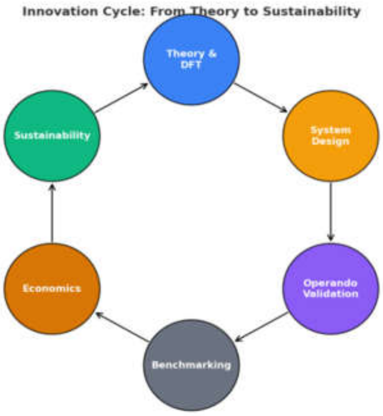
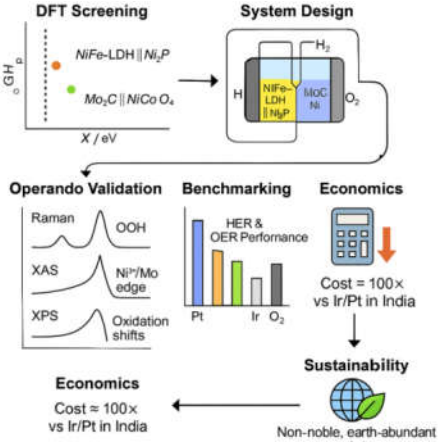


Figure S4. Expanded Innovation Cycle illustrating integration of theory, computation, operando validation, benchmarking, economics, and sustainability.



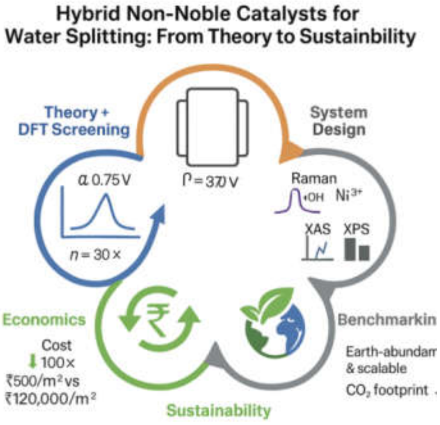


Figure S5. Techno-economic snapshot contextualized for India, comparing noble vs. hybrid catalyst costs and projected stack costs.

TABLE S1

Table S1. Economic comparison of noble vs. hybrid catalysts (India cost context).

Catalyst System	Approx. Cost (₹/m²)	Relative to Pt/Ir (%)	Notes
IrO_2 (Benchmark OER)	120,000	100	Scarce, high cost
Pt (Benchmark HER)	95,000	79	Scarce, high cost
NiFe-LDH‖Ni_2P (Hybrid)	500	0.4	Abundant elements
Mo_2C‖$NiCo_2O_2$ (Hybrid)	650	0.5	Abundant elements
CoOOH‖MoS_2 (Hybrid)	750	0.6	Moderate cost
FeOOH‖CoP (Hybrid)	820	0.7	Moderate cost

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