WP5 Report: Theories Formation and Scaling-up Potential

Executive summary

WP5 is the culminating analytical work package of the DEMADES project. Its role is to transform the experimental findings of the preceding work packages into theoretical frameworks describing catalyst formation, structure–property relationships, HER kinetics and mechanisms, and to determine how the most promising catalyst concepts could be translated from laboratory preparation to larger-area electrodes and ultimately to practical water-electrolysis systems.

The project description assigns WP5 a broad set of tasks: formulation of theoretical models for catalyst development and HER kinetics, definition of optimal synthesis conditions, establishment of structure–property–performance relationships, assessment of scale-up pathways, techno-economic feasibility, environmental implications, scale-up risks and mitigation strategies, and knowledge transfer among project partners and industrial stakeholders. WP5 is led by CEMEA SAS and implemented jointly with IMR SAS and IEE SAS.

The experimental evidence establishes several distinct catalyst-design routes. Optimized DES-electrodeposited Ni demonstrates that HER activity can be altered substantially without changing nominal composition: Sample 19_2, prepared at 30 °C and 20 mA cm^{-2}, provided the best overall pure-Ni response in the 30 °C series. Ni/MXene Sample 20, deposited at 30 °C and 25 mA cm^{-2}, gave the most favorable operating overpotentials among the extensively screened composite coatings, including $\eta 10 = 209.52$ mV. Ni/MoS_2 coatings demonstrate an interfacial route to activity enhancement, although the improvement is strongly process-dependent. Ni0.4Co0.6S demonstrates the benefit of a dual-phase heterointerface and high accessible surface area while using a very short mechanochemical synthesis. C-MoFeNiP-1200 provides the strongest direct stability/degradation evidence, including a 22 h alkaline test and post-test compositional and morphological analysis. Finally, Ni/MoS_2-modified Ni foam demonstrates the potential of three-dimensional self-supported electrodes for higher geometric current densities.

The theoretical framework proposed in this report is a process–structure–property–performance–durability chain. Synthesis variables determine nucleation, phase formation, dispersion, interface density, porosity and defect structure; these determine electronic structure, water-dissociation capability, hydrogen-binding

energetics, conductivity and mass transport; these in turn determine measurable HER descriptors such as overpotential, Tafel behavior, exchange-current density, charge-transfer resistance and high-current performance; stability and scale-up are then governed by the persistence of those beneficial structures under realistic current density, gas evolution and long operating time.

For scale-up, the most important conclusion is that the project should not attempt to scale every catalyst family equally. The first scale-up tier should emphasize low-temperature DES-electrodeposited Ni and Ni/MXene, together with Ni/MoS_2-modified Ni foam, because electrodeposition is intrinsically compatible with large conductive substrates and direct catalyst integration. $Ni_{0.4}Co_{0.6}S$ has attractive synthesis-throughput potential because the demonstrated reaction time is only ~30 s, but powder handling, coating integration and Co use require further development. C-MoFeNiP is scientifically valuable as a mechanistic and durability benchmark, but the 1200 °C treatment creates a significant scale-up energy burden that should be reduced before prioritizing large-volume manufacture.

WP5 therefore recommends a staged scale-up pathway: establish laboratory process windows and critical quality attributes; validate reproducibility on larger electrode areas; quantify catalyst loading, current efficiency, bath stability and process energy; test electrodes at ≥100 mA cm^{-2} and progressively toward several hundred mA cm^{-2}; conduct ≥100 h durability testing for lead candidates; then perform pilot-cell validation and a data-based techno-economic and environmental assessment.

Report structure

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1. WP5 mandate, scope and evidence base

1.1 Formal WP5 objectives

According to the DEMADES project description, WP5 “Theories formation and scaling-up potential”, is led by CEMEA SAS, and involves CEMEA SAS, IMR SAS and IEE SAS. Its objectives are to create comprehensive theoretical frameworks describing catalyst-development kinetics and mechanisms; derive optimal synthesis conditions and their relationship with activity and stability; develop models for HER kinetics on the newly developed electrodes; establish structure–property relationships; document scale-up strategies; assess production costs, resources and market viability; evaluate environmental effects of scale-up; identify technological and economic risks; and formulate mitigation and knowledge-transfer strategies.

The project description specifies D5.1 as the WP5 final report and D5.2 as the final comprehensive project report addressing the suitability of the developed catalysts and technologies for large-scale application. Milestone M5.1 is the meeting of all project partners for extensive discussion of data obtained in all previous work packages.

1.2 Evidence used in this report

Evidence source Contribution to WP5

Project description Formal WP5 objectives, responsibilities, deliverables, milestone, scale-up and techno-economic scope.

WP1 and WP2 data Experimental activity.

WP3 HER analysis Experimental activity, kinetic parameters, preparation-condition trends, stability evidence and catalyst-family comparisons.

WP4 sustainability analysis Derived HER energy penalties, durability framework, resource/process considerations and sustainability data gaps.

HER review from published data Theory of HER, DFT/ML/multiscale concepts, structure–property relationships, industrial-current requirements, durability and scalable synthesis principles.

Where a numerical result is not available in the project data, this report does not replace it with an assumed value. Instead, it defines the required equation, measurement or inventory needed for final validation. This distinction is particularly important for production cost, catalyst loading, current efficiency, bath lifetime, energy consumption per batch, waste generation and lifetime hydrogen output.

2. Theoretical framework for catalyst formation

2.1 Process–structure–property–performance model

The central theoretical model developed for WP5 is a causal chain linking synthesis to practical HER behavior:

Process variables → Structure / phase / interface → Physicochemical properties → HER performance → Durability → Scale-up viability

The framework is intentionally multi-scale. At the process scale, temperature, current density, time, precursor chemistry, mixing, mechanical energy and thermal history control the material that is formed. At the microstructural scale, these parameters determine grain size, phase fraction, defect density, porosity, roughness, particle dispersion, coating thickness and interface connectivity. At the electronic scale, these structures determine conductivity, local charge redistribution, adsorption energies and barriers for water activation and hydrogen adsorption/desorption. At the electrode scale, porosity, wettability, adhesion and electrical connectivity determine bubble release, current distribution and mass transport. Scale-up succeeds only if the beneficial features generated at small scale remain invariant or controllably reproducible on larger areas or batch volumes.

2.2 Formation model for DES-electrodeposited Ni

For DES-derived Ni, the WP3 data demonstrate that catalyst performance is strongly affected by deposition temperature and current density even though the nominal catalyst chemistry remains Ni. This supports a formation model in which electrochemical nucleation and growth control the catalytic microstructure. Current density changes the rate of Ni-ion reduction and surface nucleation, while temperature affects DES viscosity, ionic conductivity, diffusion and

nucleation/growth kinetics. Their coupled effect can alter grain size, nanocrystallinity, porosity, roughness, thickness and accessible active area.

The experimentally observed non-monotonic response is important. At 60 °C, increasing deposition current from 5 to 10 mA cm^{-2} improved HER performance, whereas further increases progressively reduced the advantage. Conversely, the 30 °C series produced particularly favorable performance at higher deposition current, with Sample 19_2 at 20 mA cm^{-2} providing the strongest overall pure-Ni response. Thus, there is no universal 'higher current is better' rule. Instead, each temperature establishes a process window in which nucleation density, mass transport and growth rate combine to produce a favorable surface.

The scalable form of this theory is that electrodeposition quality should be controlled through dimensionless or normalized process invariants: local current density, temperature, bath composition, water content, hydrodynamic mass transfer, electrode spacing and charge passed per unit area. Large-area scale-up should preserve these local conditions rather than merely multiplying total current.

2.3 Formation model for Ni/MoS_2 and Ni/MXene composite coatings

Composite electrodeposition introduces a second formation problem: incorporation and retention of dispersed solid particles within the growing Ni matrix. The resulting catalyst is therefore controlled by both Ni nucleation/growth and particle transport to the cathode. Particle concentration, dispersion stability, agglomeration state, surface charge, bath viscosity, convection and deposition current can all alter the amount and spatial distribution of MoS_2 or MXene incorporated into the coating.

The WP3 Ni/MoS_2 data show substantial series-to-series variation even at matched electrodeposition current density, indicating that current density alone does not fully determine composite formation. The average results nevertheless suggest that the 5–15 mA cm^{-2} range provides more favorable mean HER performance than 20 mA cm^{-2}. This supports the hypothesis that excessively rapid metal growth can reduce beneficial particle incorporation or produce less favorable composite morphology.

Ni/MXene exhibits a different optimum. Sample 20, prepared at 30 °C and 25 mA cm^{-2} with a 20 min deposition time, provided η_{10} = 209.52 mV. This indicates that under the lower-temperature DES conditions, high deposition current can still generate a highly favorable Ni/MXene architecture. The formation theory is

therefore material-specific: scale-up must control not simply average particle content but the connectivity and interfacial density of the second phase within the Ni matrix.

2.4 Formation model for mechanochemically synthesized $Ni_{1-x}Co_xS$

The Ni–Co sulfide route is governed by mechanically induced reaction, phase formation and heterointerface development. WP3 identifies a non-linear composition–activity relationship: $Ni_{0.4}Co_{0.6}S$ performs markedly better than several neighboring compositions. Its superior geometric HER activity is associated with high C_{dl}, low R_{ct} and a functional dual-phase heterointerface rather than a simple monotonic effect of Ni or Co fraction.

This result supports a formation model in which the decisive variable is not nominal composition alone but whether the mechanochemical reaction produces the required interconnected phase topology. Scale-up must therefore preserve collision energy, powder mixing, local reaction temperature, atmosphere and phase-forming conditions. The demonstrated ~30 s synthesis in a stainless-steel mixer mill is attractive for throughput, but larger batches cannot be assumed to experience identical specific mechanical energy.

2.5 Formation model for C-MoFeNiP

C-MoFeNiP formation is dominated by thermal transformation during pyrolysis. WP3 shows improved alkaline activity and reduced Rct with increasing pyrolysis temperature, with C-MoFeNiP-1200 reaching η_{10} ≈321 mV and R_{ct} ≈5.3 Ω. The corresponding theory is that higher-temperature treatment increases crystallinity, interdiffusion and formation/mixing of catalytically relevant metal-phosphide phases, while the carbon matrix contributes electrical connectivity and structural support.

However, the high-temperature route carries a scale-up penalty. Heating to 1200 °C increases furnace energy, thermal cycle time and equipment requirements. Therefore, the most important WP5 synthesis question is whether the beneficial phase assemblage and conductivity can be reproduced using lower peak temperature, shorter dwell, altered precursor chemistry or assisted thermal processing.

3. Theoretical framework for HER kinetics and structure–performance relationships

3.1 Alkaline HER kinetic model

The DEMADES materials are primarily evaluated in alkaline electrolyte, where HER requires water activation before adsorbed hydrogen can form. The elementary sequence can be represented as:

Volmer: $H_2O + e^- + * \rightarrow H^* + OH^-$

Heyrovsky: $H^* + H_2O + e^- \rightarrow H_2 + OH^- + *$

Tafel: $H^* + H^* \rightarrow H_2 + 2*$

A successful alkaline HER catalyst must therefore combine rapid water dissociation with favorable hydrogen adsorption and desorption. The processed data emphasizes the value of bifunctional and interfacial catalyst architectures in which one domain is oxophilic and promotes H–O–H cleavage while a neighboring domain provides suitable H-binding characteristics. **This theoretical concept is directly relevant to Ni/MoS_2, Ni/MXene, Ni–Co sulfides and reconstructed phosphide surfaces.**

3.2 Tafel kinetics as an empirical model

$$\eta = a + b \log_{10}|j|$$

Within a validated current-density interval, the Tafel slope b describes the additional overpotential needed for a tenfold increase in current. The intercept controls the absolute position of the Tafel relation. WP3 demonstrates why slope alone is insufficient: Ni/MXene Sample 16 had a substantially smaller slope than Sample 20, yet Sample 20 exhibited much lower operating overpotentials because the entire polarization curve was shifted to more favorable potential.

Similarly, apparent exchange current density should be used comparatively because it is obtained by extrapolation. For scale-up, directly measured operating overpotentials at technologically relevant current densities are more important than extrapolated equilibrium parameters.

3.3 Structure–property descriptors

Structural feature	Expected physicochemical effect	Expected HER consequence	Relevant DEMADES system
Nanocrystallinity / high roughness	Higher accessible area and defect density	Higher geometric current at fixed η	DES-Ni
Metal–MoS_2 interface	Charge redistribution and additional active sites	Improved water/H adsorption balance	Ni/MoS_2
Ni–MXene interface	Conductive interface, surface termination effects, dispersed active domains	Lower operating overpotential	Ni/MXene
Dual sulfide phases	Interfacial charge transfer and higher ECSA	Lower Rct and improved geometric activity	Ni0.4Co0.6S
Crystalline metal phosphides + carbon	Conductivity and active phosphide phases	Improved charge transfer; reconstructive activity	C-MoFeNiP
3D foam architecture	Higher area, bubble pathways and self-supported conduction	Improved high-current geometric response	Ni/Ni foam; Ni/MoS_2/Ni foam

3.4 Theoretical/computational tools for future model validation

The review of published and experimental data identifies density functional theory, machine learning and multiscale modeling as complementary tools for connecting atomic structure to measured activity. DFT can calculate hydrogen adsorption free energy ΔG_{H^*}, water-dissociation barriers, electronic density of states, d-band descriptors and charge transfer. For DEMADES, the highest-value DFT problems are not generic screening tasks but comparisons between experimentally realized interfaces and phases: Ni/MoS_2 boundaries, Ni/MXene terminations, Ni–Co sulfide heterointerfaces and reconstructed phosphide/oxyhydroxide surfaces.

Machine learning becomes useful after a sufficiently consistent project database exists. Inputs could include deposition temperature, current density, time, composition, morphology descriptors, XRD phase fractions, elemental ratios, C_{dl}

and R_{ct}, while outputs could include η_{10}, η_{100} and degradation rate. The aim should be interpretable process–structure prediction rather than black-box ranking. Multiscale modeling can then connect atomistic descriptors with porous-electrode transport, gas evolution and full-cell performance.

4. Theory-guided synthesis optimization of DEMADES catalyst families

4.1 Optimized DES-Ni

The preferred pure-Ni scale-up starting point is the low-temperature process represented by Sample 19_2: 30 °C and 20 mA cm^{-2}. The scale-up program should define a robust operating window around this condition rather than treat the single laboratory point as fixed. Recommended variables are 25–35 °C, current density around the demonstrated optimum, deposition charge per area, DES water content, Ni precursor concentration, substrate pretreatment and agitation.

The critical quality attributes should be coating mass per area, thickness uniformity, roughness/porosity, adhesion, phase purity, and HER overpotential. Because the strongest advantage of pure Ni is compositional simplicity, future optimization should first exhaust process control before adding further alloying elements.

4.2 Optimized Ni/MXene

Ni/MXene Sample 20 is the primary composite scale-up candidate. The demonstrated condition of 30 °C, 25 mA cm^{-2} and 20 min should be reproduced across larger substrates while monitoring MXene suspension stability. The immediate optimization target is not maximum MXene addition, but the minimum MXene content and incorporation level that maintains the low η_{10}. This reduces raw-material demand and limits the upstream burden of MXene preparation.

Scale-up trials should continuously or periodically homogenize the bath, quantify sedimentation, and measure coating composition at multiple positions on the substrate. Spatial uniformity is a key acceptance criterion because a laboratory polarization measurement on a small coupon can conceal large-area gradients.

4.3 Optimized Ni/MoS_2

For Ni/MoS_2, the best individual WP3 coating was Sample 5_3 (η_{10} ≈259.1 mV), but the matched-series averages indicate favorable behavior primarily within 5–15 mA cm^{-2} rather than at 20 mA cm^{-2}. The appropriate scale-up strategy is therefore to repeat a narrow process window using controlled MoS_2 concentration,

particle-size distribution, agitation and total deposition charge. Equal-loading pure-Ni controls are essential to demonstrate that MoS_2 provides a true interfacial benefit rather than simply altering total coating mass or roughness.

4.4 Optimized $Ni_{0.4}Co_{0.6}S$

$Ni_{0.4}Co_{0.6}S$ should be developed as the mechanochemical benchmark because its dual-phase architecture provides $\eta_{10} \approx 237$ mV, $R_{ct} \approx 9.2\ \Omega$ and the largest C_{dl} within the Ni–Co sulfide series. Its ~30 s synthesis time offers a strong throughput argument. Scale-up should preserve specific mechanical energy and phase composition while minimizing Co content. A next-generation composition series around x = 0.6 Co should test whether the same heterointerface can be maintained with further Ni substitution.

For practical electrodes, the powder route also requires a scalable integration method: ink coating, spray coating, electrophoretic deposition, roll-to-roll coating, or direct mechanochemical/thermal formation on a conductive support. The added binder and coating step must be included in future performance and cost comparisons.

4.5 Optimized C-MoFeNiP

C-MoFeNiP-1200 should remain the mechanistic durability reference, but the route should be re-optimized for thermal efficiency before scale-up. Recommended experiments include shorter dwell time at 1200 °C, lower-temperature treatment with modified precursors, rapid thermal processing, and systematic phase-property comparison. The target is to preserve low R_{ct} and stable HER behavior while decreasing thermal energy per gram of usable catalyst.

Because post-test analysis showed partial phosphorus loss and oxidation, synthesis optimization should also consider whether a deliberately pre-conditioned surface state can reduce the activation period and stabilize composition before long-term operation.

4.6 Ni-foam and self-supported electrodes

Ni foam provides the most direct architecture for practical scale-up because it combines substrate, current collector and high-area support. The WP3/WP4 analysis showed that Ni and especially Ni/MoS_2 modification substantially increased the cathodic response relative to bare foam. The next synthesis objective should be uniform penetration of catalyst through the foam without pore blockage.

For scale-up, the most important process variables are foam thickness and porosity, surface cleaning, coating mass per geometric area, coating depth, electrical contact resistance, and gas-release behavior. These electrodes should be prioritized for high-current tests because their scale-up value is primarily architectural rather than only intrinsic low-current kinetics.

5. Scaling-up potential and process translation

5.1 Scale-up criteria

A catalyst is considered scale-up-ready only when performance can be reproduced while increasing electrode area or batch size without losing critical structure. WP5 therefore proposes six scale-up criteria: reproducibility, manufacturability, resource intensity, energy intensity, electrode integration, and durability under relevant current density.

Criterion	Scale-up question	Required measurement
Reproducibility	Does the same process produce the same catalyst across batches and positions?	η_{10}/η_{100} distribution, composition, thickness, phase, loading
Manufacturability	Can the process be run on larger area/batch with available equipment?	Throughput, total current/power, agitation, furnace/mill capacity
Resource intensity	How much catalyst and critical material is required per m^2?	mg cm^{-2}, utilization yield, Co/Mo/MXene content
Energy intensity	How much manufacturing energy is used?	Wh m^{-2} or kWh kg^{-1} catalyst
Integration	Can the catalyst be applied directly to a robust current collector?	Adhesion, contact resistance, pore accessibility
Durability	Does scale-up preserve performance under realistic operation?	≥100 h CP and ≥100 mA cm^{-2} for lead systems

5.2 Electrodeposition scale-up

Electrodeposition has high scale-up potential because the catalyst can be formed directly on a conductive support, avoiding separate powder recovery, ink formulation and binder application. The fundamental scale-up relation is:

$$I_{total} = j_{dep} \times A$$

Thus, maintaining the laboratory deposition current density on a larger substrate requires proportional increase in total current. Scale-up also changes current distribution: edge effects, electrode spacing and ohmic drop can create thickness gradients. Industrial translation therefore requires current-distribution design, multiple electrical contacts, controlled agitation and bath monitoring.

The preferred route is to scale area in steps rather than jump directly from coupons to square-metre electrodes: approximately 4 cm^2 → 25–100 cm^2 → 500–1000 cm^2 → pilot plate/foam. At each stage, composition and electrochemical response should be mapped spatially.

5.3 Composite-bath scale-up

For Ni/MoS_2 and Ni/MXene, bath homogeneity becomes a primary scale-up variable. Sedimentation or particle agglomeration can cause strong vertical and longitudinal composition gradients in larger tanks. Mixing should therefore be designed to maintain suspension without creating excessive air entrainment or uncontrolled shear. Recirculation, bath filtration strategy, particle-concentration monitoring and periodic replenishment should be developed as process-control steps.

5.4 Mechanochemical scale-up

Mechanochemical scale-up is not obtained simply by using a larger jar. Collision frequency, ball-to-powder ratio, filling fraction, impact energy, heat generation and reaction propagation can all change with equipment scale. For $Ni_{0.4}Co_{0.6}S$, the relevant process invariant should be specific mechanical energy delivered per mass of powder together with XRD-confirmed phase composition. Continuous or semi-continuous mechanochemical equipment could ultimately offer greater throughput than long batch milling if the short reaction time is preserved.

5.5 Thermal-process scale-up

C-MoFeNiP scale-up is constrained by furnace energy, heating/cooling time, gas atmosphere and thermal uniformity. Larger batches can develop temperature gradients that alter phase composition. Scale-up should therefore use thermocouple mapping, controlled gas flow and mass-normalized energy accounting. The high 1200 °C peak temperature makes energy minimization a formal optimization target rather than a secondary consideration.

6. Theoretical scale-up calculations for electrode manufacture and hydrogen production

6.1 Large-area electrodeposition current demand

For a 1 m^2 electrode, 1 m^2 = 10,000 cm^2. The total current required to preserve a laboratory deposition current density is:

$$\mathbf{I_{total}(A) = j_{dep}(A\ cm^{-2}) \times 10{,}000\ cm^2}$$

Deposition current density	Total current for 1 m^2
5 mA cm^{-2}	50 A
10 mA cm^{-2}	100 A
15 mA cm^{-2}	150 A
20 mA cm^{-2}	200 A
25 mA cm^{-2}	250 A

This simple relationship shows that the favorable 30 °C conditions identified for pure Ni and Ni/MXene are electrically realistic for pilot-scale electrodeposition but require industrial rectification and current-distribution control.

6.2 Theoretical Ni deposition mass for the Ni/MXene Sample 20 condition

Ni/MXene Sample 20 was deposited at 25 mA cm^{-2} for 20 min. If all current were used for $Ni^{2+} + 2e^- \rightarrow Ni$ and current efficiency were 100%, Faraday's law gives:

$$\mathbf{m_{Ni} = I\ t\ M_{Ni} / (2F)}$$

For 1 m^2, j = 25 mA cm^{-2} corresponds to I = 250 A and Q = 300 kC over 20 min. The theoretical maximum Ni deposition is approximately 91.2 g m^{-2}. This is not the measured coating loading because actual current efficiency, side reactions and MXene incorporation are unknown. The calculation is valuable as a scale-up upper bound and identifies current efficiency as a required future measurement.

Likewise, a 20 mA cm^{-2}, 20 min Ni deposition would correspond to a theoretical maximum of approximately 73.0 g Ni m^{-2} at 100% current efficiency. If the actual current efficiency is φ, the predicted Ni mass becomes φ times this theoretical value.

6.3 Hydrogen production capacity per electrode area

Faraday's law provides a direct bridge from electrode current density to hydrogen-production capacity:

$$n_{H_2} = I \times FE / (2F)$$

$$m_{H_2} = I \times FE \times M_{H_2} / (2F)$$

Assuming 100% Faradaic efficiency for a theoretical upper-bound calculation, the hydrogen-production rate per square metre is:

HER current density	Current per 1 m^2	Theoretical H_2 production	Area required for 1 kg H_2 h^{-1}
10 mA cm^{-2}	100 A	0.00376 kg h^{-1} m^{-2}	265.9 m^2
100 mA cm^{-2}	1000 A	0.0376 kg h^{-1} m^{-2}	26.6 m^2
500 mA cm^{-2}	5000 A	0.188 kg h^{-1} m^{-2}	5.32 m^2
1 A cm^{-2}	10,000 A	0.376 kg h^{-1} m^{-2}	2.66 m^2

These calculations demonstrate why the common data emphasis on current densities above 500 mA cm^{-2} is central to scale-up. A catalyst evaluated only at 10 mA cm^{-2} would require approximately 266 m^2 of active cathode area to produce 1 kg H_2 h^{-1} at that current density, whereas operation at 500 mA cm^{-2} reduces the theoretical area to approximately 5.3 m^2. Therefore, high-current durability and bubble management are not optional secondary metrics; they determine the physical scale and capital intensity of the electrode system.

6.4 HER overpotential energy penalty

$$E_{\eta,H_2} = 2F\eta$$

Using representative WP3/WP4 η10 values, the isolated cathodic kinetic energy penalties are:

Candidate	η_{10}	HER kinetic penalty (kWh kg^{-1} H_2)	Interpretation
Ni/MoS_2/Ni foam 1-3*	≈124 mV	≈3.30	Lowest derived geometric η10; durability evidence still limited

Ni/MXene Sample 20	209.52 mV	≈5.57	Best extensively screened planar composite
Ni Sample 19_2	≈223 mV	≈5.93	Strong activity with simple composition
$Ni_{0.4}Co_{0.6}S$	≈237 mV	≈6.30	Good activity plus rapid synthesis
Ni/MoS_2 Sample 5_3	≈259.1 mV	≈6.89	Composite interfacial route
C-MoFeNiP-1200	≈321 mV	≈8.54	Strongest direct durability evidence

*Ni/MoS_2/Ni foam value is a WP4-derived value from the supplied Cycle-7 polarization dataset. These values represent only the cathodic HER overpotential contribution, not total electrolyzer electricity consumption.

7. Techno-economic framework

7.1 Scope of the techno-economic analysis

The project description explicitly requires a techno-economic analysis of catalyst production and utilization. The available WP1–WP4 information supports a structured TEA framework but does not yet contain the complete cost inventory required for defensible numerical cost-of-hydrogen results. WP5 therefore defines the calculation model and the measurements needed to populate it.

$$C_{electrode} = C_{raw\ materials} + C_{energy} + C_{labor} + C_{equipment} + C_{waste} - C_{recovery}$$

$$C_{lifetime,H_2} = (C_{initial\ electrode} + \Sigma\ C_{replacements}) / m_{H_2,lifetime}$$

For comparison of catalyst synthesis routes, the first functional unit should be cost per square metre of qualified electrode. For application-level comparison, the preferred functional unit is catalyst/electrode cost per kilogram of H_2 produced over the demonstrated lifetime.

7.2 Main economic drivers by catalyst family

Catalyst route	Potential cost advantage	Main cost/scale risk
DES-Ni	Low-cost active metal; low-temperature direct coating; no binder	DES inventory/reuse, deposition time, current efficiency, substrate cost
Ni/MXene	Low-temperature direct coating; lower η than pure Ni in best case	MXene precursor/synthesis burden, dispersion control, added material cost
Ni/MoS_2	Direct composite coating; established MoS_2 material	Particle incorporation efficiency and added Mo/S cost
$Ni_{0.4}Co_{0.6}S$	Very short ~30 s synthesis; cheaper stainless-steel milling chamber than CoS reference	Co cost/supply, powder-to-electrode integration, scale-dependent milling energy
C-MoFeNiP	Multicomponent non-PGM catalyst; demonstrated stability evidence	1200 °C thermal energy, gas handling, powder integration
Modified Ni foam	Self-supported electrode, reduced binder/current-collector complexity	Foam substrate cost, coating penetration/uniformity, high-current lifetime

7.3 Minimum dataset required for final numerical TEA

Data category	Required measurement
Raw materials	Mass and purchase cost of salts, DES components, MoS_2, MXene, Co/Ni precursors, P source, carbon and substrates
Process energy	Actual rectifier electricity, thermostating, mixing, milling, furnace heating/cooling, drying
Yield	Catalyst deposition efficiency, powder yield, rejected batches, usable electrode yield
Throughput	$m^2\ h^{-1}$ or kg catalyst h^{-1}; cycle time and batch size
Lifetime	Hours to defined degradation threshold at practical current density
Productivity	Faradaic efficiency and kg $H_2\ h^{-1}$ per m^2
Recovery	DES reuse, metal recovery, substrate reuse and recycling credit

8. Environmental and resource implications of scale-up

Scale-up can reverse an apparent laboratory sustainability advantage if energy, solvent use, washing or material losses increase disproportionately. WP5 therefore links scale-up decisions to the sustainability framework established in WP4. The review manuscript recommends consideration of material criticality, synthesis energy, life-cycle emissions, water use, toxicity, waste, durability and circularity.

8.1 DES-based electrodeposition

The environmental opportunity of DES electrodeposition is direct low-temperature coating and low volatility; however, environmental benefit must be demonstrated through bath lifetime and recovery rather than assumed from solvent identity alone. Scale-up should quantify DES make-up rate, water uptake, metal depletion, number of reuse cycles, washing water and waste-treatment requirements.

8.2 Critical materials and additive minimization

Pure Ni provides an important baseline because it avoids Mo, Co and MXene synthesis. Composite and sulfide catalysts should therefore demonstrate a performance or lifetime advantage per unit of added critical/strategic material. For $Ni_{0.4}Co_{0.6}S$, partial substitution of Co by Ni is directionally favorable, but the next objective should be to maximize hydrogen output per gram of Co rather than simply reduce nominal Co fraction.

8.3 Thermal energy

C-MoFeNiP-1200 should undergo explicit energy metering because high-temperature pyrolysis is likely to dominate its manufacturing footprint. A lower-temperature route that sacrifices a small amount of initial activity may become preferable if it greatly reduces embodied energy while preserving lifetime.

8.4 Circularity

The strongest circularity opportunities are DES bath reuse, recovery of Ni/Co/Mo from spent liquids, reuse of robust Ni-foam/current-collector substrates, and recovery of catalyst-containing scrap from coating or milling processes. These flows should be incorporated into both LCA and TEA rather than treated as end-of-project considerations.

9. Scale-up risks and mitigation strategies

Risk	Potential consequence	Mitigation strategy	Priority
Large-area current non-uniformity	Thickness/activity gradients	Multiple electrical contacts, current mapping, controlled spacing and agitation	High
Composite particle settling/agglomeration	Non-uniform MoS_2/MXene content	Recirculation, dispersion protocol, concentration monitoring, positional composition mapping	High
DES composition drift	Changing coating structure between batches	Water-content/metal-concentration monitoring, defined bath-reuse limits	High
Foam pore blockage	Mass-transfer and bubble-release losses	Loading optimization, penetration control, tomography/section imaging	High
Mechanochemical energy changes with batch size	Different phase composition	Control specific mechanical energy and XRD acceptance criteria	High
Thermal gradients in C-MoFeNiP scale-up	Phase heterogeneity	Furnace mapping, gas-flow control, smaller modular batches or rapid thermal route	High
Catalyst degradation at high current	Loss of performance/lifetime	≥100 h staged CP, dissolution monitoring, post-test characterization	High
Critical-material price/supply volatility	Unstable production cost	Minimize Co/Mo/MXene loading; qualify alternative formulations	Medium
Incomplete TEA/LCA inventory	Unreliable scale-up decision	Install process metering and mass-	High

		balance templates before pilot scale	
Scale-up schedule constraints	Delayed WP5 validation	Parallelize electrodeposition, durability and process-inventory tasks across partners	Medium

10. Candidate prioritization and scale-up roadmap

10.1 Comparative prioritization

Candidate	Technical rationale	Scale-up potential	Main unresolved issue	Recommended WP5 status
Ni Sample 19_2	Strong pure-Ni activity at 30 °C; compositionally simple	High	Long-term durability, actual loading/current efficiency	Primary electrodeposition scale-up baseline
Ni/MXene Sample 20	Lowest η_{10} among extensively screened planar coatings	High–moderate	MXene dispersion, upstream material burden and long-term stability	Primary composite scale-up candidate
Ni/MoS_2/Ni foam	Very favorable derived geometric response; self-supported 3D electrode	High	Reproducibility, high-current durability, equal-loading comparison	Primary device-integration candidate
$Ni_{0.4}Co_{0.6}S$	Good HER performance; low Rct; ~30 s synthesis	Moderate–high	Co use and scalable powder-to-electrode integration	Primary mechanochemical scale-up candidate
Ni/MoS_2 Sample 5_3	Best planar Ni/MoS_2 result	Moderate	Series variability and additive	Secondary composite route

			benefit vs optimized Ni	
C-MoFeNiP-1200	Best durability/degradation evidence; low R_{ct} in family	Moderate–low until thermal route improved	1200 °C process energy and reconstruction /dissolution	Mechanistic/durability benchmark; optimize thermal process

10.2 Proposed stage-gate roadmap

Gate	Scale	Entry criterion	Exit criterion
G1: laboratory reproducibility	4–25 cm² / gram-scale	Best WP3 synthesis condition	≥3 reproducible batches; defined composition/loading and η10
G2: enlarged electrode/batch	25–1000 cm² / 10–100 g	G1 passed	Spatial uniformity; controlled process energy and yield
G3: high-current validation	Electrode/cell scale	Stable enlarged electrode	≥100 mA cm^{-2}; staged progression toward 500 mA cm^{-2}
G4: durability qualification	Same architecture as G3	High-current activity retained	≥100 h lead test + ≥1000 cycles + post-test analysis
G5: pilot process	Pilot plate/stack or pilot batch	G4 + process inventory	Reproducible manufacturing + preliminary TEA/LCA
G6: industrial engagement	Application-specific	Pilot evidence	External manufacturing/device validation and commercial cost model

10.3 Recommended partner roles

CEMEA SAS should lead electrochemical theory, electrodeposition scale-up and cell-level HER validation. IMR SAS should lead durability interpretation, sustainability metrics and lifetime-normalized performance analysis. IEE SAS should contribute structural/chemical validation, process-resource inventories and

economic/environmental assessment. M5.1 should be used to lock common acceptance criteria and select no more than three primary candidates for the highest-cost pilot experiments.

11. WP5 theoretical models, validation plan and recommendations

11.1 Model A: synthesis–structure relationship

Structure = f(T, j_{dep}, Q/A, bath chemistry, particle transport, mechanical energy, thermal history)

Validation requires measurements of thickness/loading, morphology, phase composition, elemental distribution and surface chemistry across controlled synthesis matrices. For electrodeposition, charge per area Q/A should be reported alongside current density and time because it provides a more transferable scale-up variable.

11.2 Model B: structure–HER relationship

HER performance = f(ECSA, interface density, conductivity, water-activation ability, H-binding energetics, transport)

Validation requires η_{10}/η_{100}, Tafel parameters, EIS, C_{dl}/ECSA proxy, Faradaic efficiency and structural descriptors. DFT should be targeted toward the experimentally identified interfaces and reconstructed phases rather than generic ideal surfaces.

11.3 Model C: scale-up performance

$j_{effective}$ = f($j_{intrinsic}$, active area, bubble coverage, ionic/electronic resistance, mass transport)

This model explains why a catalyst with strong low-current laboratory activity may underperform in a larger electrode. Bubble coverage, local heating, electrolyte distribution and contact resistance become increasingly important with current density and area. Porous Ni foam is expected to benefit from gas-release pathways, but only high-current testing can validate this hypothesis.

11.4 Model D: lifetime-normalized scale-up value

Scale-up value $\propto$ (H_2 output × lifetime × FE) / (material use × synthesis energy × replacement burden)

This is intentionally a framework rather than a single universal score. It identifies the variables that must be measured before a defensible economic or environmental ranking can be produced.

11.5 Specific recommendations

• Use Sample 19_2 as the pure-Ni process baseline and scale the 30 °C DES route first because it combines strong activity, compositional simplicity and direct electrode integration.

• Advance Ni/MXene Sample 20 as the highest-priority planar composite, but optimize MXene loading downward and verify bath dispersion and large-area composition uniformity.

• Advance Ni/MoS_2-modified Ni foam directly into high-current testing because its practical value depends on three-dimensional transport and bubble management.

• Scale $Ni_{0.4}Co_{0.6}S$ through controlled specific mechanical energy and phase acceptance criteria; simultaneously develop a scalable method to integrate the powder with an electrode.

• Retain C-MoFeNiP-1200 as a durability/reconstruction benchmark, while treating reduction of pyrolysis energy as the principal scale-up optimization task.

• Measure catalyst loading, deposition current efficiency, process electricity, bath reuse and material yield for all scale-up candidates; without these data, TEA and LCA remain qualitative.

• Adopt ≥100 mA cm^{-2} as the next mandatory activity benchmark for enlarged electrodes and progressively test toward ≥500 mA cm^{-2} for the most robust self-supported architectures.

• Use ≥100 h steady-state testing and ≥1000 accelerated cycles for lead candidates, combined with dissolution analysis and pre/post SEM/XPS/XRD.

• Apply DFT to the actual experimentally observed interfaces/phases and use ML only after a standardized project database has been assembled.

• At M5.1, select a maximum of three scale-up leaders using a common matrix covering activity, durability, process reproducibility, resource intensity, synthesis energy and electrode integration.

12. Conclusions

WP5 integrates the DEMADES experimental results into a coherent theoretical and scale-up framework. The project data support the central conclusion that HER performance is governed by coupled synthesis–structure relationships rather than composition alone. For DES-Ni and composite electrodeposition, temperature and current density control catalyst formation in a non-monotonic manner. For Ni–Co sulfides, phase connectivity and interface formation dominate over nominal composition. For C-MoFeNiP, pyrolysis controls phase formation and charge transfer but creates an energy-intensive manufacturing route. Three-dimensional Ni foam introduces an architectural pathway in which transport and bubble management become as important as intrinsic catalytic kinetics.

The strongest near-term scale-up platform is direct low-temperature electrodeposition because it is compatible with large conductive substrates, compositionally simple Ni, and composite incorporation. The best-supported starting conditions are the 30 °C pure-Ni and Ni/MXene regimes identified in WP3. Ni/MoS_2-coated Ni foam should be prioritized for practical high-current validation. $Ni_{0.4}Co_{0.6}S$ offers an unusually short synthesis route and should be developed in parallel as a high-throughput powder catalyst. C-MoFeNiP provides the most mature degradation evidence but requires lower-energy thermal processing to improve scale-up attractiveness.

The theoretical scale-up calculations show the importance of operating current density. At 500 mA cm^{-2}, one square metre of cathode can theoretically produce about 0.188 kg H_2 h^{-1} at 100% Faradaic efficiency, whereas at 10 mA cm^{-2} the production rate is only about 0.00376 kg h^{-1} m^{-2}. This factor-of-50 difference demonstrates why future decisions must be based on high-current electrode performance and lifetime rather than η_{10} alone.

A complete numerical techno-economic and environmental assessment cannot yet be finalized because several project-specific inventories are missing, including actual catalyst loading/current efficiency, process electricity, bath-reuse data, manufacturing yield, long-duration lifetime at practical current density, and recovery/recycling performance. WP5 therefore establishes the equations, scale-up metrics, candidate priorities and experimental program required to generate those inputs. This fulfills the theory-formation role of WP5 while defining a practical path from laboratory catalyst discovery to pilot-scale hydrogen electrodes.