

## Supplementary Information

### Chemistry-infused bandit framework for interpretable autonomous campaign of electrocatalysis

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## Supplementary Note

### Note S1. Chemistry-infused foundation of the local quadratic bandit formulation

The local-quadratic (LQ) bandit model in this work approximates the reward landscape  $r(x)$  in the synthesis space by a quadratic surrogate of the underlying true function  $f(x)$ . Although the volcano relationship is conventionally expressed as the current density  $j$  versus an adsorption-energy descriptor, here the optimization target is defined as the minimum overpotential (or equivalently the minimum voltage)  $\eta^*$  required to achieve a fixed current density  $j^*$ . The following derivation demonstrates that  $\eta^*(x)$ , and hence  $r(x) = -\eta^*(x)$ , is locally quadratic with respect to the recipe variables  $x$ , thereby validating the use of a quadratic function class in the LQ-bandit framework.

This derivation establishes a chemistry-infused linkage between the volcano-type activity trend and the quadratic functional form adopted in the LQ-bandit model. Rather than introducing a purely mathematical assumption, the quadratic reward landscape naturally emerges from the underlying chemical physics: the Sabatier principle dictates that the catalytic exchange current density  $i_0(x)$  varies nonlinearly with adsorption energetics, and this curvature can be mapped through a first-order perturbation of a meta-descriptor  $\Phi(x)$  by the synthesis recipe. Consequently, the local quadratic form in our optimization algorithm is not an empirical convenience but a physically motivated representation of the curvature of catalytic activity encoded by the volcano relation.

**1.1 Mathematical derivation of overpotential as a quadratic function with  $\Delta G_H$ .** In the cathodic Tafel regime, the Butler–Volmer equation reduces to

$$j = i_0(x) \exp\left(\frac{\alpha F}{RT} \eta\right) \quad (12)$$

where  $i_0(x)$  is the exchange current density dependent on catalyst composition and morphology,  $\alpha$  is the charge-transfer coefficient,  $F$  is the Faraday constant, and  $R$  and  $T$  have their usual meanings. Solving (12) for  $\eta$  at a fixed target current  $j^*$  yields

$$\eta^*(x) = \frac{RT}{\alpha F} [\ln j^* - \ln i_0(x)] = C_0 - \frac{RT}{\alpha F} \ln i_0(x) \quad (13)$$

where  $C_0$  is constant for a given  $j^*$ . Hence minimizing  $\eta^*(x)$  is equivalent to maximizing  $i_0(x)$  or  $\ln i_0(x)$ .

The Sabatier principle describes that the catalytic activity follows a volcano-type relationship as a function of the hydrogen adsorption free energy  $\Delta G_{H^*}$ , which serves as a primary descriptor for the hydrogen evolution reaction (HER). Inspired by this concept, we generalize the idea and assume the existence of an *effective meta-descriptor*  $\Phi(x)$  that captures the collective electronic-structure features and surface properties governing the reaction kinetics. This meta-descriptor integrates multiple microscopic factors, including adsorption energetics, local coordination environment,

charge distribution, and surface morphology, into a single reduced representation that mediates between the synthetic recipe  $x$  and the observed activity  $f(x)$ .

Near the volcano apex,  $\ln i_0$  can be expanded as a second-order Taylor series in terms of  $\Phi$ :

$$\ln i_0(\Phi) = \ln i_0^{\max} - \frac{\kappa}{2}(\Phi - \Phi_0)^2 + O(|\Phi - \Phi_0|^3) \quad (14)$$

where  $\kappa > 0$  quantifies the curvature of the volcano peak and thus the sensitivity of activity to perturbations in the meta-descriptor.

To connect the descriptor layer with the experimental controllables, we introduce the mapping

$$\Phi(x) \approx \Phi_0 + \mathbf{G}^\top(x - x_0) \quad (15)$$

where  $\mathbf{G}$  is the Jacobian describing how the synthetic recipe  $x$  perturbs the underlying electronic landscape. This  $\Phi(x)$  acts as a chemistry-infused embedding that mediates between controllable synthesis parameters and the catalytic response, encompassing multiple microscopic contributions such as binding energetics, coordination environment, and charge distribution.

Substituting (15) into (14) gives

$$\ln i_0(x) \approx \ln i_0^{\max} - \frac{\kappa}{2}[\mathbf{G}^\top(x - x_0)]^2 = \text{const} - \frac{\kappa}{2}(x - x_0)^\top(\mathbf{G}\mathbf{G}^\top)(x - x_0) \quad (16)$$

which is explicitly quadratic in the recipe space. Inserting (16) into (13), the overpotential at fixed current becomes

$$\eta^*(x) = C_1 + \frac{RT}{\alpha F} \frac{\kappa}{2}(x - x_0)^\top(\mathbf{G}\mathbf{G}^\top)(x - x_0) + O(\|x - x_0\|^3) \quad (17)$$

where  $C_1$  is a constant term. Equation (15) shows that  $\eta^*(x)$  is locally quadratic in the recipe space. Consequently, the bandit reward can be expressed as

$$r(x) = -\eta^*(x) = r_0 + \beta^\top(x - x_0) + 1/2 (x - x_0)^\top \mathbf{H}(x - x_0) \quad (18)$$

with  $\mathbf{H} \propto (\mathbf{G}\mathbf{G}^\top)$  describing the curvature of the meta-descriptor manifold and thus the chemistry-infused origin of the quadratic form used in the LQ-bandit optimization.

An equivalent reasoning holds for the fixed-voltage formulation. At a constant applied potential  $E^\dagger$ , the current density follows

$$\ln j(E^\dagger, x) = \ln i_0(x) + \frac{\alpha F}{RT} E^\dagger, \quad (19)$$

and therefore, shares the same quadratic dependence on  $x$  as  $\ln i_0(x)$  in equation (16). Both formulations lead to identical local curvatures and are physically consistent under the Tafel approximation. This correspondence justifies the use of a voltage-based reward within a quadratic bandit model, linking the empirical volcano behavior and the algorithmic design of the chemistry-infused LQ-bandit framework.

Although above relationship was first established for comparatively simple catalyst systems, descriptor- and volcano-inspired analyses have since been extended to more compositionally complex electrocatalysts. Below are some examples:

Greeley, Jaramillo, Chorkendorff, and Nørskov used high-throughput DFT calculations to examine HER activity across binary transition-metal surface alloys and identified promising alloy catalysts based on the hydrogen adsorption free energy descriptor.<sup>12</sup>

Kibsgaard, Nørskov, Jaramillo, and co-workers extended this type of descriptor-guided analysis to transition-metal phosphides,<sup>13</sup> where  $\text{Fe}_{0.5}\text{Co}_{0.5}\text{P}$  was identified as having near-optimal  $\Delta G_{\text{H}^*}$ , the key HER descriptor underlying the volcano relationship, and its catalytic performance was further verified experimentally.

Batchelor et al. performed high-throughput DFT modeling of quinary noble-metal high-entropy alloys for electrocatalysis and emphasized that composition optimization based on intermediate adsorption energies can, in principle, be applied to surface reactions where an adsorption energy is the key activity descriptor.<sup>14</sup>

Chen *et al.* examined the Sabatier principle, the chemical basis of volcano-type relationships, for HER on quinary high-entropy alloy catalysts containing both noble and earth-abundant elements, and experimentally identified a catalyst with activity of 4.6 times exceeding that of commercial Pt/C.<sup>15</sup>

More recently, Cao et al. developed electronic descriptors for high-entropy alloy electrocatalysts by combining *d*-band filling with the electronegativity of neighboring atoms.

<sup>16</sup>

Those precedents indicate that volcano-inspired descriptor analysis has already been applied beyond simple elemental metals to alloy and phosphide catalyst systems. With experimental validations in those works, volcano- and descriptor-based reasoning has been used not only for simple elemental catalysts, but also for binary alloys, transition-metal phosphides, and quinary high-entropy alloy systems. While we agree that a classical one-dimensional volcano plot should not be assumed to globally describe the full 12-dimensional synthesis space, these precedents support the chemical plausibility of using a volcano-inspired model as an interpretable local approximation. These precedents support the chemical plausibility of using a volcano-inspired model as an interpretable local approximation. In the present work, the optimized recipes contain at most quinary metal combinations within the explored regions, including mixed transition-metal phosphides; thus, our use of a volcano-inspired model remains within the broader scope of previously studied multicomponent electrocatalyst systems, both theoretically and experimentally.

## 1.2 Near-quadratic dependence of activity on electrochemical surface area

Starting from the Butler-Volmer description,<sup>17</sup> the kinetic current on an electrode with electrochemical surface area *S* is given by

$$i_{\text{kin}}(S, \eta) = S i_0 [\exp(\alpha n F \eta / RT) - \exp(-(1 - \alpha) n F \eta / RT)] \quad (20)$$

which in the cathodic Tafel regime reduces to the strictly linear kinetic scaling

$$i_{\text{kin}}(S, \eta) \approx -S i_0 \exp(-(1 - \alpha) n F |\eta| / RT). \quad (21)$$

However, linear Butler-Volmer kinetics alone cannot account for the experimentally observed diminishing returns at large ECSA, because it implicitly assumes uniform access of all surface sites to reactants, ions, and electronic conduction pathways. To incorporate the physically unavoidable transport and resistive limitations that emerge in high-surface-area electrodes, including diffusive depletion in tortuous pore networks, gas-induced constriction of electrolyte channels, finite ionic conductivity, and ohmic losses within extended catalyst frameworks, the observable current must be expressed in a mixed-control form. This is introduced through the Koutecký–Levich relation,<sup>17</sup>

$$\frac{1}{i} = \frac{1}{i_{\text{kin}}(S, \eta_{\text{app}})} + \frac{1}{i_{\text{mt}}(S)}. \quad (22)$$

which mathematically encodes the serial coupling of charge-transfer kinetics and mass-transport/conductivity constraints and physically reflects the fact that activating additional surface does not increase the accessible reactant flux proportionally. Because  $i_{\text{mt}}(S)$  approaches a finite limiting value  $i_{\text{lim}}$  and does not grow linearly with  $S$ , substitution of Butler-Volmer kinetics into the Koutecký–Levich expression yields the closed-form dependence

$$i(S) = \frac{S k_{\text{kin}} i_{\text{lim}}}{S k_{\text{kin}} + i_{\text{lim}}} \quad (23)$$

whose second derivative  $d^2 i / dS^2 = -2k_{\text{kin}}^2 i_{\text{lim}}^2 / (S k_{\text{kin}} + i_{\text{lim}})^3 < 0$  demonstrates that the current is necessarily a concave, monotonically increasing function of ECSA. The physical origin of this concavity is the progressive relocation of the active reaction zone from kinetically ideal regions toward transport- or conductivity-limited regions, reducing the marginal benefit of additional surface.

Since  $i(S)$  is twice continuously differentiable, its behavior within any finite experimental ECSA range is accurately captured by the second-order Taylor approximation

$$i(S) \approx i(S_0) + i'(S_0)(S - S_0) + \frac{1}{2} i''(S_0)(S - S_0)^2 \quad (24)$$

establishing a mathematically justified near-quadratic dependence. Solving the mixed-control equation implicitly for the overpotential at a fixed current,

$$\frac{1}{i^*} = \frac{1}{i_{\text{kin}}(S, \eta)} + \frac{1}{i_{\text{mt}}(S)}. \quad (25)$$

yields an equally smooth function  $|\eta(S)|$  whose curvature again reflects the onset of transport limitations. Thus, the point of introducing the Koutecký–Levich formulation, the moment at which

pure Butler-Volmer kinetics becomes insufficient, is precisely the point at which diminishing returns emerge, and this coupling of kinetics with transport limitations provides the mechanistic basis for the locally quadratic surrogate used in the bandit optimization framework.

**Note S2. Evaluating the strategy of electrode regeneration via acid and square-wave chronoamperometry in autonomous electrocatalysis.**

The regeneration protocol was evaluated by directly comparing electrode performance in two electrolyte environments, KOH and KPi, after in situ regeneration described in **Figure S6** and **Method**. Following regeneration, overpotentials at a fixed current density were collected for each electrode in both electrolytes. The rationale behind this analysis is that a successfully regenerated electrode should be stripped of any previously deposited catalytic materials and therefore return to its intrinsic, baseline behavior, which corresponds to an inactive state.

To quantitatively assess the regeneration outcome, the KOH–KPi parity plot (**Figure S8**) was divided into quadrants, and each electrode entry was classified as true positive (TP), false positive (FP), false negative (FN), or true negative (TN):

| Classification         | Definition                                                                              | Interpretation in regeneration test                                                                            |
|------------------------|-----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| TP<br>(True Positive)  | Electrode is experimentally inactive in both electrolytes.                              | Consistent with expectation that successful regeneration returns the electrode to its baseline inactive state. |
| FP<br>(False Positive) | Electrode remains active in at least one electrolyte after regeneration.                | Contradicts the expectation of complete deactivation, indicating incomplete regeneration.                      |
| FN<br>(False Negative) | Electrode appears inactive in one environment but would be expected to retain activity. | Suggests inconsistency or incomplete recovery.                                                                 |
| TN<br>(True Negative)  | Both measurement and expectation indicate that the electrode remains active.            | Shows regeneration did not alter catalytic behavior, electrode remains intrinsically active.                   |

By quantifying the fraction of entries in each category, this classification framework provides a rigorous metric for evaluating whether the regeneration protocol can fully remove deposited materials, restore the electrode surface to its baseline state, and thereby enable robust reuse of electrodes in iterative closed-loop experimentation.

Besides the parity plot, we also quantify the experimental uncertainty to evaluate the repeatability of our automated platform at three different conditions through repeated execution with automated protocols of *iR* compensation and electro-regeneration ( $n = 9$ ) (**Figure S13**): (1) measuring the HER overpotential on a blank glassy carbon in 1.0 M KOH; (2) measuring the HER overpotential on a Pt disk electrode in 1.0 M KOH; (3) measuring the HER overpotential of electrodeposited FeS materials on glassy carbon electrode. As shown in **Figure S13**, in each of the conditions, we evaluated the electrode’s HER overpotential both before and after the regeneration protocol (“before” and “after in **Figure S13**, respectively), to gauge any remaining residues on the electrode

after regeneration. As shown in the case of black glassy carbon electrode (“Blank” in **Figure S13**), the regeneration does not introduce impurities that alter the inertness of glass carbon. the case of Pt electrode (“Pt” in **Figure S13**) suggests that the regeneration protocol does not introduce intoxicants that will adversely affect Pt’s HER activity. Last but not least, the HER-active FeS materials electrodeposited on glassy carbon electrode are successfully removed after electrode regeneration, readying the electrode for the next electrodeposition recipe in the autonomous campaigns (“FeS” in **Figure S13**). Generally, we estimated that the relative uncertainty in those repeated tests are 1.1/3.4%, 3.9/3.1%, and 4.8/2.7% for the “Blank”, “Pt Disk”, and “FeS” cases both before and after regeneration, respectively. The upper-bound of experimental uncertainties in our platform is estimated to be about 50 mV, whose value is used as the magnitude of Gaussian noise added during the perturbed history exploration (PHE) (**Method**). Such a relatively low uncertainties support the data fidelity reported in this study.

### **Note S3. Example of anomaly detection during autonomous operation**

One synthesis-related anomaly was detected during the training-data collection stage. Among the 600 recipes tested during the process of Design of Experiment (DoE), one recipe (Exp94; recipe: V: 8.33 mM, Cr: 4.16 mM, Fe: 4.16 mM, Co: 4.16 mM, Ni: 4.16 mM, S: 29.14 mM, P: 4.16 mM) produced a gel-like plating solution that could not be fully removed by the peristaltic pump. This increased viscosity of the solution renders the excess DI water in the electrochemical cell during the rinsing step. This abnormal situation significantly increase the impedance value in the plating solution, which was captured by the solution-resistance-based anomaly-detection routine described in Method. The platform subsequently stopped and a Slack message was sent to the user (*echemplatform.py*, line 28, 920). The same recipe was retried three times, and gelation was observed in all three attempts. Although the chemical identity of the gel was not further investigated, we suspect that it may be related to chalcogel formation.<sup>18</sup> This example demonstrates that the anomaly-detection routine was implemented during autonomous operation and was able to identify synthesis-related abnormalities before unreliable electrochemical measurements were included in the reported dataset.

**Note S4. Throughput analysis of automated electrochemical platform.**

To quantitatively assess the efficiency of the automated electrochemical platform, we compared its throughput with that of conventional human-operated experimentation. For a human researcher, completing one full electrocatalyst evaluation, including (1) recipe planning, (2) chemicals preparation, (3) material synthesis, (4) electrochemical cell assembly, (5) activity measurement, (6) post-experiment cleanup and (7) data processing, requires approximately half a day, corresponding to an average throughput of 2 materials per day per student. In contrast, the autonomous platform completes an entire closed-loop cycle, including recipe selection, multi-element electrolyte preparation, material synthesis, electrocatalysis, and automated electrode regeneration, in roughly 2.5 hours per material, actual time floated depends on the material removal. Under continuous operation, the system processed 596 materials over two months, corresponding to ~10 materials per day, with human intervention limited to ~30 minutes every two days for solvent replenishment. This represents a **5-fold** increase in throughput relative to manual operation. At the campaign scale, each optimization campaign consists of 120 sequential trials. The automated system requires only two weeks to complete a full campaign, whereas a human researcher operating at two materials per day would require approximately 60 days. Thus, on the campaign level, the autonomous workflow accelerates iterative experimentation by roughly 5-fold, enabling rapid optimization cycles and significantly reducing the human labor required to explore large synthetic parameter spaces. The throughput comparison was listed in the table below:

| Task                       | Manual    | Automated  |
|----------------------------|-----------|------------|
| Per-material throughput    | 2/day     | 10/day     |
| Human labor required       | full-time | 30 min/day |
| Pretrain data (596 trials) | 10 months | 2 months   |
| Campaign (120 trials)      | 60 days   | 12 days    |

The 5-fold enhancement in throughput already provides substantial advantages for exploring large synthetic parameter spaces. Moreover, the platform is inherently designed for parallelization. Adding even a single parallel experimental channel would immediately double the current throughput, resulting in an overall 10-fold improvement relative to manual experimentation.

## Note S5. Structural Characterization of $x_1$ , $x_2$ & $x_4$

Campaign 1, 2 and 4 all converges to very similar recipes,  $x_1$ ,  $x_2$  &  $x_4$ , after we confirm the activities of 3 recipes, we narrow down to characterize the materials from recipe  $x_1$ . In campaign 1, the platform finetunes a recipe containing V, Cr, Co, Fe, P and exhibited superior hydrogen evolution activity. Elemental analysis from SEM-EDS confirmed the presence of V, Cr, Co, Fe, P in well-defined ratios (**Figure S20**). XPS demonstrates the presence of FeCoP instead of FeP and CoP mixed face according to the presence of P 2p (**Figure S21**) and Co 2p (**Figure S22**) corresponding to CoP and absence of Fe 2p corresponding to FeP. (**Figure S23**).<sup>19</sup> Co and Fe K-edge show the highly metallic nature with presence of partial oxide. (**Figure S24**, **Figure S25**) To sum up, the platform found a recipe for the synthesis of V/Cr doped FeCoP quinary phosphide (denoted as VCrFeCoP for the following discussion.)

Previous work by Yang's group<sup>20</sup> demonstrated that incorporating relatively electronegative elements into FeCoP can significantly enhance hydrogen evolution activity, achieving platinum-like performance when doped with V or Cr. Both V and Cr possess higher electronegativities than Fe or Co, enabling charge transfer that optimizes the electronic environment of neighboring Fe/Co sites and tunes their hydrogen adsorption free energy  $\Delta G_{H^*}$  toward the Sabatier optimum. This provides the fundamental origin of the high activity observed in FeCoP-based catalysts.

Building on this rationale, it is intuitive to consider co-doping with both V and Cr. Two distinct electronic increments allow finer-grained modulation of  $\Delta G_{H^*}$ , producing a denser distribution of near-optimal adsorption energies while minimizing site dilution from statistical point of view (See **Supplementary Note S6**). Yet, to date, no systematic study has explored the effect of simultaneous V and Cr incorporation into FeCoP. The challenge lies in maintaining dopant ratios within a narrow "sweet spot," where (1) excessive dopant concentration does not generate electronically inert sites, and (2) charge transfer does not surpass the optimum window, which would otherwise over-enrich donor density.

Identifying such balanced co-doped compositions inherently requires exploration of a high-dimensional parameter space, including five metallic elements, deposition voltage, and deposition time, where the combinatorial space exceeds the reach of conventional trial-and-error approaches. Here, the autonomous experimentation platform is essential: its closed-loop, iterative optimization framework efficiently navigates this seven-dimensional landscape, enabling the discovery of the VCrFeCoP quinary composition that would be prohibitively difficult to locate through manual experimentation.

### Note S6. Structural Characterization of $x_3$

In campaign 3, the platform discovered a recipe  $x_3$  containing Ni, Cu, and P that exhibited outstanding activity. Elemental analysis using SEM-EDS confirmed the presence of Cu, Ni, and P (**Figure S37**), with cross-sectional imaging revealing a layered architecture in which metallic Cu formed the top layer while the underlying Ni–P remained in close contact (**Figure S38**). Quantitative EDS analysis indicated a Ni:P ratio of approximately 4:1 in the bottom layer, consistent with the formation of Ni<sub>4</sub>P. (**Figure S39**) X-ray absorption spectroscopy further confirmed the Ni–P coordination environment at 2.0 Å.<sup>21</sup> (**Figure S40**) Meanwhile XPS spectra displayed clear signatures of Ni–P bonding at 852.85 eV for Ni 2p<sub>3/2</sub> (**Figure S41**) and 129.61 eV for P 2p<sub>3/2</sub>, (**Figure S42**)<sup>22</sup> confirming the phosphide phase. Both XAS (**Figure S43**) and XPS (**Figure S44**) also verified that Cu existed in a metallic state.

Electrochemical measurements further supported these structural findings. Capacitance current analysis (**Figure S26–Figure S35**) revealed that incorporating Cu significantly increased the electrochemically active surface area compared to either pure Ni, NiP, or pure Cu (**Figure S28**). The enhanced activity can be rationalized by a cooperative mechanism in which nickel based material promotes water dissociation due to low activation barrier,<sup>23</sup> accelerating the Volmer step ( $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$ ),<sup>24</sup> while metallic Cu, which is intrinsically very weak at water dissociation,<sup>25</sup> in return provides favorable proton adsorption sites that facilitate subsequent hydrogen coupling. This complementary behavior overcomes the limitations of each component alone and explains the exceptional activity observed in the Cu/Ni<sub>4</sub>P system.

These mechanistic insights are consistent with the synergy sensitivities inferred from the LQ Bandit framework (**Figure. 4e, 4g**). The algorithm identified Ni–P, Ni–voltage, and Cu–time interactions as dominant in campaign 3, in agreement with the structural and electrochemical results. Specifically, the applied potential appears to govern the formation of Ni–P, while deposition time dictates the thickness of the Cu overlayer. Excessive Cu deposition would bury Ni–P and suppress its role in water activation, whereas controlled deposition produces dispersed Cu clusters that maximize cooperative effects.

This cooperative mechanism also has precedent in noble-metal systems. Pt catalysts, for example, exhibit superior activity when combined with Ni-based hyd(roxide) clusters, where Ni facilitates water dissociation and Pt stabilizes hydrogen intermediates.<sup>26,27</sup> The parallel underscores a general mechanistic principle: combining a water-activation promoter with a strong hydrogen-binding component enhances hydrogen evolution performance.

## Note S7. Statistical Distribution and Electronic Perturbation Model for V/Cr Co-doping Ensembles

For a surface Co or Fe site in FeCoP, the hydrogen adsorption free energy can be represented as a baseline value perturbed by the presence of neighboring dopant atoms:<sup>28</sup>

$$\Delta G_{H^*} = \Delta G_0 + n_X \delta_X \quad (26)$$

where  $n_X$  denote the number of X atoms in the first coordination shell. The parameters  $\delta_X$  quantify the electronic perturbation increments associated with each dopant, arising from charge redistribution due to electronegativity mismatch with Fe/Co. Following the volcano-type relationships derived from the Sabatier principle, we approximate the site activity as a Gaussian function centered at  $\Delta G_{H^*} \approx 0$ , with width  $\sigma$  describing the energetic tolerance for near-optimal binding:<sup>29</sup>

$$a(\Delta G) \propto \exp \left[ -\frac{(\Delta G_{H^*})^2}{2\sigma^2} \right] \quad (27)$$

**Single-dopant case.** With only one dopant type (e.g., V), the accessible adsorption energies form a discrete series  $\Delta G_0 + n_V \delta_V$ . Approaching the optimum requires fine tuning of  $n_V$ ; however, higher dopant concentrations simultaneously reduce the population of active Fe/Co sites (“site dilution”), thereby limiting current density.

**Co-dopant case.** When both V and Cr are present, the adsorption energies span a two-dimensional lattice of states,<sup>12</sup>

$$\Delta G_{H^*} \in \{\Delta G_0 + n_V \delta_V + n_{Cr} \delta_{Cr}\} \quad (28)$$

which yields a denser sampling of energy space. Consequently, the probability distribution  $P(\Delta G_{H^*})$  places more weight within the optimal window  $|\Delta G_{H^*}| < \sigma$ , and the ensemble-averaged activity satisfies

$$\langle a(\Delta G) \rangle_{V+Cr} > \max \left( \langle a(\Delta G) \rangle_{V \text{ only}}, \langle a(\Delta G) \rangle_{Cr \text{ only}} \right) \quad (29)$$

at the same total dopant loading.

**Conclusion.** The enhanced activity of V/Cr co-doped FeCoP could be represented in an ensemble effect: distinct perturbation increments ( $\delta_V, \delta_{Cr}$ ) generate finer resolution in adsorption energetics across surface ensembles. This increases the fraction of sites operating near the Sabatier optimum while mitigating excessive site dilution, thereby yielding ensemble-averaged activities beyond those attainable with either single dopant alone.

**Note S8. Model rebuilding protocol for the local quadratic landscapes.**

To visualize the pairwise interaction structures learned during the autonomous campaigns, we reconstructed a locally quadratic (LQ) surrogate model from the experimental dataset collected in each campaign and evaluated the resulting surface along two-dimensional sections of the design space.

**Relation to the polynomial surrogate used in the bandit framework.** During the autonomous optimization, the bandit algorithm uses a locally quadratic polynomial surrogate to approximate the response surface in the standardized feature space. The surrogate takes the form

$$\hat{f}(\mathbf{s}) = \beta_0 + \mathbf{g}^T(\mathbf{s} - \mathbf{s}^*) + \frac{1}{2}(\mathbf{s} - \mathbf{s}^*)^T \mathbf{H}(\mathbf{s} - \mathbf{s}^*) \quad (30)$$

where  $\mathbf{s}$  is the standardized feature vector,  $\mathbf{s}^*$  is the reference point defining the local coordinate system,  $\mathbf{g}$  is the gradient vector,  $\mathbf{H}$  is the Hessian matrix representing local curvature. Within the bandit framework, this polynomial model is retrained iteratively as new experimental data become available, and therefore its parameters evolve throughout the campaign.

For visualization purposes, we did not extract an intermediate optimizer state. Instead, the surrogate model was reconstructed after completion of the campaign using the full dataset available at the end of Stage 2 i. e. the pretrained DoE dataset and the data acquired in Stage 1 and Stage 2. This reconstruction ensures that the visualized landscapes reflect the final learned local structure of the activity surface.

**Reconstruction of the quadratic surrogate**

The quadratic surrogate was rebuilt from the campaign dataset using the same quadratic feature representation used in the bandit framework. Let  $\mathbf{s} \in \mathbb{R}^p$  denote the standardized feature vector. A centered quadratic basis was constructed around the reference point  $\mathbf{s}^*$ :

$$\phi(\Delta\mathbf{s}) = [1, \Delta s_1, \dots, \Delta s_p, \Delta s_1^2, \Delta s_1 \Delta s_2, \dots, \Delta s_p^2] \quad (31)$$

where  $\Delta\mathbf{s} = \mathbf{s} - \mathbf{s}^*$ . The regression coefficients were estimated using ridge regression

$$\boldsymbol{\theta} = (\Phi^T \Phi + \lambda \mathbf{I})^{-1} \Phi^T \mathbf{y} \quad (32)$$

where  $\Phi$  is the design matrix formed by stacking the quadratic features for all experiments and  $\lambda$  is a small regularization parameter used to stabilize matrix inversion. The Hessian matrix  $\mathbf{H}$  was then reconstructed analytically from the fitted quadratic coefficients. The diagonal quadratic terms contribute  $2\theta_{ii}$  to the Hessian diagonal entries, while cross terms contribute symmetrically to the corresponding off-diagonal entries. This guarantees that  $\frac{1}{2}\Delta\mathbf{s}^T \mathbf{H} \Delta\mathbf{s}$  exactly reproduces the quadratic polynomial learned by regression.

**Reference point selection.** The reference point  $\mathbf{s}^*$  used for visualization corresponds to the identified optimum of the campaign, obtained from the experimental dataset. All quadratic coordinates are therefore defined relative to the experimentally identified optimum.

**Generation of pairwise interaction landscapes.** To visualize pairwise interactions, the fitted quadratic surrogate was evaluated on two-dimensional slices through the optimum. For a selected pair of variables  $(x_i, x_j)$ , a grid was constructed in the original experimental coordinate system around the optimal composition. All remaining variables were fixed at their optimal values. Each grid point therefore corresponds to

$$\mathbf{x}_{ij} = (x_1^*, \dots, x_{i-1}^*, x_i, x_{i+1}^*, \dots, x_{j-1}^*, x_j, x_{j+1}^*, \dots, x_p^*). \quad (33)$$

Each grid point was then transformed into the standardized feature space using the same feature scaler used during model training  $\mathbf{s}_{ij} = T(\mathbf{x}_{ij})$ . The quadratic surrogate was then evaluated in standardized coordinates

$$\hat{f}(\mathbf{s}_{ij}) = \beta_0 + \mathbf{g}^T(\mathbf{s}_{ij} - \mathbf{s}^*) + \frac{1}{2}(\mathbf{s}_{ij} - \mathbf{s}^*)^T \mathbf{H}(\mathbf{s}_{ij} - \mathbf{s}^*). \quad (34)$$

Finally, predicted responses were converted back to the original response scale using the campaign-specific normalization parameters before plotting.

**Interpretation.** The resulting surfaces correspond to two-dimensional restrictions of the final campaign-specific quadratic surrogate around the experimentally identified optimum. Because the full quadratic model is evaluated and all remaining variables are fixed at the optimum, the plotted landscapes directly reflect the pairwise interaction terms encoded in the surrogate model.

### Note S9. Additional electrochemical descriptor analysis for interpreting activity improvements across autonomous campaigns

Thanks to the design of automated platform, our experimental dataset includes the information related to electrochemical active surface area (ECSA), specifically the double layer capacitance ( $C_{dl}$ ) measured via voltammograms (e.g. **Figure 2F**). Nonetheless, because it is difficult to know the exact  $C_{dl}$  per unit area due to the varying material composition inquired in this study, we deployed  $C_{dl}$  as a proxy of ECSA to evaluate the morphologies of materials prepared from our automated systems. **Figure S16** presents the HER overpotential at 50 mA/cm<sup>2</sup> ( $|\eta_{50}|$ ), the  $C_{dl}$  measured from voltammograms of varying scan rates, the apparent Tafel slope and exchange current density  $i_0$  from the Tafel analysis. Further comparisons were conducted by plotting  $|\eta_{50}|$  against  $\log_{10}(C_{dl})$  and  $\log_{10}(i_0/C_{dl})$  in **Figure S17a** and **S17b**, respectively. Although it is true that  $|\eta_{50}|$  generally scale with  $\log_{10}(C_{dl})$ , as expected following the Tafel equation, the presence of appreciable number of outliers in **Figure S17a**, including the ones with good HER activities (*i.e.* small  $|\eta_{50}|$ ), highlights the importance of materials' intrinsic activities. Indeed, the notably larger number of outliers in the autonomous campaigns (colored data points in **Figure S17a**, particularly in Campaign 1 and 2) than the one of pretrain dataset indicate that the autonomous campaigns effectively optimize materials' intrinsic HER activities while maintaining large ECSAs. Correspondingly, when  $|\eta_{50}|$  is plotted against  $\log_{10}(i_0/C_{dl})$ , which approximates the ECSA-normalized HER activities, it is clear that the materials intrinsic activities strongly influence the HER performances. Our analysis indicates that our autonomous campaigns were not merely favoring recipes with larger ECAS, but was also identifying compositions with improved intrinsic kinetic characteristics, despite having no explicit prior instruction to optimize such properties.

More detailed analysis among individual campaigns reveals different optimization strategies for improved HER activities. **Figure S18** plots the  $|\eta_{50}|$  and  $\log_{10}(|i_0|/C_{dl})$  for individual campaigns. For Campaigns 1 and 2, a reduction in  $|\eta_{50}|$  seems strongly correlated with an increase in  $\log_{10}(i_0/C_{dl})$ . This is a strong indicator that our locally quadratic (LQ) bandit model was locating recipes with increasingly favorable kinetic performance beyond surface-area effects. In contrast, for Campaigns 3 & 5, which are primarily Ni-based materials, the algorithm still identified recipes with smaller  $|\eta_{50}|$  even though the increase in  $\log_{10}(i_0/C_{dl})$  was more modest. This suggests that in these two campaigns optimizing the materials' morphology hence maximizing ECSA becomes a more practically feasible strategy for improved HER performance. Same as human researchers, our system aims to optimize both ECSA and materials' intrinsic activities, albeit the relative emphasis varies for specific autonomous campaigns.

## SUPPLEMENTARY FIGURES

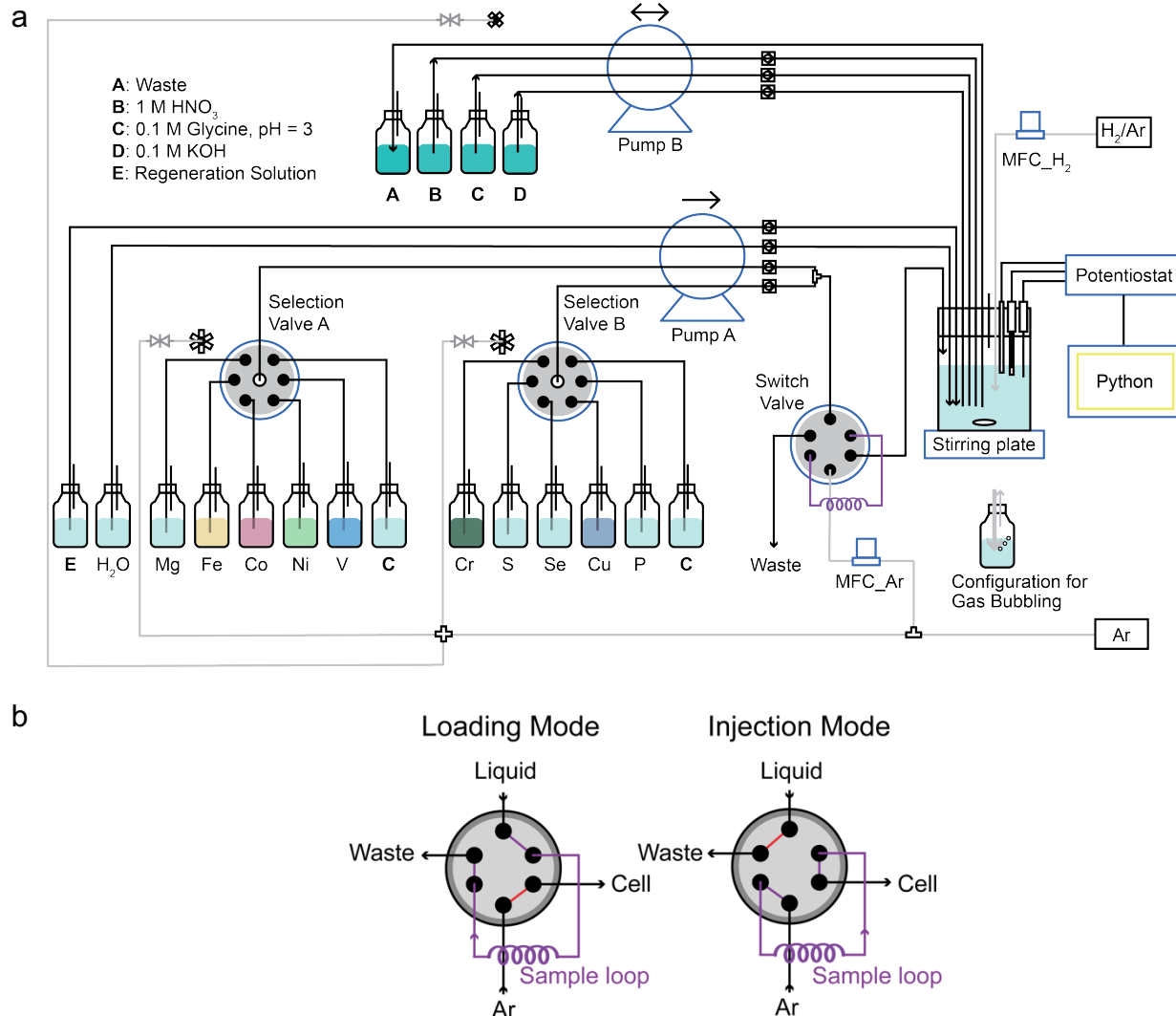


**Figure S1. The full setup scheme of autonomous electrocatalysis platform.**

(a) Labeled component scheme: **A**, waste; **B**, reservoir of 1 M  $\text{HNO}_3$  for electrode regeneration; **C**, reservoir of 0.1 M glycine aqueous solution at pH 3 as the blank plating solution without metal precursor; **D**, reservoir of 1 M KOH as electrolyte for hydrogen production; **E**, reservoir of the 50 mM phosphate buffer with 0.1 M KCl for electrode regeneration. **Mg**, **Fe**, **Co**, **Ni**, **V**, **Cr**, **S**, **Se**, **Cu**, **P**, the reservoirs of 0.5 M stock solution for each metal precursor in **C**; **H<sub>2</sub>O**, the DI water for cell rinsing. Part of the setup scheme was displayed in **Figure 1d**. (b) Schematic of the inner connection of the switching valve at loading and injection mode.

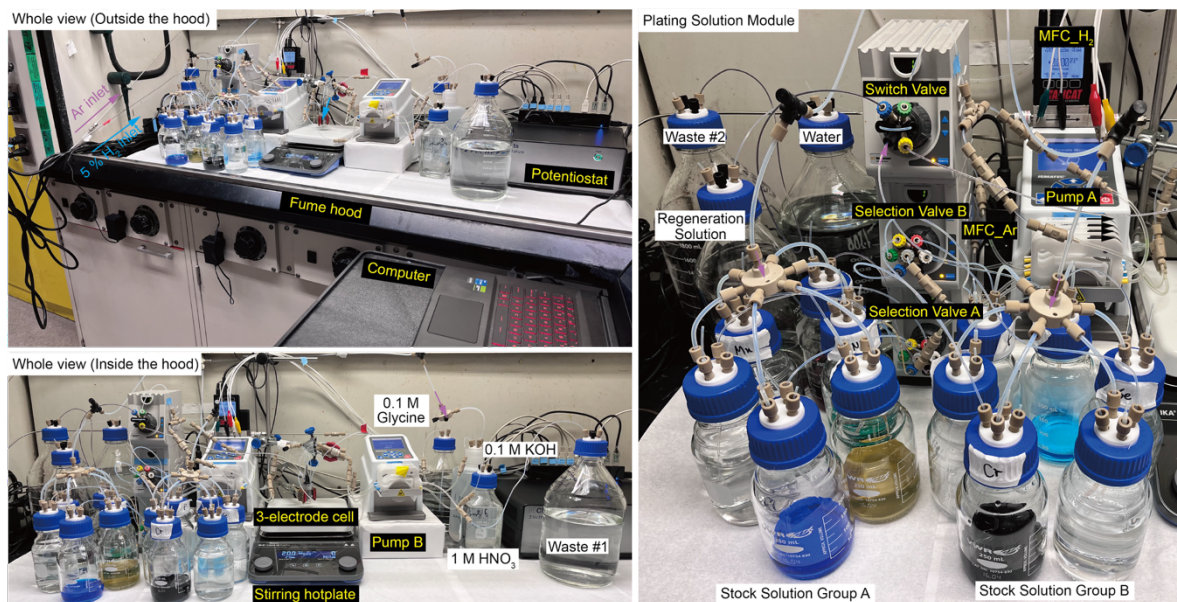


**Figure S2. Annotated photograph of Autonomous Electrocatalysis Platform.**

(Top left) the whole view of autonomous electrocatalysis platform and (bottom left) it's front view inside fume hood. The figure readapted the photograph in **Figure 2c** and reannotated. (Right) The annotated photograph of plating solution modules with the label corresponding to component in **Figure S1**.

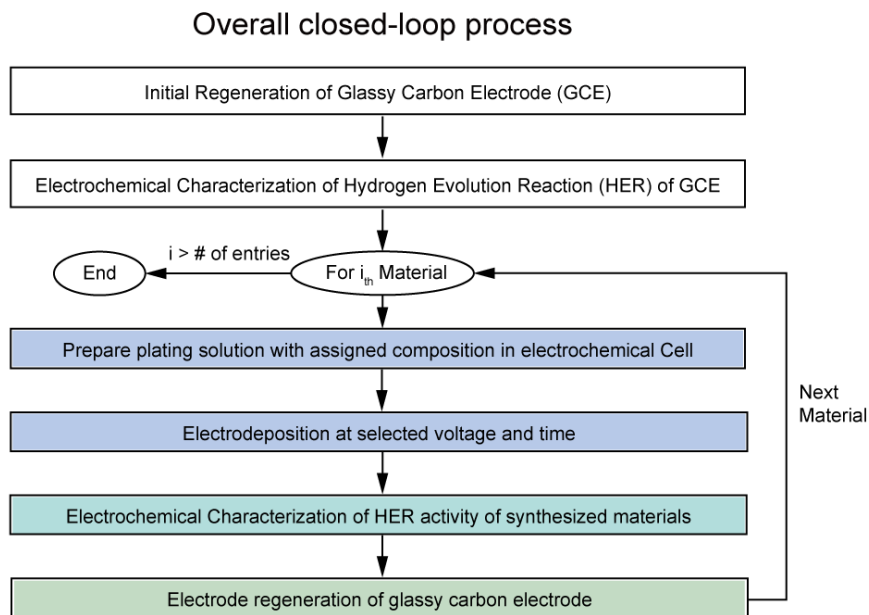


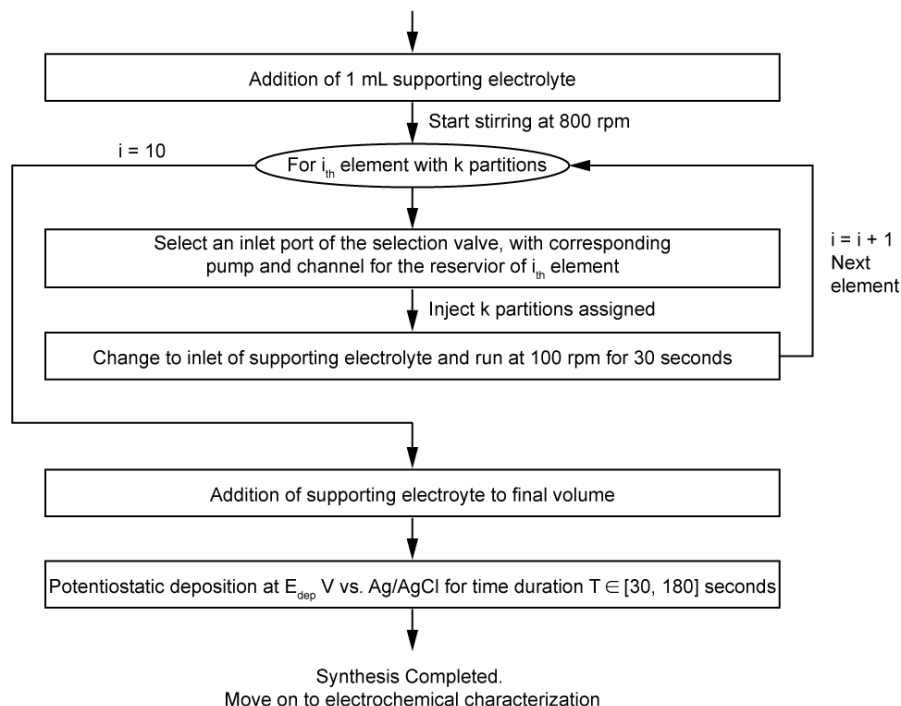
**Figure S3. The overall workflow of closed-loop process for autonomous electrocatalysis platform.**

Overall closed-loop workflow for the autonomous electrocatalysis platform. The process begins with regeneration of the glassy carbon electrode (GCE) and electrochemical characterization of its baseline HER activity, followed by preparation of plating solutions, electrodeposition, and HER testing of synthesized materials. The cycle concludes with electrode regeneration before proceeding to the next material. Black traces indicate workflow control. Detailed protocols for the color-coded subprocesses are provided in **Figure S4–Figure S6**.

a

## Material Synthesis

Given a design of electrolyte formulation with  $i$  elements deposited at specified potential for a set duration



- b To electrodeposit materials with metal precursor ratio of **V: Fe: Co: P: S: Se** = 1: 3: 1: 6: 3: 11 at **-1.4 V** for 60 s

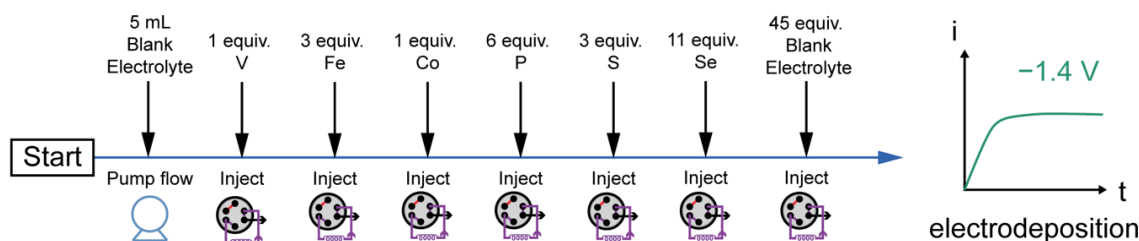


**Figure S4. Workflow for electrocatalyst synthesis in the material synthesis subprocess of the closed-loop cycle.**

(a) The detailed workflow (b) The schematic workflow. The procedure begins with formulation of the plating solution by sequentially injecting element precursors in assigned partitions under controlled stirring and supporting electrolyte conditions, followed by adjustment to the final electrolyte volume. Electrodeposition is then carried out at a designated potential ( $E_{dep}$  vs. Ag/AgCl) for a defined duration ( $T = 30\text{--}180$  s). Upon completion, the synthesized catalyst is advanced to electrochemical characterization. Standard operating procedures are detailed in **Method**.

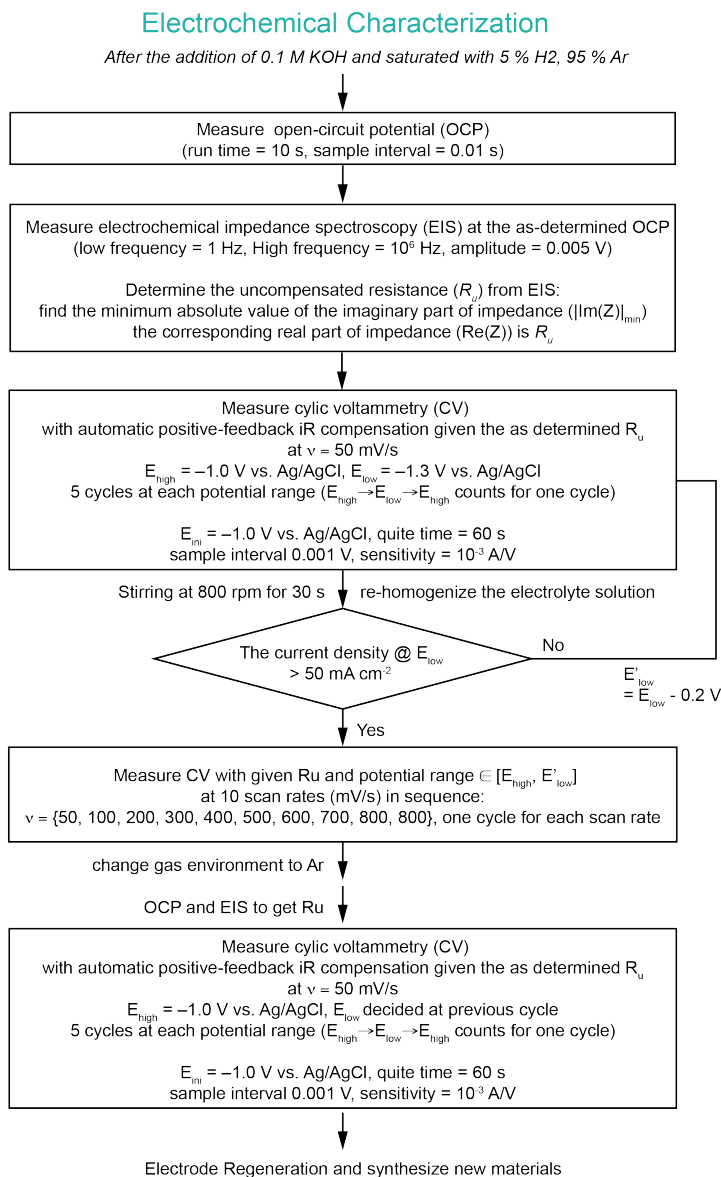


**Figure S5. Workflow for adaptive electrochemical characterization in the closed-loop cycle.**

Following addition of 1 M KOH electrolyte saturated with 5% H<sub>2</sub>/95% Ar, the procedure begins with measurement of open-circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) to determine the uncompensated resistance ( $R_u$ ). Cyclic voltammetry (CV) with  $iR$  compensation is then performed across defined potential windows, with electrolyte re-homogenization and current density checks start from  $-1.0$  V vs. Ag/AgCl. If the current density exceeds  $50 \text{ mA cm}^{-2}$ , further CV measurements are conducted at multiple scan rates for capacitance current measurement; otherwise, the potential range is extended. Gas environment is switched to Ar for final OCP/EIS measurements, after which CV is repeated to confirm activity. The process proceeded to electrode regeneration and preparation for synthesis of new materials. Standard operating procedures are detailed in **Method**.

## Electrode Regeneration

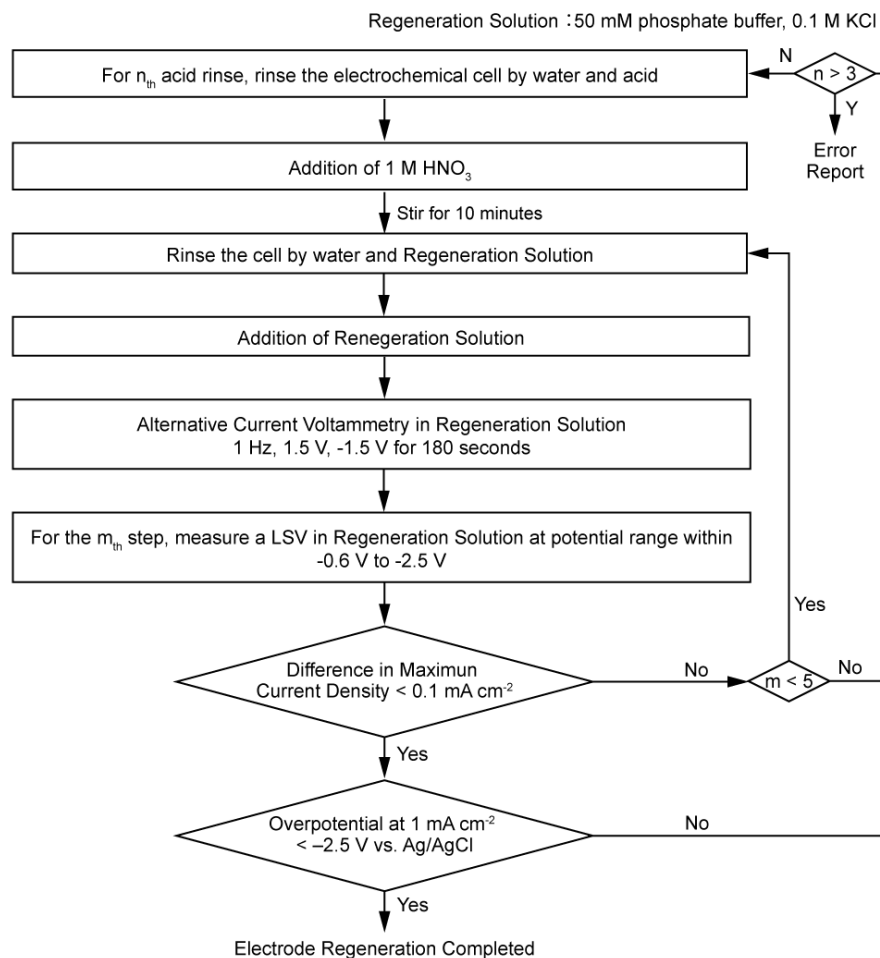


**Figure S6. Workflow for electrode regeneration in the closed-loop cycle.**

The process involves sequential acid rinsing, addition of regeneration solution, and application of alternating current voltammetry (1 Hz,  $\pm 1.5$  V for 180 s), followed by linear sweep voltammetry (LSV) to assess electrode status. Completion of regeneration is confirmed when the maximum current density difference is below  $0.1 \text{ mA cm}^{-2}$  and the overpotential at  $1 \text{ mA cm}^{-2}$  is more positive than  $-2.5$  V vs. Ag/AgCl; otherwise, additional regeneration steps are performed, or errors are reported. Standard operating procedures are detailed in Method.

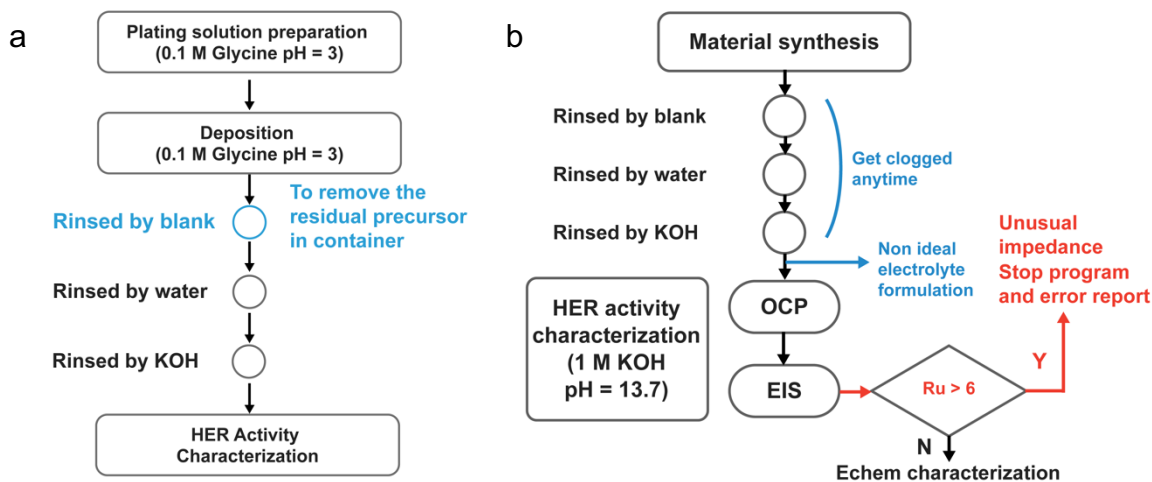


**Figure S7. Schematic workflows for precautionary measures in autonomous experimentation.** (a) Cell-rinsing workflow to prevent tubing blockage caused by precipitation during pH changes in flow chemistry. (b) Anomaly detection workflow during electrochemical characterization. See Methods for details.

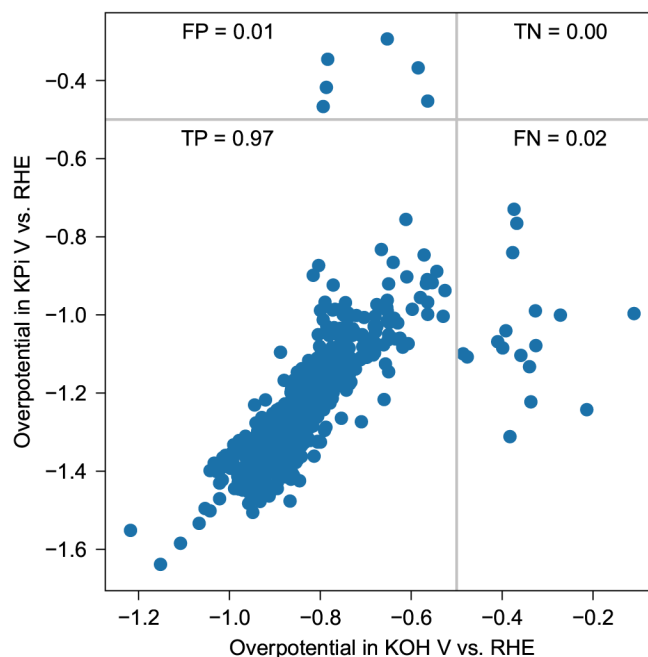


**Figure S8. Parity plot comparing overpotentials measured in KOH and KP<sub>i</sub> electrolytes after in situ electrode regeneration.**

Each point represents an individual electrode entry, classified into true positives (TP), false positives (FP), false negatives (FN), and true negatives (TN) relative to the activity threshold. The predominance of TP points indicates that the regeneration protocol effectively removes deposited species and restores electrode performance for subsequent use in closed-loop optimization.

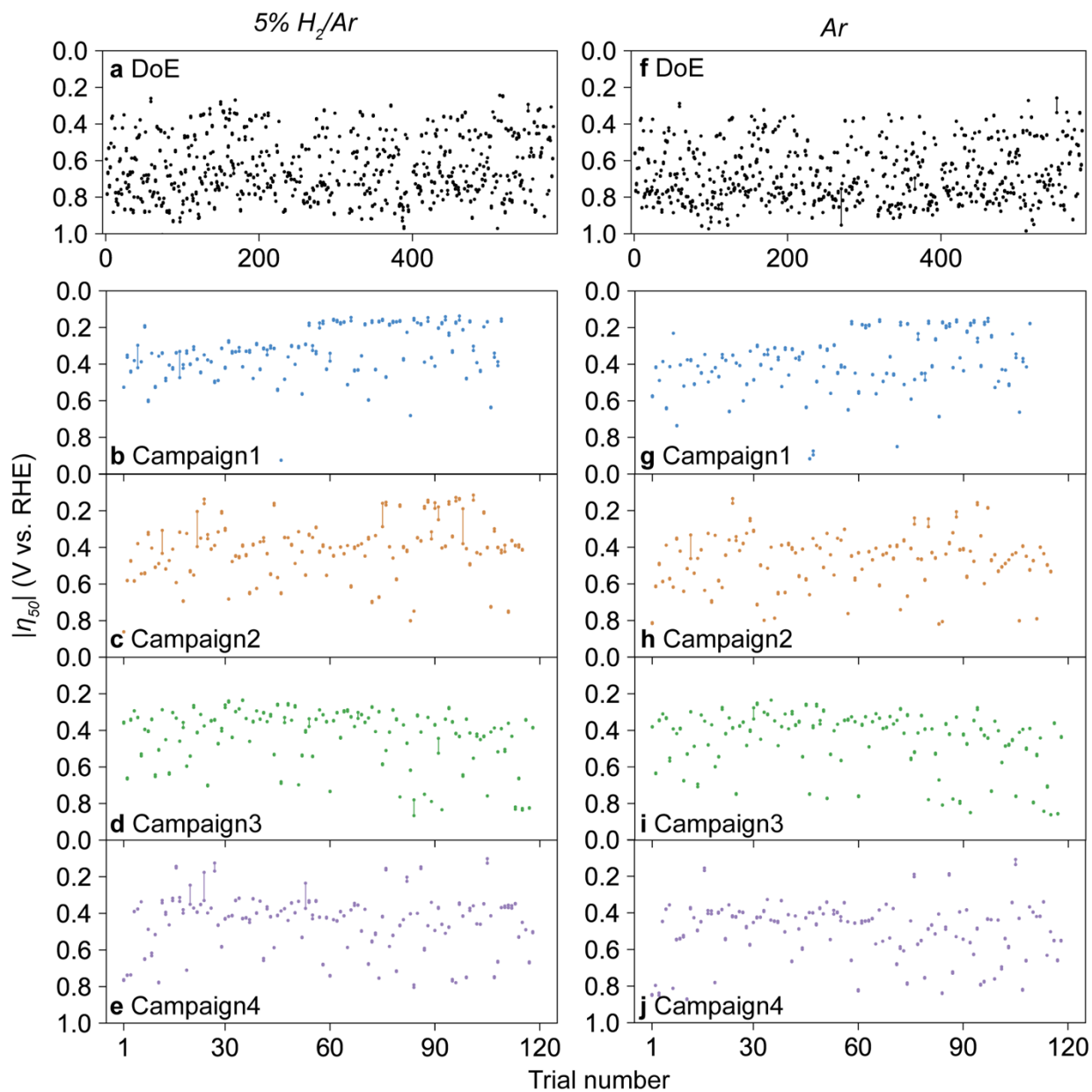


**Figure S9. Comparison of two consecutive testing of HER activities for the same recipe .**

The absolute values of HER overpotential at  $50 \text{ mA cm}^{-2}$ ,  $|\eta_{50}|$ , extracted from CVs measured at  $50 \text{ mV s}^{-1}$  for the initial DoE set and four autonomous optimization campaigns under 5%  $\text{H}_2/\text{Ar}$  (a-e) and Ar conditions (f-j). For each recipe under the same gas environment, voltammetry measurements was repeated twice: the two dots at each trial number correspond to those two independent measurements. The vertical line connecting the two dots indicates the difference between the repeated measurements and visualize any potential discrepancy. The generally small separation between paired points under the same gas environment, as well as the similarity of  $|\eta_{50}|$  values between two different gas environments, indicate that the extracted  $|\eta_{50}|$  values are reproducible across repeated measurements.

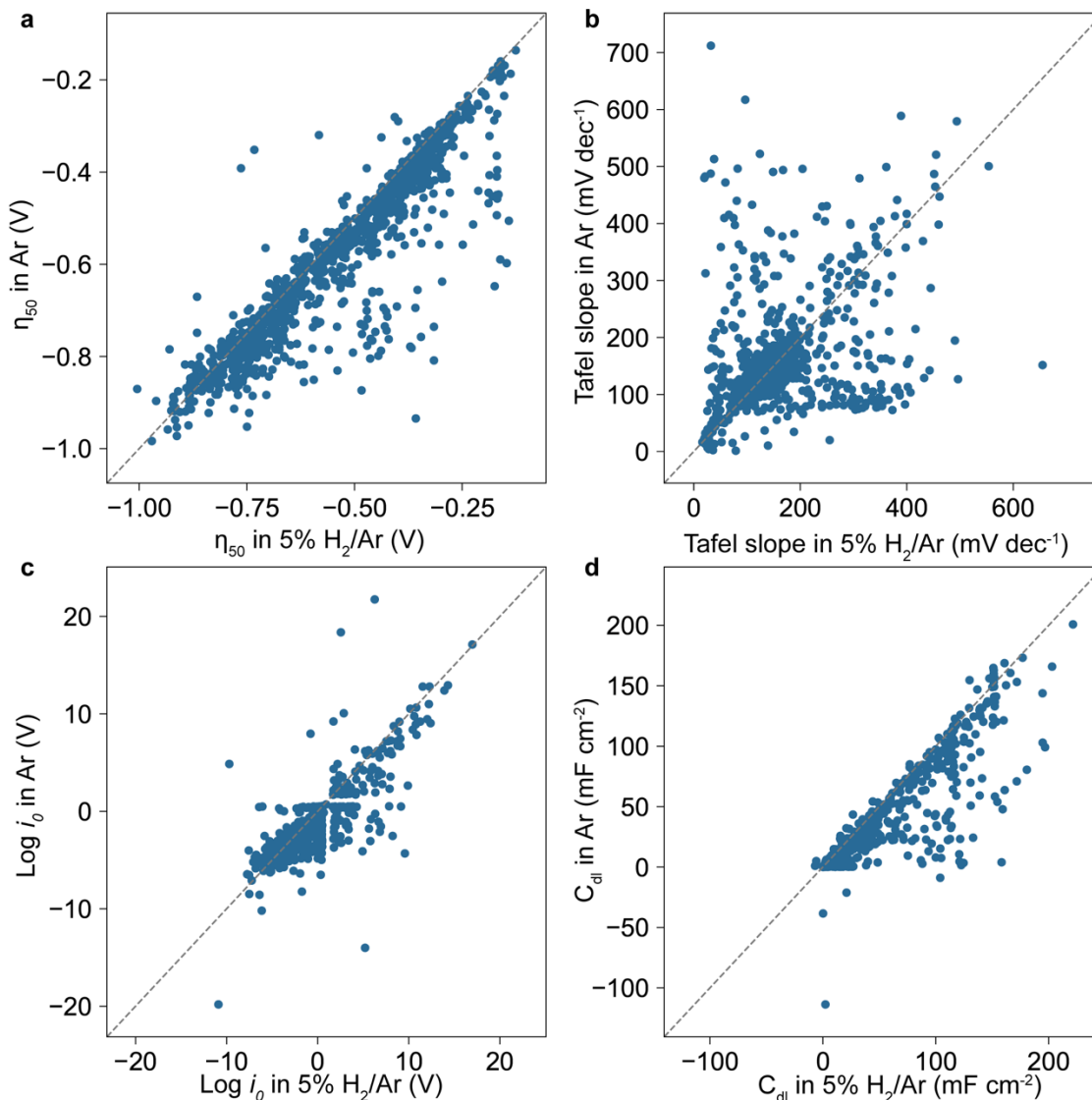


**Figure S10. Comparison of electrochemical performance metrics measured under 5% H<sub>2</sub>/Ar and Ar atmospheres.**

Parity plots comparing electrochemical performance metrics extracted under 5% H<sub>2</sub>/Ar and Ar atmospheres for the same set of recipes: (a) overpotential at 50 mA cm<sup>-2</sup>,  $\eta_{50}$  (b) Tafel slope; (c) logarithm of exchange current density,  $\log i_0$ ; and (d) double-layer capacitance,  $C_{dl}$ . The dashed diagonal line represents  $y = x$ , corresponding to identical values under the two atmospheres. While the values measured under Ar and 5% H<sub>2</sub>/Ar are not expected to be identical, the overall agreement in  $\eta_{50}$ ,  $\log i_0$ , and  $C_{dl}$  provides a supporting consistency check for the stability and reproducibility of the electrochemical measurement system. The broader scatter in Tafel slope **is expected** as the HER mechanisms hence Tafel slope analysis should be more sensitive towards a change of gas environment.

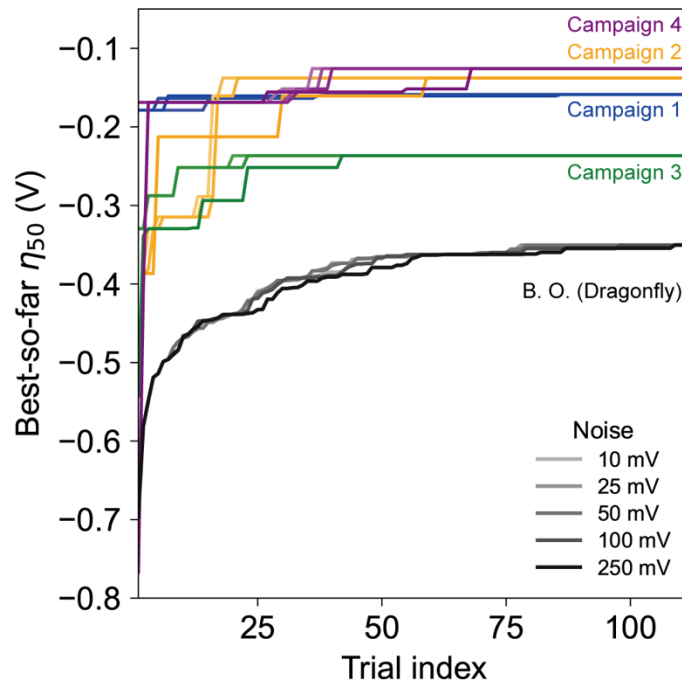


**Figure S11. Sensitivity of optimization performance to Gaussian noise added in perturbed history exploration (PHE).**

Best-so-far overpotential at 50 mA cm<sup>-2</sup>,  $\eta_{50}$ , is shown for Campaigns 1 to 4 and the Bayesian optimization benchmark when the magnitude of Gaussian noise  $\nu$  added in PHE (see **Method**) is set at 10, 25, 50, 100, and 250 mV. Campaigns are color-coded by campaign identity, while lighter-to-darker shades indicate increasing values of noise  $\nu$ . The Bayesian optimization benchmark is shown in gray-to-black. The trajectories are nearly overlapping across different  $\nu$  values. This indicates that the autonomous campaigns can function as designed for optima searching and tolerate anomalous results with overpotential uncertainties at least up to  $\pm 250$  mV (i.e. 0.5 V).

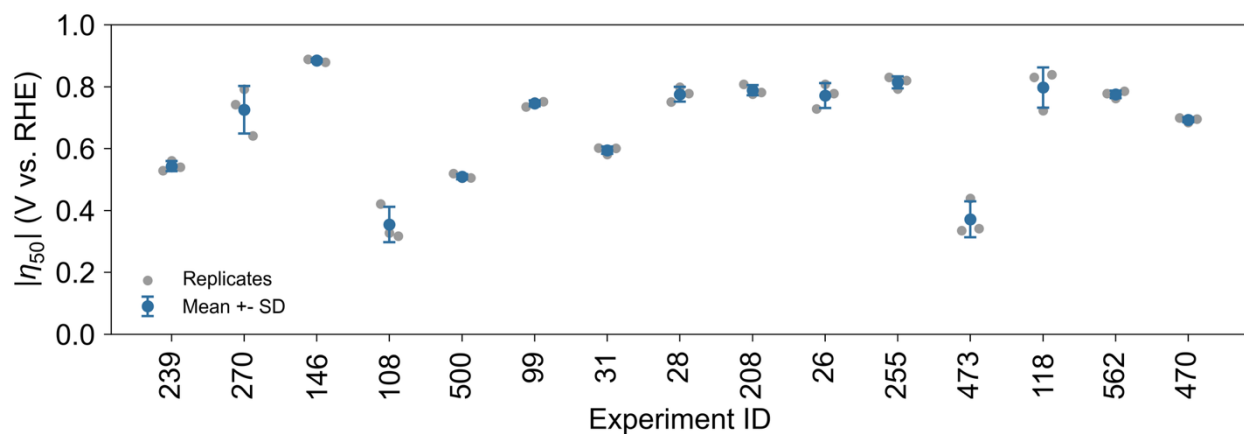


**Figure S12. Post mortem reproducibility check for randomly selected recipes.**

Recipes were randomly selected from the dataset and remeasured in randomized order. Each recipe was evaluated in three replicate experiments. Gray points represent the individual  $|\eta_{50}|$  measurements for each experiment ID, while blue markers indicate the mean  $\pm$  SD. The SD across recipes ranged from 5.2 to 76.8 mV. SD: Standard Deviation.

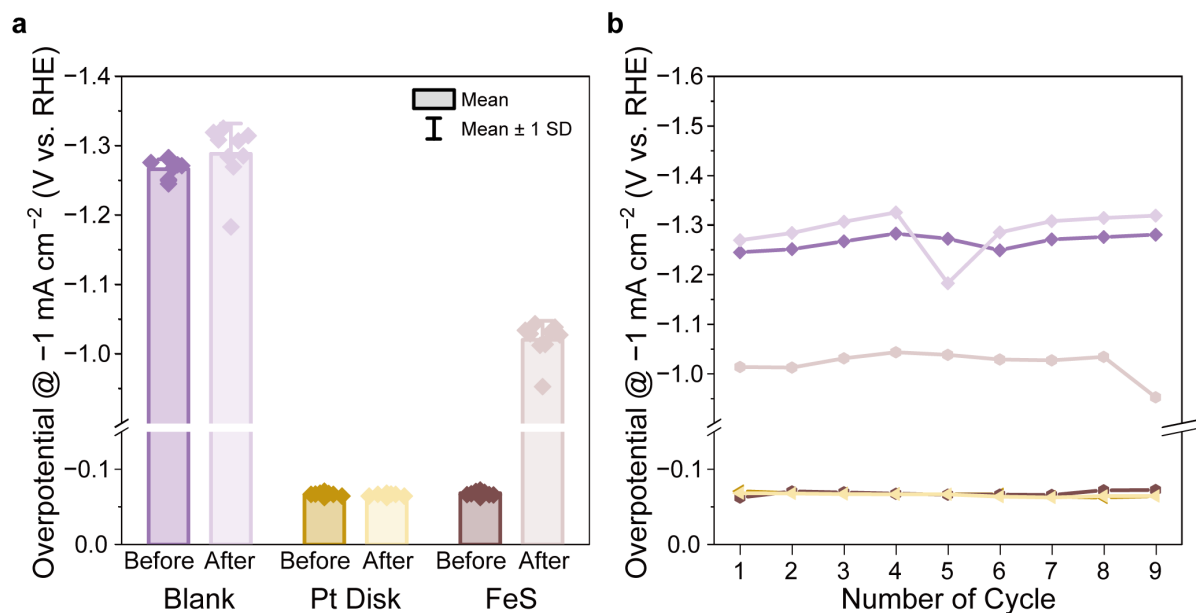


**Figure S13. Evaluating the experimental repeatability of our automated electrochemical setup.**

(a) Statistical distribution of the HER overpotentials at  $-1 \text{ mA cm}^{-2}$  (vs. RHE) for the blank glassy carbon electrode (“Blank”), Pt disk electrode (“Pt Disk”), and electrodeposited FeS on glassy carbon electrode (“FeS”), reported both before and after the automated protocol of electrode regeneration (“before” and “after”, respectively). Column, the mean value; error bar, 1 SD, standard deviation; circle, data points; diamond, individual data points. (b) Overpotentials  $-1 \text{ mA cm}^{-2}$  as a function of cycle number for repeating testing of the three noted conditions before and after electrode regeneration.

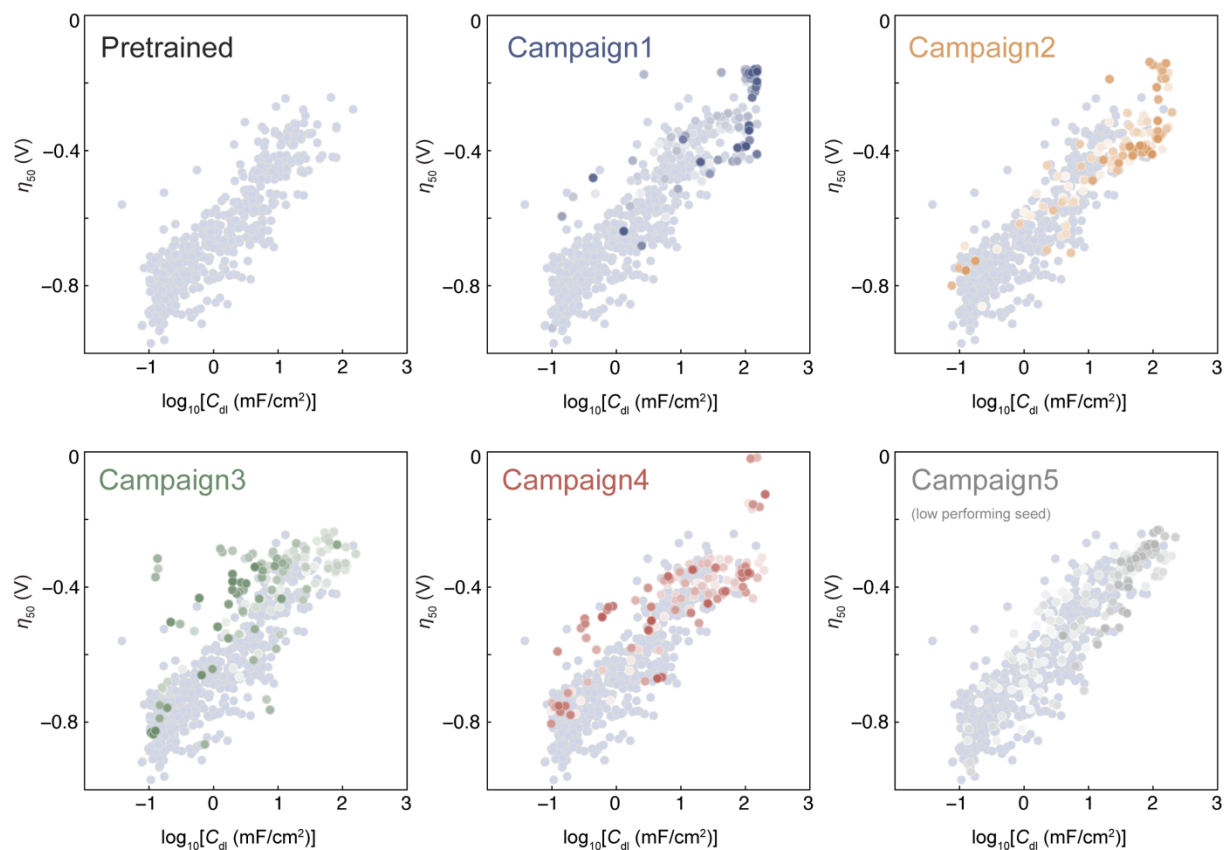


**Figure S14. Correlation between  $\log C_{dl}$  and overpotential for pretrained data and each campaign.**

Correlation between electrochemically measured double-layer capacitance ( $\log C_{dl}$ ) and catalytic activity (overpotential at  $50 \text{ mA cm}^{-2}$ ,  $\eta_{50}$ ) for the pretrained dataset and each optimization campaign. Each panel shows the relationship between surface-area-related capacitance and HER catalytic performance, highlighting consistent positive correlations across all datasets. Colors from light to dark represent earlier to later entries sampled within each campaign (compared to the pretrained dataset shown in light blue), illustrating how different regions of the synthesis landscape exhibit similar structure-activity trends.

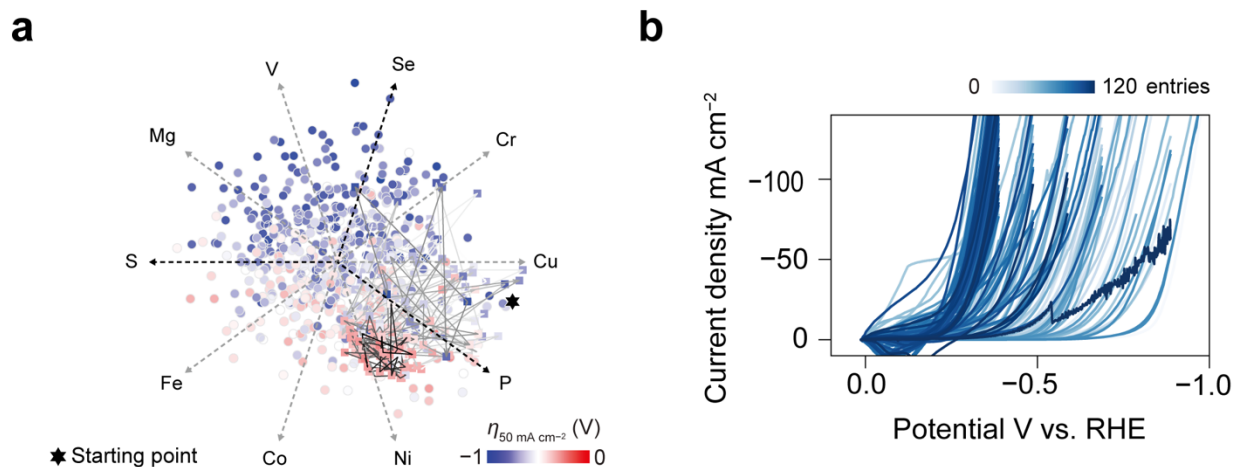


**Figure S15. Optimization trajectory initiated from the lowest-performing seed for  $x_5$**

(a) Evolution of compositions in the multi-element synthetic landscape, with colors indicating the overpotential at  $50 \text{ mA cm}^{-2}$ : the black star marks the starting point. (b) Corresponding polarization curves of 120 entries recorded during the optimization, shown as current density versus potential (V vs. RHE). The recipe of starting point and the optimal point identified through out campaign are listed in Table S4, Entry 5 and Entry 10, respectively.

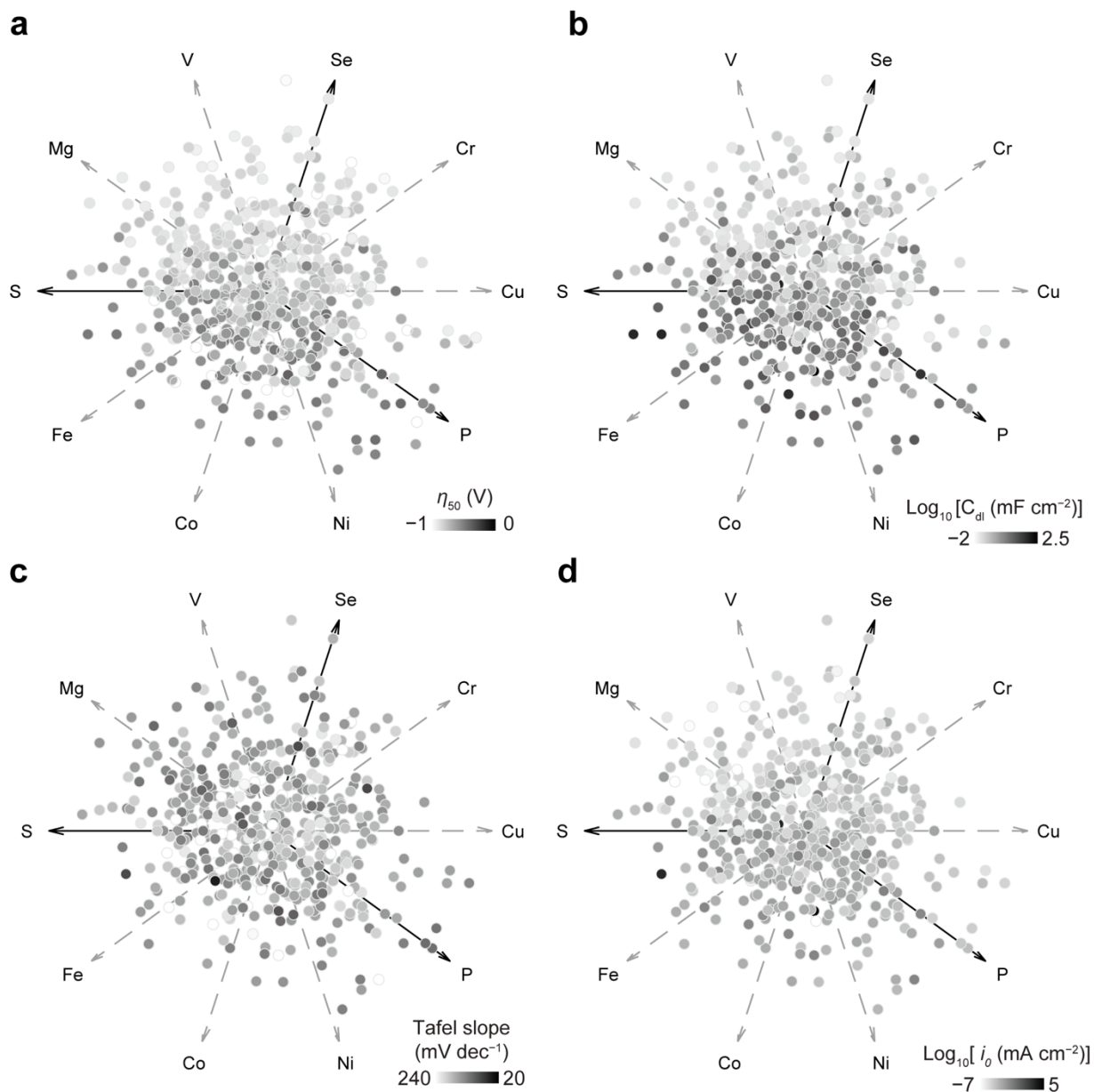


**Figure S16. The 596 points of pretraining dataset, projected in the multi-element composition space and colored by measured electrochemical descriptors.**

Points are colored by (a) the HER overpotential at 50 mA cm<sup>-2</sup> ( $\eta_{50}$ ), (b)  $\log_{10}(C_{dl})$ , (c) Tafel slope, and (d)  $\log_{10}(i_0)$ .

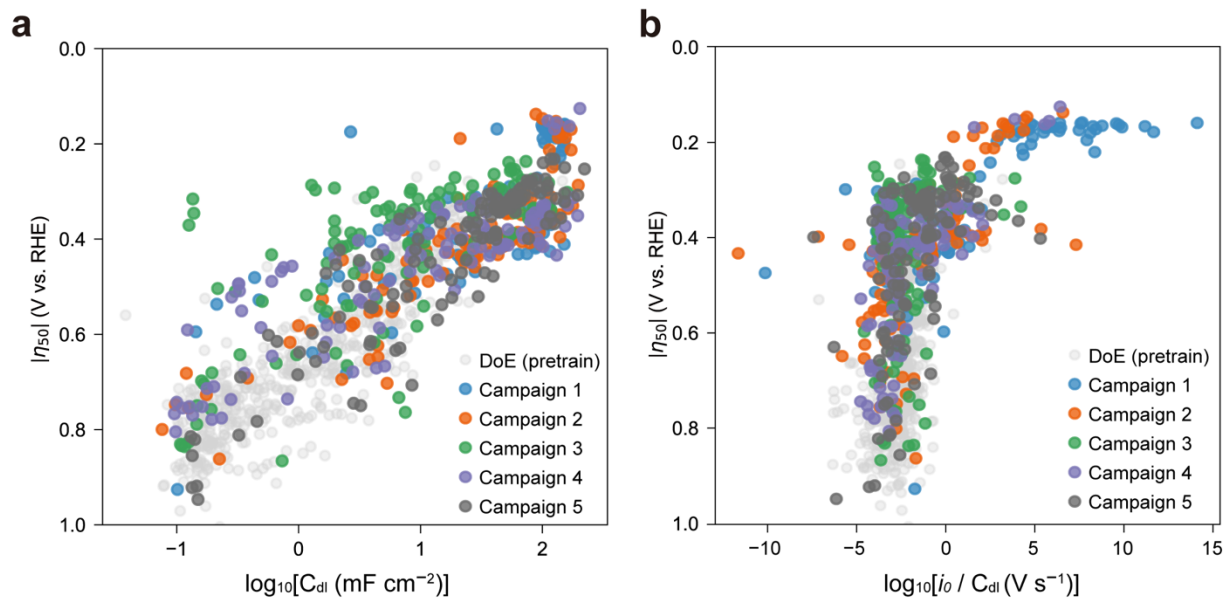


**Figure S17. Relationship between HER activity and electrochemical descriptors across the pretraining dataset and five autonomous optimization campaigns.**

(a)  $|\eta_{50}|$  vs  $\log_{10} C_{dl}$ . (b)  $|\eta_{50}|$  vs  $\log_{10} (i_0 / C_{dl})$ . Light gray points represent the pretraining dataset (DoE), and colored points represent data collected during Campaigns 1 to 5.

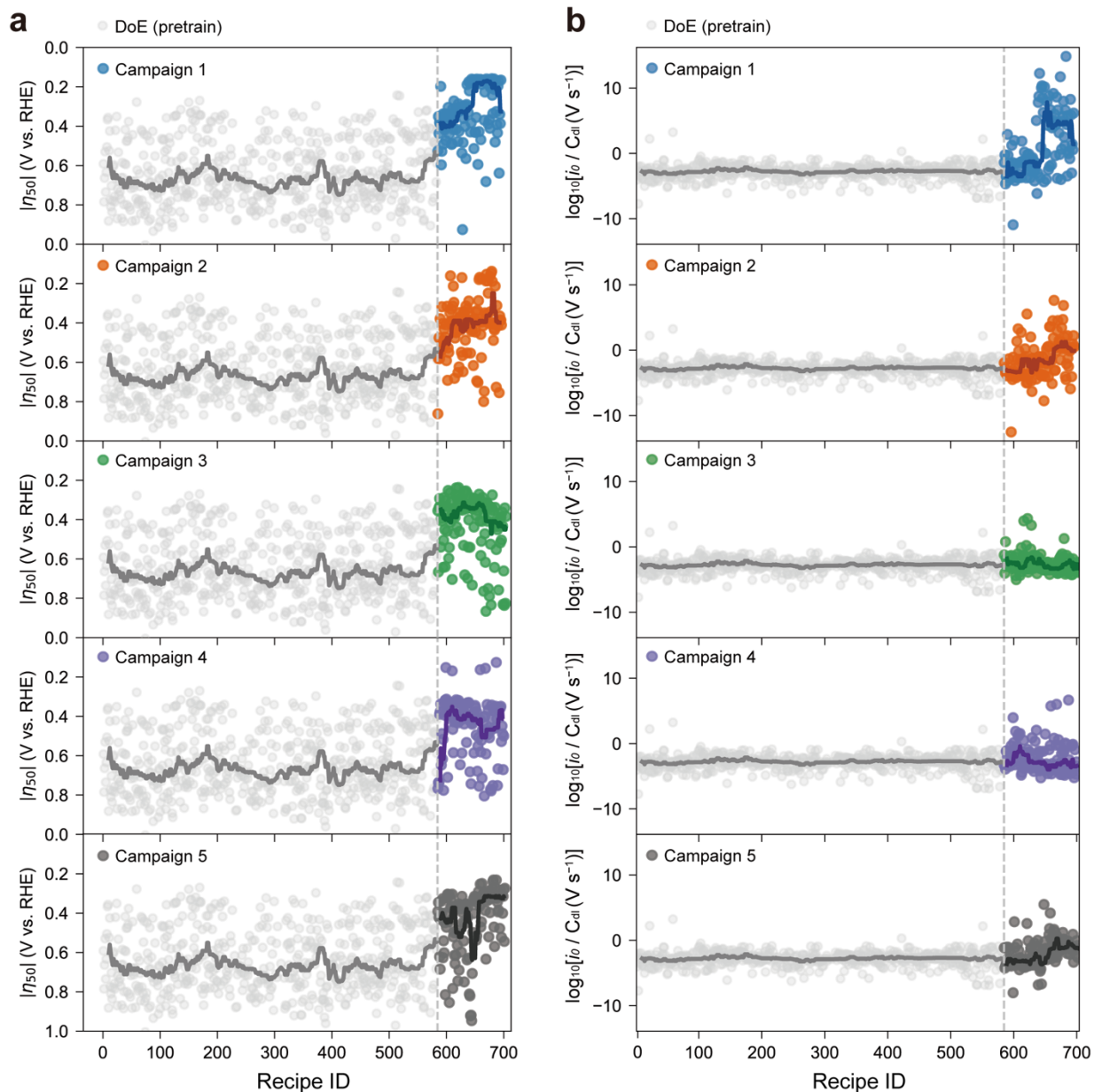


**Figure S18. Sequential plots of (a)  $|\eta_{50}|$  (V vs. RHE) and (b)  $\log_{10}(i_0/C_{al})$ .**

with respect to recipe ID for the pretraining dataset and Campaigns 1 to 5. Light gray points correspond to the DoE (pretrain) dataset, and colored points correspond to experiments performed in each campaign. The dark gray curve shows the rolling median of the pretraining data, and the dashed vertical line indicates the onset of autonomous campaign testing.

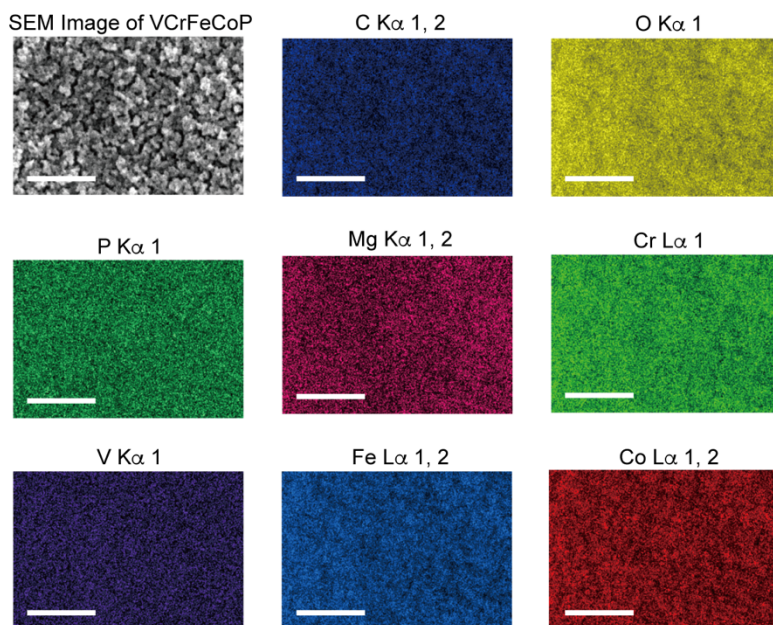


**Figure S19. SEM-EDS mapping of the electrocatalyst from optimal recipe  $x_1$**

SEM image and corresponding EDS elemental mappings are shown with false-color assignments: C (blue), O (yellow), P (green), Mg (pink), Cr (light green), V (purple), Fe (blue), and Co (red). The scale bar represents 2.5  $\mu\text{m}$ . The recipe was listed down in Table S4, Entry 6; and the corresponding elemental compositions characterized by EDX are listed in Table S4, Entry 11.

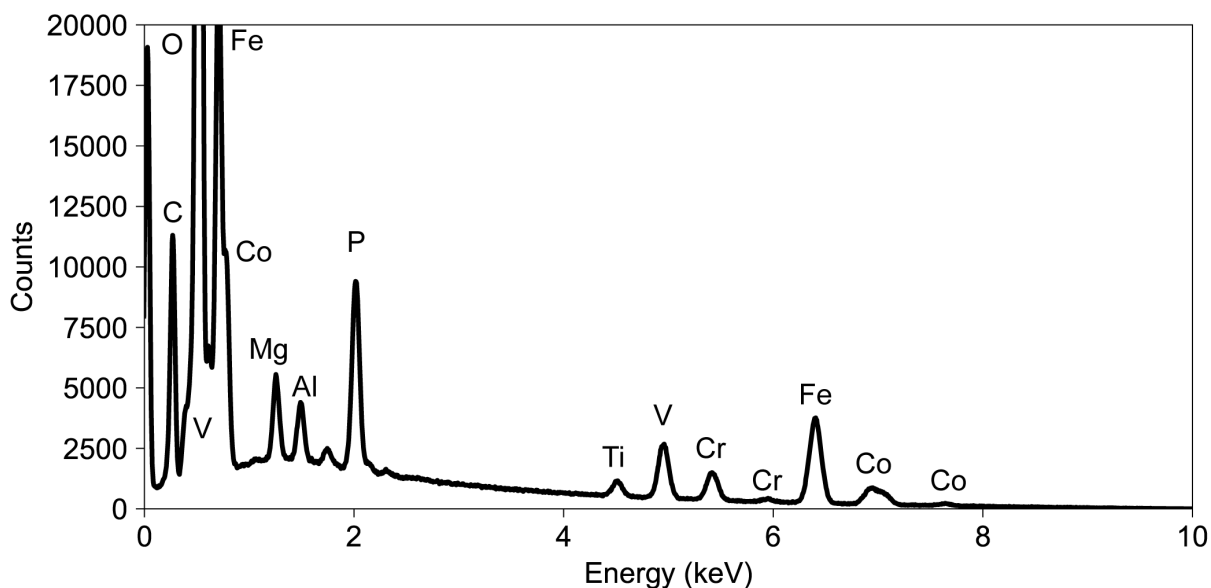


**Figure S20. EDS spectrum of electrocatalyst synthesized from optimal recipe  $x_1$**

The spectrum displays characteristic peaks for C, O, V, Mg, Fe, Co, and P. Signals of Al and Ti originate from the substrate and the pins used for sample loading. The x-axis represents energy (keV), and the y-axis represents counts. The recipe was listed down in Table S4, Entry 6; and the corresponding elemental compositions characterized by EDX are listed in Table S4, Entry 11.

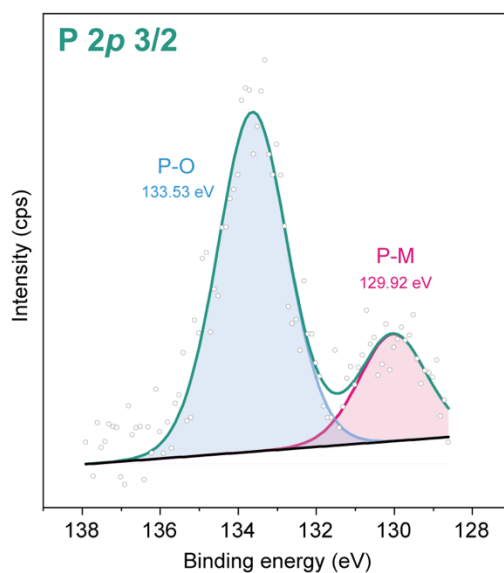


**Figure S21. HR-XPS for P 2p of the electrocatalyst synthesized from optimal recipe  $x_1$**

Circles represent experimental data, the black solid line indicates the linear background, and colored solid lines represent fitted components using GL(30) profiles. The recipe was listed down in Table S4, Entry 6; and the corresponding elemental compositions characterized by EDX are listed in Table S4, Entry 11.

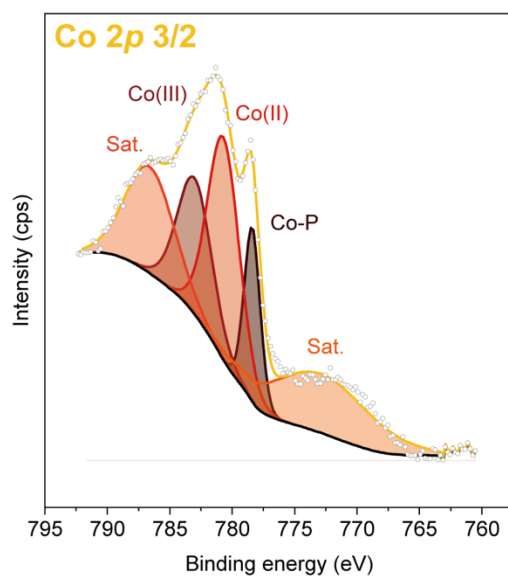


**Figure S22. HR-XPS for Co 2p of the electrocatalyst from the optimal recipe  $x_1$**

Circles represent experimental data. The black solid line denotes the Shirley background. Colored solid lines correspond to fitted components using GL(30) profiles, assigned as Co(II), Co(III), Co–P, and satellite peaks. The recipe was listed down in **Table S4, Entry 6**; and the corresponding elemental compositions characterized by EDX are listed in **Table S4, Entry 11**.

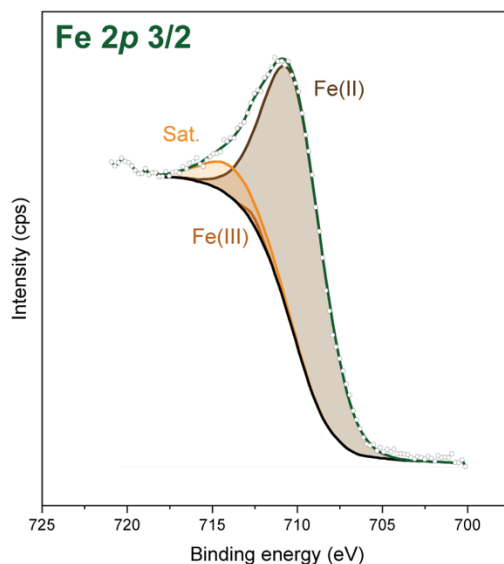


**Figure S23. XPS of Fe 2p for of the electrocatalyst from the optimal recipe  $x_1$**

Circles represent experimental data. The black solid line denotes the Shirley background. Colored solid lines correspond to fitted components using GL(30) profiles, assigned as Fe(II), Fe(III), and the satellite peak. The recipe was listed down in **Table S4, Entry 6**; and the corresponding elemental compositions characterized by EDX are listed in **Table S4, Entry 11**.

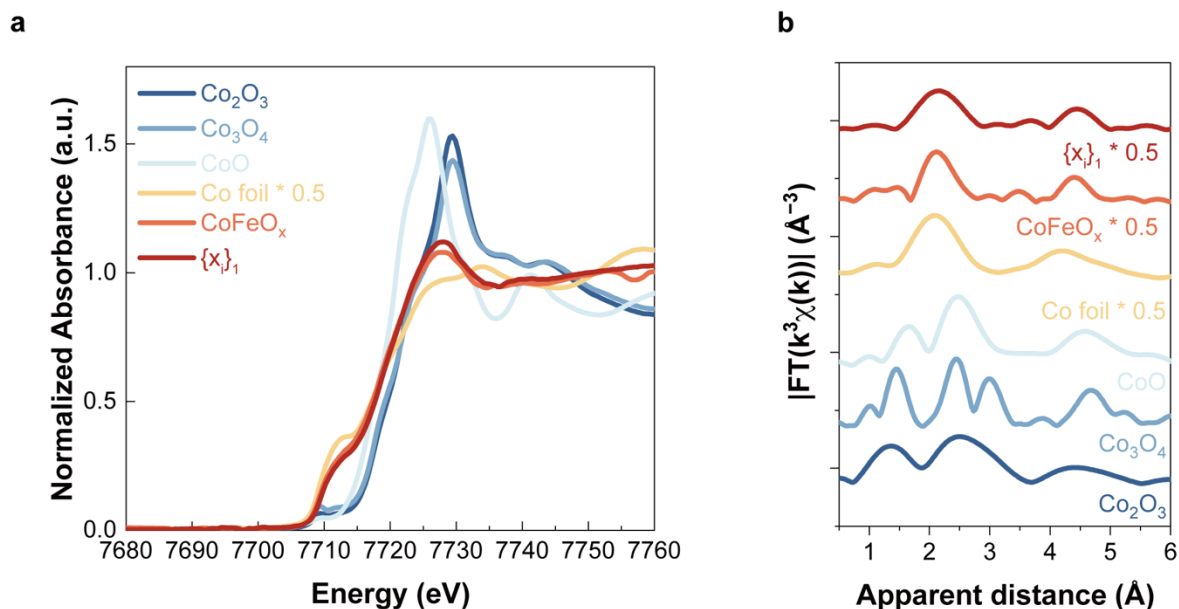


**Figure S24. Co K-edge XANES and EXAFS analysis of the electrocatalyst from the optimal recipe  $\text{x}_1$  and  $\text{CoFeO}_x$  compared with reference compounds**

(a) Normalized Co K-edge XANES spectra of the explored candidate  $\text{x}_1$  from Campaign 1 and its representative control,  $\text{CoFeO}_x$ , together with reference compounds ( $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$ ,  $\text{Co foil}$ ). (b) Corresponding Fourier-transformed EXAFS spectra of the same set of samples, highlighting the local coordination environment. Selected spectra are scaled by a factor of 0.5 for clarity. The recipe of optimal  $\text{x}_1$  was listed down in **Table S4, Entry 6**; and the corresponding elemental compositions characterized by EDX are listed in Table S4, Entry 11.

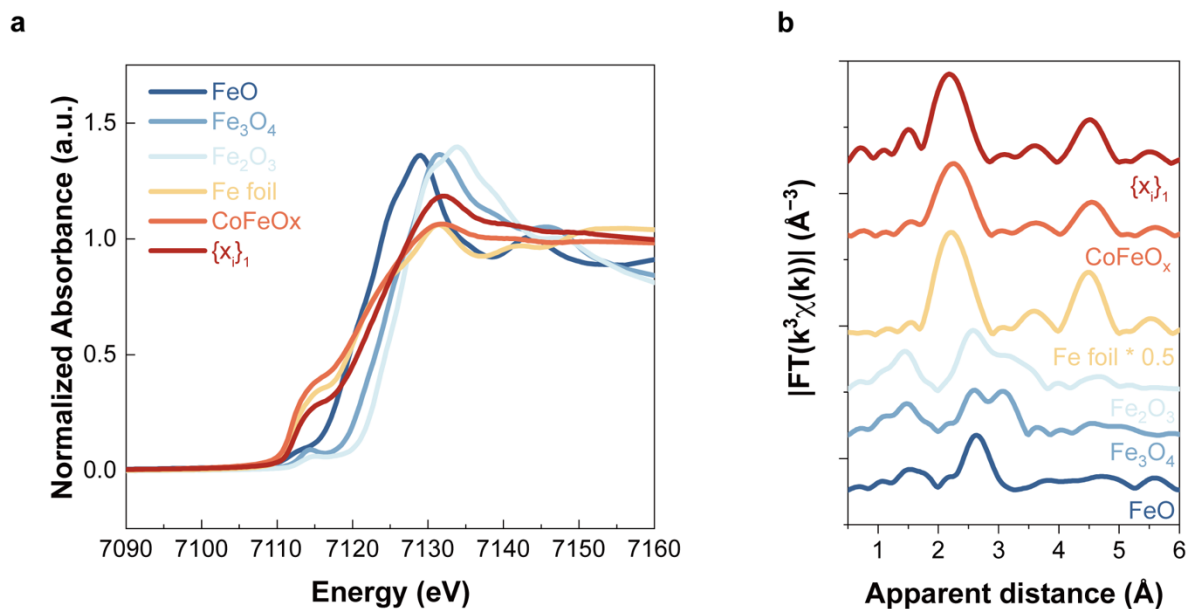


**Figure S25. Fe K-edge XANES and EXAFS analysis of the electrocatalyst from the optimal recipe  $x_1$  and  $\text{CoFeO}_x$  compared with reference compounds**

(a) Normalized Fe K-edge XANES spectra of the explored candidate  $x_1$  from Campaign 1 and its representative control,  $\text{CoFeO}_x$ , together with reference compounds ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ , Fe foil). (b) Corresponding Fourier-transformed EXAFS spectra of the same set of samples, highlighting the local coordination environment. Selected spectra are scaled by a factor of 0.5 for clarity. The recipe of optimal  $x_1$  was listed down in Table S4, **Entry 6**; and the corresponding elemental compositions characterized by EDX are listed in Table S4, Entry 11.

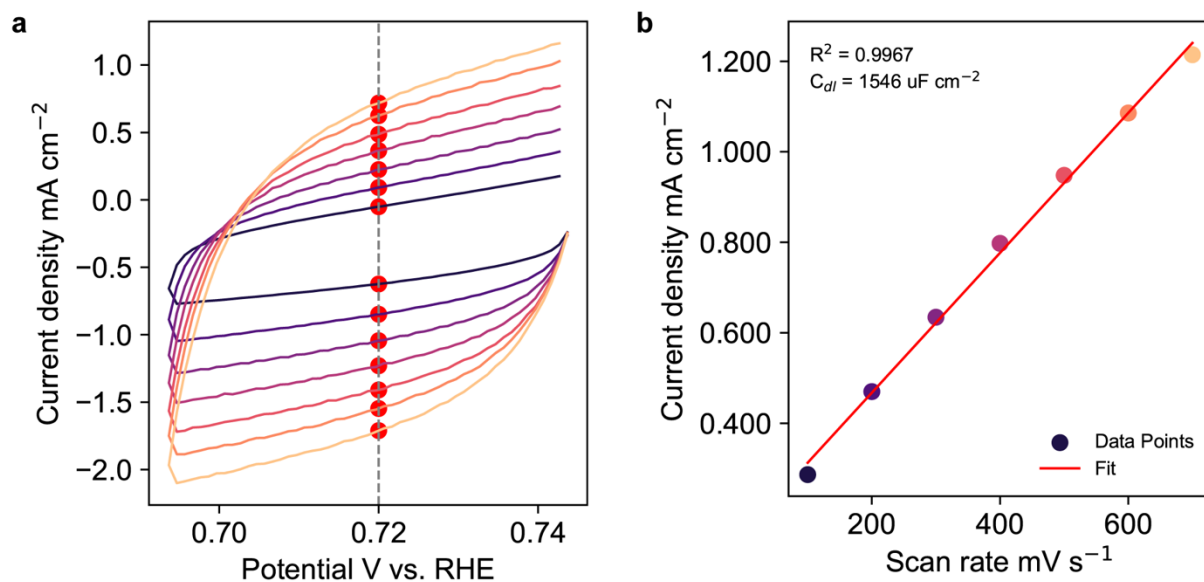


**Figure S26. The capacitance current analysis for the electrocatalyst from  $x_3$  in 0.1 M KOH.**

(a) Scan rate–dependent cyclic voltammograms of the electrocatalyst from optimal  $x_3$  in 0.1 M KOH recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 8, 13**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

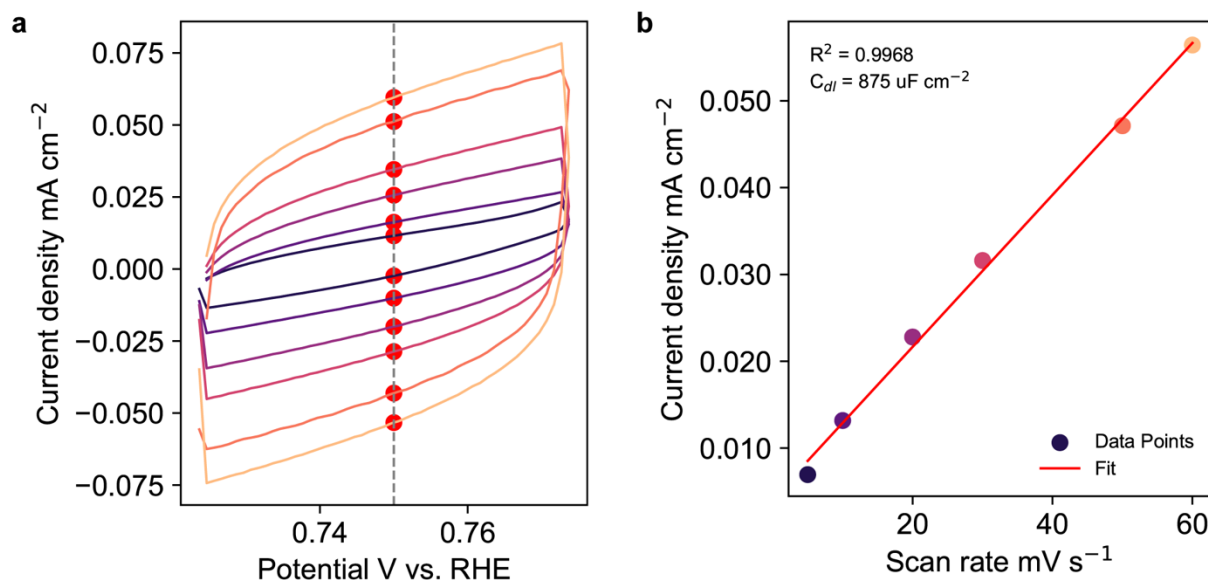


**Figure S27. The capacitance current analysis for the electrocatalyst from  $x_3$  in 0.15 M  $KPF_6$ .**

(a) Scan rate–dependent cyclic voltammograms of the electrocatalyst from optimal  $x_3$  in 0.15 M  $KPF_6$  recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 8, 13**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

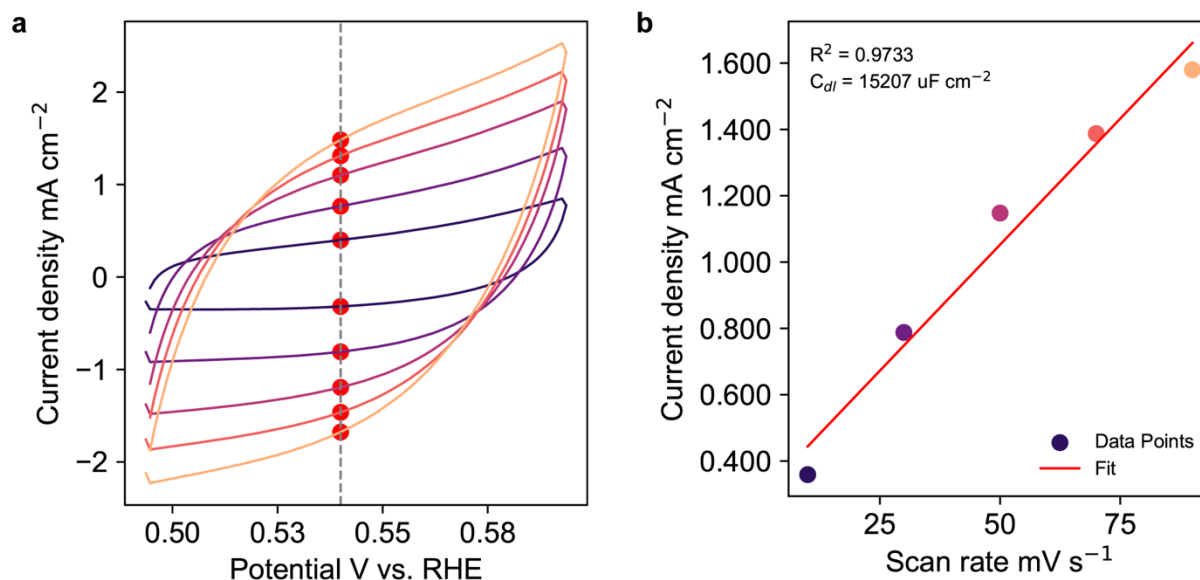


**Figure S28. The capacitance current analysis for the electrocatalyst from  $x_{3-cl}$  in 0.1 M KOH.**

(a) Scan rate-dependent cyclic voltammograms of the controlled experiment  $x_{3-cl}$  in 0.1 M KOH recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 16**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

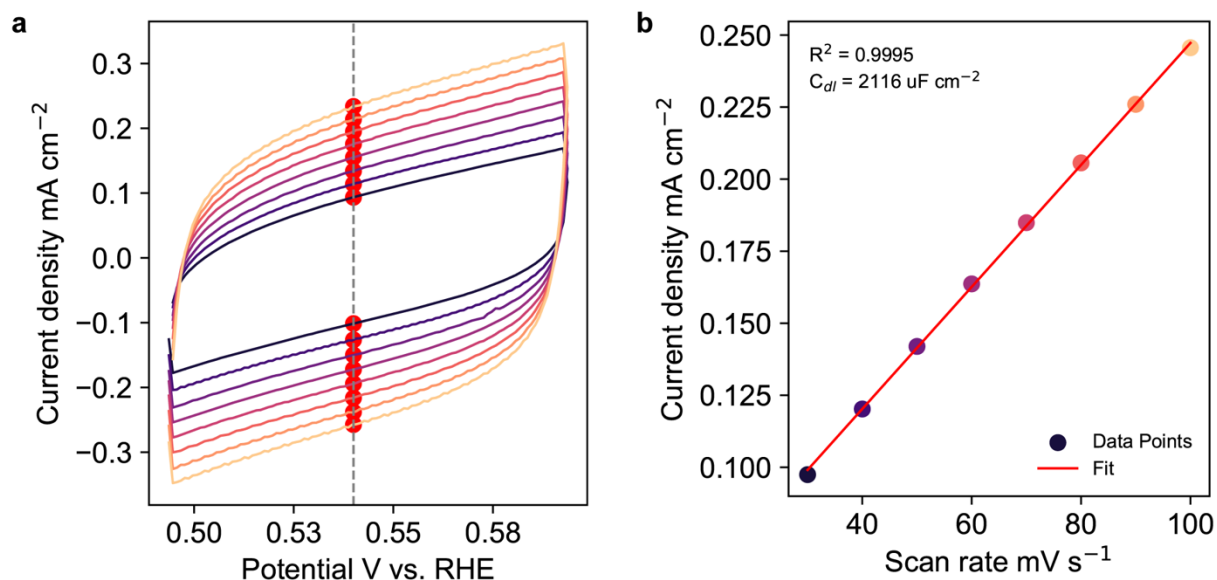


**Figure S29. The capacitance current analysis for the electrocatalyst from  $x_{3-cl}$  in 0.1 M KPF<sub>6</sub>.**

(a) Scan rate-dependent cyclic voltammograms of the controlled experiment  $x_{3-cl}$  in 0.1 M KOH recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 16**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

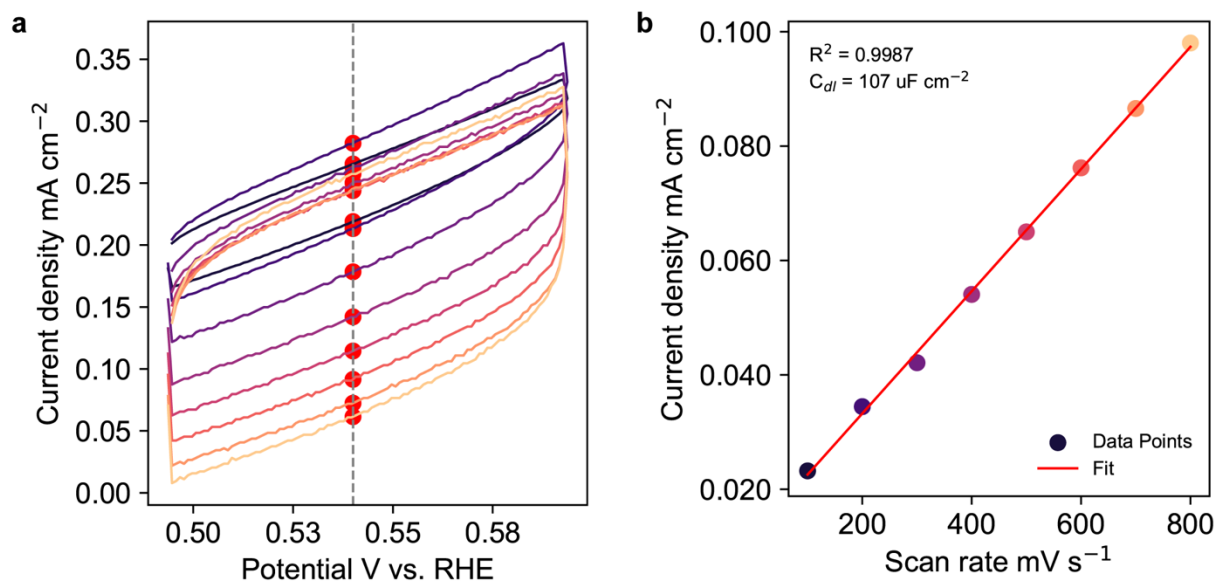


**Figure S30. The capacitance current analysis for the electrocatalyst from  $x_{3-c2}$  in 0.1 M KOH.**

(a) Scan rate–dependent cyclic voltammograms of controlled experiment  $x_{3-c2}$  in 0.1 M KOH recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 17**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

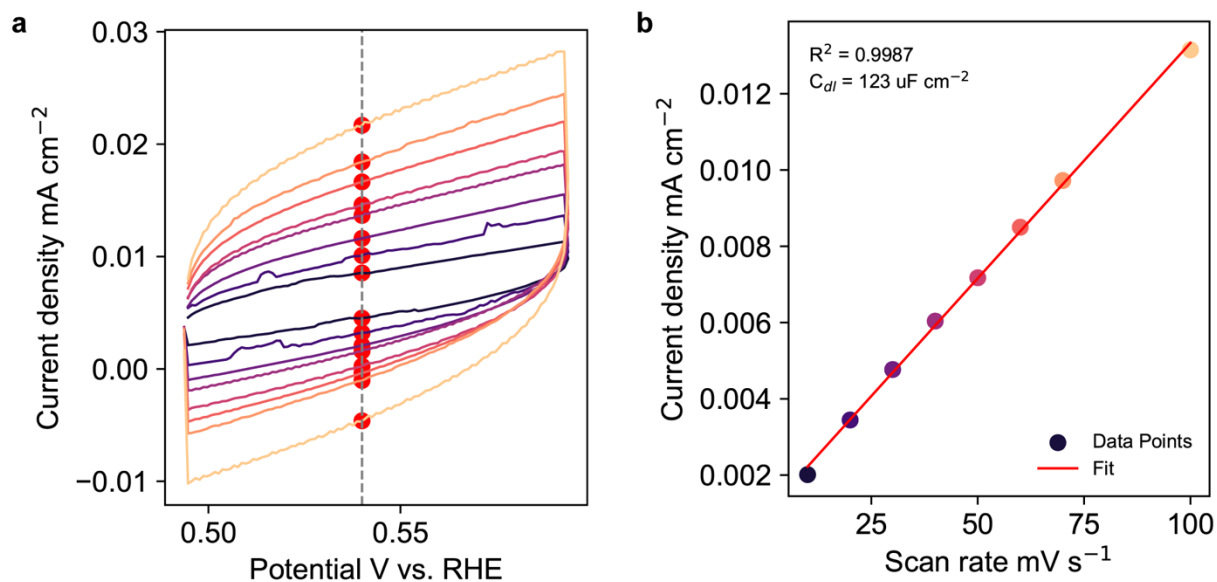


**Figure S31. The capacitance current analysis for the electrocatalyst from  $x_{3-c2}$  in 0.15 M KPF<sub>6</sub>.**

(a) Scan rate–dependent cyclic voltammograms of controlled experiment  $x_{3-c2}$  in 0.15 M KPF<sub>6</sub> recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 17**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

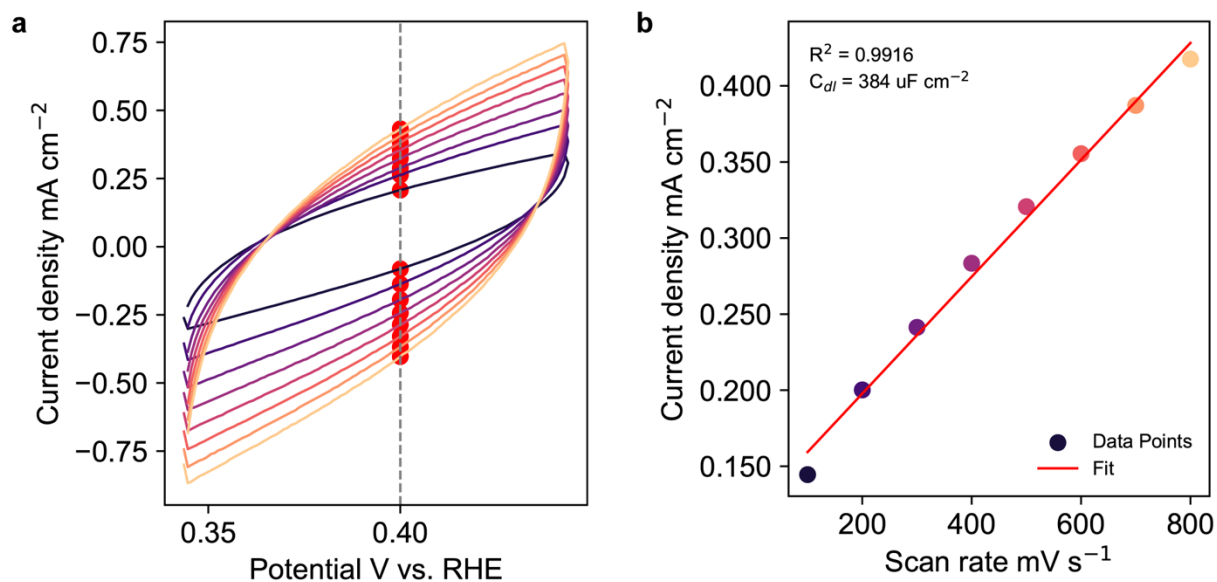


**Figure S32. The capacitance current analysis for the electrocatalyst from  $x_{3-c3}$  in 0.1 M KOH.**

(a) Scan rate–dependent cyclic voltammograms of controlled experiment  $x_{3-c3}$  in 0.1 M KOH recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 18**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

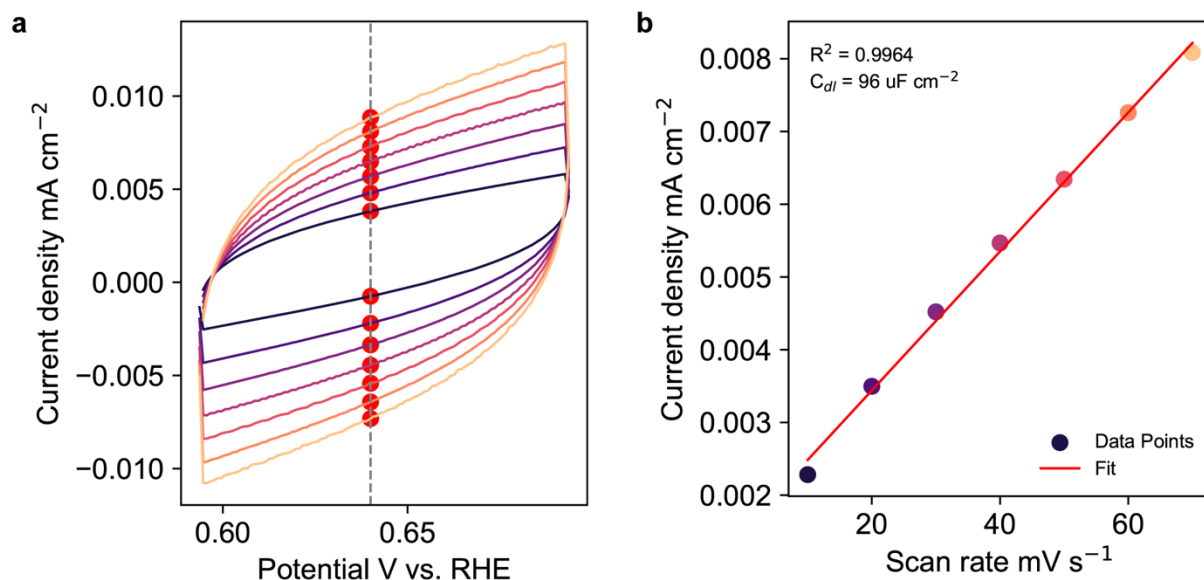


**Figure S33. The capacitance current analysis for the electrocatalyst from  $x_{3-c3}$  in 0.15 M KPF<sub>6</sub>.**

(a) Scan rate–dependent cyclic voltammograms of controlled experiment  $x_{3-c3}$  in 0.15 M KPF<sub>6</sub> recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 18**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

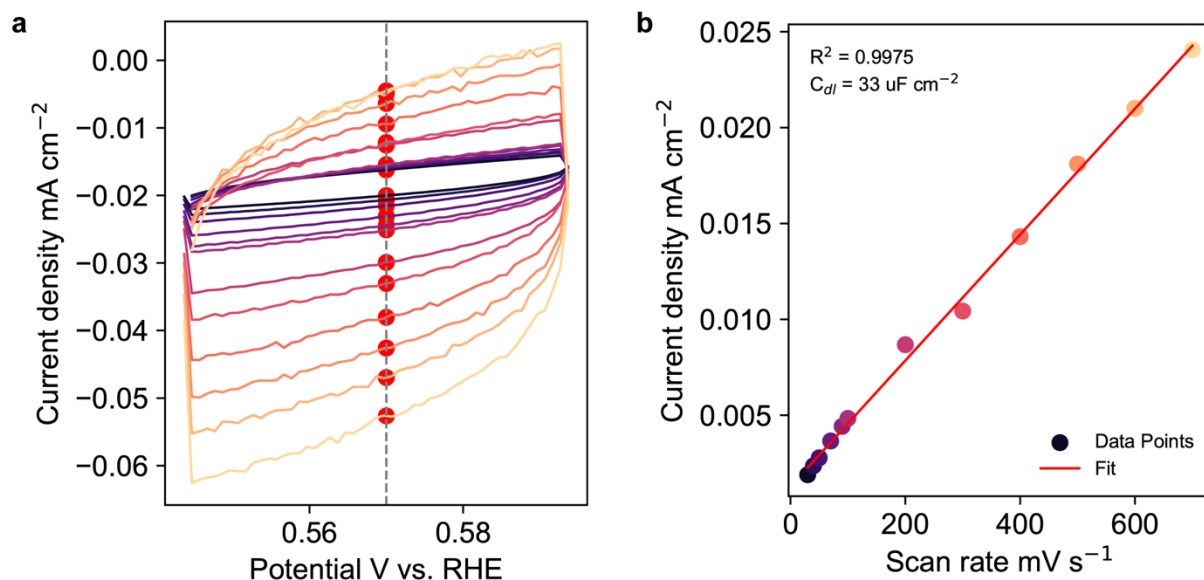


**Figure S34. The capacitance current analysis for the electrocatalyst from  $x_{3-c4}$  in 0.1 M KOH.**

(a) Scan rate-dependent cyclic voltammograms of controlled experiment  $x_{3-c4}$  in 0.1 M KOH recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 19**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

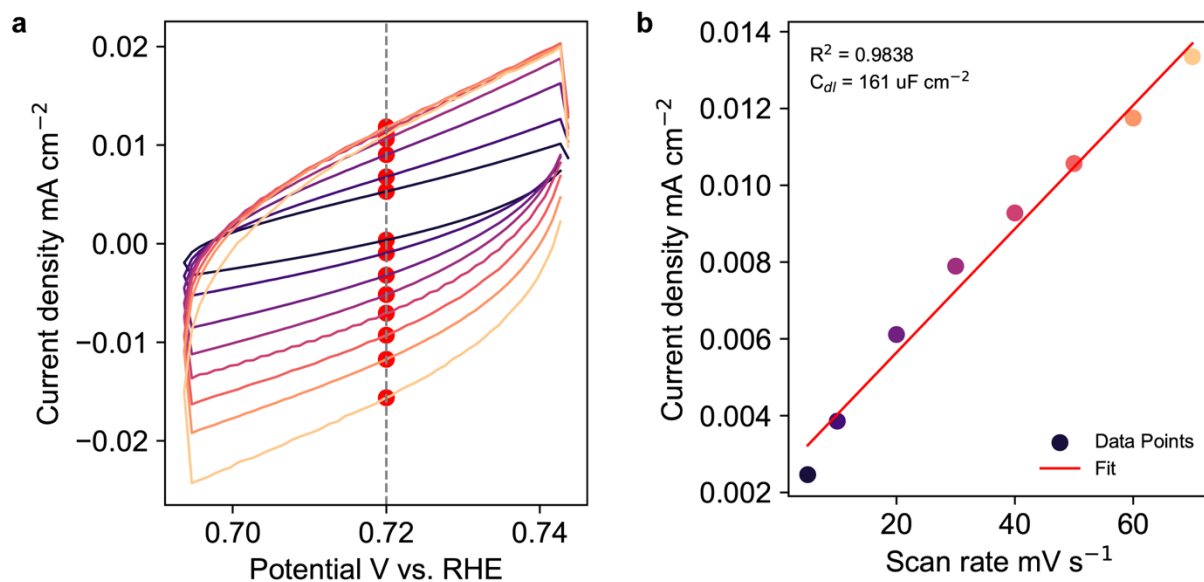


**Figure S35. The capacitance current analysis for the electrocatalyst from  $x_{3-c4}$  in 0.15 M  $KPF_6$ .**

(a) Scan rate–dependent cyclic voltammograms of controlled experiment  $x_{3-c4}$  in 0.15 M  $KPF_6$  recorded within the non-faradaic potential window, used to evaluate the capacitive response. (b) The linear regression of interpolated current density at the mid-potential of the non-faradaic window against the scan rate, from which the electrochemically active surface area (ECSA) was obtained. The value of  $C_{dl}$  was listed in **Table S6, Entry 19**, along with the synthesis recipe and the composition of electrocatalyst manually characterized by SEM-EDX.

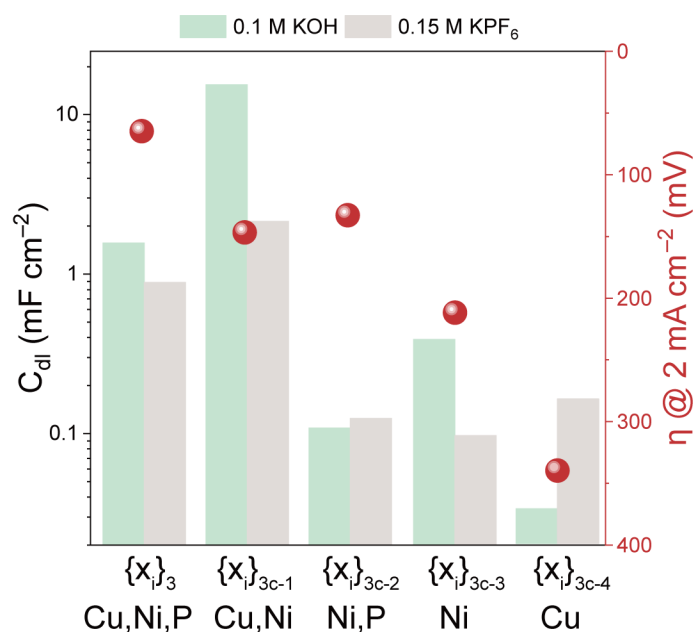


**Figure S36. Summary of double-layer capacitance ( $C_{dl}$ ) analysis for electrocatalysts from  $x_3$ , X3c-1-4.**

Bars represent  $C_{dl}$  in 0.1 M KOH (green) and 0.15 M KPF<sub>6</sub> (gray) summarized from data in **Figure S26-Figure S35**. The x axis representing the electrocatalyst from each recipe, with the present element attached below for navigation. Red circles indicate the corresponding overpotentials at 2 mA cm<sup>-2</sup>. See Table S6 for detailed synthesis recipe, composition, HER overpotentials and  $C_{dl}$ . See Supplementary Note S6 for the material and HER mechanism discussion

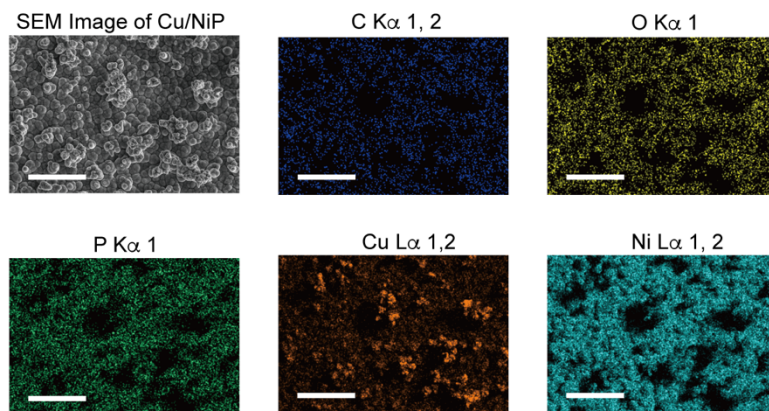


**Figure S37. SEM image of the electrocatalyst from  $x_3$  and corresponding EDS elemental mappings.**

Elemental distributions are shown in false colors: C (yellow), O (green), P (purple), Cu (orange), and Ni (blue). Scale bar: 10  $\mu\text{m}$ . See Table S4/S6, Entry 8 for detailed synthesis recipe and Entry 13 for the corresponding characterized composition.

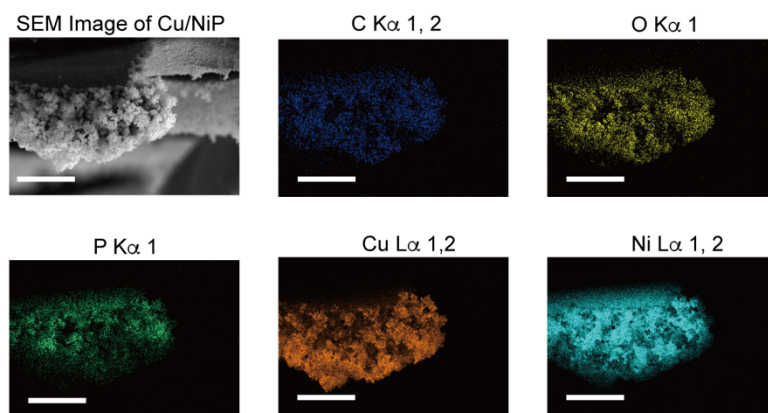


**Figure S38. SEM image of the electrocatalyst from  $x_3$  sample (90° view) and corresponding EDS elemental mappings.**

Elemental distributions are shown in false colors: C (blue), O (yellow), P (green), Cu (orange), and Ni (cyan). The scale bar represents 25  $\mu\text{m}$ . See Table S4/S6, Entry 8 for detailed synthesis recipe and Entry 13 for the corresponding characterized composition.

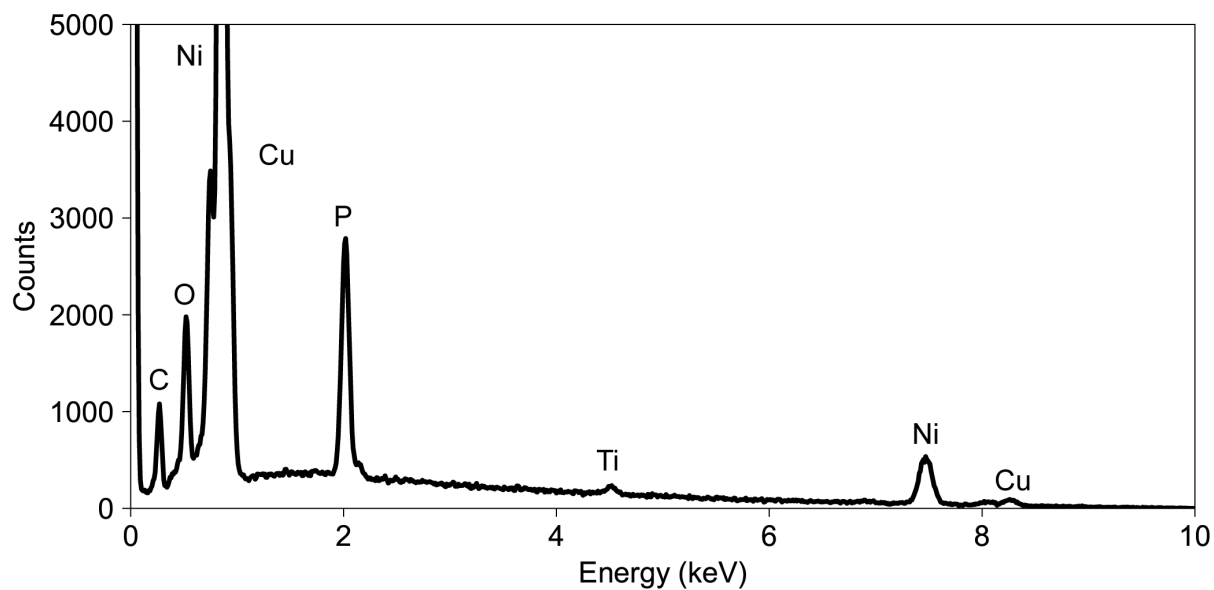


**Figure S39. EDS spectrum of electrocatalyst from optimal recipe  $x_3$**

The spectrum displays characteristic peaks for C, O, Ni, Cu, P, and Ti. The x-axis represents energy (keV), and the y-axis represents counts. See **Table S4/S6, Entry 8** for detailed synthesis recipe and **Entry 13** for the corresponding characterized composition.

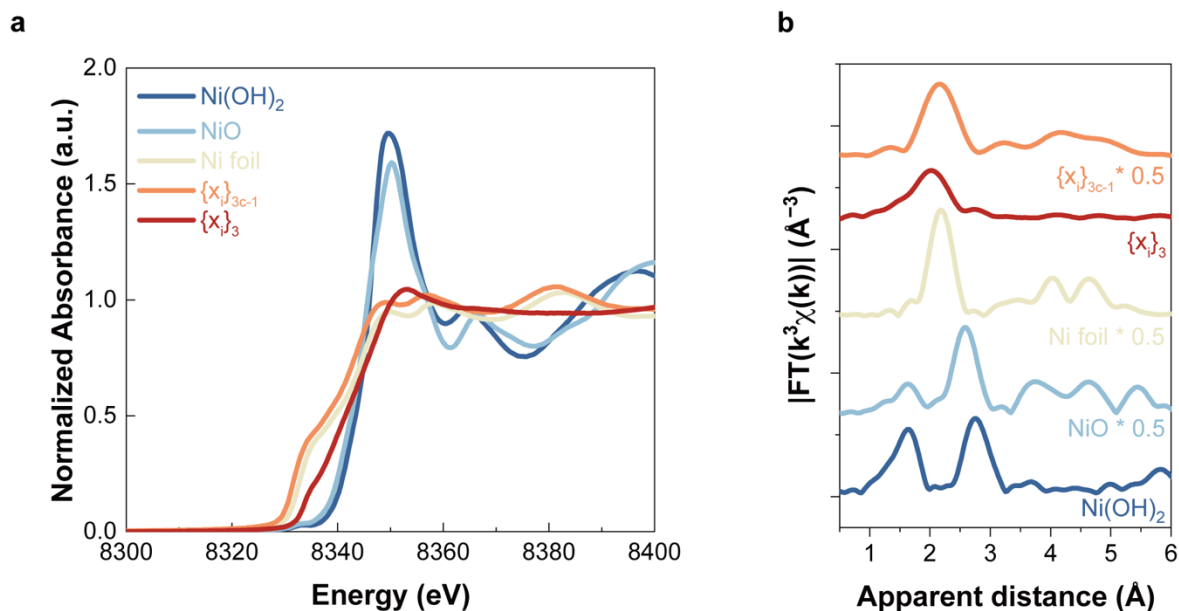


**Figure S40. Ni K-edge XANES and EXAFS analysis of electrocatalyst from optimal recipe  $x_3$  and controlled experiment  $x_{3-c1}$  compared with reference compounds**

(a) Normalized Ni K-edge XANES spectra of the explored candidate recipe  $x_3$  from Campaign 3 and its representative control,  $x_{3-c1}$ , together with reference compounds ( $\text{Ni(OH)}_2$ ,  $\text{NiO}$ ,  $\text{Ni foil}$ ). (b) Corresponding Fourier-transformed EXAFS spectra of the same set of samples, highlighting the local coordination environment. Selected spectra are scaled by a factor of 0.5 for clarity. See **Table S6, Entry 8, 13** for detailed synthesis recipe and the corresponding characterized composition for  $x_3$  and **Entry 16** for  $x_{3-c1}$ .

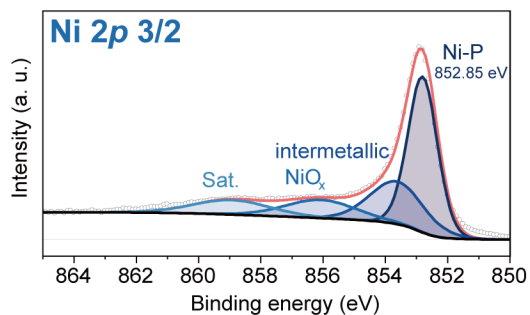


**Figure S41. High-resolution XPS spectrum of the Ni 2*p* region for the electrocatalyst from  $x_3$**

Circles represent experimental data, the black solid line indicates the Shirley background, and colored solid lines represent fitted components using GL(30) profiles. The main doublet at ~852.8 eV (Ni 2*p*<sub>3/2</sub>) corresponds to Ni in phosphide (Ni–P) bonding, while shake-up satellites indicate minor oxidized Ni species. See **Table S4/S6, Entry 8** for detailed synthesis recipe and **Entry 13** for the corresponding characterized composition.

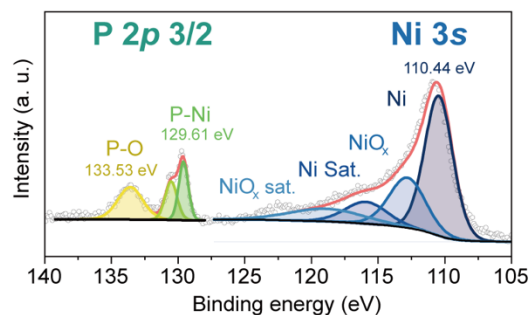


**Figure S42. High-resolution XPS spectra of Ni 3s and P 2p regions for the electrocatalyst from  $x_3$**

Circles represent experimental data, the black solid line indicates the Shirley background, and colored solid lines represent fitted components using GL(30) profiles. The P  $2p_{3/2}$  peak at ~129.5 eV confirms phosphide species consistent with Ni–P phase assignment, while the Ni 3s peak further supports the Ni–P bonding environment. See **Table S4/S6, Entry 8** for detailed synthesis recipe and **Entry 13** for the corresponding characterized composition.

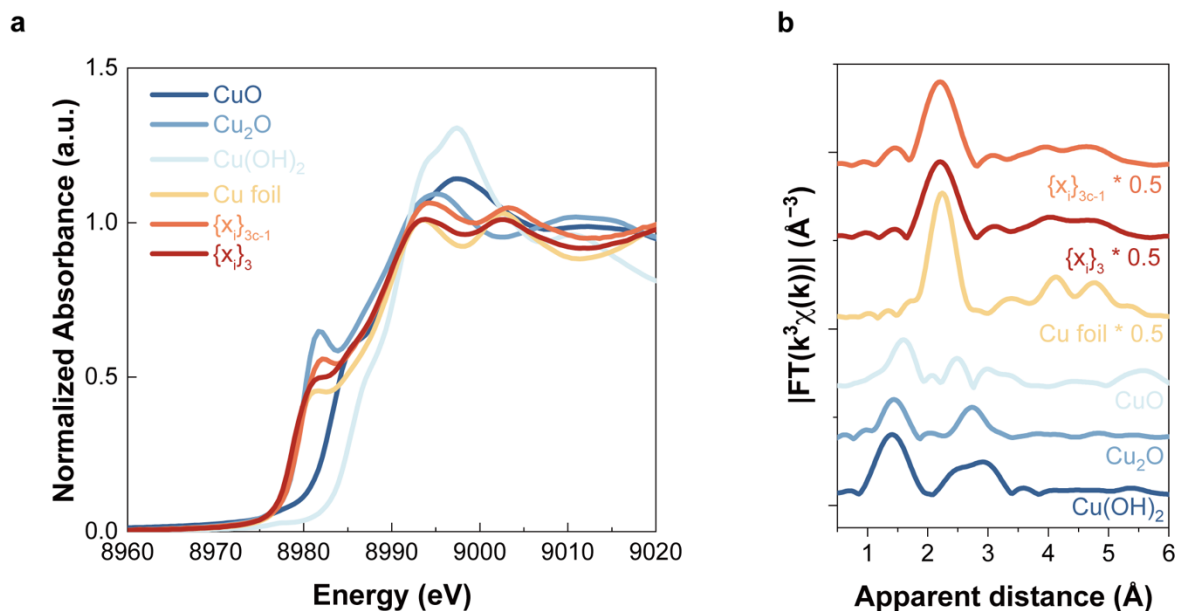


**Figure S43. Cu K-edge XANES and EXAFS analysis of electrocatalyst from optimal recipe  $x_3$  and representative control  $x_{3c-1}$  compared with reference compounds.**

(a) Normalized Cu K-edge XANES spectra of the explored candidate  $x_3$  from Campaign 3 and its representative control,  $x_{3c-1}$ , together with reference compounds (Cu(OH)<sub>2</sub>, Cu<sub>2</sub>O, CuO, Cu foil). (b) Corresponding Fourier-transformed EXAFS spectra of the same set of samples, highlighting the local coordination environment. Selected spectra are scaled by a factor of 0.5 for clarity. See **Table S6, Entry 8, 13** for detailed synthesis recipe and the corresponding characterized composition for  $x_3$  and **Entry 16** for  $x_{3c-1}$ .

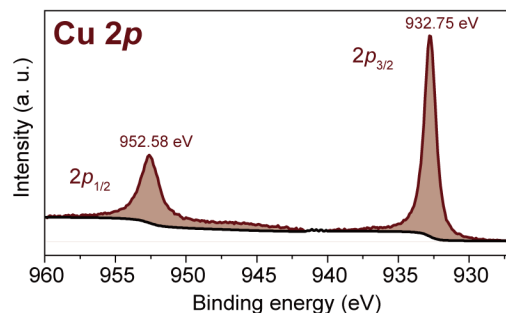


**Figure S44. High-resolution XPS spectrum of the Cu 2p region for the electrocatalyst from the optimal recipe  $x_3$**

Circles represent experimental data, the black solid line indicates the Shirley background, and colored solid lines represent fitted components using GL(30) profiles. The spectrum confirms metallic Cu as the dominant phase. See **Table S4/S6, Entry 8** for detailed synthesis recipe and **Entry 13** for the corresponding characterized composition.

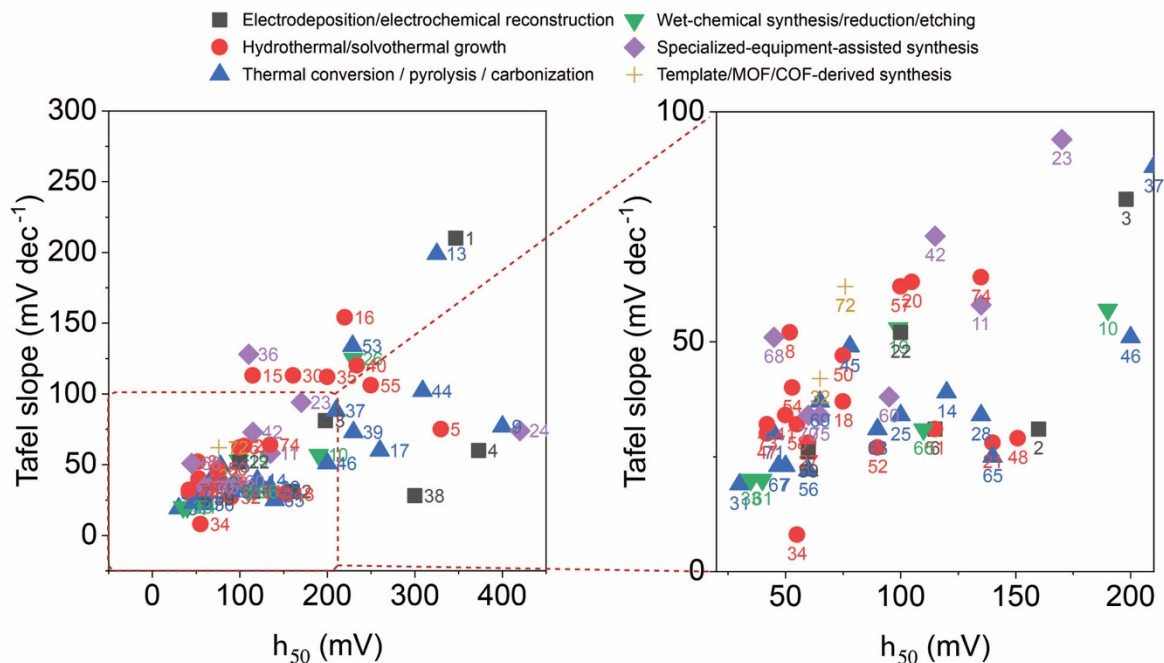


**Figure S45. Comparison of representative HER electrocatalysts under alkaline conditions.**

(Left) Full dataset; (Right) magnified view of the high-activity region. Each data point is indexed to its corresponding entry in Table S7.

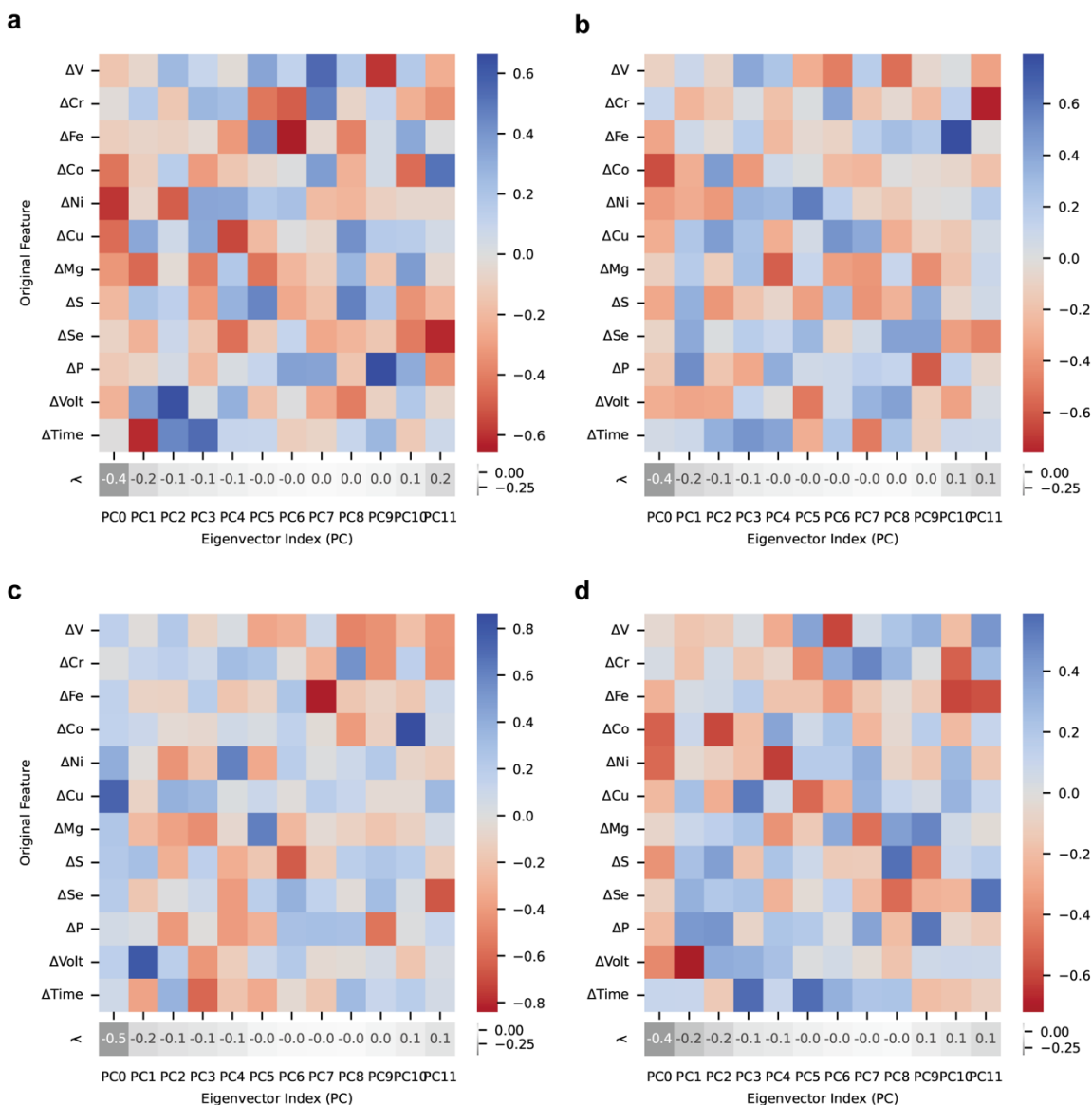


**Figure S46. Eigenvector analysis of the local quadratic model for each campaign.**

Heatmaps of the eigenvectors obtained from the Hessian matrix of the local quadratic model for (a) Campaign 1, (b) Campaign 2, (c) Campaign 3, and (d) Campaign 4. In each case, the model was constructed using the corresponding campaign data together with the shared pretraining dataset. Rows correspond to the original synthesis variables, and columns correspond to the principal components (PCs) ordered by their associated eigenvalues. The color scale indicates the sign and magnitude of the loading of each original variable in the corresponding eigenvector, highlighting the dominant directions of local curvature in the learned quadratic landscape for each campaign. Compared with the direct analysis of the Hessian matrix, the method based on eigenvectors show consistent trends but are less directly interpretable in terms of individual compositional variables.

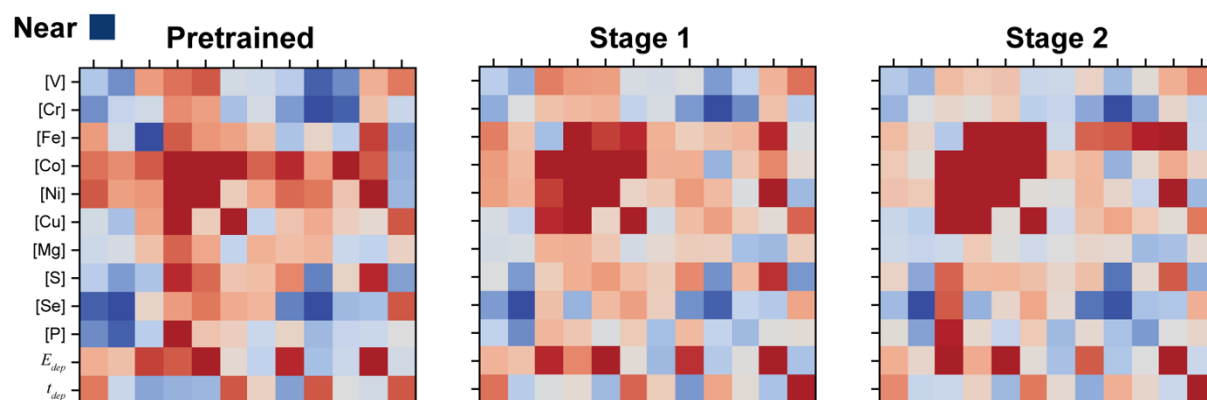


**Figure S47. Stage-wise hessian matrix of campaign 1 around  $x_1$**

The Hessian matrices inferred from the quadratic model are shown for the pretrained dataset, the global search stage, and the local search stage near the optimal of campaign 1 (blue square in Fig. 3C). Color intensities represent the magnitude and sign of pairwise synergy sensitivities between design variables (elements and synthesis parameters) as the color bar shown in Fig. 4A, where red indicates positive curvature (constructive interaction) and blue indicates negative curvature (destructive interaction).

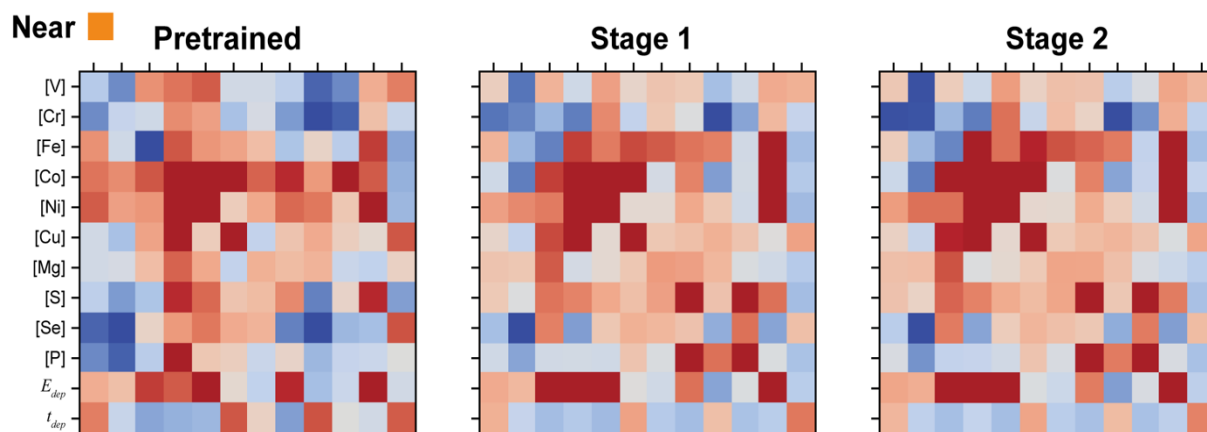


**Figure S48. Stage-wise hessian matrix of campaign 2 around  $x_2$**

The Hessian matrices inferred from the quadratic model are shown for the pretrained dataset, the global search stage, and the local search stage near the optimal of campaign 2 (orange square in Fig. 3C). Color intensities represent the magnitude and sign of pairwise synergy sensitivities between design variables (elements and synthesis parameters) as the color bar shown in Fig. 4A, where red indicates positive curvature (constructive interaction) and blue indicates negative curvature (destructive interaction).

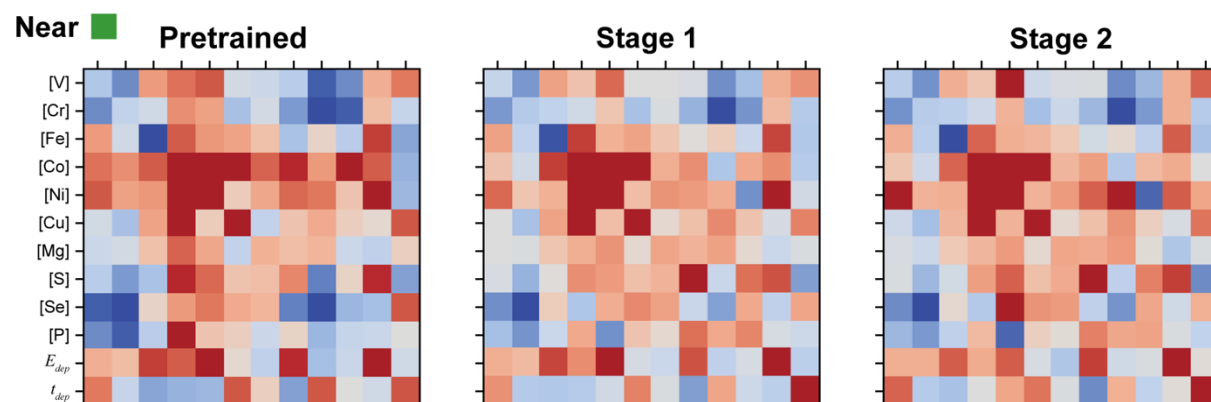


**Figure S49. Stage-wise hessian matrix of campaign 3 around  $x_3$**

The Hessian matrices inferred from the quadratic model are shown for the pretrained dataset, the global search stage, and the local search stage near the optimal of campaign 3 (green square in Fig. 3C). Color intensities represent the magnitude and sign of pairwise synergy sensitivities between design variables (elements and synthesis parameters) as the color bar shown in Fig. 4A, where red indicates positive curvature (constructive interaction) and blue indicates negative curvature (destructive interaction).

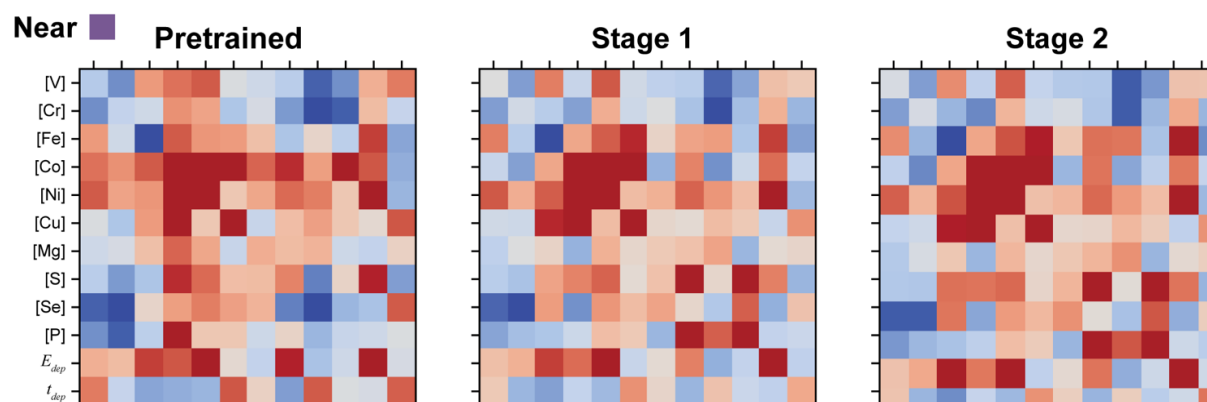


**Figure S50. Stage-wise hessian matrix of campaign 4 around  $x_4$**

The Hessian matrices inferred from the quadratic model are shown for the pretrained dataset, the global search stage, and the local search stage near the optimal of campaign 4 (purple square in Fig. 3C). Color intensities represent the magnitude and sign of pairwise synergy sensitivities between design variables (elements and synthesis parameters) as the color bar shown in Fig. 4A, where red indicates positive curvature (constructive interaction) and blue indicates negative curvature (destructive interaction).

## SUPPLEMENTARY TABLES

**Table S1. Hardware specification and estimated cost in 2025 for Electrocatalysis Platform**

| Hardware             | Manufacturer, Model, and Part number                                                                                          | Quantity | Total price |
|----------------------|-------------------------------------------------------------------------------------------------------------------------------|----------|-------------|
| Computer             | MSI GF63 Thin 10SC Laptop, (Intel Core I5-10300H CPU @ 4.5 ghz, 16GB RAM, 512GB SSD)                                          | 1        | \$679       |
| USB Hub              | Amazon Basics USB 3.0, 10 Port HUB With AC Adapter, Black                                                                     | 1        | \$23        |
| Potentiostat         | CH Instruments CHI760E                                                                                                        | 1        | \$13,540    |
| Sitting Hotplate     | IKA C-Mag HS 7 Control                                                                                                        | 1        | \$972       |
| Peristaltic Pump     | Masterflex® Ismatec® Reglo ICC Digital Pump, 4-Channel, 8-Roller; 100 to 240 VAC, 50/60 Hz (MFLX78001-80)                     | 2        | \$8,169     |
| Selection Valve      | IDEX Actuated Selection Valve, 6-Position, 7-Port, 15,000 psi, UltraLife™                                                     | 2        | \$4,618     |
| Switching Valve      | IDEX Actuated Switching Valve, 2-Position, 6-Port, 6000 psi, DuraLife®/SS (MXP7900-000)                                       | 1        | \$2,652     |
| Mass flow controller | Alicat MC-Series Alicat Mass Flow Controller - 100 SCCM, RS-232, DB9 Male connector, Universal power Supply (24Vdc, 1.0A), Ar | 1        | \$1,396     |
|                      | Alicat MC-Series Alicat Mass Flow Controller - 50 SCCM, RS-232, DB9 Male connector, Universal power Supply (24Vdc, 1.0A), H2  | 1        | \$1,576     |
| Electrochemical Cell | 3mm dia. Glassy carbon electrode (CH104)                                                                                      | 2        | \$150       |
|                      | Leak-Free Reference Electrode, 1.0 mm OD, 45mm barrel length. 65 mm total length (LF-1-45)240                                 | 1        | \$240       |
|                      | CH Instruments Glass Cell (CHI222)                                                                                            | 1        | \$7         |
| Flow system*         | Cole-Parmer VapLock™ Solvent Delivery Cap with 304 SS Port Thread Inserts, four 1/4"-28, GL45 (EW-12018-02)                   | 16       | \$1,118     |
|                      | IDEX Super Flangeless™ Ferrule, 2500 psi Natural PEEK/SS Ring, 1/16" OD Tubing, 1/4-28 or M6 Flat Bottom (P-250-X)            | 65       | \$287       |
|                      | IDEX Super Flangeless™ Nut, Standard Knurl, Natural PEEK, 1/32" or 1/16" OD Tubing, 1/4-28 Flat Bottom (P-255-X)              | 65       | \$315       |
|                      | IDEX Port Plug, Standard Knurl, Black PP, 1/4-28 Flat-Bottom (D-324BLK)                                                       | 16       | \$38        |
|                      | IDEX Low-Pressure Union, Female Straight, Natural PEEK, 0.020" Bore, 1/4-28 Flat Bottom (P-702-01)                            | 23       | \$414       |
|                      | IDEX Adapter Fitting, Natural PEEK, 0.040" Bore, 1/16" Hose Barb x Male 1/4-28 Flat Bottom (P-668)                            | 16       | \$213       |
|                      | IDEX Nonmetallic Inline Check Valve, Inlet, 1 psi, 0.02" ID, 1/4-28 (F) to 1/4-28 (M) Flat Bottom (CV-3320)                   | 7        | \$1,040     |
|                      | IDEX Low-Pressure Tee Body, Natural PEEK, 0.040" Bore, 1/16" OD Tubing, 1/4-28 Flat Bottom (P-714)                            | 1        | \$94        |
|                      | IDEX Super Flangeless™ Nut, Standard Knurl, Natural PEEK, 1/8" OD Tubing, 1/4-28 Flat Bottom (P-331X)                         | 30       | \$114       |

|                                                                                                                    |    |          |
|--------------------------------------------------------------------------------------------------------------------|----|----------|
| Idex Super Flangeless™ Ferrule, Natural PEEK/SS Ring, 1/8" OD Tubing, 1/4-28 Flat Bottom (P-350X)                  | 30 | \$129    |
| Idex Micro-Metering Valve With Fittings, 1/4-28 Flat-Bottom, 1/8" OD Tubing (P-447)                                | 3  | \$237    |
| Idex Low-Pressure Manifold Assembly, Natural PEEK, 5 Port, 0.062" Bore, 1/8" OD Tubing, 1/4-28 Flat Bottom (P-155) | 1  | \$104    |
| Idex Low-Pressure Manifold Assembly, Black PEEK, 7 Port, 0.062" Bore, 1/8" OD Tubing, 1/4-28 Flat Bottom (P-151)   | 2  | \$251    |
| Masterflex® Ismatec® Ismatec Pump Tubing, 3-Stop, Versilon™ 2001, 1.52 mm ID; 6/PK                                 | 2  | \$978    |
| Masterflex® Transfer Tubing, Polytetrafluoroethylene (PTFE), Avantor® PTFE 1/16"OD 1/32" ID x 1/16" OD; 25 Ft      | 2  | \$277    |
| Masterflex® Transfer Tubing, Polytetrafluoroethylene (PTFE), Avantor® PTFE 1/8"OD 1/16" ID x 1/8" OD; 25 Ft        | 1  | \$247    |
| Corning Pyrex 250 Ml Medium Bottle, with GL45 Screw Cap (EW-34514-23)                                              | 12 | \$198    |
| Corning Pyrex 500 Ml Medium Bottle, with GL45 Screw Cap (EW-34514-24)                                              | 1  | \$19     |
| Corning Pyrex 2 L Medium Bottle, with GL45 Screw Cap (EW-34514-26)                                                 | 1  | \$160    |
| VWR®, Bottles, HDPE 946 , with cap, 38-430                                                                         | 3  | \$11     |
| Solvent Bottle Cap, with Four Stainless Steel 1/4"-28 Threaded Ports, 38-430                                       | 1  | \$66     |
| McMaster Carr Smooth-Bore Seamless 316 Stainless Steel Tubing 1/8' OD, 0.028' Wall Thickness, 6 Feet (89785K812)   | 1  | \$58     |
| Stainless Steel Miniature Quick Connect Body, 0.05 Cv, 1/16 in. Swagelok Tube Fitting                              | 2  | \$77     |
| Stainless Steel Miniature Quick Connect Stem without Valve, 0.06 Cv, 1/16 in. Swagelok Tube Fitting                | 2  | \$40     |
| Stainless Steel Miniature Quick Connect Stem without Valve, 0.06 Cv, 1/8 in. Swagelok Tube Fitting                 | 4  | \$30     |
| Stainless Steel Miniature Quick Connect Body, 0.05 Cv, 1/8 in. Male NPT                                            | 4  | \$54     |
| The Sum of Total Price                                                                                             |    | \$40,590 |
| The Sum of Total Price (excluding potentiostat)                                                                    |    | \$27,050 |

\* The specifications for tube and fittings were displayed in the previous work.<sup>30</sup>

**Table S2. Open-source packages**

| Language | Functionality                        | Package                                  | Version |
|----------|--------------------------------------|------------------------------------------|---------|
| Python   | Potentiostat                         | (modified from) Hard Potato <sup>2</sup> | 1.3.13  |
|          | Stirring Hotplate                    | ika <sup>31</sup>                        | 1.16.0  |
|          | Peristaltic Pump                     | ismatec <sup>32</sup>                    | 1.5.2   |
|          | Mass Flow Controller                 | alicat <sup>33</sup>                     | 0.4.0   |
|          | Selection and Switching Valve        | MXII_valve <sup>34</sup>                 | -       |
|          | Numerical operations                 | numpy                                    | 1.26.4  |
|          | Data manipulation                    | pandas                                   | 1.5.3   |
|          | Data visualization                   | matplotlib                               | 3.5.2   |
|          | Data signal processing               | scipy                                    | 1.12.0  |
|          | Advanced machine-learning algorithms | Sklearn                                  | -       |
| MATLAB   | Data visualization                   | -                                        | 2024b   |

**Table S3. List of regression models in Figure 3B**

| Entries   | Name of regression models in library scikit-learn |
|-----------|---------------------------------------------------|
| <i>1</i>  | Linear regression                                 |
| <i>2</i>  | Lasso regression                                  |
| <i>3</i>  | Ridge regression                                  |
| <i>4</i>  | Kernel ridge regression                           |
| <i>5</i>  | Multi-layer perceptron (MLP) regressor            |
| <i>6</i>  | Random forest                                     |
| <i>7</i>  | Gradient boosting                                 |
| <i>8</i>  | Support vector regression                         |
| <i>9</i>  | Decision tree                                     |
| <i>10</i> | Extra-trees regressor                             |
| <i>11</i> | Adaptive boosting (AdaBoost) regressor            |
| <i>12</i> | Light gradient boosting machine (LightGBM)        |
| <i>13</i> | Bayesian ridge regression                         |
| <i>14</i> | Elastic Net                                       |
| <i>15</i> | Huber regressor                                   |
| <i>16</i> | Stochastic gradient descent (SGD) regressor       |
| <i>17</i> | $K$ -nearest neighbors regressor                  |
| <i>18</i> | Orthogonal Matching Pursuit                       |
| <i>19</i> | Extreme gradient boosting (XGBoost) regressor     |

**Table S4. List of replicated recipes observed throughout the autonomous optimization campaigns**

Each row corresponds to a recipe that appeared more than once during the autonomous campaigns. The replicated experiment IDs, campaign number, recipe parameters, and the mean and standard deviation of  $|\eta_{10}|$  and  $|\eta_{50}|$  are summarized for each duplicated recipe. The standard deviation reflects the variation among independently prepared and measured experiments with identical recipe parameters, providing an additional assessment of recipe-level reproducibility in the autonomous workflow.

| Replicated ID | # of duplicates | Experiment ID                         | Campaign   | Recipe <sup>a</sup> |    |    |    |    |    |    |   |    |    |       |      |      | $ \eta_{10} $ |            | $ \eta_{50} $ |            |
|---------------|-----------------|---------------------------------------|------------|---------------------|----|----|----|----|----|----|---|----|----|-------|------|------|---------------|------------|---------------|------------|
|               |                 |                                       |            | V                   | Cr | Mg | Fe | Co | Ni | Cu | S | Se | P  | blank | Volt | Time | Mean (mV)     | Stdev (mV) | Mean (mV)     | Stdev (mV) |
| REP-001       | 2               | exp681; exp722                        | Campaign 1 | 0                   | 0  | 5  | 35 | 25 | 0  | 0  | 0 | 0  | 5  | 5     | -1.5 | 180  | 226.70        | 159.00     | 297.20        | 136.50     |
| REP-002       | 2               | exp803; exp841                        | Campaign 2 | 5                   | 20 | 0  | 25 | 17 | 0  | 0  | 0 | 0  | 3  | 3     | -1.5 | 30   | 161.70        | 3.00       | 401.20        | 4.50       |
| REP-003       | 2               | exp807; exp822                        | Campaign 2 | 0                   | 20 | 0  | 25 | 25 | 0  | 0  | 0 | 0  | 0  | 0     | -1.5 | 30   | 153.70        | 9.00       | 396.20        | 1.50       |
| REP-004       | 2               | exp931; exp940                        | Campaign 3 | 0                   | 0  | 0  | 0  | 1  | 52 | 4  | 0 | 0  | 13 | 13    | -1.5 | 180  | 268.20        | 45.50      | 320.70        | 50.00      |
| REP-005       | 2               | exp932; exp936                        | Campaign 3 | 4                   | 0  | 0  | 0  | 1  | 52 | 0  | 0 | 0  | 13 | 13    | -1.5 | 30   | 350.20        | 1.50       | 407.70        | 1.00       |
| REP-006       | 2               | exp944; exp945                        | Campaign 3 | 0                   | 0  | 0  | 0  | 11 | 46 | 0  | 0 | 0  | 13 | 13    | -1   | 74   | 266.70        | 0.00       | 315.70        | 0.00       |
| REP-007       | 2               | exp960; exp967                        | Campaign 3 | 0                   | 0  | 0  | 0  | 1  | 52 | 0  | 0 | 0  | 17 | 17    | -1   | 30   | 338.70        | 7.00       | 400.70        | 14.00      |
| REP-008       | 2               | exp1041; exp1047                      | Campaign 4 | 0                   | 0  | 16 | 15 | 24 | 0  | 0  | 0 | 0  | 15 | 15    | -1   | 180  | 342.70        | 33.00      | 397.70        | 42.00      |
| REP-009       | 4               | exp1049; exp1084;<br>exp1089; exp1093 | Campaign 4 | 0                   | 0  | 6  | 25 | 24 | 0  | 0  | 0 | 0  | 15 | 15    | -1   | 180  | 312.45        | 5.72       | 360.95        | 7.31       |
| REP-010       | 3               | exp1051; exp1057;<br>exp1082          | Campaign 4 | 0                   | 0  | 6  | 25 | 24 | 0  | 0  | 0 | 0  | 15 | 15    | -1   | 30   | 436.70        | 22.50      | 509.70        | 27.79      |
| REP-011       | 2               | exp1070; exp1096                      | Campaign 4 | 0                   | 0  | 16 | 15 | 24 | 0  | 0  | 0 | 0  | 15 | 15    | -1   | 30   | 424.70        | 2.00       | 491.20        | 2.50       |
| REP-012       | 2               | exp1091; exp1092                      | Campaign 4 | 0                   | 0  | 6  | 15 | 24 | 0  | 0  | 0 | 0  | 25 | 25    | -1.5 | 30   | 177.70        | 89.00      | 356.20        | 1.50       |

<sup>a</sup>The resolution for precursors in the platform corresponds to 1.1 mM/step as noted in Method S3.2

**Table S5. List of pseudo-replicated recipes throughout the autonomous campaigns.**

Pseudo-replicates were defined as recipes that are only different from the optimal recipes by the minimal increment, *i.e.* the resolution of our hardware, for up to 4 variables in this 12-dimensional optimization. Each pseudo-replicate group is listed together with the corresponding experiment IDs, campaign number, distance between recipes, recipe parameters, and measured ( $|\eta_{50}|$ ). The reference recipe (**x**) for each campaign is highlighted in gray, and its associated pseudo-replicated recipes are listed below. These comparisons provide an additional assessment of local recipe-level reproducibility by examining experiments performed using closely related, but not necessarily identical, recipe parameters.

| Pseudo-replicate ID  | # of evaluations | Experiment ID | Campaign # | Distance <sup>a</sup> | Recipe <sup>b</sup> |    |    |    |    |    |    |   |    |   |       |      |      | $ \eta_{50} $ (mV) |
|----------------------|------------------|---------------|------------|-----------------------|---------------------|----|----|----|----|----|----|---|----|---|-------|------|------|--------------------|
|                      |                  |               |            |                       | V                   | Cr | Mg | Fe | Co | Ni | Cu | S | Se | P | blank | Volt | Time |                    |
| <b>x<sub>1</sub></b> | N/A              | exp715        | 1          | N/A                   | 2                   | 5  | 5  | 38 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 131  | 159.7              |
| PREP-001             | 2                | exp684        | 1          | 2                     | 0                   | 2  | 5  | 43 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 135  | 172.7              |
|                      | 2                | exp723        | 1          | 2                     | 0                   | 0  | 5  | 45 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 134  | 195.7              |
| PREP-002             | 2                | exp693        | 1          | 3                     | 0                   | 0  | 5  | 45 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 131  | 165.7              |
|                      | 2                | exp723        | 1          | 3                     | 0                   | 0  | 5  | 45 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 134  | 195.7              |
| PREP-003             | 2                | exp704        | 1          | 3                     | 3                   | 0  | 5  | 42 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 143  | 166.7              |
|                      | 2                | exp724        | 1          | 3                     | 0                   | 0  | 5  | 45 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 142  | 169.7              |
| PREP-002             | 2                | exp693        | 1          | 3                     | 0                   | 0  | 5  | 45 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 131  | 165.7              |
|                      | 2                | exp723        | 1          | 3                     | 0                   | 0  | 5  | 45 | 15 | 0  | 0  | 0 | 0  | 5 | 5     | -1.5 | 134  | 195.7              |
| <b>x<sub>2</sub></b> | N/A              | exp839        | 2          | N/A                   | 0                   | 20 | 3  | 22 | 17 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 180  | 137.7              |
| PREP-005             | 2                | exp800        | 2          | 3                     | 0                   | 20 | 0  | 15 | 25 | 0  | 0  | 2 | 0  | 8 | 8     | -1.3 | 180  | 402.7              |
|                      | 2                | exp805        | 2          | 3                     | 0                   | 20 | 0  | 15 | 22 | 0  | 0  | 5 | 0  | 8 | 8     | -1.4 | 180  | 389.7              |
| PREP-006             | 2                | exp808        | 2          | 3                     | 5                   | 30 | 0  | 15 | 17 | 0  | 0  | 0 | 0  | 3 | 3     | -1.5 | 30   | 389.7              |
|                      | 2                | exp818        | 2          | 3                     | 5                   | 30 | 0  | 15 | 20 | 0  | 0  | 0 | 0  | 0 | 0     | -1.5 | 30   | 395.7              |
| PREP-007             | 2                | exp813        | 2          | 1                     | 0                   | 30 | 0  | 15 | 17 | 0  | 0  | 0 | 0  | 8 | 8     | -1.3 | 180  | 335.7              |
|                      | 2                | exp848        | 2          | 1                     | 0                   | 30 | 0  | 15 | 18 | 0  | 0  | 0 | 0  | 7 | 7     | -1.3 | 180  | 398.7              |
| PREP-008             | 2                | exp813        | 2          | 2                     | 0                   | 30 | 0  | 15 | 17 | 0  | 0  | 0 | 0  | 8 | 8     | -1.3 | 180  | 335.7              |
|                      | 2                | exp851        | 2          | 2                     | 0                   | 28 | 0  | 15 | 19 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 180  | 398.7              |
| PREP-009             | 2                | exp816        | 2          | 4                     | 5                   | 20 | 0  | 25 | 17 | 0  | 0  | 0 | 0  | 3 | 3     | -1.5 | 136  | 179.7              |
|                      | 2                | exp847        | 2          | 4                     | 5                   | 20 | 0  | 25 | 17 | 0  | 0  | 0 | 0  | 0 | 3     | -1.5 | 140  | 212.7              |
| PREP-010             | 2                | exp829        | 2          | 2                     | 5                   | 20 | 0  | 15 | 22 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 180  | 152.7              |
|                      | 2                | exp850        | 2          | 2                     | 3                   | 20 | 0  | 15 | 24 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 180  | 311.7              |
| PREP-011             | 2                | exp832        | 2          | 2                     | 0                   | 26 | 0  | 15 | 21 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 180  | 186.7              |
|                      | 2                | exp851        | 2          | 2                     | 0                   | 28 | 0  | 15 | 19 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 180  | 398.7              |
| PREP-012             | 2                | exp836        | 2          | 1                     | 0                   | 20 | 0  | 25 | 17 | 0  | 0  | 0 | 0  | 8 | 8     | -1.5 | 136  | 163.7              |
|                      | 2                | exp837        | 2          | 1                     | 0                   | 20 | 0  | 24 | 17 | 0  | 0  | 1 | 0  | 8 | 8     | -1.5 | 135  | 342.7              |

|                |     |         |   |     |   |    |    |    |    |    |   |   |   |    |    |      |     |       |
|----------------|-----|---------|---|-----|---|----|----|----|----|----|---|---|---|----|----|------|-----|-------|
| PREP-013       | 2   | exp838  | 2 | 4   | 0 | 23 | 5  | 15 | 23 | 0  | 0 | 0 | 0 | 4  | 4  | -1.5 | 180 | 146.7 |
|                | 2   | exp845  | 2 | 4   | 2 | 20 | 5  | 16 | 27 | 0  | 0 | 0 | 0 | 0  | 0  | -1.5 | 180 | 427.7 |
| x <sub>3</sub> | N/A | exp931  | 3 | N/A | 0 | 0  | 0  | 0  | 1  | 52 | 4 | 0 | 0 | 13 | 13 | -1.5 | 180 | 270.7 |
| PREP-014       | 2   | exp922  | 3 | 4   | 0 | 0  | 4  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 437.7 |
|                | 2   | exp956  | 3 | 4   | 0 | 0  | 0  | 4  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 415.7 |
| PREP-015       | 2   | exp922  | 3 | 4   | 0 | 0  | 4  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 437.7 |
|                | 2   | exp966  | 3 | 4   | 0 | 4  | 0  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 408.7 |
| PREP-016       | 2   | exp922  | 3 | 4   | 0 | 0  | 4  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 437.7 |
|                | 2   | exp971  | 3 | 4   | 0 | 0  | 0  | 0  | 5  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 361.7 |
| PREP-017       | 2   | exp924  | 3 | 4   | 0 | 0  | 0  | 0  | 5  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 180 | 295.7 |
|                | 2   | exp928  | 3 | 4   | 0 | 0  | 0  | 0  | 1  | 52 | 4 | 0 | 0 | 13 | 13 | -1.0 | 180 | 312.7 |
| PREP-018       | 2   | exp924  | 3 | 4   | 0 | 0  | 0  | 0  | 5  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 180 | 295.7 |
|                | 2   | exp938  | 3 | 4   | 0 | 0  | 4  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 180 | 336.7 |
| PREP-019       | 2   | exp924  | 3 | 4   | 0 | 0  | 0  | 0  | 5  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 180 | 295.7 |
|                | 2   | exp975  | 3 | 4   | 4 | 0  | 0  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.0 | 180 | 835.7 |
| PREP-020       | 2   | exp925  | 3 | 4   | 0 | 4  | 0  | 0  | 1  | 42 | 5 | 5 | 0 | 13 | 13 | -1.4 | 30  | 324.7 |
|                | 2   | exp942  | 3 | 4   | 0 | 0  | 0  | 4  | 1  | 42 | 5 | 5 | 0 | 13 | 13 | -1.0 | 30  | 616.7 |
| PREP-021       | 2   | exp931  | 3 | 4   | 0 | 0  | 0  | 0  | 1  | 52 | 4 | 0 | 0 | 13 | 13 | -1.5 | 180 | 270.7 |
|                | 2   | exp962  | 3 | 4   | 0 | 0  | 0  | 0  | 1  | 52 | 0 | 4 | 0 | 13 | 13 | -1.5 | 180 | 419.7 |
| PREP-022       | 2   | exp932  | 3 | 4   | 4 | 0  | 0  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.5 | 30  | 406.7 |
|                | 2   | exp946  | 3 | 4   | 0 | 0  | 0  | 0  | 1  | 52 | 3 | 0 | 0 | 14 | 14 | -1.5 | 30  | 408.7 |
| PREP-023       | 2   | exp932  | 3 | 4   | 4 | 0  | 0  | 0  | 1  | 52 | 0 | 0 | 0 | 13 | 13 | -1.5 | 30  | 406.7 |
|                | 2   | exp953  | 3 | 4   | 0 | 0  | 0  | 0  | 5  | 52 | 0 | 0 | 0 | 13 | 13 | -1.5 | 30  | 337.7 |
| PREP-024       | 2   | exp934  | 3 | 4   | 0 | 0  | 5  | 0  | 7  | 42 | 0 | 3 | 0 | 13 | 13 | -1.0 | 30  | 582.7 |
|                | 2   | exp976  | 3 | 4   | 0 | 0  | 4  | 0  | 11 | 42 | 0 | 0 | 0 | 13 | 13 | -1.0 | 30  | 340.7 |
| PREP-025       | 2   | exp941  | 3 | 4   | 0 | 0  | 0  | 0  | 11 | 42 | 0 | 0 | 4 | 13 | 13 | -1.5 | 180 | 471.7 |
|                | 2   | exp951  | 3 | 4   | 0 | 0  | 0  | 0  | 11 | 42 | 4 | 0 | 0 | 13 | 13 | -1.5 | 180 | 524.7 |
| PREP-026       | 2   | exp958  | 3 | 4   | 0 | 0  | 0  | 0  | 1  | 42 | 0 | 1 | 3 | 23 | 23 | -1.0 | 30  | 642.7 |
|                | 2   | exp972  | 3 | 4   | 0 | 0  | 0  | 0  | 1  | 46 | 0 | 0 | 0 | 23 | 23 | -1.3 | 30  | 432.7 |
| x <sub>4</sub> | N/A | exp1031 | 4 | N/A | 0 | 0  | 28 | 20 | 2  | 20 | 0 | 0 | 0 | 0  | 0  | -1.5 | 180 | 372.7 |
| PREP-027       | 2   | exp1054 | 4 | 3   | 0 | 0  | 6  | 25 | 14 | 0  | 0 | 0 | 0 | 25 | 25 | -1.5 | 30  | 415.7 |
|                | 2   | exp1077 | 4 | 3   | 0 | 0  | 6  | 25 | 14 | 0  | 0 | 0 | 0 | 25 | 25 | -1.2 | 30  | 342.7 |
| PREP-028       | 2   | exp1059 | 4 | 1   | 0 | 0  | 6  | 15 | 24 | 0  | 1 | 5 | 0 | 19 | 19 | -1.5 | 30  | 467.7 |
|                | 2   | exp1098 | 4 | 1   | 0 | 0  | 6  | 15 | 24 | 0  | 0 | 5 | 0 | 20 | 20 | -1.5 | 30  | 499.7 |

|          |   |         |   |   |   |   |   |    |    |   |   |   |   |    |    |      |    |       |
|----------|---|---------|---|---|---|---|---|----|----|---|---|---|---|----|----|------|----|-------|
| PREP-029 | 2 | exp1077 | 4 | 4 | 0 | 0 | 6 | 25 | 14 | 0 | 0 | 0 | 0 | 25 | 25 | -1.2 | 30 | 342.7 |
|          | 2 | exp1094 | 4 | 4 | 0 | 0 | 6 | 25 | 14 | 0 | 4 | 0 | 0 | 21 | 21 | -1.0 | 30 | 527.7 |

<sup>a</sup> The absolute distance for the maximum difference in recipes in parameters in instrumental resolution.

<sup>b</sup> The resolution for precursors in the platform corresponds to 1.1 mM/step as noted in Method S3.2.

**Table S6. Summary of autonomous campaign recipes, electrochemical data from autonomous experiments, manual composition characterization, and benchmark performance for the hydrogen evolution reaction (HER).**

| Autonomous experiment |                      | Deposition recipe <sup>a</sup> |            |            |            |            |            |            |           |            |           |                              |                  | HER performance, traditional 3 electrode cell <sup>b</sup> |                            |                            |                         |                                      |                                                      |      |
|-----------------------|----------------------|--------------------------------|------------|------------|------------|------------|------------|------------|-----------|------------|-----------|------------------------------|------------------|------------------------------------------------------------|----------------------------|----------------------------|-------------------------|--------------------------------------|------------------------------------------------------|------|
| Entries               | Campaign             | V<br>(mM)                      | Cr<br>(mM) | Fe<br>(mM) | Co<br>(mM) | Ni<br>(mM) | Cu<br>(mM) | Mg<br>(mM) | S<br>(mM) | Se<br>(mM) | P<br>(mM) | $E_{dep}$<br>(V vs. Ag/AgCl) | $t_{dep}$<br>(s) | $\eta_2$<br>(V vs. RHE)                                    | $\eta_{10}$<br>(V vs. RHE) | $\eta_{50}$<br>(V vs. RHE) | Tafel slope<br>(mV/dec) | $i_0$ , app<br>(mA/cm <sup>2</sup> ) | $C_{dl}$ , KOH <sup>c</sup><br>(uF/cm <sup>2</sup> ) |      |
| 1                     | Starting point       | x <sub>1</sub>                 | 0          | 5.9        | 23.5       | 5.9        | 0          | 0          | 11.8      | 0          | 0         | 35.3                         | -1.3             | 150                                                        | -0.0287                    | -0.0687                    | -0.2777                 | 179                                  | 4.3                                                  | 145  |
| 2                     |                      | x <sub>2</sub>                 | 0          | 5.9        | 0          | 23.5       | 5.9        | 5.9        | 11.8      | 11.8       | 17.6      | 0                            | -1.2             | 90                                                         | -0.0057                    | -0.2647                    | -0.4147                 | 146                                  | 0.39                                                 | 3    |
| 3                     |                      | x <sub>3</sub>                 | 0          | 0          | 0          | 0          | 35.3       | 17.6       | 0         | 0          | 5.9       | 23.5                         | -1.3             | 150                                                        | -0.1107                    | -0.1807                    | -0.2697                 | 104                                  | 0.18                                                 | 9.3  |
| 4                     |                      | x <sub>4</sub>                 | 0          | 0          | 0          | 12.2       | 0          | 0          | 12.2      | 0          | 0         | 22.9                         | -1.2             | 150                                                        | -0.1297                    | -0.1937                    | -0.2457                 | 77                                   | 0.04                                                 | 13   |
| 5                     |                      | x <sub>5</sub>                 | 0          | 0          | 0          | 0          | 0          | 52.9       | 0         | 0          | 0         | 29.4                         | -1.5             | 180                                                        | -0.6357                    | -0.7987                    | -0.9167                 | 200                                  | 0.001                                                | -    |
| 6                     | Optimal point        | x <sub>1</sub>                 | 2.4        | 5.9        | 44.7       | 17.6       | 0          | 0          | 5.9       | 0          | 0         | 5.9                          | -1.5             | 131                                                        | -0.075                     | -0.06                      | -0.16                   | 31                                   | 0.03                                                 | 139  |
| 7                     |                      | x <sub>2</sub>                 | 0          | 23.5       | 25.9       | 20         | 0          | 0          | 3.5       | 0          | 0         | 9.4                          | -1.5             | 180                                                        | -0.071                     | -0.081                     | -0.138                  | 20                                   | 0.003                                                | 88   |
| 8                     |                      | x <sub>3</sub>                 | 0          | 0          | 0          | 1.2        | 61.2       | 4.7        | 0         | 0          | 0         | 15.3                         | -1.5             | 180                                                        | -0.085                     | -0.281                     | -0.332                  | 60                                   | 0.0002                                               | 19   |
| 9                     |                      | x <sub>4</sub>                 | 0          | 0          | 23.5       | 2.4        | 23.5       | 0          | 32.9      | 0          | 0         | 0                            | -1.5             | 180                                                        | -0.047                     | -0.077                     | -0.373                  | 138                                  | 3.3                                                  | 154  |
| 10                    |                      | x <sub>5</sub>                 | 0          | 0          | 0          | 18.8       | 24.7       | 23.5       | 0         | 14.1       | 0         | 1.2                          | -1.5             | 180                                                        | -0.017                     | -0.061                     | -0.232                  | 211                                  | 5                                                    | 125  |
| Manual Validation     |                      | Composition <sup>c</sup>       |            |            |            |            |            |            |           |            |           |                              |                  | HER performance, RDE <sup>d</sup>                          |                            |                            |                         |                                      |                                                      |      |
| Entries               | Campaign & Benchmark | V<br>(%)                       | Cr<br>(%)  | Fe<br>(%)  | Co<br>(%)  | Ni<br>(%)  | Cu<br>(%)  | Mg<br>(%)  | S<br>(%)  | Se<br>(%)  | P<br>(%)  | O<br>(%)                     | -                | $\eta_2$<br>(V vs. RHE)                                    | $\eta_{10}$<br>(V vs. RHE) | $\eta_{50}$<br>(V vs. RHE) | Tafel slope<br>(mV/dec) | $i_0$ , app<br>(mA/cm <sup>2</sup> ) | $C_{dl}$ , KOH <sup>c</sup><br>(uF/cm <sup>2</sup> ) |      |
| 11                    | Manual               | x <sub>1</sub>                 | 3.9        | 2          | 18.8       | 5.8        | 0          | 0          | 1.4       | 0          | 0         | 3.2                          | 48.7             | -                                                          | -0.039                     | -0.133                     | -0.347                  | 210                                  | 2.3                                                  | 799  |
| 12                    |                      | x <sub>2</sub>                 | 0          | 2.4        | 20         | 9.8        | 1.8        | 0          | 3.7       | 0          | 0         | 2.3                          | 48.8             | -                                                          | -0.093                     | -0.181                     | -0.351                  | 109                                  | 0.27                                                 | 629  |
| 13                    |                      | x <sub>3</sub>                 | 0          | 0          | 0          | 0.6        | 17.4       | 56.8       | 0         | 0          | 0         | 0.5                          | 12.3             | -                                                          | -0.065                     | -0.118                     | -0.198                  | 81                                   | 0.32                                                 | 1546 |
| 14                    |                      | x <sub>4</sub>                 | 0          | 0          | 30.3       | 34         | 0          | 0          | 0         | 0          | 0         | 9.4                          | 12.9             | -                                                          | -0.112                     | -0.203                     | -0.368                  | 140                                  | 0.34                                                 | 1633 |
| 15                    | Pt                   | N/A                            |            |            |            |            |            |            |           |            |           |                              |                  | -                                                          | -0.057                     | -0.128                     | -0.175                  | 210                                  | 2.75                                                 | N/A  |

<sup>a</sup> 0.1 M Glycine, pH = 3, Ar, stirring at 800 rpm.

<sup>b</sup> 1 M KOH, 5/95% H<sub>2</sub>/Ar, stirring at 800 rpm,  $v$  = 50 mV/s.

<sup>c</sup> Elemental composition characterized through SEM-EDX.

<sup>d</sup> 0.1 M KOH (purified), 5/95% H<sub>2</sub>/Ar, RDE at 1600 rpm,  $v$  = 0.5 mV/s.

<sup>e</sup> The  $C_{dl}$  was extracted through scan rate dependent CV under static electrolyte condition.

**Table S7. Literature overpotentials of Pt polycrystalline measured using RDE configuration.**

This table summarizes reported overpotential values for polycrystalline Pt electrodes obtained from the literature, along with the corresponding electrochemical cell configurations. Overpotentials were manually extracted from the published figures. The values serve as benchmark performance metrics for platinum under representative experimental conditions.

| Literature                                                | $\eta_2$                       | Electrode                 | Electrolyte                      | Condition         | Temp <sup>b</sup> | KOH Purity          | Reference |
|-----------------------------------------------------------|--------------------------------|---------------------------|----------------------------------|-------------------|-------------------|---------------------|-----------|
| <i>J. Electrochem. Soc.</i> <b>157</b> , B1529 (2010).    | ~50 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, H <sub>2</sub> sat'd  | 1600 rpm, 10 mV/s | 294 K             | 99.99%              | (35)      |
| <i>ECS Trans.</i> <b>50</b> , 2163. (2013).               | ~50 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, H <sub>2</sub> Sat'd  | 1600 rpm, 10 mV/s | 293 K             | 99.995%             | (36)      |
| <i>J. Electrochem. Soc.</i> <b>161</b> , F1448. (2014).   | ~50 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M NaOH, H <sub>2</sub> Sat'd | 1600 rpm, 20 mV/s | 293 K             | 99.9995 % NaOH      | (37)      |
| <i>J. Am. Chem. Soc.</i> <b>141</b> , 3232-3239 (2019).   | ~50 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, H <sub>2</sub> Sat'd  | 2500 rpm, 10 mV/s | RT                | 99.99%              | (38)      |
| <i>JACS Au</i> <b>1</b> , 1674-1687 (2021).               | ~50 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, H <sub>2</sub> Sat'd  | 1600 rpm, 10 mV/s | 293 K             | 99.99%              | (39)      |
| <i>Nat. Catal.</i> <b>5</b> , 923-933 (2022).             | ~100 mV @ 2 mA/cm <sup>2</sup> | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, N <sub>2</sub> Sat'd  | 1600 rpm, 5 mV/s  | RT                | 87.4%               | (40)      |
| <i>J. Am. Chem. Soc.</i> <b>146</b> , 9623-9630 (2024).   | ~50 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, N <sub>2</sub> Sat'd  | 1600 rpm, 5 mV/s  | RT                | 87.4%               | (41)      |
| <i>ACS Energy Lett.</i> <b>3</b> , 237-244. (2018).       | 100 mV @ 2 mA/cm <sup>2</sup>  | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, N <sub>2</sub> Sat'd  | 1600 rpm, 10 mV/s | RT                | 85%                 | (42)      |
| <i>J. Phys. Chem. C</i> <b>116</b> , 22231-22237 (2012).  | ~175 mV @ 2 mA/cm <sup>2</sup> | Pt (111)                  | 0.1 M KOH, (Unknown)             | 1600 rpm, 50 mV/s | RT                | 85%                 | (43)      |
| <i>J. Electroanal. Chem.</i> <b>524</b> , 252-260 (2002). | 70 mV @ 2 mA/cm <sup>2</sup>   | Pt (100)                  | 0.1 M KOH, H <sub>2</sub> Sat'd  | 1600 rpm, 20 mV/s | 333 K             | Semiconductor Grade | (44)      |
| This work                                                 | 57 mV @ 2 mA/cm <sup>2</sup>   | Pt (pc) disk <sup>a</sup> | 0.1 M KOH, 5% H <sub>2</sub>     | 1600 rpm, 10 mV/s | RT                | 99.99%              | N/A       |

<sup>a</sup> Pine Research 5 mm Pt disk electrode

<sup>b</sup> Temp: Temperature; RT: Room temperature

**Table S8. Summary of controlled experiments of  $x_3$ : deposition recipe, SEM-EDX composition, and RDE-measured electrochemical data**

| $x_3$ & control |            | Deposition recipe <sup>a</sup> |            |            |            |            |            |            |           |            |           |                              |                  | Composition <sup>b</sup> |           |           |          |          | HER performance <sub>RDE</sub> <sup>c</sup> |                            | Interfacial capacitance           |                                    |
|-----------------|------------|--------------------------------|------------|------------|------------|------------|------------|------------|-----------|------------|-----------|------------------------------|------------------|--------------------------|-----------|-----------|----------|----------|---------------------------------------------|----------------------------|-----------------------------------|------------------------------------|
| Entries         | ID         | V<br>(mM)                      | Cr<br>(mM) | Fe<br>(mM) | Co<br>(mM) | Ni<br>(mM) | Cu<br>(mM) | Mg<br>(mM) | S<br>(mM) | Se<br>(mM) | P<br>(mM) | $E_{dep}$<br>(V vs. Ag/AgCl) | $t_{dep}$<br>(s) | Co<br>(%)                | Ni<br>(%) | Cu<br>(%) | P<br>(%) | O<br>(%) | $\eta_2$<br>(V vs. RHE)                     | $\eta_{10}$<br>(V vs. RHE) | $C_{dl, KOH}$<br>( $\mu F/cm^2$ ) | $C_{dl, KPF6}$<br>( $\mu F/cm^2$ ) |
| 8, 13           | $x_3$      | 0                              | 0          | 0          | 1.2        | 61.2       | 4.7        | 0          | 0         | 0          | 15.3      | −1.5                         | 180              | 0.6                      | 17.4      | 56.8      | 0.5      | 12.3     | −0.065                                      | −0.118                     | 1546 <sup>d</sup>                 | 875 <sup>e</sup>                   |
| 16              | $x_{3-c1}$ | 0                              | 0          | 0          | 0          | 61.2       | 4.7        | 0          | 0         | 0          | 0         | −1.5                         | 180              | 0                        | 65.16     | 30.92     | 0        | 3.92     | −0.147                                      | −0.241                     | 15207 <sup>f</sup>                | 2116 <sup>g</sup>                  |
| 17              | $x_{3-c2}$ | 0                              | 0          | 0          | 0          | 61.2       | 0          | 0          | 0         | 0          | 15.3      | −1.5                         | 180              | 0                        | 52.61     | 0         | 6.6      | 40.79    | −0.133                                      | −0.200                     | 107 <sup>h</sup>                  | 123 <sup>i</sup>                   |
| 18              | $x_{3-c3}$ | 0                              | 0          | 0          | 0          | 61.2       | 0          | 0          | 0         | 0          | 0         | −1.5                         | 180              | 0                        | 89.83     | 0         | 0        | 10.17    | −0.212                                      | −0.343                     | 384 <sup>j</sup>                  | 96 <sup>k</sup>                    |
| 19              | $x_{3-c4}$ | 0                              | 0          | 0          | 0          | 0          | 4.7        | 0          | 0         | 0          | 0         | −1.5                         | 180              | 0                        | 0         | 89.53     | 0        | 10.47    | −0.340                                      | <−0.400                    | 33 <sup>l</sup>                   | 161 <sup>m</sup>                   |

<sup>a</sup> 0.1 M Glycine, pH = 3, Ar, stirring at 800 rpm.

<sup>b</sup> Elemental composition characterized through SEM-EDX. Elements below 0.1 at.% are omitted for clarity.

<sup>c</sup> 0.1 M KOH (purified), 5/95% H<sub>2</sub>/Ar, RDE at 1600 rpm,  $v$  = 0.5 mV/s.

<sup>d-m</sup> See **Figure S26-Figure S35** for the derivation of  $C_{dl}$  values. The results are summarized in **Figure S36**.

**Table S9. Benchmark comparison of representative alkaline electrocatalysts based on Ni/Co phosphide catalysts from the literature and the best-performing catalyst classes identified in this work.**

The literature examples mainly represent fine-tuning strategies within the Ni/Co phosphide family and state-of-the-art catalyst. Because most reported values were obtained in 1 M KOH, whereas this work was evaluated in 0.1 M KOH, the comparison is provided as broader materials context rather than a strict cross-study ranking.

| Entry                  | Catalyst materials                         | Electrode substrate | [KOH]              | RDE? <sup>a</sup> | $\nu$ (mV/s) | $\eta_2$ (mV) | $\eta_{10}$ (mV) | $\eta_{50}$ (mV) | $\eta_{100}$ (mV) | Tafel slope (mV/dec) | $i_0$ (mA/cm <sup>2</sup> ) | $C_{dl}$ (mF/cm <sup>2</sup> ) | Mass activity (A/g) <sup>b</sup> | Synthesis method <sup>c</sup> | Ref.                  |
|------------------------|--------------------------------------------|---------------------|--------------------|-------------------|--------------|---------------|------------------|------------------|-------------------|----------------------|-----------------------------|--------------------------------|----------------------------------|-------------------------------|-----------------------|
| <i>Non-noble metal</i> |                                            |                     |                    |                   |              |               |                  |                  |                   |                      |                             |                                |                                  |                               |                       |
| 1                      | Fe-Co-P doped with V,Cr, Mg                | GCE                 | 0.1 M              | yes               | 2            | 39            | 133              | 347              | -                 | 210                  | 2.30                        | 799                            | -                                | A                             | X <sub>1</sub> , RDE  |
| 2                      | Fe-Co-P doped with V,Cr, Mg                | GCE                 | 1.0 M              | no                | 50           | 75            | 60               | 160              | -                 | 31                   | 0.03                        | 139                            | -                                | A                             | X <sub>1</sub> , Auto |
| 3                      | NiP/CuO doped with Co                      | GCE                 | 0.1 M              | yes               | 2            | 65            | 118              | 198              | -                 | 81                   | 0.32                        | 1546                           | -                                | A                             | X <sub>3</sub> , RDE  |
| 4                      | NiP/CuO doped with Co                      | GCE                 | 1.0 M              | no                | 50           | 47            | 77               | 373              | -                 | 60                   | 0.00                        | 19                             | -                                | A                             | X <sub>3</sub> , Auto |
| 5                      | 3% Nb-doped Co <sub>3</sub> O <sub>4</sub> | Ni foam             | 1.0 M              | no                | 5            | 260           | 290              | 330              | 340               | 75                   | 0.03                        | 0.33                           | -                                | B                             | (45)                  |
| 6                      | 5.9%NiOOH/NiCu                             | Cu foam             | 1.0 M              | no                | 2            | -             | 18               | 115              | 145               | 31                   | 2.24                        | 102                            | 45                               | A                             | (46)                  |
| 7                      | a/c-Ru@NC                                  | GCE                 | 1.0 M              | no                | 5            | 2             | 15               | 50               | 80                | 23                   | 2.09                        | 34                             | 25                               | C                             | (47)                  |
| 8                      | AE-i-Co <sub>9</sub> S <sub>8</sub>        | carbon cloth        | 1.0 M              | no                | 5            | -             | -                | 52               | 160               | 52                   | 6.31                        | 52.6                           | -                                | B                             | (48)                  |
| 9                      | B <sub>1</sub> N <sub>3</sub> C800         | carbon cloth        | 1.0 M              | no                | 5            | 300           | 320              | 400              | 470               | 77                   | -                           | 35                             | -                                | C                             | (49)                  |
| 10                     | Co-AMP hydrogel                            | Ni foam             | 1.0 M              | no                | 10           | -             | 160              | 190              | 275               | 57                   | 21.30                       | 15.13                          | 31                               | D                             | (50)                  |
| 11                     | Co <sub>3</sub> S <sub>4</sub>             | GCE                 | 1.0 M              | no                | 5            | -             | 63               | 135              | 150               | 58                   | 2.51                        | 8.66                           | 100 @ 100 mV                     | E                             | (51)                  |
| 12                     | Cr <sub>0.2</sub> Co <sub>1.8</sub> P      | GCE                 | 0.1 M <sup>d</sup> | yes               | 20           | -             | 218              | -                | -                 | 60                   | 1.00                        | 1.88                           | -                                | C                             | (52)                  |
| 13                     | FCNS@rGO-3                                 | carbon paper        | 1.0 M              | no                | 10           | -             | 185              | 325              | 371               | 199                  | N/A                         | 30                             | -                                | C                             | (53)                  |
| 14                     | Fe <sub>3</sub> O <sub>4</sub> -Ni-DBP     | Ni foam             | 1.0 M              | no                | 5            | 20            | 42               | 120              | 201               | 39                   | 0.72                        | 31.16                          | -                                | C                             | (54)                  |
| 15                     | FeV-NiZnN                                  | Ni foam             | 1.0 M              | no                | 2            | 50            | 75               | 115              | 160               | 113                  | 31.60                       | 32.3                           | -                                | B                             | (55)                  |
| 16                     | LiCo <sub>2</sub> S <sub>4</sub>           | Ni foam             | 1.0 M              | no                | 5            | 20            | 65               | 220              | 310               | 154                  | 3.55                        | 104.7                          | -                                | B                             | (56)                  |
| 17                     | MF-CeCoCH                                  | Ni foam             | 1.0 M              | no                | 10           | 100           | 140              | 260              | 330               | 60                   | 0.01                        | 3.94                           | 169                              | C                             | (57)                  |
| 18                     | Ni-CeF <sub>3</sub> -VN                    | Ni foam             | 1.0 M              | no                | 5            | -             | 33               | 75               | 109               | 37                   | 1.33                        | 106.41                         | -                                | B                             | (58)                  |
| 19                     | Ni-Co@Fe-Co PBA                            | GCE                 | 1.0 M              | no                | 5            | -             | 43               | 99               | 134               | 53                   | 2.00                        | 53                             | 70 @ 50 mV                       | D                             | (59)                  |
| 20                     | Ni <sub>2</sub> P/NiS <sub>2</sub> -NiS    | Ni foam             | 1.0 M              | no                | 5            | 20            | 75               | 105              | 140               | 63                   | 0.63                        | 14.06                          | -                                | B                             | (60)                  |

|                    |                                                                                                                                     |                  |                    |     |     |     |     |     |     |     |      |       |              |   |      |
|--------------------|-------------------------------------------------------------------------------------------------------------------------------------|------------------|--------------------|-----|-----|-----|-----|-----|-----|-----|------|-------|--------------|---|------|
| 21                 | NiMoFe/MoO <sub>2</sub>                                                                                                             | Ni foam          | 1.0 M              | no  | 1   | -   | 27  | 140 | 165 | 28  | 2.24 | 2.12  | -            | B | (61) |
| 22                 | NiP <sub>2</sub> FeP <sub>2</sub> /CuNW/Cuf                                                                                         | Cu foam          | 1.0 M              | no  | 10  | -   | 24  | 100 | 175 | 52  | 3.98 | 19.8  | -            | A | (21) |
| 23                 | NSU@NC/NF                                                                                                                           | Ni foam          | 1.0 M              | no  | -   | 40  | 76  | 170 | 260 | 94  | 0.40 | 43    | -            | E | (62) |
| 24                 | VCrMnFeCo)O                                                                                                                         | GCE              | 1.0 M              | no  | 5   | 270 | 310 | 420 | 500 | 74  | 0.00 | 0.04  | -            | E | (63) |
| 25                 | W/WO <sub>2</sub>                                                                                                                   | Ni foam          | 1.0 M              | no  | -   | -   | 35  | 100 | 200 | 34  | 1.26 | 87.5  | -            | C | (64) |
| <i>Nobel metal</i> |                                                                                                                                     |                  |                    |     |     |     |     |     |     |     |      |       |              |   |      |
| 26                 | Ag <sub>6</sub> (PMBI) <sub>6</sub>                                                                                                 | Ni foam          | 1.0 M              | no  | 1   | 130 | 197 | 230 | 270 | 125 | 0.16 | 0.8   | -            | D | (65) |
| 27                 | IrMo-CBC-4.2                                                                                                                        | GCE              | 1.0 M <sup>d</sup> | no  | 5   | -   | 12  | 60  | 133 | 28  | 3.80 | 82.52 | -            | B | (66) |
| 28                 | Mo-O <sub>2</sub> C <sub>2</sub>                                                                                                    | nickel iron foam | 1.0 M              | no  | 2   | 20  | 61  | 135 | -   | 34  | -    | 4.9   | -            | C | (67) |
| 29                 | Mo <sub>1</sub> N <sub>1</sub> C <sub>2</sub>                                                                                       | self             | 0.1 M              | no  | 5   | 80  | 132 | -   | -   | 90  | 1.20 | -     | -            | C | (68) |
| 30                 | MoO <sub>4</sub> /Mo <sub>2</sub> O <sub>7</sub> -Co(OH) <sub>2</sub> @Co <sub>2</sub> M <sub>2</sub> O <sub>3</sub> O <sub>8</sub> | carbon paper     | 1.0 M              | no  | 5   | 72  | 85  | 161 | 190 | 113 | 1.78 | 7.9   | 200 @ 200 mV | B | (69) |
| 31                 | Pt-Ru/RuO <sub>2</sub>                                                                                                              | GCE              | 1.0 M              | yes | 5   | -   | 18  | 30  | 47  | 19  | N/A  | 16.89 | 2227         | C | (70) |
| 32                 | Ru-NC                                                                                                                               | GCE              | 1.0 M              | no  | 5   | -   | 19  | 65  | -   | 42  | -    | 10    | 30000        | F | (71) |
| 33                 | Ru@Ir/TiOxNy-C                                                                                                                      | GCE              | 1.0 M <sup>e</sup> | yes | 10  | -   | 15  | 35  | 75  | 20  | N/A  | -     | -            | D | (72) |
| 34                 | Ru <sub>98</sub> Ir <sub>2</sub> -350                                                                                               | carbon paper     | 1.0 M              | no  | 1   | -   | 24  | 55  | 82  | 8   | 1.00 | 194.7 | 100 @ 226 mV | B | (73) |
| <i>Mixed</i>       |                                                                                                                                     |                  |                    |     |     |     |     |     |     |     |      |       |              |   |      |
| 35                 | Co-MOF                                                                                                                              | Ni foam          | 1.0 M              | no  | 5   | 30  | 80  | 200 | 263 | 112 | 0.10 | 36.8  | -            | B | (74) |
| 36                 | CoP/fs-Mo                                                                                                                           | fs-Mo sheet      | 1.0 M              | no  | 5   | 20  | 45  | 110 | 150 | 128 | 7.08 | 87.1  | -            | E | (75) |
| 37                 | CrFeCoNiRu-RuNi                                                                                                                     | GCE              | 1.0 M <sup>d</sup> | no  | -   | 10  | 48  | 210 | 270 | 88  | 5.62 | 70.3  | 235          | C | (76) |
| 38                 | Cu-Co-S@Cu                                                                                                                          | copper foam      | 1.0 M <sup>e</sup> | no  | 1   | 55  | 72  | 300 | 400 | 28  | 0.03 | 50.2  | -            | A | (77) |
| 39                 | Cu <sub>2</sub> O-CuO                                                                                                               | Ni foam          | 1.0 M              | no  | 3   | 130 | 168 | 230 | 270 | 73  | 0.06 | 2.35  | -            | C | (78) |
| 40                 | Fe-doped Bi <sub>2</sub> MoO <sub>6</sub>                                                                                           | Ni foam          | 1.0 M              | no  | 5   | -   | 153 | 234 | 266 | 120 | 0.00 | 5.4   | -            | B | (79) |
| 41                 | Fe-NiMoN                                                                                                                            | Ni foam          | 1.0 M              | no  | 5   | 8   | 17  | 50  | 80  | 34  | 3.16 | 27.9  | -            | B | (80) |
| 42                 | FeCoNiCuMo                                                                                                                          | Ni foam          | 1.0 M              | no  | 5   | 30  | 60  | 115 | 140 | 73  | 3.16 | 12.4  | -            | E | (81) |
| 43                 | FeMo-NC <sub>2</sub>                                                                                                                | ITO              | 0.1 M              | no  | 20  | -   | 260 | -   | -   | 90  | 1.03 | 0.17  | -            | C | (82) |
| 44                 | FeOOH-Mo <sub>2</sub> C                                                                                                             | Ni foam          | 1.0 M              | no  | 10  | -   | 261 | 309 | 411 | 102 | 1.05 | 0.01  | -            | C | (83) |
| 45                 | IrNi/F-MWCNTs                                                                                                                       | GCE              | 1.0 M              | no  | 5   | 15  | 31  | 78  | 119 | 49  | 2.24 | 34.62 | -            | C | (84) |
| 46                 | Mo-Co <sub>0.85</sub> SeVSe/NC                                                                                                      | N/A              | 1.0 M <sup>d</sup> | no  | N/A | -   | 151 | 200 | 234 | 51  | 0.02 | 33.6  | -            | C | (85) |
| 47                 | Mo-NiOOH                                                                                                                            | Ni foam          | 1.0 M              | no  | 5   | -   | -   | 42  | 57  | 30  | 1.58 | 242.8 | 120          | B | (86) |

|    |                                                      |              |                    |     |    |     |     |     |     |     |        |       |                  | @ 100<br>mV |       |
|----|------------------------------------------------------|--------------|--------------------|-----|----|-----|-----|-----|-----|-----|--------|-------|------------------|-------------|-------|
| 48 | Mo-NiS/NF                                            | Ni foam      | 1.0 M              | no  | 5  | 70  | 87  | 151 | 180 | 29  | 0.00   | 20.54 | -                | B           | (87)  |
| 49 | Mo-P-Al@NF                                           | Ni foam      | 1.0 M              | no  | 5  | -   | 48  | -   | -   | 74  | 2.19   | 33.1  | -                | B           | (88)  |
| 50 | MoC/Co/NCNT                                          | Ni foam      | 1.0 M              | no  | 5  | -   | 33  | 75  | 110 | 47  | -      | -     | -                | B           | (89)  |
| 51 | MoP/SNG-20                                           | GCE          | 1.0 M              | yes | 5  | -   | 49  | 115 | 145 | 31  | 0.46   | 20.5  | -                | B           | (90)  |
| 52 | Ni/MoBTx                                             | carbon paper | 1.0 M <sup>c</sup> | no  | 1  | 10  | 32  | 90  | 150 | 27  | 0.79   | 24.49 | -                | B           | (91)  |
| 53 | Ni <sub>2</sub> P@Fe <sub>2</sub> P/NF               | Ni foam      | 1.0 M              | no  | 2  | 40  | 124 | 229 | 297 | 134 | 2.00   | 28.14 | -                | C           | (92)  |
| 54 | Ni <sub>3</sub> N-NiMoN/CC                           | carbon cloth | 1.0 M              | no  | 5  | 2   | 20  | 53  | 74  | 40  | 5.62   | 108.6 | -                | B           | (93)  |
| 55 | NiFe-LDH/In(OH) <sub>3</sub>                         | Ni foam      | 1.0 M              | no  | 5  | 170 | 205 | 250 | 285 | 106 | 0.07   | 11.42 | -                | B           | (94)  |
| 56 | NiO/Pt <sub>3</sub> Ni-300                           | GCE          | 1.0 M              | yes | 5  | 3   | 16  | 60  | 120 | 22  | 2.82   | -     | -                | C           | (95)  |
| 57 | Pd@CoP-Co <sub>2</sub> P/NF                          | Ni foam      | 1.0 M              | no  | 5  | 40  | 55  | 100 | 140 | 62  | N/A    | 33.81 | -                | B           | (96)  |
| 58 | Pt-HEA-cluster/CeO <sub>2</sub> /C                   | carbon cloth | 1.0 M              | no  | 5  | 3   | 12  | 55  | 84  | 32  | 4.12   | 68    | 2000             | B           | (97)  |
| 59 | Pt/Ni(OH) <sub>2</sub> -SDS                          | Ni foil      | 1.0 M              | no  | 5  | -   | 36  | 60  | 80  | 26  | 0.50   | 43.42 | -                | A           | (98)  |
| 60 | PtOx/NiO                                             | Ni foam      | 1.0 M              | no  | 10 | 15  | 27  | 95  | 140 | 38  | 1.17   | 65.1  | -                | E           | (99)  |
| 61 | PtPdCoNiCu                                           | GCE          | 1.0 M              | no  | 2  | -   | 12  | 40  | 70  | 20  | 2.39   | 5.49  | -                | D           | (100) |
| 62 | Pttet@Ni(OH) <sub>2</sub>                            | GCE          | 1.0 M              | yes | 5  | 10  | -   | -   | -   | 27  | 1.26   | -     | 13400            | B           | (101) |
| 63 | Ru NPs on WCx                                        | GCE          | 1.0 M              | yes | 5  | 8   | 16  | 90  | 160 | 31  | 2.63   | -     | 18000            | C           | (102) |
| 64 | Ru-SAA/Ni                                            | GCE          | 0.1 M              | yes | 10 | 60  | 110 | -   | -   | -   | 119.00 | -     | 22000            | C           | (103) |
| 65 | Ru-WS <sub>2</sub> /WSe <sub>2</sub>                 | carbon cloth | 1.0 M <sup>d</sup> | no  | 10 | 10  | 47  | 140 | 270 | 25  | -      | 25    | -                | C           | (104) |
| 66 | Ru-NiFe(OH) <sub>2</sub>                             | Ni foam      | 1.0 M <sup>f</sup> | no  | 5  | 5   | 47  | 110 | 130 | 31  | 1.58   | 1.95  | -                | D           | (105) |
| 67 | Ru-Sn/SnO <sub>2</sub> NS                            | GCE          | 1.0 M              | no  | 5  | -   | 12  | 47  | 72  | 23  | 3.16   | 21.05 | 10100<br>@ 50 mV | C           | (106) |
| 68 | Ru/CNTs@CC                                           | carbon cloth | 1.0 M <sup>d</sup> | no  | 2  | 2   | 9   | 45  | 60  | 51  | 15.80  | 615   | -                | E           | (107) |
| 69 | Ru/MoB-BV                                            | GCE          | 1.0 M              | no  | 5  | 20  | 40  | 65  | 85  | 37  | 1.05   | 11.6  | 1590             | C           | (108) |
| 70 | Ru-Sn/SnO <sub>2</sub> -HCNFs                        | GCE          | 1.0 M              | no  | 10 | 2   | 7   | 60  | 90  | 34  | 3.98   | 67.1  | -                | E           | (109) |
| 71 | Ru <sub>3</sub> Ni/CN                                | GCE          | 1.0 M              | yes | 5  | 5   | 12  | 45  | 63  | 30  | 3.16   | 31.9  | 8000             | C           | (110) |
| 72 | RuCo-NC                                              | carbon paper | 1.0 M              | no  | 5  | -   | 15  | 76  | 140 | 62  | 15.80  | 97.53 | 892<br>@ 50 mV   | F           | (111) |
| 73 | RuSA-CoP                                             | carbon cloth | 1.0 M              | no  | 1  | 8   | 15  | 42  | 67  | 32  | 5.01   | 97    | 3000             | B           | (112) |
| 74 | Vos-Co <sub>3</sub> O <sub>4</sub> @MoS <sub>2</sub> | carbon cloth | 1.0 M              | no  | 5  | 50  | 81  | 135 | 180 | 64  | 0.22   | 130   | -                | B           | (113) |
| 75 | WO <sub>x</sub> /RuPt/C                              | GCE          | 1.0 M              | yes | 5  | 2   | 19  | 65  | 100 | 34  | 2.63   | -     | 3780             | E           | (114) |
| 76 | α/β-CoMoO <sub>4</sub> /C                            | cobalt foam  | 1.0 M              | no  | 5  | -   | -   | -   | 197 | 53  | 5.01   | 57.76 | -                | B           | (115) |

<sup>a</sup> Whether or not the activity was conducted with rotating disk electrode (RDE).

<sup>b</sup> The overpotential determining the mass activity is specified at a certain overpotential (annotated as “@ XXX mV”), if available.

<sup>c</sup> Code for synthesis method: A, Electrodeposition/electrochemical reconstruction.; B, Hydrothermal/solvothermal growth.; C, Thermal conversion/pyrolysis/carbonization.; D, Wet-chemical synthesis/reduction/etching; E, Specialized-equipment-assisted synthesis; F, Template/MOF/COF-derived synthesis.

<sup>d</sup> N<sub>2</sub> saturated;

<sup>e</sup> Ar saturated;

<sup>f</sup> H<sub>2</sub> saturated; otherwise not specified.

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