

Facet-Dependent Hydrogen Evolution Reaction on M_2P ($M = \text{Ni, Co, Fe}$) Single Crystals

Seongyoung Kong,^{a,b} Dhruv Raturi,^{b,c} Bryan Owens-Baird,^{a,b} Weiran Zheng,^{d,e,f} Yury V. Kolen'ko,^g Prashant Singh,^b Duane D. Johnson,^{b,c} and Kirill Kovnir^{a,b,*}

^a *Department of Chemistry, Iowa State University, Ames, IA 50011, USA*

^b *Ames National Laboratory, U.S. Department of Energy, Ames, IA 50011, USA*

^c *Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011, USA*

^d *Department of Chemistry, Guangdong Technion-Israel Institute of Technology, Shantou 515063, PR China*

^e *Guangdong Provincial Key Laboratory of Materials and Technologies for Energy Conversion, Guangdong Technion-Israel Institute of Technology, Shantou 515063, PR China*

^f *Technion-Israel Institute of Technology, Haifa 32000, Israel*

^g *Nanochemistry Research Group, International Iberian Nanotechnology Laboratory, Braga 4715-330, Portugal*

ABSTRACT

Transition-metal phosphides (*MPs*) are promising earth-abundant catalysts for hydrogen evolution reactions (HER) due to remarkable activity and stability. To further improve their properties, facet control is a key strategy. Growth of shape-selected nanoparticles may substantially enhance electrocatalytic activity, but this approach requires fundamental studies of facet-specific catalytic properties. There are only a few reports on facet effects of *MPs*, which leads to a limited understanding of activity of each facet and hampers catalyst design. Here, we grew large hexagonal-prism-shaped single crystals of three representative M_2P ($M = \text{Ni, Co, Fe}$) catalysts using metal-flux routes. Two facets of M_2P single crystals were tested to study facet-dependent HER activities, and it was consistently demonstrated that for all M_2P crystals, a tip facet [(0001) for $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ and (010) for Co_2P] had a higher activity than side facet [(10 $\bar{1}$ 0) for $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ and (100) for Co_2P]. HER activity comparison between the same facet elucidated the activity ordered between different transition metals as $\text{Fe}_2\text{P} > \text{Co}_2\text{P} > \text{Ni}_2\text{P}$ under low potential regions. At high applied potentials this trend is reversed due to the differences in Tafel slopes, with Ni_2P becoming the most active catalyst, such that activity of the (0001) facet of Ni_2P approaches that of Pt. The calculated surface density of states (DOS) of each facet and its local curvature were found to be a useful descriptor for the activity trends among different transition metals of the same facets.

Keywords: phosphides; hydrogen evolution reaction; single crystals; facet; Fe_2P ; Co_2P ; Ni_2P .

INTRODUCTION

Heterogeneous catalysts are the heart of current energy conversion/storage area, i.e., Haber-Bosch process ($\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$), methanol synthesis, CO_2 reduction, hydrogen-evolution reaction (HER), and more. However, only certain elements or compounds can be utilized for specific catalysis.¹ For instance, Fe is a conventional catalyst in Haber-Bosch process and Pt is the standard material for HER. The reason behind this can be explained by Sabatier's principle, postulating that catalytic activity is determined by adsorption energies of the active sites to the intermediates.^{2,3} If the adsorption energy to the adsorbents/intermediates is too strong or weak, desorption or adsorption processes become a rate-determining step, reducing the activity.⁴ It's thus important to have a balanced adsorption energy to maximize the rate of catalysis, and it explains why only certain elements or compounds meet those specific criteria.

One of the simplest electrocatalytic reactions, HER (in acid), is composed of two stages: initially, the Volmer step ($\text{H}^+ + * + \text{e}^- \rightarrow \text{H}^*$, where “ $*$ ” represents an active site) occurs, succeeded by a recombination step, either Tafel ($\text{H}^* + \text{H}^* \rightarrow \text{H}_2$) or Heyrovsky ($\text{H}^+ + \text{e}^- + \text{H}^* \rightarrow \text{H}_2$), depending on the number of available sites on the surface.⁵ Notably, Pt exhibits almost zero-adsorption energy to hydrogen intermediates, resulting in the highest HER activity among transition metals. *d*-band theory explains the trend in that the proper energy level of 5*d* band of Pt provides optimum bonding/antibonding electron filling when overlapping with 1s orbital of hydrogen.⁶ It is a perspective of a bulk model that such a theory can elucidate why the adsorption energy of Au or Cu is weak and that of Ni or Co is strong. However, as catalytic reactions occur on the catalyst's surface, the activity of a single catalyst often significantly varies depending on an exposed crystal structure termination due to the different geometries of the active sites. Therefore, it is important to understand not only the contribution of the bulk structure but also that of the surface facets to HER activity for the rational design of improved electrocatalysts.

While extensive facet studies have been conducted on many other electrocatalysts, the progress on HER catalyst is quite static. One of the first facet studies on HER can be found in Pt single-crystal case that demonstrated the superior activity of (110) facet compared to those of (100) and (111) facets by lowering the H adsorption energy close to zero.⁷⁻⁹ Even with that appreciable enhancement, there are only few additional studies, possibly due to the sufficiently high activity of platinum-group metals and their alloys.¹⁰ Despite its excellent performance, Pt is scarce and

expensive, and 3d transition-metal phosphides (TMPs) have recently emerged as alternatives because of their superior activity and robustness over other main group catalysts.^{11,12} In addition, their structural versatility have led many researchers to investigate diverse compositions of TMPs such as M_3P , M_2P , MP , and MP_2 ($M = \text{Ni, Co, Fe}$), but most studies are focused on analysis of the bulk structure and attempts to compare the different facets are scarce.^{13–17} A few reports shows that Ni_2P nanoparticles and nanorods, mainly exposing (0001) and $(21\bar{3}0)$ or $(\bar{1}120)$ facets, displays different HER activity.^{18,19} There are also some calculation reports on HER activity of different facets, yet experimental evidence is limited.^{20–26}

To trace the effects of surface facets on HER activity, single crystals are required because they possess well-defined surface areas of distinct facets while maintaining the same bulk composition. Their millimeter-scale surfaces make it possible to isolate the contribution of individual facets, which is difficult to achieve with nanocrystals. Moreover, single crystal studies can reveal trends among different transition metals by enabling direct comparisons of HER activity at the same facets. However, growing large enough crystals is challenging and to our best knowledge there are only few reports on TMP catalysts.^{27–30} Although M_2P binary phases ($M = \text{Ni, Co, Fe}$) are commonly regarded as representative compositions of TMP catalysts, no comparative study using single crystals has been conducted to date. It could be due to challenges of growing large crystals from the common synthesis methods generally applied in TMP catalysts such as wet chemical, solvothermal, or metal organic framework (MOF) based routes.^{31,32} Therefore, it is imperative to develop the synthesis routes to grow sufficiently large M_2P single crystals to access the HER activity of the isolated facets and understand the activity trend across different facets and transition metals.

In this study, we combined solid-state chemistry and catalysis expertise. We developed the method to grow *mm*-size single crystals of three Ni_2P , Co_2P , and Fe_2P catalysts via indium (In) and tin (Sn) flux methods. This study is the first to report the use of In flux for growing single crystals of Ni_2P , as In is typically employed as a reactive flux for synthesizing metal indides or indium-containing pnictides.^{33–36} Sn-flux is a common source to grow single crystals of binary or polyphosphides with high P content, such as FeP_4 , CoP_3 , CrP_4 , or $\text{Cu}_4\text{SnP}_{10}$, but the examples of metal-rich phase are rare.^{37–40} Ni_2P and Fe_2P have the same hexagonal crystal system (structure type: Fe_2P , space group: $P\bar{6}2m$, Pearson symbol: $hP-9$) and Co_2P is a distorted hexagonal structure

and is crystallized as orthorhombic structure (structure type: TiNiSi , space group: $Pnma$, Pearson symbol: $oP-12$).⁴¹ All M_2P crystals were grown as elongated hexagonal prisms and their tip $[(0001)$ for Ni_2P and Fe_2P , (010) for Co_2P] and side $[(10\bar{1}0)$ for Ni_2P and Fe_2P , (100) for Co_2P] facets were investigated under HER catalysis for facet-dependent and metal-dependent activities. Our computed descriptors explain activity trends among different transition metals of the same facets and the tip and side facets.

EXPERIMENTAL SECTION

Growth of M_2P ($M = \text{Ni, Co, Fe}$) single crystals

Elemental Ni (99.995%, Alfa Aesar), Co (99.8%, Alfa Aesar), Fe (99.9%, Alfa Aesar), and red phosphorus (98.7%, Alfa Aesar) powder were used for single crystal growth. Bi (99.998%, Alfa Aesar) and In chunk (99.99%, Metal shipper) were utilized as fluxes for Ni_2P crystal growth and Sn shots (99.80%, Alfa Aesar) were utilized as flux for Co_2P and Fe_2P crystal growth. For Ni_2P crystal growth, In flux produced better crystal size and quality compared to the Bi flux, and the optimized ratio of Ni:P:In was 2:1:50 in 7g total scale. The reactants were loaded in the 9 mm (I.D.)/11 mm (O.D.) fused silica ampoule, and silica wool and pieces were added on the top of the reactants for further centrifuging the molten flux. Then, the reaction ampoule was flame-sealed under vacuum below 50 μTorr . For Co_2P and Fe_2P crystal growth, the optimized element ratio was 2:1:25 for Co:P:Sn in a total of 10 g scale and 2:1:75 for Fe:P:Sn in a total of 30 g scale, respectively. For the Co_2P crystal growth, the silica ampoule of the same size used for Ni_2P crystal growth was utilized, while for the Fe_2P crystal growth, two different sizes of silica ampoules were used in the form of plugs to make tube sealing easier. A 20 mm (I.D.)/ 23 mm (O.D.) silica ampoule was used as a bottom part where all the reactants can be placed and a 17 mm (I.D.)/ 19 mm (O.D.) silica ampoule was turned upside down and plugged into the bottom tube so that a whole assembly can be flame-sealed by sealing the attaching part of the two ampoules. For both reactions, silica wool and small pieces were also added on the top of the reactants to save the product after centrifuging. The reaction ampoules were flame-sealed under vacuum below 50 μTorr . The sealed reaction ampoules were placed in a muffle furnace and the reaction temperature was the same for all M_2P crystal growths as follows: heating to 1100 °C for 12 h, dwelling for 24 h, slow cooling to 600 °C for 120 h, and then centrifuging the flux. The ampoules were opened in the air and grown crystals were immersed in dilute acid ($\text{HCl:H}_2\text{O} = 1:1$ for In and Sn flux, Acetic acid: $\text{H}_2\text{O:H}_2\text{O}_2 =$

3:2:1 for Bi flux, all volume ratios) overnight to remove the residual flux. After filtration and drying in the air overnight, needle-shaped mm-long M_2P crystals were obtained.

Powder X-ray diffraction (PXRD)

The in-house PXRD analysis of all samples was done using bench top MiniFlex600 diffractometer (Rigaku) equipped with a Cu- K_α X-ray source ($\lambda = 1.540593 \text{ \AA}$) with Ni- K_β filter. For sample preparation, a Si holder with zero background was utilized.

***In situ* PXRD**

For In flux reaction of Ni_2P , *in situ* PXRD experiment was carried out at 28-ID-2 beamline at the NSLS II at Brookhaven National Laboratory. The 2:1:2 ratio of Ni:P:In was ground and placed in a 0.5 mm (I.D.)/ 0.7 mm (O.D.) silica capillary. Then, the reaction capillary was evacuated, and flame-sealed. At the beamline, two heating coils were placed next to the side of the capillary and temperature was measured through IR camera. The difference between the setting and actual temperature was corrected by using CeO_2 reference and estimated temperature error was $\pm 20 \text{ }^\circ\text{C}$. The wavelength of X-ray beam was $0.1824 \text{ \AA}$ and diffraction was collected using a 16" two-dimensional detector with CsI coated scintillator panels. The heating profile was heating to $900 \text{ }^\circ\text{C}$ with a rate of $25 \text{ }^\circ\text{C/min}$ and then cooling to $600 \text{ }^\circ\text{C}$ with the same rate. For the Sn flux reaction of three M_2P s, *in situ* PXRD was collected at 17-BM beamline at the APS at Argonne National Laboratory. The 2:1:5 ratio of M :P:Sn was ground and prepared in the same way as *in situ* In flux reaction. At the beamline, two heating coils were placed at the side of the capillary and the thermocouple was placed at the tip of the capillary. The deviation of actual temperature from setting value increases as temperature increases and it was corrected through extrapolation. The wavelength of the X-ray beam was $0.24141 \text{ \AA}$ and the diffraction data was collected using Varex 4343CT detector. The heating profile of Ni_2P was heating to $890 \text{ }^\circ\text{C}$ at a rate of $40 \text{ }^\circ\text{C/min}$ and cooling to $470 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C/min}$. Co_2P was heated to $1000 \text{ }^\circ\text{C}$ at a rate of $40 \text{ }^\circ\text{C/min}$ cooling to $500 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C/min}$. Fe_2P was heated to $1000 \text{ }^\circ\text{C}$ at a rate of $40 \text{ }^\circ\text{C/min}$ cooling to $780 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C/min}$ due to beam time constraints. All collected data of *in situ* PXRD was integrated and analyzed through GSAS-II software.⁴²

Single-crystal X-ray diffraction (SCXRD)

To index the facets of the crystals, APEX II diffractometer (Bruker, Cu- K_α : $1.5418 \text{ \AA}$) was used for Ni_2P and Fe_2P , and D8 Venture diffractometer (Bruker, Mo- K_α : $0.7107 \text{ \AA}$) was utilized for

Co₂P. The data were collected with a 1° step of φ and ω scans at 173 K and Bruker APEX 3 software package was used to determine the unit cell and index the facets.

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX)

To analyze the composition of the crystals, Quanta 250 field emission SEM (FEI) was utilized at 15 kV and the detector was X-Max 80 EDX (Oxford Instruments). The obtained data were processed using Aztec software package.

Atomic Force Microscopy (AFM)

AFM images were acquired using a Cypher ES scanning probe microscope (Oxford Instruments Ltd.) equipped with a 160AC-NA cantilever in tapping mode. The M₂P crystal surface was cleaned by washing with ethanol (EtOH) and deionized (DI) water three times in succession to ensure the removal of residual contaminants. The cleaned crystal surface was then dried under a nitrogen (N₂) atmosphere. Image processing and analysis were performed using the Gwyddion software package.

Working electrode fabrication

Figure S1 represents schematic procedure of electrode fabrication. The selected crystal was attached to the Au wire (99.95%, 0.1 mm, Thermo Scientific Chemicals) using conductive epoxy (H20E, Epoxy Technology) in a proper orientation according to the facet of interest. The conductive epoxy was cured in a vacuum oven at 150 °C for 10 min and naturally cooled down. The connected assembly was molded by insulating epoxy to secure the crystal at the desired orientation and protect the joint part from the electrolyte. A Teflon rod was embedded in the epoxy mold to help hold the whole working electrode. To expose the surface of the side crystal facet, a razor blade was carefully used to remove or peel off the epoxy under the microscope. Because other facets were embedded in the epoxy while the desired facet was oriented toward the surface of the epoxy, the facet of interest can be exposed by cutting the surface part of the epoxy that covers it. The epoxy does not adhere strongly to the flat crystal surface, so it was easily peeled away when cut along the facet edges. For the tip crystal facet, both the epoxy and crystal were cut through using a razor blade. Then, the exposed crystal facet was rinsed by sonicating with water and ethanol for 3 min each. Few Ni₂P crystals were tested for polishing, and they were polished using alumina dispersion (Allied high-tech products. Inc) with sizes of 1 μm , 0.3 μm , and 0.05 μm , and the sonication with water and ethanol was done for 3 min each between the polishing steps.

The tip facets of Co₂P and Fe₂P could not be polished due to their brittle nature, which leads to crystal fracture upon polishing attempts.

Electrochemical analysis

A potentiostat 1010E (Gamry) and a three-electrode setup were used for all electrochemical analyses. The setup included a saturated calomel electrode (SCE, Gamry) as the reference electrode, a lab-made cathode as the working electrode, and a graphite rod as the counter electrode in a three-neck flask (**Figure S2**). A stir bar was placed in the flask to facilitate bubble removal, and the electrode was positioned at a sufficient distance to ensure that turbulence from stirring did not affect the measurements. 0.5 M H₂SO₄ was used as the electrolyte, and hydrogen gas was purged for 30 min prior to the measurement. Cyclic voltammetry was conducted from the range of −0.25 V to −1.55 V vs SCE with a scan rate of 5 mV/s for side facet measurement and the range of −0.25 V to −1.15 V vs SCE with the same scan rate. iR_u compensation was not applied due to instrumental limitations for measuring EIS of small surface area of the electrode. To convert the SCE to the reversible hydrogen potential (RHE), the following equation was used:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.244 \text{ V} + 0.059 \times \text{pH}$$

Density Functional Theory (DFT) calculations

Density Functional Theory (DFT), as implemented in the Vienna *ab initio* simulation package (VASP), was used for spin-polarized electronic-structure calculations.^{43,44} The exchange-correlation functional by Perdew, Burke, and Ernzerhof (PBE), with a kinetic-energy cutoff of 520 eV was used for the plane-wave basis set.⁴⁵ Experimental structures taken from ICSD were used for Fe₂P, Co₂P, and Ni₂P (ICSD-44345, 624592, and 43395, respectively).⁴⁶ Supercells representing all possible surface-facet terminations for a given orientation were automatically generated from these cells using *Pymatgen*.⁴⁷ Terminations for the side facet of Fe₂P and Ni₂P had their lattice transformed into an orthogonal lattice. All surface slabs had a minimum thickness of 10 Å, vacuum thickness of 15 Å, and 3 Å thick region near the surface on one side where ionic positions were fully relaxed. Structural relaxation of atomic coordinates was performed until energy and forces converged to 10^{−5} eV and 10^{−2} eV/Å, respectively. Monkhorst-Pack *k*-mesh grid of (7×7×1) was used to sample the Brillion zone during relaxation, while mesh density was increased to (15×15×2) for reliable surface energies.⁴⁸ The same energy and force convergence criteria were used during structural relaxation of these larger supercells, but the Monkhorst-Pack

k-mesh grid was reduced to (3×3×1) during relaxation and subsequently increased to (7×7×2) for charge self-consistency, reliable binding energies, and density of states (DOS) results. Gaussian smearing of 0.01 eV was used for total-energy calculations, whereas smearing of 0.15 eV was used to determine DOS. *Vaspkit* was used to analyze the DOS and charge density differences.⁴⁹

Facet-dependent Surface Energies: Predicting stable surface structures for a given M_2P facet required computing surface energy using Eqs. 1-3,⁵⁰ where γ [J/m²] and A [m²] represent surface energy and surface area, respectively. Spin-polarized DFT calculations were performed on slabs created via cleavage of a periodic bulk supercell, noting that terminations of slabs are generally not symmetric. The resulting surface energies are invariant with respect to chemical potentials of the constituents.

$$\gamma = (E_{\text{cleavage}} + E_{\text{relax}})/A \quad \text{Eq. 1}$$

$$E_{\text{cleavage}} = (E_{\text{unrelaxed}}^{\text{DFT}} - n_b E_{\text{bulk}}^{\text{DFT}})/2 \quad \text{Eq. 2}$$

$$E_{\text{relax}} = E_{\text{relaxed}}^{\text{DFT}} - E_{\text{unrelaxed}}^{\text{DFT}} \quad \text{Eq. 3}$$

These values of surface energies at 0 K are tabulated in **Tables S3** and **S4** and used as a proxy for surface stability under synthesis conditions. The termination with the lowest value was selected as the model surface to narrow the scope of further analysis: tip facets for all M_2P are T1 terminations; and side facet for Ni_2P is T6, Fe_2P are competing T2 and T5; and Co_2P is T2 (**Table S6**). Our DFT surface-energy results find side (10 $\bar{1}$ 0) facets are comparable (Ni, Fe) or lower (Co) than the tip (0001) facet for all M_2P crystals, observed here as needle-shaped samples. This result is consistent with findings from ultrafast crystal growth in pure metal melts in which the lowest-energy facet of the pure metal (Ni with (111) facet) is a template for barrierless growth.⁵¹ Growth for M_2P under this mechanism is (10 $\bar{1}$ 0) side facets, as observed. See result for more details.

RESULTS AND DISCUSSION

Single-crystal growth of M_2P ($M = \text{Ni, Co, Fe}$)

For the growth of all M_2P single crystals, a considerable excess of metal flux was used to ensure dissolving all reactants and maximizing the chances of growing crystals. To grow Ni_2P single crystals, Bi flux was initially investigated due to a high solubility to Ni (**Figure S3**).⁵² Sn could also be a potential flux due to high solubility of both Ni and P in Sn, but it was avoided because Sn flux growth attempts form undesirable Ni-Sn-P ternary phases.⁵³ However, there is a small temperature region where Ni_2P crystals can grow with Sn flux, as will be shown later. The various ratios of Ni:P:Bi were explored and then optimized to 2:1:50, with maximum heating temperature of 1150°C, followed by dwelling and slow cooling to 500°C. The summary of attempted ratios, temperature profiles, and corresponding crystal shapes are listed in **Table S1 and Figure S3**. With all different conditions, however, Bi flux consistently grew Ni_2P crystals in thin, sharp needle shapes, making them unsuitable for use as electrodes. It could be attributed to a poor solubility of P in Bi flux. It was observed that large Ni_2P crystals did not grow and formed powder when the maximum heating temperature was below the Ni_2P melting point of 1122 °C (**Figure S3 H**). To ensure good solubility for both Ni and P and to avoid forming unwanted flux-containing phases, indium (In) flux was used for the first time in this study to grow Ni_2P single crystals. Indium flux is commonly used as a reactive flux to grow metal indide crystals, but there have been no reports of using it to grow metal phosphide crystals. This may be due to the expected formation of a stable InP phase or other Ni-In binary phases. But, there is a report that a reaction between Ni and InP powder forms a Ni-In-P ternary phases at temperatures as low as 470°C, despite a reported melting point of InP of 1055°C.^{54,55} It is also reported that other Ni-P binary phases, such as Ni_3P , $\alpha\text{-Ni}_5\text{P}_2$, and Ni_{12}P_5 , are also present in the reaction between Ni and In-P at 600°C, indicating that InP can react at lower temperatures.⁵⁴ As ternary Ni-In-P phases generally have a lower melting point, they could decompose at moderate temperatures and lead to the formation of Ni_2P . As a result, using indium flux did not produce any of the concerning phases, but rather it grew larger and wide enough Ni_2P single crystals which are suitable for catalyst testing (**Figure 1**). The optimized ratio of Ni:P:In was 2:1:50 and the maximum heating temperature was 1100°C. Decreasing the molar ratio of In resulted in poorly shaped crystals, while increasing it led to the growth of heavily twinned crystals. Despite high solubility of Ni and P in the In flux the maximum temperature was kept at 1100°C to ensure complete dissolution of the reactants in the flux.

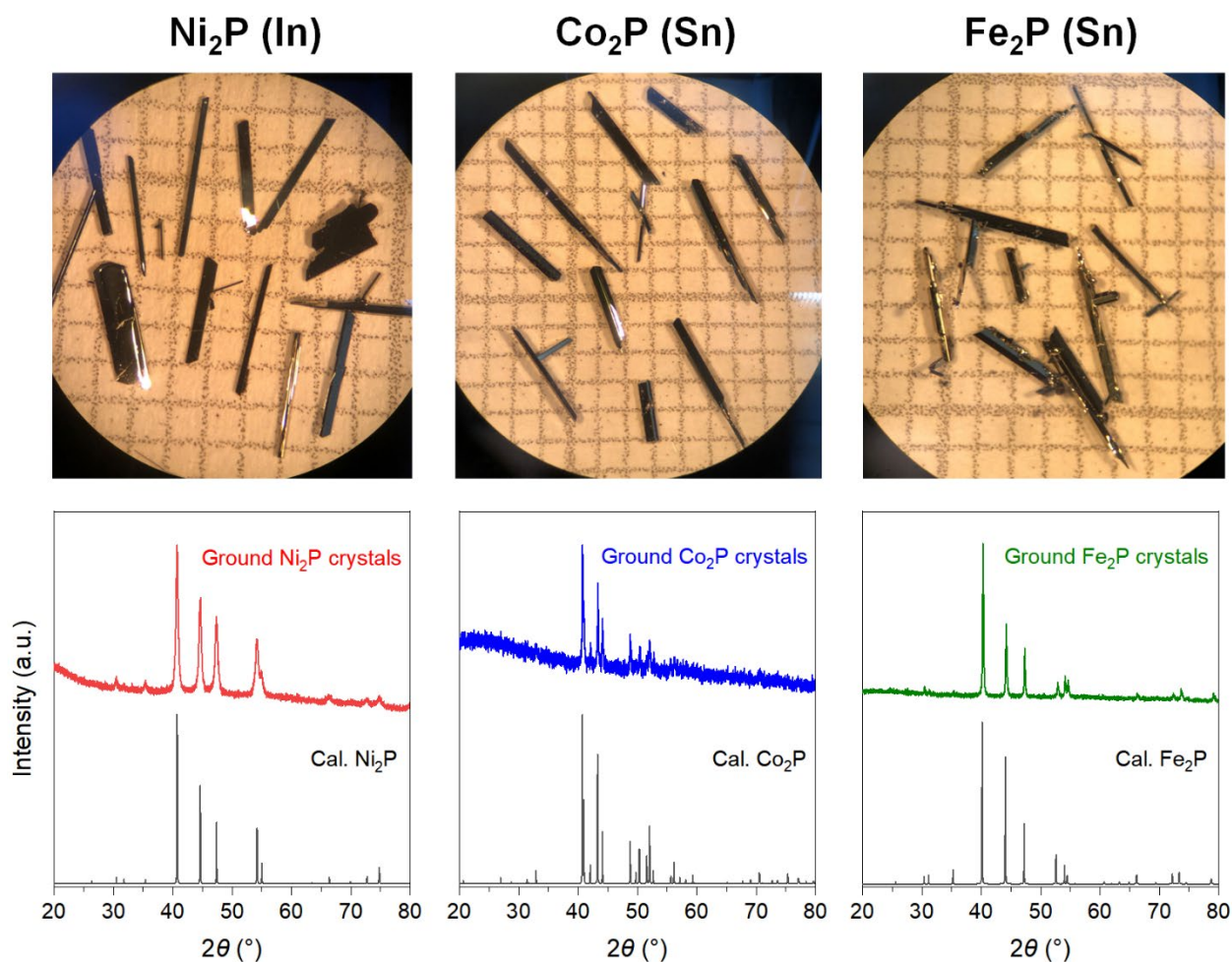


Figure 1. The upper panel displays photographs of selected $M_2\text{P}$ single crystals grown from different metal fluxes given in parenthesis. The background is mm paper. The lower panel represents the powder X-ray diffraction (PXRD) patterns of calculated (black) and ground single crystals (red: Ni_2P , blue: Co_2P , green: Fe_2P) of $M_2\text{P}$ obtained in the same batches.

For growth of Co_2P and Fe_2P single crystals, the Sn flux was found to be suitable for both, as Sn exhibits good solubility for both metals and P, and there is no reported Co-Sn-P or Fe-Sn-P ternary phases. Interestingly, the optimal ratio of Sn differed for the two metal phosphides: for Co_2P , the ratio was 2:1:25 (Co:P:Sn), while for Fe_2P it was 2:1:75 (Fe:P:Sn). Selected Co_2P and Fe_2P crystals are shown in **Figure 1**. For Co_2P crystal growth, increasing the molar ratio of Sn reduced the formation of Co_2P powder and increased crystal yield, but the crystals tended to become thinner and agglomerated. Conversely, reducing the molar ratio of Sn produced smaller crystals. For Fe_2P crystal growth, increasing the molar ratio of Sn up to 75 produced Fe_2P powder and decent-quality crystals. However, beyond this ratio, the crystals began to grow thinner, and reducing the Sn ratio

led to smaller crystals like Co_2P crystal growth. The copious amount of Sn flux for growing Fe_2P crystals increased the overall scale of the reaction to 30 g. The temperature profile used for the growth of all three $M_2\text{P}$ single crystals was the same as described in the experimental section. From PXRD patterns of ground single crystals, the phase purity was confirmed as shown in **Figure 1**. SEM images and EDS analysis of three $M_2\text{P}$ single crystals are shown in **Figure S4**. Elemental analysis confirmed the M:P stoichiometry without presence of foreign elements, such as Si from the reaction ampoule or elements from fluxes. AFM studies of the roughness of crystal surface (**Figure S5**) show the very low RMS of 0.42, 0.27, and 0.79 nm for the side facets of Ni_2P , Co_2P , and Fe_2P , respectively. For the tip facets, the RMS values were as low as 0.18, 0.20, and 0.15 nm for Ni_2P , Co_2P , and Fe_2P , respectively, validating that the cutting-based sample preparation method produces smooth surfaces. **Figure S6** shows the PXRD patterns of Ni_2P single crystal that was placed on the sample holder in parallel and the patterns show that main intense peaks are from (0 k 0) plane. It demonstrates that the large area of exposed side facets of Ni_2P corresponds to (0 k 0) facet and crystal was grown along the [0001] direction. Likewise, facet indexing of single crystal XRD confirms that Co_2P and Fe_2P crystals were also grown along similar directions with large side facets.

***In situ* powder X-ray diffraction (PXRD)**

To understand the mechanism of Ni_2P formation in In flux, we have performed *in situ* PXRD on the mixture of Ni, P, and In powders with a 2:1:2 ratio (**Figure 2a**). Temperatures were recorded only between approximately 220 °C and 900 °C during heating and cooling due to instrument limitations. Upon heating, the melted In flux (melting point: 156.6 °C) reacted with Ni and P, and it produced $\text{In}_{6.4}\text{Ni}_3$ and Ni_2InP phases at 228 °C. As the temperature increased, $\text{In}_{6.4}\text{Ni}_3$ further reacted with Ni and transformed into Ni-rich phase, In_3Ni_2 , at 415 °C, which is consistent with the In-Ni phase diagram ($\text{In}_{6.4}\text{Ni}_3$ decomposition temperature: 404 °C).⁵⁶ It was noted that Ni_2P started to form at the temperature as low as 455 °C, and In_3Ni_2 began to be rapidly consumed. Provided that the peritectic temperature of In_3Ni_2 is 865°C, it could react with P and form Ni_2P at a lower temperature. As Ni_2P was formed, unknown intermediate phases appeared up to 635 °C, and the Ni_2InP phase completely disappeared at 513 °C. The reported melting point of Ni_2InP is 526 °C.⁵⁴ One of the unidentified peaks may correspond to $\text{Ni}_{57}\text{In}_{22}\text{P}_{21}$ phase as it was detected at both 470 °C and 600 °C isotherm in a previous study.⁵⁴ Above 740 °C, all remaining elemental Ni and In_3Ni_2 reacted completely, leaving the Ni_2P as a single phase. Even after cooling to 224°C, Ni_2P was the

only phase present. It demonstrates that Ni_2P is the most thermodynamically stable phase in the Ni-In-P system, and it is essential to raise the temperature above $\sim 750^\circ\text{C}$ or extend the dwelling time to prevent the formation of potential competing phases. Due to the instrument limitations, the highest temperature that can be reached was $\sim 900^\circ\text{C}$, and the ratio of In was significantly smaller than the actual crystal growth conditions. Those are the reasons the full melting of all components was not achieved. From the actual synthesis profile, the temperature is ramped up to 1100°C and the In ratio increased by more than 10 times, which could be sufficient to decompose all intermediate phases and ensure full melt, allowing Ni_2P to grow into large, well-faceted crystals.

Sn flux reaction of three $M_2\text{P}$ was also investigated with *in situ* PXRD (**Figures S7-S9**) and all existing phases during heating and cooling are summarized in **Figure 2b**. The used ratio was 2:1:5 for all $M:\text{P}:\text{Sn}$. Reaction of Ni_2P with Sn flux showed different features compared to In flux. It showed the full melt region at relatively low temperatures, appearing above 938°C when heating and above 849°C when cooling. The difference between the two melting points could be due to the delay of phase transformation caused by the fast heating/cooling rates. The presence of full melt at lower temperatures indicates that Ni and P have good solubility in Sn. The most competing phase was the ternary Ni_2SnP phase, and it started to form $\sim 423^\circ\text{C}$ during heating and fully decomposed at around 796°C , making Ni_2P present as a single phase above that temperature. After melting, there was a small region where Ni_2P could possibly precipitate between 675°C and 849°C , but the peak intensity was very faint. It suggests that centrifuging the flux at even this temperature region would not produce a noticeable yield of crystals. Below 675°C , the Ni_2SnP phase started to form and became the major phase when cooled down to 222°C . This result demonstrates that Sn flux is not a suitable medium to grow Ni_2P single crystals. For Co_2P and Fe_2P reaction with Sn flux (**Figures S8,S9**), unlike Ni_2P , no complete sample melting was observed during heating up to the maximum temperature, $\sim 1060^\circ\text{C}$, and it corroborates the Fe-Sn and Co-Sn phase diagrams.⁵⁷⁻⁵⁹ Ni shows the lowest liquidus behavior and can form a liquid phase with $\sim 67\%$ Sn at 1000°C , while Co requires $\sim 73\%$ Sn and Fe requires $\sim 90\%$ Sn. It also explains why Fe needs the highest Sn ratio for single crystal growth compared to others. Co_2P reaction with Sn formed Sn_4P_3 at 271°C and CoSn_2 intermetallic at 348°C . Then both compounds decomposed at 533°C and formed an unknown phase until 678°C . The study of this unknown phase is currently ongoing. After 678°C , Co_2P became the major phase and there was a small amount of CoP present. After cooling below 798°C , the intensity of the CoP pattern began to increase, and remained at

245 °C. This suggests that the concentration of Sn flux needs to be optimized to avoid the formation of CoP. In the Fe₂P reaction, any Fe-Sn intermetallic phases were not observed, and as Sn₄P₃ decomposed, Fe₂P and FeP began to form at 589°C. This may indicate that the formation of binary Fe-P phases is more favorable throughout the reactions. The amount of FeP was minute and didn't show any increment during heating or cooling. It is hypothesized that in actual synthesis, higher temperature and higher Sn flux rate would ensure melting and slow precipitation of Co₂P and Fe₂P, growing large single crystals.

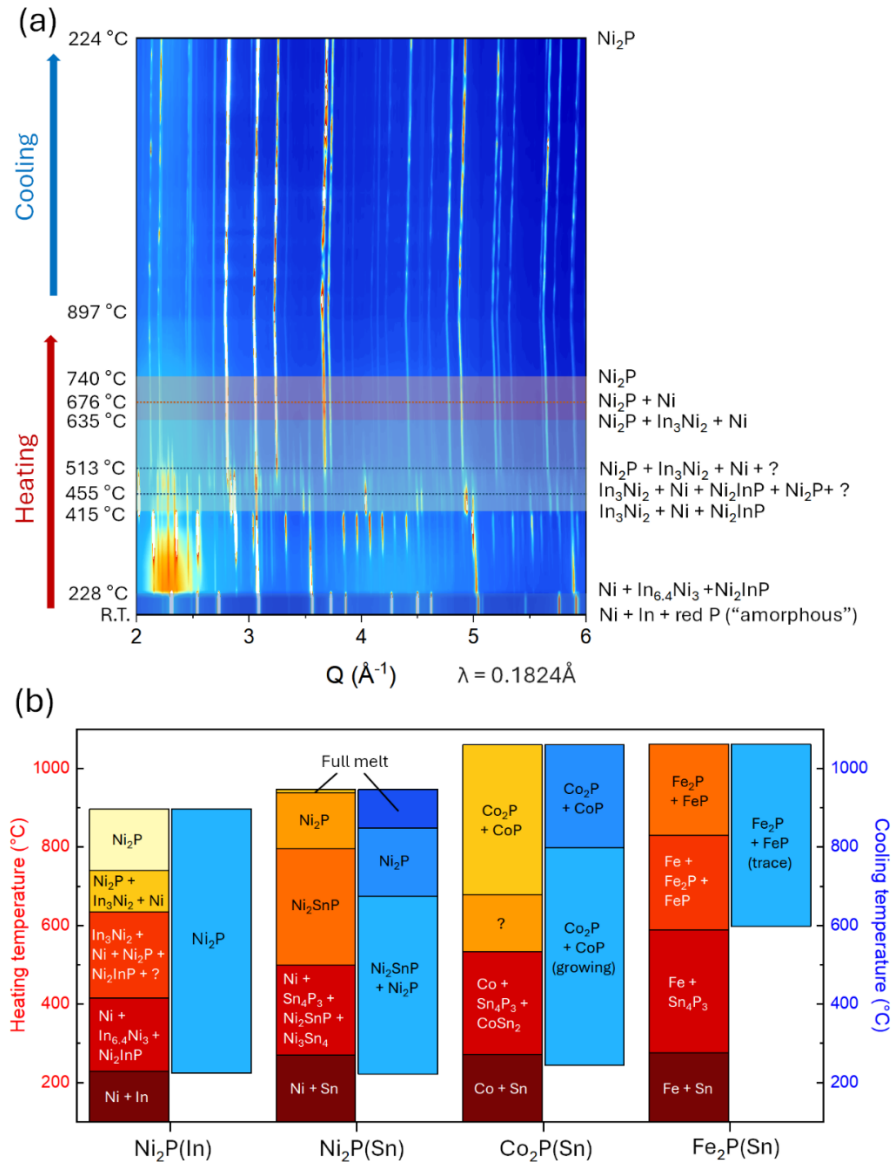


Figure 2. *In situ* powder X-ray diffraction of different metal flux for M₂P synthesis. (a) Contour plot of Ni₂P formation in In flux and (b) summarized histograms of existing phases during heating (red column) and cooling (blue column) for M₂P formation in different fluxes. The ratio used for the reaction was 2:1:2 for Ni:P:In and 2:1:5 for Ni:P:Sn, Co:P:Sn, and Fe:P:Sn.

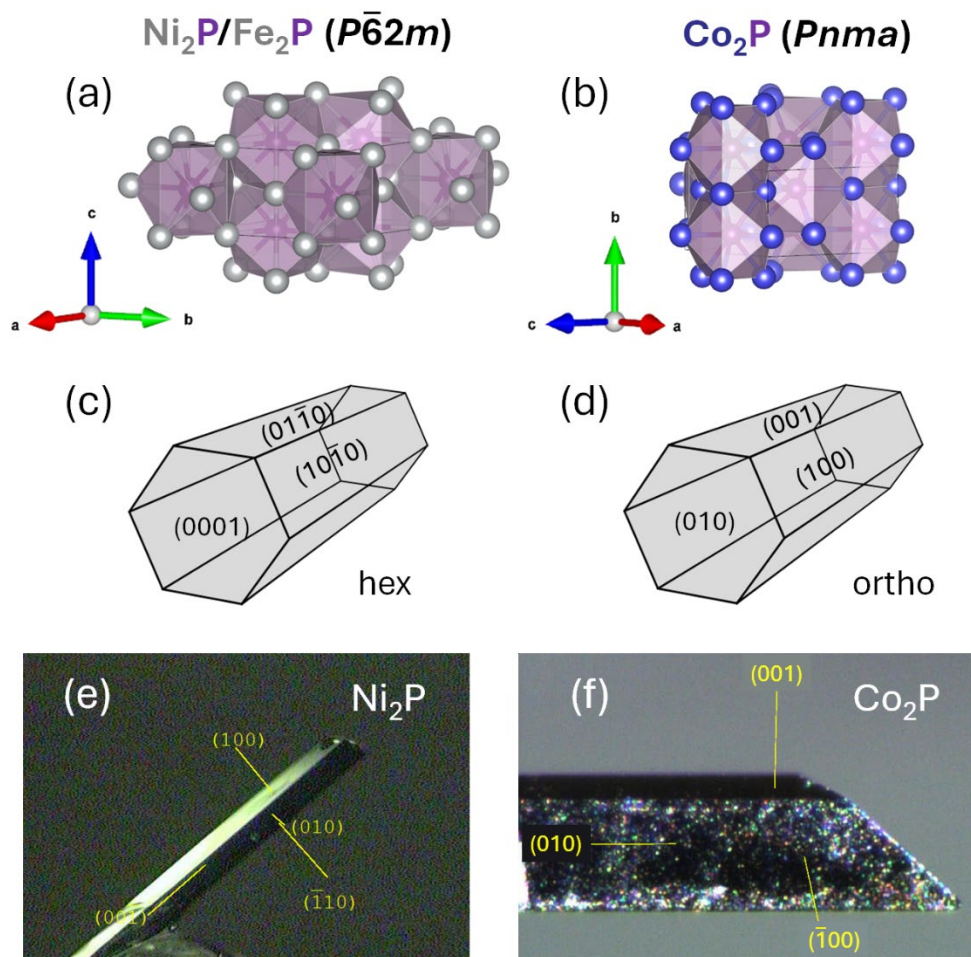


Figure 3. Crystal structure of (a) Ni_2P and Fe_2P and (b) Co_2P and schematic facet indexing of (c) $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ and (d) Co_2P . Indexed facets of (e) Ni_2P and (f) Co_2P crystals via single crystal XRD. Facet indexing of Fe_2P is shown in **Figure S10**, and extra indexing of multiple $M_2\text{P}$ crystals is provided in **Figure S11**.

Facet indexing of $M_2\text{P}$ single crystals and electrode fabrication

The crystal structures of $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ and Co_2P are related to each other as Co_2P is an orthorhombically distorted version of hexagonal Fe_2P structure. They share similar structure building blocks, P surrounded by 9 metal atoms with tricapped trigonal prism configurations, those $\text{P}@M_9$ polyhedra are tiled via face and edge sharing. The difference is that the base vector of growth direction of those polyhedra is c axis for $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ (**Figure 3a**) and b axis for Co_2P (**Figure 3b**). This is because of the conventions of different space groups of crystal structure, $P\bar{6}2m$ (c axis) and $Pnma$ (b axis) as shown in **Figure 3c,d**. Facet indexing was conducted using single crystal XRD. Since $M_2\text{P}$ crystals grow as hexagonal pillars, there was one tip facet, which was indexed as (0001) for $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ (**Figure 3c** and **Figures S10,S11**) and as (010) for Co_2P (**Figures 3d,S11**).

The side facets of $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ are mainly indexed as $(10\bar{1}0)$, $(01\bar{1}0)$, and $(\bar{1}100)$, and those of Co_2P are indexed as (100) and (001) . Note that the structure of Co_2P is centrosymmetric, which makes the $(\bar{1}00)$ and (100) directions identical. For convenience, we'll denote both facets as (100) . Also, two side facets, $(10\bar{1}0)$ and $(01\bar{1}0)$, of hexagonal structure are symmetrically equivalent with have the identical atomic configuration. It was found that the side facet with the largest surface area was $(10\bar{1}0)$ for Ni_2P and Fe_2P , and was (100) for Co_2P , respectively, as also shown from PXRD results of Ni_2P (**Figure S6**). These $(10\bar{1}0)$ and (100) side facets and (0001) and (010) tip facets were further tested for HER.

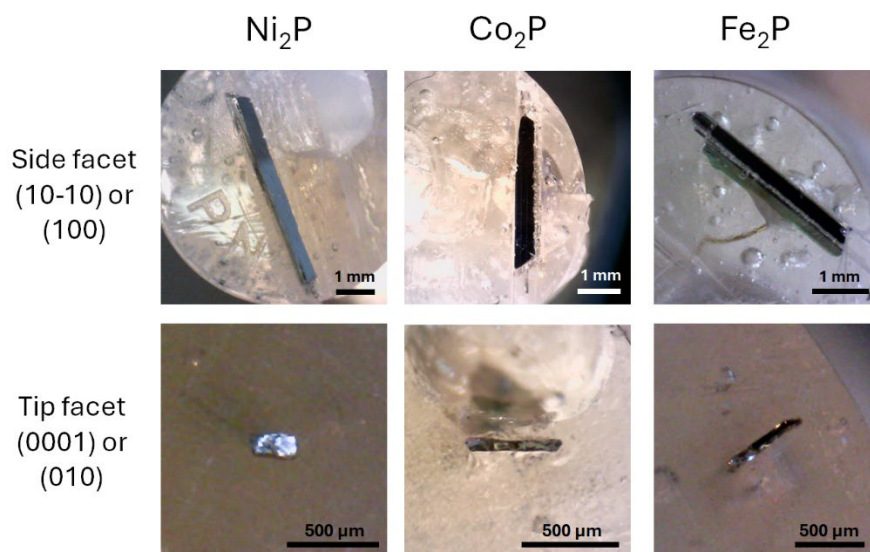


Figure 4. Pictures of fabricated electrode using single crystals that expose a side facet (top row) and a tip facet (bottom row).

Selected crystals were attached to the Au wire by conductive epoxy, and the whole assembly was molded in non-conductive epoxy (**Figure S1**). Molding the electrodes from non-conductive epoxy was beneficial because it allowed only the desired side to be exposed and placed the electrodes close to the stir bar, effectively removing hydrogen bubbles from the surface. After molding, the side facet was exposed using the blade by carefully removing the epoxy part that covers it. The tip facet was exposed by cutting the electrode perpendicular to the side facets of the crystal. Indexing of multiple crystals was performed prior to electrode fabrication, because, after electrode fabrication retrieving crystals for further SCXRD analysis was not feasible. Indexing consistently showed that the direction perpendicular to the crystal needle corresponds to the (0001) facet for $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ and the (010) facet for Co_2P . **Figure S11** and **Table S3** present the indexing of multiple crystals and unit cell parameters used for facet identification. We confirmed that the as-cut surface

of the tip facet of Ni_2P had similar activity compared to the polished one (**Figure S12**). The tip facet of Co_2P and Fe_2P was not polished as the crystals were brittle and broken by polishing. The remaining portion of the Au wire outside the mold was connected to Cu wire and wrapped with parafilm to prevent it from contacting the electrolyte. **Figure 4** shows the exposed facets of fully fabricated electrodes of three $M_2\text{P}$ single crystals and the surface area of the facets is listed in **Table S2**. The electrode and the electrochemical measurement setup are shown in **Figure S2**. Note that the electrode and stir bar were positioned at a distance sufficient to avoid turbulence from stirring, ensuring that the electrochemical measurements were not disturbed.

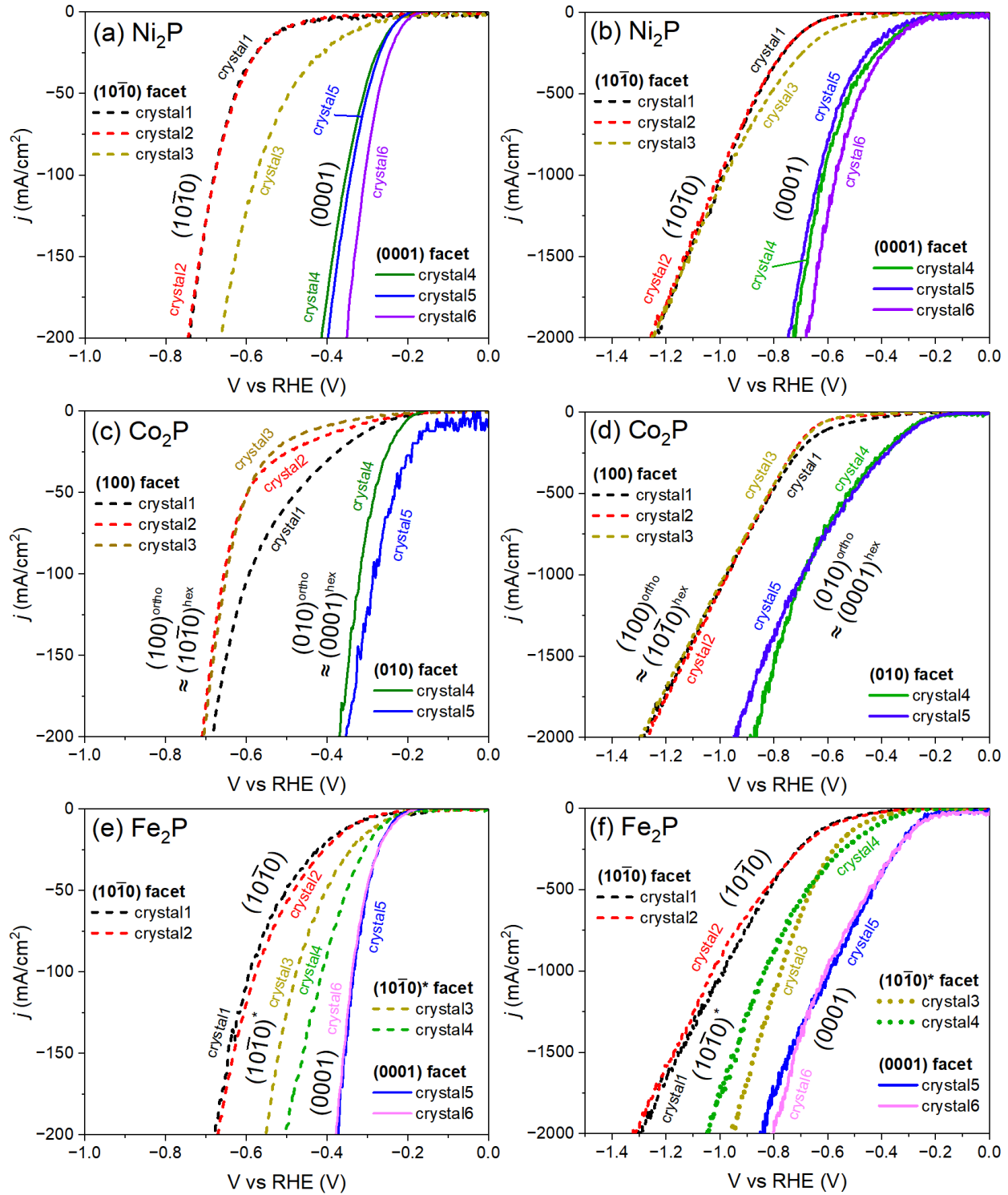


Figure 5. Polarization curves of two different facets of (a,b) Ni₂P, (c,d) Co₂P, and (e,f) Fe₂P single crystals. Left panels (a,c,e) correspond to the low current density region ($j = <200$ mA/cm²) and the right panels (b,d,f) correspond to the high current density region ($j = <2000$ mA/cm²). For Fe₂P, two side facets are assigned as (10 $\bar{1}$ 0) and (10 $\bar{1}$ 0)* since the latter facet, (10 $\bar{1}$ 0)*, consistently showed higher activity than the first facet, (10 $\bar{1}$ 0). The side facets are represented as dotted lines and the tip facets as solid lines.

Facet-dependent HER activity of M_2P single crystals

Each facet of the three M_2P crystals was tested for HER activity, and each facet was measured several times with different crystals to ensure reproducibility (**Figure 5**). Because of the small surface area of the electrodes, some electrodes showed a current density of more than -10 mA/cm^2 in non-faradaic regions. To improve clarity in determining the onset potentials of each facet, the tip facets were remeasured under conditions that minimized noise in the low current density region and replotted together with the original side facet (**Figures 5a, 5c, and 5e**). The overpotential values of measured facets are summarized in **Table S2** and the mean and standard deviation of them are shown as histograms in **Figure S13**. Note that the side facet of orthorhombic Co_2P is (100), which corresponds to $(10\bar{1}0)$ of hexagonal $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$ and the tip facet of Co_2P is (010), which corresponds to (0001) of $\text{Ni}_2\text{P}/\text{Fe}_2\text{P}$. One of the important observations of this test was the superior HER activity of the tip facet compared to the side facet from all M_2P single crystals (**Figure 5 and Table S2**). The average η_{100} of $(10\bar{1}0)$ facet of Ni_2P was $646(\pm 58) \text{ mV}$ whereas that of (0001) facet was $326(\pm 22) \text{ mV}$ and the overpotential differences between the two facets increased as applied potential increased (**Figures 5a, 5b, and S13**). For Co_2P , the average η_{100} of the (100) facet was $633(\pm 34) \text{ mV}$, while that of the (010) facet was $291(\pm 7) \text{ mV}$, consistently exhibiting the more efficient HER activity of the tip facet (**Figure 5c, 5d**). Fe_2P also had a higher activity of the (0001) facet, but some of $(10\bar{1}0)$ facets (denoted as $(10\bar{1}0)^*$ with asterisk) showed activity close to that of the (0001) facet at high potential regions. For example, η_{2000} of $(10\bar{1}0)$ facet of crystal3 was 959 mV while that of (0001) facet of crystal5 was 854 mV and the difference between two was only 105 mV (**Figure 5e, 5f**). It is substantially smaller compared to the η_{2000} difference of two facets from Ni_2P (531 mV) and Co_2P (375 mV). This may be attributed to the stronger H adsorption properties of Fe than Ni and Co, the explanation of which is presented later along with the calculation results. . The results clearly show that the onset point and η_{10} values of the tip facets appeared at smaller overpotential regions compared to the side facets. Overall, these results demonstrate the facet-dependent HER activity of three M_2P single crystals, demonstrating that tip $[(0001)^{\text{hex}}$ or $(010)^{\text{ortho}}]$ facet is more efficient than side $[(10\bar{1}0)^{\text{hex}}$ or $(100)^{\text{ortho}}]$ facet. It is known that the tip facet of hexagonal M_2P has the M 3-fold hollow active sites where H adsorption is relatively moderate among other reported sites such as M - M bridge, M - P bridge, and on-top M or P atom sites.^{21,24,60,61} Whitmire group presented that $(10\bar{1}0)$ facet of Fe_2P has Fe-Fe bridge sites where the H adsorption energy is stronger than that of Fe_3P termination of (0001) facet and lower

than that of Fe_3P_2 termination. It indicates that depending on its termination, the H adsorption energy of the side facet of $M_2\text{P}$ could be larger or smaller than that of tip facet. The stable termination of each facet, along with the corresponding electronic structure and adsorption energy, will be discussed in the calculation section to explain the observed activity behavior.

Metal-dependent HER activity at the same facets

The same facets of three $M_2\text{P}$ single crystals were analyzed as shown in **Figure 6**. There are few reports comparing the three $M\text{Ps}$, as their morphologies and surface areas vary and thus it is difficult to compare even under the same synthesis conditions.⁶² However, single crystals have flat and well-defined surfaces, thus, the comparison becomes reliable. The polarization curves were selected from those that closely match the average value of each facet. **Figure 6a** shows the polarization curves of $(10\bar{1}0)$ facets of three $M_2\text{P}$ single crystals up to the current density of 500 mA/cm^2 . Note that the $(10\bar{1}0)^*$ facet of Fe_2P represents one that showed higher activity than the other $(10\bar{1}0)$ facets. In low potential range, Ni_2P was found to require the highest overpotential, followed by Co_2P and Fe_2P . For instance, η_{300} of $(10\bar{1}0)$ facet of Ni_2P was 786 mV, that of Co_2P was 751 mV, and that of Fe_2P was 734 mV, suggesting that Fe_2P was the most efficient. A similar trend was found in the HER activity of the (0001) facet of three $M_2\text{P}$ in that Ni_2P showed the largest η_{300} overpotential, followed by Co_2P and Fe_2P (**Figure 6c**). Tao Wu *et al.* compared the (111) and (100) facets of CoPS single crystals and showed that the lower overpotential of the (100) facet in early potential region is due to its higher H adsorption energy compared to the (111) facet, as H adsorption is rate-determining step in that potential range.²⁹ It was reported that the H adsorption strength was highest for element Fe, followed by Co and Ni and Mou *et al.* showed that the H adsorption energy of Co terminal (0001) facet of hexagonal NiCoP is stronger than that of Ni terminal.^{24,63,64} This is because the d -band center of Co and Fe is closer to the Fermi level compared to that of Ni, providing less electron filling to the antibonding state when overlapping with hydrogen orbital.⁶ Interestingly, the HER activity trend of the same facets of $M_2\text{P}$ follows the same trend as the H adsorption strength of the transition metal, indicating that stronger H adsorption energy benefits HER overall in the low potential region. The geometric activity order of $\text{Fe}_2\text{P} > \text{Co}_2\text{P} > \text{Ni}_2\text{P}$ in lower potential regions is in line with previous study.⁶⁵ We observed strong correlations between the surface electronic structure properties and overpotentials among different metals (*vide infra*). When it comes to the high applied potential range up to the current

density of 2000 mA/cm², activity crossover occurs and the overpotential of Ni₂P becomes lower than that of Co₂P and Fe₂P in both facets (**Figures 6b, 6d**). The η_{2000} of the tip facet was 748 mV for Ni₂P, 873 mV for Co₂P, and 811 mV for Fe₂P. This crossover occurred around 1500 mV/cm² for (10 $\bar{1}$ 0) facet and around 1250 mA/cm² for (0001) facet. As shown in previous report, the rate determining step became H desorption at high potential region and lower H adsorption energy could become beneficial.²⁹ We performed a similar electrocatalytic activity test on the molded Pt wire with similar to tip facets surface area. At high current densities the activity of Ni₂P (0001) facet approaches that of Pt wire measured at identical conditions (**Figure 6d**).

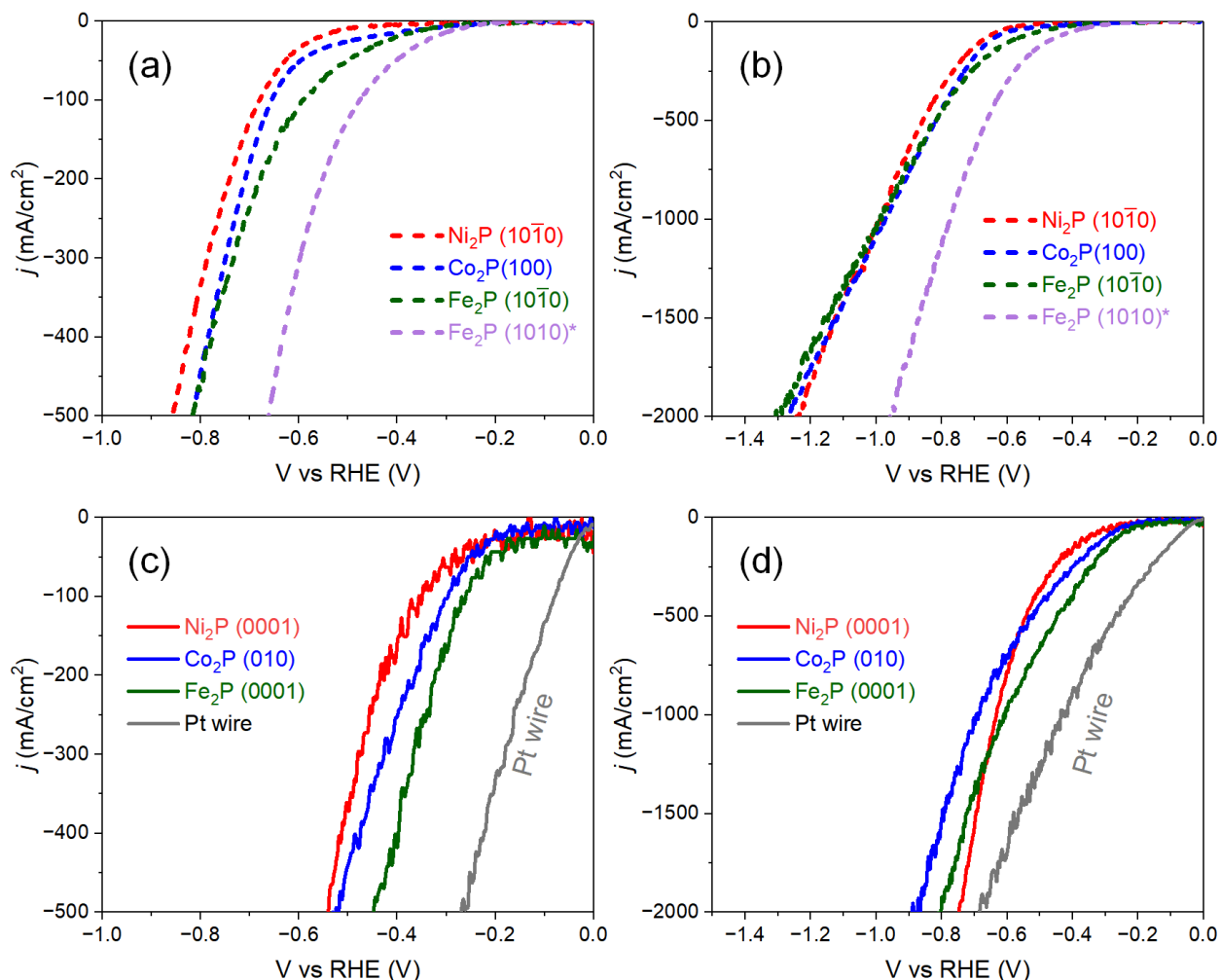


Figure 6. Representative polarization curves of the (a, b) side facet and (c, d) tip facet of M_2P single crystals in different current density ranges. (a) and (c) show the current density range of <500 mA/cm² while (b) and (d) show the current density range of <2000 mA/cm². The HER activity of tip of Pt wire was measured and compared to other tip facet of M_2P crystals in (c) and (d).

Kinetic analyses and long-term duration testing

Tafel slope and Nyquist plot analyses were carried out as indicators of mechanistic and kinetic behaviors (**Figure 7a–d**). The range of Tafel slopes was chosen to indicate the linear region and the representative Tafel slope of each facet (see **Figure S14** for the wider range).^{66,67} The range of Tafel slopes of the tip facets appeared at lower overpotentials than those of the side facets, consistent with their earlier onset points (**Figure 7a, 7b**). Notably, the Tafel slope of tip facets was consistently lower than that of the side facets. For the tip/side facets in mV/dec: Ni₂P (65/174), Co₂P (74/193), and Fe₂P (77/268{205*}). It suggests that the facile HER process occurs at the tip facets and supports the superior activity of tip facets in not only low potential regions but also at high applied potentials. When it comes to metal-dependence, Ni₂P showed the lowest Tafel slopes compared to Co₂P and Fe₂P in both facets, explaining the origin of activity crossover in high potential regions.

Electrochemical impedance spectroscopy (EIS) was performed at –0.35 V vs. RHE. To account for the different surface areas of each crystal, the charge-transfer resistance (R_{ct}) values obtained from the Nyquist plots were normalized by multiplying with the geometric surface area of the electrodes (**Figure 7c, 7d** and **Table S4**).⁶⁸ For facet-dependence, the R_{ct} of tip facets was consistently lower than that of side facets, indicating a lower kinetic barrier and consequently higher activity of the tip facets. Regarding metal dependence, Fe₂P exhibited the lowest R_{ct} , while Ni₂P showed the highest, consistent with the activity trend of Fe₂P > Co₂P > Ni₂P in the lower potential region for both facets. Together with the Tafel slope results, the tip facets exhibited lower values in R_{ct} as well as Tafel slopes compared to the side facets throughout the M_2P , representing its favorable kinetics. On the other hand, Ni₂P exhibited the highest R_{ct} among other M_2P s, but the smallest Tafel slopes in both tip and side facets. It indicates that the high charge transfer barriers in the early potential region are effectively overcome in the high potential region resulting in the highest activity, especially at the (0001) facet becoming comparable to Pt measured at identical conditions.

To evaluate the long-term behavior of the crystal electrodes, chronoamperometry was conducted at –0.35 V vs. RHE for 10 h (**Figures 7e, 7f** and **Table S5**). It was noted that the generated current density was substantially reduced in an hour, likely due to the flat surfaces of the single crystals being more susceptible to poisoning effects, a similar behavior also observed in electrodes fabricated from dense polycrystalline pellets. Nevertheless, the current density order after 10 h

remained consistent with the previously observed activity trends. For facet dependence, the tip facets consistently generate higher current densities than the side facets for all M_2P crystals. In terms of metal dependence, Fe_2P exhibited the highest current density, followed by Co_2P and Ni_2P for both facets. These results confirm that the activity trends of the M_2P crystals are preserved over the extended operation time in the low-potential region.

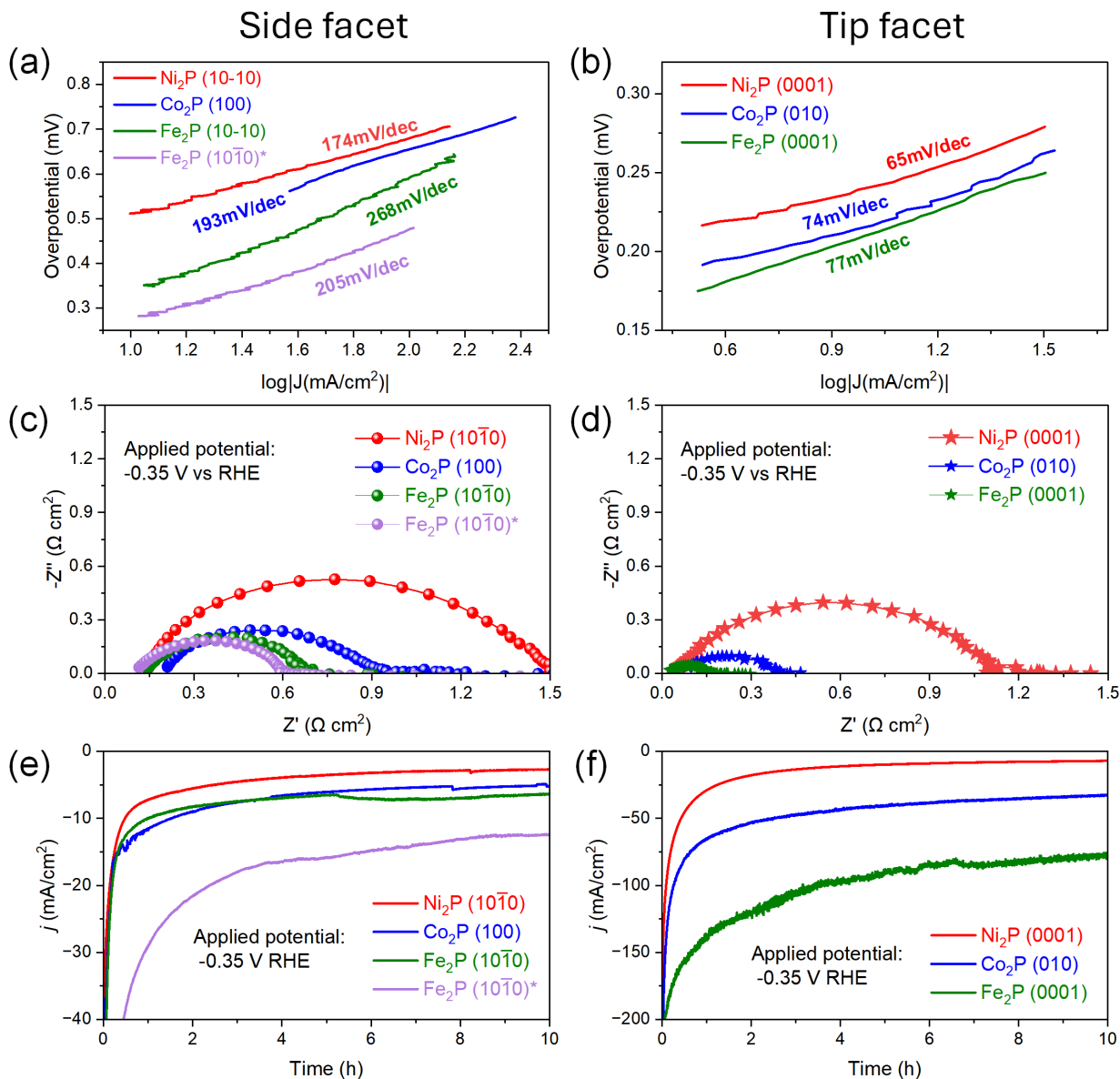


Figure 7. Tafel slope, Nyquist plot, and chronoamperometry of (a,c,e) side facets and (b,d,f) tip facets. For electrochemical impedance spectroscopy measurement (EIS), the applied potential was -0.35 V vs RHE in 0.5 M H_2SO_4 . For chronoamperometry measurement, the same potential was applied for 10 h.

DFT-derived surface energy calculations

Table S6 summarizes the calculated surface energy for each possible surface termination for a given M_2P ($M = \text{Fe, Co, Ni}$) surface and the most stable terminations were identified for further analysis. There are two Fe_2P facets that have close surface energy and Fe_2P and Fe_2P^* correspond to T2 and T5 termination, respectively. The crystal structure of selected surface terminations is shown in **Figure S15**. Using pristine surface structures identified by surface-energy DFT values (see **Table S6**), we confirm earlier computational findings that report *hollow* active sites consisting of 3-4 exposed metal atoms as the most stable site for a non-interacting adsorbed hydrogen.^{21,60,69,70}

The computed surface energies of the side facets are either comparable ($M = \text{Ni, Fe}$) or lower ($M = \text{Co}$) than for the tip facets for all M_2P crystals. Notably, the overall form of the experimentally grown crystals is needle-shaped, such that the geometric surface area of the side facet is significantly greater than that of the tip facet. This contradiction with DFT [i.e., the tip facet is lower in energy than the side facet] is resolved when considering findings on crystal growth.⁵¹ Ultrafast crystal growth in pure metal melt (like Ni) is governed by a barrierless ordering process that permits the metal crystalline interface to impose its inherent structure onto an adjacent liquid, e.g., *fcc* Ni(111) is lowest facet forming a *hcp* [0001] template for growth in melt. The expectation of these studies for crystal growth governed by such a non-equilibrium process is that nucleation favors the lowest facet in the melt [here (0001) tip facets] but growth occurs orthogonally [here (10 $\bar{1}$ 0) side facets], as experimentally observed.

Electronic behavior of isolated active sites

Motivated by the work of Santos and Schmickler, which suggested that the accumulation of charge in active orbitals at a facet may stabilize transition-state H from the electrolyte⁷¹, we qualitatively correlate the experimental charge-transfer resistance (R_{ct}) and overpotential (η_{100}) with the calculated density of states (DOS) at the Fermi energy, $n(\varepsilon_F)$, for *d*-orbitals (d_{xz}, d_{yz}, d_{z^2}) protruding from the M_2P facet near the adsorption site (**Figure 8**). In **Figure 8a**, a clear correlation to measured R_{ct} is found with the calculated $n(\varepsilon_F)$ because at low applied potential the perturbations to calculated $n(\varepsilon_F)$ are expected to be small.

At low overpotential, as for the tip facets, a significant linear correlation is found (**Figure 8b**), similar to R_{ct} from EIS measurements, as the potential-driven perturbation to $n(\varepsilon_F)$ is expected to be small. As the DFT-calculated (zero-potential) $n(\varepsilon_F)$ does not resolve the non-equilibrium

effects, the side facets that have a higher η_{100} show a poorer linear correlation, and qualitatively different than the correlation with R_{ct} ,

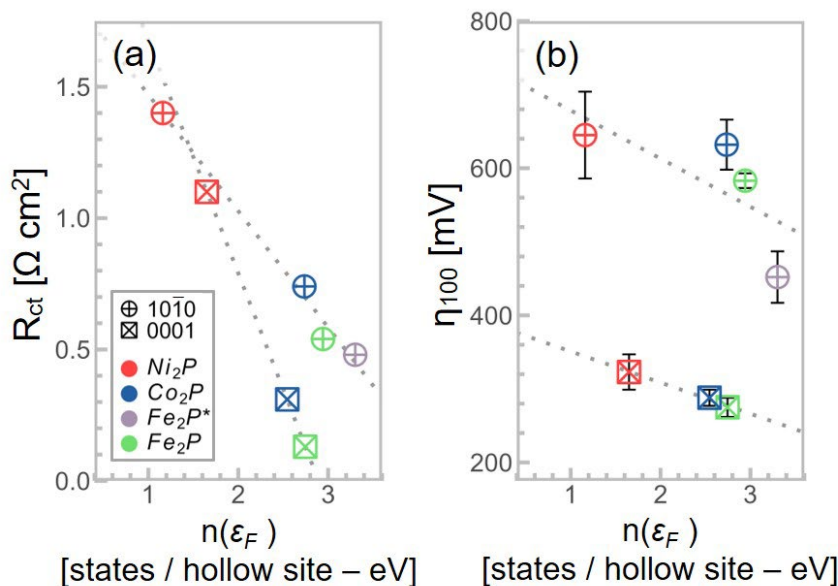


Figure 8: Activity of M_2P surfaces – as measured by (a) charge-transfer resistance (R_{ct}) and (b) overpotential to drive a current density of 100 mA/cm² – versus $n(\epsilon_F)$ associated with active d -band states protruding from a facet surface. This descriptor correlates with measured activity of M_2P surfaces at low potentials if the facets (side or tip) are grouped separately.

We show that $n(\epsilon_F)$ qualitatively correlates HER activity for the same (side or tip) facets, offering a computationally efficient descriptor to optimize HER performance for these systems. Note that a build-up of charge near the Fermi energy that is shown to decrease charge-transfer resistance of the surface will also generally increase surface energies of the facet. This suggests that unstable surfaces can broadly be considered better catalysts. The correlation of $n(\epsilon_F)$ with observed overpotential depends on the current density at which the overpotential is measured. As current density increases above 2000 mA/cm², the $n(\epsilon_F)$ descriptor correlation with observed overpotentials is gradually lost (**Figure S16**).

Coverage effects on electronic descriptor

To use of $n(\epsilon_F)$ to describe HER activity at high current densities, this descriptor must account for potential-driven increases in surface coverage on M_2P facets. Here, we assess the implication for HER activity at large current densities by analyzing changes in $n(\epsilon_F)$ and DOS behavior near ϵ_F

(e.g., stabilization due to forming a pseudo-gap) due to coverage. Details of fully covered structures are reported in **Table S8** and based on calculations discussed elsewhere.

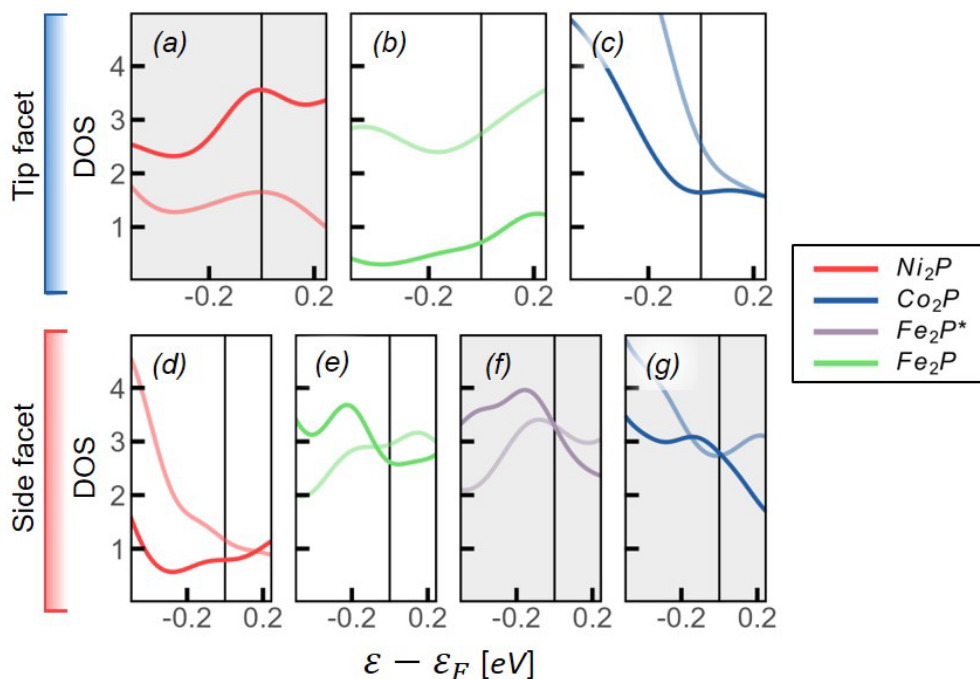


Figure 9: DOS for d -orbitals (d_{xz}, d_{yz}, d_{z^2}) protruding from the facet (per adsorption-site per eV) are plotted for tip (a-c) and side (d-g) facets with a *single H* (lighter lines) and *full coverage* (darker lines). At full coverage, facets with near constant or increasing $n(\epsilon_F)$ should remain as active (a,f,g shaded grey). At full coverage, facets with decreasing $n(\epsilon_F)$ should become more inert.

From **Figure 9**, we observe that M_2P facets may be grouped based on the change in $n(\epsilon_F)$ from single H to full coverage (plots shaded grey). The $n(\epsilon_F)$ increases with coverage in the case of the Ni_2P tip facet, while Fe_2P^* and Co_2P side facets remain near constant as compared to single H near active sites (all shaded grey). As a result of the presence of more states at ϵ_F , these facets are expected to be more active at higher coverages. This expectation agrees with the observed higher HER activity for Ni_2P tip facet relative to other M_2P facets. In contrast, $n(\epsilon_F)$ decreases or remains unchanged in all other cases, so these facets (not shaded) are expected to be more inert with higher coverage.

Notably, besides enhancement of $n(\epsilon_F)$, a secondary feature of the DOS is its curvature at ϵ_F due to H coverage. Presence of a local minimum in the DOS at full coverage indicates that the system is stabilized upon coverage and that this increases activation energy required for OPD H to destabilize or dissociate chemisorbed H via either the Tafel or Heyrovsky reactions. Fully covered

Ni₂P tip facet has a negative curvature of $n(\varepsilon_F)$, suggesting resistance to active site poisoning across a wide range of current densities (**Figure 9a**). Similar to Ni₂P tip facet, Fe₂P* side facet also has a negative curvature (**Figure 9f**) regardless of coverage, potentially explaining its observed high activity over a wide range of current densities. While Fe₂P (**Figure 9e**) and Co₂P (**Figure 9g**) side facet at full coverage have similar $n(\varepsilon_F)$, they differ in their stability. Co₂P side facet shows a stabilized curvature for non-interacting H (single H case), but at full coverage the curvature indicates instability (hinders poisoning). In contrast, Fe₂P side facet becomes positively curved upon full coverage indicating enhanced stability (potentially poison active sites). This coverage effect agrees with enhanced HER activity for Co₂P side facets versus Fe₂P side facets, even though $n(\varepsilon_F)$ are similar for both materials.

CONCLUSIONS

In this study, new synthetic routes to grow mm-sized Ni₂P, Co₂P, and Fe₂P single crystals were presented using different metal-flux growth methods. Selected crystals of three M_2 P were tested for facet-dependent HER activity. All M_2 P crystals consistently revealed that tip facets had a superior HER activity compared to side facets. The HER activity of the three M_2 P compounds was compared using the same facets, showing that Ni₂P exhibited the lowest activity at small overpotentials. However, this trend reverses at high overpotential regime, where Ni₂P exhibited the highest activity for both facets. Moreover, the activity of (0001) tip facet of Ni₂P approaches that of Pt measured at identical conditions at high applied potentials. Tafel slope and charge-transfer resistance (R_{ct}) analyses revealed that the superior activity of the tip facets originates from their lower kinetic barriers in both the HER mechanism and electron transfer across the M_2 P crystal surfaces. In terms of metal dependence, Ni₂P exhibited the highest R_{ct} while Fe₂P showed the lowest, consistent with the activity order of Fe₂P > Co₂P > Ni₂P at low applied potentials. However, the lowest Tafel slopes of Ni₂P resulted in the activity crossover at higher applied potentials. From DFT, we correlated HER activity and R_{ct} with a density of states analysis for M_2 P tip and side facets when non-equilibrium distortions to these electronic states are expected to be small. This study provides insights for shape-selective growth of M_2 P nanocrystals – aiming at hexagonal discs with enhanced exposed (0001) facets should result in improved activities. Furthermore, synthesizing nanocrystals to expose the facets identified through this type of single-crystal study

could be an integrated approach to designing efficient catalysts, especially when adding DFT-based descriptors, as identified, used to guide improved HER activity.

AUTHOR INFORMATION

Corresponding Author

Kirill Kovnir, kovnir@iastate.edu

Author Contributions

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Supporting Information

The Supporting Information is available free of charge: Additional synthetic and computational details and figures and tables pertaining to crystal images, powder X-ray diffraction, in-situ PXRD maps, atomic force and scanning electron microscopies, HER tests, and electronic structure calculations.

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