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Nanocrystalline Ni$_5$P$_4$: A hydrogen evolution electrocatalyst of exceptional efficiency in both alkaline and acidic media


Cite this: DOI: 10.1039/sx000000x
Received 00th January 2012, Accepted 00th January 2012
DOI: 10.1039/sx000000x
www.rsc.org/

Producing hydrogen (H$_2$) by splitting water with fossil-free electricity, is considered a grand challenge for developing sustainable energy systems and a carbon dioxide free source of renewable H$_2$. Renewable H$_2$ may be produced from water by electrolysis with either low efficiency alkaline electrolyzers that suffer 50-65% losses, or by more efficient acidic electrolyzers with rare platinum group metal catalysts (Pt). Consequently, research has focused on developing alternative, cheap, and robust catalysts made from earth-abundant elements. Here, we show that crystalline Ni$_5$P$_4$ evolves H$_2$ with geometric electrical to chemical conversion efficiency on par with Pt in strong acid (33 mV/dec Tafel slope and -62 mV overpotential at -100 mA/cm$^2$ in 1 M H$_2$SO$_4$). The conductivity of Ni$_5$P$_4$ microparticles is sufficient to allow fabrication of electrodes without conducting binders by pressing pellets. Significantly, no catalyst degradation is seen in short term studies at current densities of -10 mA/cm$^2$, equivalent to ~10% solar photoelectrical conversion efficiency. The realization of a noble metal-free catalyst performing on par with Pt in both strong acid and base offers a key step towards industrially relevant electrolyzers competing with conventional H$_2$ sources.

1. Introduction

Although H$_2$ can be produced by electrochemical water-splitting, commercial alkaline electrolyzers rely on metallic nickel (Ni) electrodes that have low efficiencies and suffer electrochemical corrosion, which are acceptable only because of the low cost of Ni metal. Recent advances include the use of electrodeposited NiMo alloy catalysts with yet undisclosed stability/longevity under commercial conditions. Commercial Proton Exchange Membrane (PEM)-type electrolyzers use platinum (Pt) particles on carbon, the archetypical catalyst for the H$_2$ evolution reaction (HER). On pure Pt [110] the reaction has the highest efficiency, being thermodynamically reversible in acids, and each additional 29 mV of applied potential increases the current ten-fold (Tafel slope of 29 mV/dec), which is the lowest electrical loss reported. However, platinum group metals (PGM) are among the scarcest elements on Earth that are stable below 800°C. Recently, Popczun et al. described its superior efficiency as an HER catalyst as well as other advances in earth-abundant HER catalysts from earth-abundant elements. Here, we show that crystalline Ni$_5$P$_4$ evolves H$_2$ with geometric electrical to chemical conversion efficiency on par with Pt in strong acid (33 mV/dec Tafel slope and -62 mV overpotential at -100 mA/cm$^2$ in 1 M H$_2$SO$_4$). The conductivity of Ni$_5$P$_4$ microparticles is sufficient to allow fabrication of electrodes without conducting binders by pressing pellets. Significantly, no catalyst degradation is seen in short term studies at current densities of -10 mA/cm$^2$, equivalent to ~10% solar photoelectrical conversion efficiency. The realization of a noble metal-free catalyst performing on par with Pt in both strong acid and base offers a key step towards industrially relevant electrolyzers competing with conventional H$_2$ sources.
H$_2$SO$_4$ and 1 M NaOH—an unique attribute among PGM-free HER catalysts.

2. Results:

2.1. Synthesis & Characterization: We synthesized micron sized particles of Ni$_5$P$_4$ (Ni$_5$P$_4$ MPs) and Ni$_2$P NPs as single phase crystalline particles by adapting previously reported solvothermal methods. Special attention to prevent formation of the other 6 crystalline phases of nickel phosphides was necessary to achieve high purity.

![PXRD analysis of Ni$_5$P$_4$ (A) and Ni$_2$P (B) comparing the observed (black) and difference (blue) at room temperature. The Bragg positions (vertical lines) correspond to the crystallographic reflections. The Ni$_5$P$_4$ structure is refined in a hexagonal unit-cell, space group P63mc (#186), with unit-cell parameters a = 6.78822(15) Å, c = 11.0086(4) Å. No additional peaks, indicative of impurities are observed, showing that Ni$_5$P$_4$ is the only crystalline component (details in S.I.). The small differences between fit and data are due to the size range of the particles from 20 nm-1.8 µm, see HRTEM. The Ni$_2$P NP structure refinement used the Ni$_2$P reference pattern (PDF 03-065-3544), refining the following parameters: zero-point, scale factor, positional and thermal factors, and unit-cell parameters. Graphs are vertically displaced for clarity.](image)

Rietveld refinement of the Ni$_5$P$_4$ reference pattern to the Ni$_5$P$_4$ MPs PXRD pattern shown in Fig. 1A, shows that both the peak positions and intensities agree with the fit, establishing that Ni$_5$P$_4$ is the only crystalline component within the ~2% detection limit. The Scherrer equation indicates an average particle size of ~20 nm. Rietveld refinement of the PXRD also confirmed Ni$_2$P as phase-pure nanoparticles (NPs) with a particle size of 5–6 nm from the Scherrer equation, see Fig. 1B.

![TEM image of Ni$_5$P$_4$ MPs before catalysis. (A) TEM image at low magnification (insert) zoom in on MP edge showing the particles nano-roughness. (B) HRTEM image of a single nanoparticle of MP particle agglomerate.](image)

HRTEM further confirmed both the Ni$_5$P$_4$ phase from lattice spacings (see Table S4, ESI) and the NP crystallite size range 5–20 nm (Fig. 2B). Ni$_5$P$_4$ NPs were found to have fused together to form larger spherical MPs, size 0.3–1.8 µm (Fig. 2A). HRTEM shows that individual particles are encapsulated in a thin (1.1 ± 0.5 nm), amorphous shell. The transmission dependence on atomic number, suggests that this shell is amorphous carbon, likely produced from breakdown of the organophosphine precursor, as reported previously for similar syntheses.

2.2. Electrochemical activity measurement: As Ni$_5$P$_4$ converts into Ni$_2$P when heated above 350°C, the procedure used by Popczun et al. to prepare thin-film electrodes by sintering Ni$_2$P onto Ti-foil could not be applied here. Instead, electrodes were made by pressing 50 mg of catalyst into a 6 mm diameter pellet (at 5 tons) and sealing it in epoxy so that only the top surface of the electrode contacted the solution (see Methods & ESI). The electric conductivity of the Ni$_5$P$_4$ MP pellets are measured by the 4-point probe technique. The obtained resistivity of 6.3 µΩm and using a representative pellet thickness of 480 µm and geometric area of 0.021 cm$^2$ the electrode resistance attributable to the pellet design was only...
1.4 m\(\Omega\). High frequency EIS measurements were used to estimate the uncompensated resistance at 12.4 \(\Omega\) in 1 M \(\text{H}_2\text{SO}_4\), which is \(10^4\) greater than the resistance to conduction through the pellet — thus indicating that the limiting resistance is from the solution not the electrode assembly. A polished Pt foil (Pt) served as a control (see ESI).

2.2. Electrochemical Characterization: Fig. 3A plots the voltammograms of pellet-electrodes made with Ni\(_2\)P NPs or Ni\(_5\)P\(_4\) MPs, compared to Pt foil in 1 M \(\text{H}_2\text{SO}_4\) or 1 M \(\text{NaOH}\) under 1 atm \(\text{H}_2\) gas. The potentials (vs. RHE) required to produce current densities of \(j = -10\) and \(-100\) mA/cm\(^2\) and Tafel slopes are summarized in Table 1. Ni\(_5\)P\(_4\) MPs were preconditioned at \(j = -10\) mA/cm\(^2\) for 16 hr prior to measurements. In contrast, both Pt and Ni\(_2\)P NPs were measured using pristine samples due to poisoning or corrosion instability, respectively, for these samples. For Ni\(_5\)P\(_4\) MPs the potential (mV vs. RHE) required for \(j = -10\) mA/cm\(^2\) in 1 M acid is \(-23\) vs. \(-42\) for Ni\(_2\)P NPs, and \(-27\) for Pt. This performance difference is maintained at -100 mA/cm\(^2\) (Fig. 3A). In 1 M alkali, the potentials increase relative to acid, but still favors Ni\(_5\)P\(_4\) MPs over Ni\(_2\)P NPs; the values at \(j = -10\) mA/cm\(^2\) are \(-49\), \(-69\), & \(-82\) mV for Ni\(_5\)P\(_4\), Ni\(_2\)P, and NiMo NPs\(^{26}\), respectively. This performance difference is maintained at -100 mA/cm\(^2\) and is actually better than Ni\(_2\)P NPs (1 mg/cm\(^2\) thin-film) in the literature\(^8\), attributable to the increased loading (177 mg/cm\(^2\)).

Fig. 3B plots the logarithm of current density vs. overpotential (\(\eta\)) from which the slope (electrical potential cost per decade of current) reveals the HER kinetics (Tafel slope). We performed the Tafel analysis for Ni\(_5\)P\(_4\) MPs, Pt, and Ni\(_2\)P NPs in the interval \(-\text{Tafel slope/2} < \eta < -\text{Tafel slope}\), as recommended by Sheng et al.\(^{34}\). In acid electrolyte this yields differences of only 5–6 mV/dec, illustrating the similarities in reaction kinetics for

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the 3 catalysts. Above this region, slopes increase as diffusion limitations begin to influence the Tafel kinetics. By contrast, in 1 M alkali the Tafel slope of Ni₅P₄ MPs is 20 mV/dec smaller than of the Ni₅P NP. At larger applied potentials, Tafel slopes again increase as diffusion limitations begin to influence the kinetics. The Tafel slope of Ni₅P NP pellet-electrodes agrees reasonably well with the Ni₅P/Ti-foil-electrodes described by Popczun et al.8 (see ESI). The Tafel slope of Ni₅P MPs in 1 M acid (33 mV/dec) and in 1 M base (98 mV/dec) should be compared to those for Pt (29 mV/dec, in acid) and bulk NiMo alloy (132 mV/dec, in base). Thus, the Tafel kinetics of Ni₅P MPs is essentially indistinguishable from the best reported values for the HER kinetics, i.e. Pt in acid and greatly improved over the bulk NiMo alloy in alkali.

Table 1. Performance of electrocatalysts.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Potentiala required for j = -10-100 mA/cm² / [mV vs. RHE]</th>
<th>Tafel slope / [mV/dec]</th>
<th>HER Faradaic efficiency, % H₂ yield</th>
<th>Estimated TOF / [mol H₂ / mol electrocatalytic surface atoms / s] (η = 100 mV/200mV)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₅P₄ (pellet)</td>
<td>-23/-62 (acid)</td>
<td>33 (acid)</td>
<td>100%±1% H₂ (acid)c</td>
<td>3.59/0.8 (acid)</td>
</tr>
<tr>
<td></td>
<td>-49/-202 (base)</td>
<td>98 (base)</td>
<td>100%±5% H₂ (base)c</td>
<td>0.79/2.9 (base)</td>
</tr>
<tr>
<td>Ni₅P (pellet)</td>
<td>-42/-101 (acid)</td>
<td>38 (acid)</td>
<td>unstableb</td>
<td>0.015/0.064 (acid)d</td>
</tr>
<tr>
<td></td>
<td>-69/-220 (base)</td>
<td>118 (base)</td>
<td>unstableb</td>
<td>0.004/0.014 (base)</td>
</tr>
<tr>
<td>Bulk Pt foil</td>
<td>-27/-55 (acid)</td>
<td>29 (acid)</td>
<td>100%±2% H₂ (acid)d</td>
<td>329 (N/A)</td>
</tr>
<tr>
<td>NiMo alloy⁸</td>
<td>-82/N/A (base)</td>
<td>132 (base)⁹</td>
<td>N/A</td>
<td>0.05/0.36 (base)²⁶,⁶</td>
</tr>
</tbody>
</table>

a. Values are obtained from Fig. 2A, thus reflecting the kinetic current at 1 mV/s and not the steady state potentials. 
b. TOF was estimated by assuming all the catalyst was active, then normalization to the known value of Ni₅P NP on Ti foil, to account for the lower active loading (see ESI for details). 
c. A second Tafel slope of 82 mV/dec is reported in literature at larger values for Ni₅P MP and Ni₅P NPs. 
d. Literature³⁵ NiMo Tafel slopes are reported for polycrystalline bulk alloy, whereas overpotentials and TOFs refer to NPs. 
e. H₂ and O₂ were determined by GC after passing 6 C (coulombs) in a one compartment cell (see ESI). 
f. Faradaic yield measurements were conducted on Pt/C/Nafion composites (see ESI). 
g. Popczun et al.⁸ reports TOF = 0.015 s⁻¹ at η = 100 mV and TOF = 0.5 s⁻¹ at 200 mV using NPs of Ni₅P on Ti-foil. 
h. Ni₅P corrodes during electrolysis, making long term H₂ yields time-dependent.

Far greater loadings of earth-abundant catalysts can be used compared to PGMs (Pt is more than 10³ more expensive than Ni). Therefore, it is the geometric current density for earth-abundant catalysts which shows the true potential in applied energy harvesting. However, the intrinsic catalytic rate, albeit harder to determine, gives the activity of a single active site (turn-over frequency, TOF) and therefore is an alternative comparison to literature values. For new catalysts like the nickel phosphides—and indeed many earth-abundant catalysts—neither the nature of the active site nor its relative abundance are known. Hence, we have adopted the method used by Popczun et al.⁸ to estimate the number of catalytic sites per surface area (see ESI for method details) using the crystal structure, the BET surface area of the catalyst powder, and the activity at η = 100 mV and η = 200 mV. Using this method we arrived at an estimated 1.9·10¹⁵ atoms per cm² of surface Ni₅P₄ (2.0·10¹⁵ atoms/cm² for Ni₅P). For polished Pt foil we used the same method as for the nickel phosphides to estimate surface atom density, obtaining 4.1·10¹⁵ surface atoms/cm², close to the literature value of 1.5·10¹⁵ surface atoms/cm² for Pt[111]⁶⁰. Using the geometric surface area we obtained a TOF of 329 s⁻¹ for Pt foil.

Estimating the total electroactive surface area of catalyst in contact with the electrolyte is complicated for the solid pellet electrodes used here as they may be semi-porous. Initially, lower and upper bounds to the electrocatalytically active surface area were estimated assuming either the geometric surface area of the electrode or the volume of the full pellet (geometric area times the thickness of the solid pellet) times the measured N₂ BET surface areas (1m²/g for Ni₅P MP and 69.4 m²/g for Ni₅P NPs), neither of which were known to be the electrocatalytical area. Hence, to compare to literature reports we estimated the absolute TOFs by normalization of pellet electrodes to the reported TOF for thin-film Ni₅P NPs,⁸ for which the accurate active catalyst loading was known. This normalization was then applied to the Ni₅P MPs, as these could not be prepared as thin-films due to the high temperature cracking of pellets (Fig. 3D), similar to the previous study.⁸ This comparison shows that the TOF of Ni₅P₄ MP exceeds that of Ni₅P by 200 fold in both acid and base. Additionally, Ni₅P MP have a 10 fold greater TOF than the previously reported values for state-of-the-art NiMo alloy⁸,⁶⁰, with the latter TOFs 0.05 s⁻¹ and 0.36 s⁻¹ at η = 100 mV and η = 200 mV under alkaline conditions. The estimated TOF of Ni₅P MP is about two orders of magnitude lower than that of the Pt-foil in acid at η = 100 (assuming an atomically flat surface).

Steady-state activity and electrode degradation (corrosion) were investigated during 16 hr chronopotentiometric (CP) electrolysis at -10 mA/cm² in both acid and base. This current density has been widely adopted as a standard condition as it is equal to a photoelectrochemical cell operating at ~10 % solar efficiency.³⁷,³⁸ Fig. 3C shows the time dependence of the CP potential of unconditioned pellet electrodes of Ni₅P₄ and Ni₅P foil (details in ESI). In acid, both Ni₅P₄ MPs and Ni₅P NPs exhibit short term increase in activity over ~2 hr to steady-state values (conditioning). The current for Ni₅P NP sometimes become unstable during 16 hr as shown (Fig. 3C) due to corrosion, which is in contrast to the stable current of Ni₅P MP. In base, both Ni₅P₄ MPs and Ni₅P NPs exhibit conditioning over ~2 hr to steady-state values that favor Ni₅P₄ by 21 mV after 16 hr. A similar trend, of smaller amplitude was reported previously for Ni₅P NPs on Ti.³⁸ During electrolysis, Ni₅P pellets physically degrade as seen by visible swelling and cracking of pellets (Fig. 3D), similar to the previous study.⁸
albeit with minimal potential change, see Fig. 3C. The reason for the apparent CP stability is the large amount of catalyst used to make electrode pellets. In contrast, the Ni₅P₄ pellets retain their metallic luster and show little to no visible change, indicating stability against corrosion in both acid and base over 16 hr.

To corroborate the visual and electrochemical analysis of electrode stability, the electrolyte was sampled at time intervals and analyzed by ICP-MS elemental analysis for Ni (Fig. 4). This analysis shows no Ni dissolves from the Ni₅P₄ electrode in 1 M NaOH over the 16 h electrolysis period. In 1 M H₂SO₄ a sharp initial increase in dissolved Ni is observed that levels off at 14.3% within this same period. We attribute the initial loss in acid to the dissolution of other Ni products (residual precursor from the synthesis, or a surface layer of phosphate formed by air exposure) that does not dissolve in alkali. As this dissolution shows no correlation with the catalytic activity of the electrode, we conclude that the active Ni₅P₄ MP sample is stable during H₂ evolution. For comparison, an electrode pressed from Ni₃P NPs was investigated in 1 M H₂SO₄. As expected from the visual and electrochemical analysis, significant dissolution (50.5% after ~19 hr) was observed for this sample.

### 2.3. Post electrolysis characterization:

Lastly, Fig. 5 shows HRTEM images of particles obtained from the surface layer of an Ni₅P₄ MP electrode after 6 hr of electrolysis in acid (A) and base (B) vs. before electrolysis (C). The particles show no visible sign of surface reconstruction and the presence of the amorphous carbon coating before and after catalysis indicates that particle size and shape are retained. Six lattice spacings compiled from multiple locations in both acid and base electrolyzed samples were found to agree well with the lattice spacings for Ni₅P₄ from PXRD (see ESI), while not agreeing with any of the other low temperature nickel phosphide or nickel oxide phases, thus precluding the formation of new phases. Surface analysis by SEM-EDXS at multiple locations gave the average composition: Ni₅.01P₄.19 and Ni₅.02P₄.20 after electrolysis in acid and base, respectively, further confirming retention of the initial catalyst composition. SEM images also corroborate the unchanged range of particle sizes and morphology between samples electrolyzed in acid and base (see Fig. 5(D) and (E)). All lines of evidence indicate chemical and electrochemical stability of Ni₅P₄ in both acid and base.

![HRTEM images](image.png)

**Fig. 5** HRTEM after 6 hr CP analysis at -10 mA/cm² in (A) 1 M H₂SO₄ and (B) 1 M NaOH, and (C) shows Ni₅P₄ before CP analysis, scale bar 5 nm. SEM images after 6 hr CP analysis at -10 mA/cm² in (D) 1 M H₂SO₄ and (E) 1 M NaOH, scale bar 2 μm.

### 3. Discussion:

The observed Tafel slope of 33 mV/dec in acid for Ni₅P₄ MPs can be compared to theoretical expressions derived for H₂ formation kinetics on an idealized planar surface having a single catalytic site in aqueous acid (such as crystalline Pt)\(^{39}\). Within the experimental uncertainty, the measured Tafel slope is comparable to the limiting Tafel slopes of 29 and 39 mV/dec. By contrast, a Tafel slope of 118 mV/dec is theoretically predicted when the RLS is the capture of a hydronium ion from solution and an electron from the metal conducting band onto an empty site (the discharge reaction), which therefore can be excluded as the RLS.

According to previously published electronic structure calculations (DFT) on Ni₅P \(^{110}\), the HER mechanism in acid could proceed in three steps as shown in Fig. 6A. The first step (I) is the energetically favored electron transfer to a proton bound to a trigonal Ni₃ site, the second step (II) is an electron transfer to a bridging proton at a Ni–P bond—this step was identified as being the rate-determining HER step\(^{28}\). The nature of the RDS suggests that the Ni–P bond length could be a reasonable reactivity descriptor—as increase of this bond length will favor greater electron localization on the P and therefore reduce the barrier to proton binding (greater basicity than Ni).
In summary, we have shown that Ni₅P₄ MPs exhibit exceptionally high TOFs, greater than that of Ni₅P NPs in 1 M H₂SO₄ and 1 M NaOH and the previously reported value for NiMo NPs in 1 M NaOH, in combination with low electrical impedance losses and high corrosion resistance during electrolysis. Ni₅P₄ also exhibits indistinguishable rate-limiting kinetics compared to Pt in acid at low current densities. This combination of superior efficiency and stability in both strong acid and strong alkali is unique among earth-abundant HER electrocatalysts and makes Ni₅P₄ a promising candidate for the future development of renewable H₂ via water splitting.

5. Experimental:
5.1. Catalyst synthesis: Nanoparticulate Ni₅P and Ni₅P₄ were synthesized by a solvothermal method starting from nickel acetate and tri-octylphosphine using octylether/oleylamine and tri-octylphosphine oxide as solvents. Details are given in ESI.

5.2. Electrochemical testing: Electrochemical cells were pre-cleaned in piranha (1:3 35% H₂O₂ and conc. H₂SO₄) and after chronopotentiometric testing of Pt, in aqua regia, prior to the piranha cleaning. CV and CP analyses were conducted in a three-compartment cell with glass-frit separating the compartments. A luggin compartment holds the reference electrode. A boron-doped diamond thin-film counter electrode (~1 cm², elementsix) and a home-made Ag/AgCl (3 M KCl) reference electrode were used. The working compartment was purged with 1 atm. H₂ prior to and during measurements. Working electrodes were made from 50 mg nickel phosphide powder, pressed into pellets (6 mm diameter) under 5 tons, back-connected to Ti-foil with Ag-paste (SPI), attached to a copper wire, and sealed in a glass tube with Loctite Hysol 1C epoxy exposing an electrode area of ~0.02–0.04 cm².

All electrochemical potentials are reported vs. the reversible hydrogen electrode (RHE) by measuring the open circuit potential of a clean Pt electrode under 1 atm. H₂ in the electrolyte of interest at each pH. Potentials measured by CV are further corrected for IR-drop, while CP measurements are corrected only for pH and reference potential (not uncompensated IR drop).

5.3. Faradaic efficiency: Product measurements are conducted in a 1 compartment cell using a B-doped diamond counter electrode in a two-electrode configuration. A charge of 6 C at 1.96 mA corresponding to j ~10-100 mA/cm² depending on the electrode area. Prior to measurements the electrode was preconditioned by passing 6 C at the above conditions, followed by Ar purging for ≥ 20 min. H₂ (and O₂) in the headspace were quantified by gas chromatography (GC). Commercial Pt nanoparticles supported on Vulcan carbon and dispersed in Nafion composite was used for comparison of faradaic efficiencies (see ESI for this electrode preparation). The faradaic yields of 89-92% were obtained for Pt.

5.4. Elemental analysis: ICP-OES (Perkin-Elmer Optima 7100) was used for the elemental analysis of the electrolyte at selected times during CP measurement, this was used to determine the leaching of Ni from the Ni₅P₄ and Ni₅P pellet electrodes (see ESI for details).
Acknowledgements
The authors acknowledge funding from the AFOSR contract FA9550-11-1-0231, NATCO Pharma, NSF-MRSEC (DMR-0819860) to the Princeton Center for Complex Materials (N.Y.) for imaging facilities, and Rutgers University for a fellowship to ABL.

Notes and references

Water splitting, powered by renewable electricity, is promising for producing clean hydrogen. Unfortunately, renewable energy coming from either sunlight or wind power is ill correlated with consumer demand, hence requiring storage, e.g. as a fuel in the form of hydrogen. Water splitting may be carried out electrocatalytically in electrolysers using electricity from photovoltaics or wind power. However, acidic electrolysers use scarce PGM metal catalysts (often Pt) for the hydrogen evolution reaction (HER). Although platinum is highly efficient, research efforts are directed towards replacing this catalyst with more earth abundant materials. State of the art alkaline electrolysers use Ni-based catalysts but show lower efficiencies due to inefficient catalysis and therefore have high operating costs. Recently, transition metal phosphides, especially of Ni and Co, have been shown to be promising for the replacement of platinum in acidic solutions. While these materials are cheap, abundant, and active for the HER, not all forms are stable during catalysis. This paper shows that a new member of this family, Ni₅P₄, show an excellent activity, not only in acid, but also in alkali as well as being stable during electrolysis.