

Non-precious metal hydrogen catalyst in commercial polymer electrolyte membrane electrolyzers

Authors:

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Abstract:

We demonstrate the translation of a low cost, non-precious metal cobalt phosphide (CoP) catalyst from 1 cm² lab-scale experiments to a commercial-scale 86 cm² polymer electrolyte membrane (PEM) electrolyser. A 2-step bulk synthesis was adopted to produce CoP on a high surface area carbon support that was readily integrated into an industrial PEM electrolyser fabrication process. The performance of the CoP was compared head-to-head with a platinum-based PEM under the same operating conditions (400 psi, 50 °C). CoP was found to be active and stable, operating at 1.86 A.cm⁻² for >1700 hours of continuous hydrogen production while providing substantial material cost savings relative to platinum. This work illustrates a potential pathway for non-precious hydrogen evolution catalysts developed in past decades to translate to commercial applications.

Main Text:

The modern-day commercialisation of large-scale polymer electrolyte membrane (PEM) water electrolyzers represents the culmination of decades of fundamental scientific studies involving catalysts, membranes, electrode architectures, and membrane electrode assemblies (MEAs) among other key advancements. Commercial PEM electrolyzers utilise expensive platinum group catalysts such as platinum and iridium, despite their high costs and scarcity, to achieve and maintain high activity over 50,000 h. Terawatt-scale deployment of electrolyzers envisioned for grid resilience require significant reduction of platinum group catalysts and/or replacement by alternative non-platinum group (NPG) catalysts within the device ¹. This goal presents many challenges, including the need to tailor catalyst inks, tune deposition methods, and provide stable activity at elevated temperatures, pressures, and current densities, all while demonstrating high activity and durability over the lifetime expected of a commercial system. In this study, we bridge the gap between decades of lab-scale, solution-based, NPG catalyst development and industrial-scale electrolyser operation. We report the integration of a highly active NPG catalyst (cobalt phosphide, CoP) into a commercial grade PEM electrolyser with >1700 hours of continuous operation and negligible loss in activity. We briefly discuss the economic trade-off of replacing the traditional Pt cathode with a NPG catalyst while emphasising the promise of NPG materials to supersede precious metal catalysts in commercial PEM electrolyzers.

Recent technoeconomic analyses suggest that PEM electrolysis is a promising technology for widespread renewable hydrogen production, hinging on capital cost reductions that would make this technology competitive in the hydrogen market ¹. Overcoming this challenge requires cost reductions across many system components, demanding substantial innovation in material design, engineering, and manufacturing. Reducing precious metal content has been a major R&D effort among manufacturers of PEM electrolyzers, as doing so would reduce capital costs while also mitigating issues of material scarcity. While Pt and Ir catalysts constitute ~8% of the total stack cost today, price inelasticity, and therefore volatility, of these precious metals hinder future TW-scale deployment of PEM electrolysis ². This motivates the development of active and stable NPG hydrogen evolution reaction (HER) catalysts, the best-case scenario for reducing Pt content in PEM electrolyzers.

Inspired by hydrogen-producing enzymes such as nitrogenase, molybdenum disulphide (MoS_2) emerged as one of the first promising NPG HER catalysts ^{3,4}. Subsequently, researchers pursued similar classes of materials, including transition metal phosphides, which exhibit favourable activities and stabilities in lab scale demonstrations ⁵⁻⁷. Significant advances in the activities of NPG catalysts have been accomplished by tuning the morphology, chemical composition, and crystal structure via synthesis methods ^{5,6}. Universal to nearly all published NPG HER literature are the electrochemical testing protocols used to measure catalyst activity and stability (linear sweep voltammetry, cyclic voltammetry, chronoamperometry, and/or chronopotentiometry) ⁸. Such methodologies provide figures of merits such as onset potential, exchange current densities, and Tafel slopes which enable benchmarking, as well as provide insightful fundamental knowledge. However, relatively few studies have translated NPG catalysts to PEM electrolyser devices ⁹⁻¹² and to the best of our knowledge, there are no reports demonstrating their integration in commercial-scale systems at relevant sizes, current densities, pressures, and temperatures.

CoP synthesis and characterisation. Herein, to the best of our knowledge we report the first translation of a NPG HER catalyst into a commercial-scale PEM electrolyser. Thanks to the development efforts of many, there were a multitude of potential NPG catalyst candidates ^{5,13,14}. For this initial demonstration we selected CoP, as experimental and theoretical studies have shown it to have promising HER activity in the acidic environments relevant for PEM electrolyzers ¹⁵⁻¹⁹. The CoP was prepared by wetness impregnation of cobalt nitrate onto Vulcan carbon followed by vapour phase phosphidation. The phosphidation step was adapted from a previous report wherein a CoP thin film was fabricated on a silicon substrate ¹⁸. The direct growth of the phosphide on the carbon support facilitates mechanical adhesion of the catalyst to the substrate and enhances uniform electrical conductivity and dispersion of the catalyst ⁶. Our simple 2-step synthesis produced >1.1 gram powder catalyst batch sizes, amenable to MEA fabrication using ink-based methods. This method has the potential for orders of magnitude scale-up, as batch size was only limited by the reactor size employed. Synthetic details are provided in the supplementary information.

Shown in Fig. 1A is the X-ray diffraction (XRD) pattern of the as-synthesised catalyst, confirming that our developed method generates a phase-pure catalyst (FeAs-type CoP). X-ray photoelectron spectroscopy (XPS) of the as-prepared catalyst shows the presence of CoP, cobalt oxide, and phosphate species (Supplementary Fig. 1), which are commonly reported for CoP²⁰. The loading of CoP on the Vulcan carbon support was ~21wt% with a Co:P molar ratio of 1:1, determined using inductively coupled plasma mass spectrometry (ICP-MS) (Supplementary Tables 1-2).

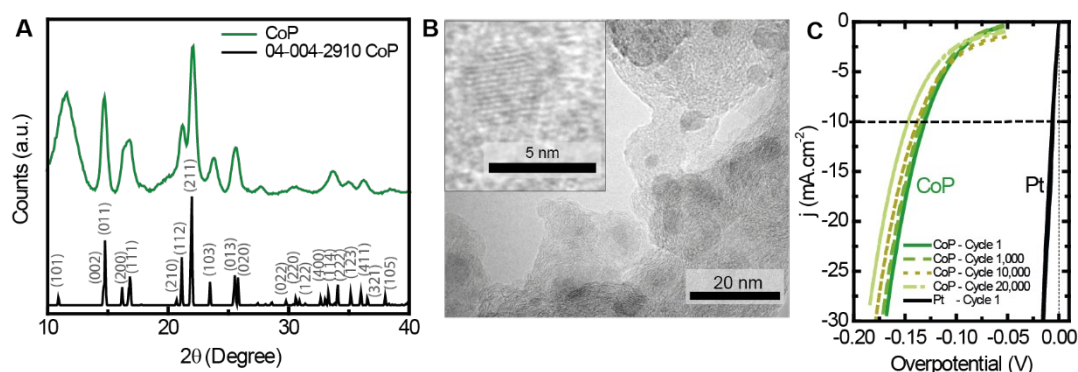


Fig. 1. Physical and electrochemical characterisation of the CoP catalyst. (A) Powder XRD of the CoP sample (green solid line) and reference pattern (black solid line). (B) TEM micrograph. Inset shows a higher magnification micrograph of a CoP nanoparticle. (C) Linear sweep voltammograms (LSVs) (iR-corrected) of the CoP catalyst ($0.12 \text{ mg}_{\text{CoP}}.\text{cm}^{-2}$) and commercial Pt catalyst ($0.12 \text{ mg}_{\text{Pt}}.\text{cm}^{-2}$) drop cast onto carbon paper and tested in a 3-electrode electrochemical cell in $0.5 \text{ M H}_2\text{SO}_4$. LSVs are shown for the as-prepared CoP (green coloured lines) and commercial Pt (black solid line, cycle 1), as well as after 1,000, 10,000 and 20,000 cycles of accelerated cyclic voltammograms for the CoP catalyst.

The morphology of the catalyst was examined with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Fig. 1B and Supplementary Fig. 2). TEM enables clear identification of CoP nanoparticles with an average diameter of ~5 nm (Fig. 1B). HR-TEM (Fig. 1B inset) confirms lattice plane spacing of 2.5 \AA which matches FeAs-type CoP (111)¹⁶. Lower magnification TEM micrographs show that CoP is well-dispersed on the Vulcan carbon support (Supplementary Fig. 3). Thus, we report a facile synthesis route, consisting of simple precursors and few processing steps, which yields a high surface area nanoparticulate CoP catalyst that is amenable to scaled-up MEA fabrication requiring minimal technical changes.

Lab-scale activity and durability. Lab-scale measurements, in acidic electrolyte (Fig. 1C) revealed excellent activity and stability of the CoP catalyst (Supplementary Figs. 4-5), in-line with previous studies ^{21,22}. For comparison, the activity of a commercial Pt catalyst of similar loading is also shown (Fig. 1C). While the activity of the CoP catalyst does not rival that of Pt, CoP showed little degradation under lab-scale cyclic voltammetry durability testing conditions and reasonable onset potentials. It is well known that 3-electrode stability measurements do not necessarily translate into MEA stability ²³⁻²⁵, which motivated further examination of the CoP catalyst in a MEA. Although CoP is not the most active catalyst in the literature ⁵, it represents a platform for performing these initial and important feasibility screenings of NPG catalysts within a commercial-grade electrolyser, motivating exploration of other NPG catalysts within these systems.

Commercial-scale activity and durability. To fabricate cathode gas diffusion electrodes (GDEs), the catalyst was dispersed in a suspension of Nafion ionomer, IPA, and water, then spray coated onto carbon paper gas diffusion layers. The anode GDE used IrO_x as the baseline material, a known durable catalyst, which isolated any observed performance changes in the electrolyser to the NPG cathode. A Nafion 117 proton exchange membrane was used in the MEA, placed between the anode and cathode GDEs. The MEAs were assembled in Proton OnSite's commercial 86 cm² active area PEM-electrolyser cell stack (Fig. 2A) along with a baseline all-PGM cell (Pt black-based GDE) for direct comparison under identical operating conditions. All tests were conducted at 400 psi hydrogen differential pressure and at elevated temperatures with liquid water fed to the anode side of the cell. Supplementary Table 3 highlights the distinct differences between the 3-electrode lab-scale setup and the commercial-grade testing protocol.

The CoP catalyst was loaded at 1.0 mg_{CoP}.cm⁻² on the GDE, equivalent to 4.5 mg.cm⁻² total catalyst loading including the carbon support. The electrolyser was first characterised by stepping the current from 100 mA.cm⁻² (1.54V) to 1.86 A.cm⁻² (2.27 V) at 50 °C (Fig. 2B). Interestingly, the polarisation curve shows this non-precious catalyst can reach the same high current densities as the Pt-containing cell at reasonable potentials. Assuming that every unit of CoP is active for the HER, a conservative estimate for the turnover frequency (TOF) of CoP is 0.87 H₂.s⁻¹. More likely, only the surface bound CoP units (~10 %) participate in the reaction, leading to an estimated TOF_{avg} of 8.7 H₂.s⁻¹. Comparatively, the TOF for the Pt

catalyst is estimated to be $1.88 \text{ H}_2\cdot\text{s}^{-1}$ conservatively, or $28.8 \text{ H}_2\cdot\text{s}^{-1}$ assuming only surface atoms participate in the reaction. Details of the calculations are shown in the supplementary information.

The all-PGM baseline GDE shows that the Pt PEM required 2.05 V to reach a current density of $1.86 \text{ A}\cdot\text{cm}^{-2}$ (Fig. 2B). This result reflects operating efficiencies of 55% and 61% respectively for the CoP- and Pt-based electrolyzers based on the lower heating value (see supplementary information for details). While the fact that the Pt system performs 220 mV better than the NPG catalyst is not surprising given the 3-electrode measurements (Fig. 1C), this small difference is impressive considering the commercially relevant high current densities employed. Future work will explore electrode engineering to maximise the performance of NPG based electrolyzers. Optimisation of catalyst loading and ionomer content, for example, will only help to narrow the performance gap between PGM and NPG catalysts in commercial electrolyser platforms. This gap will continue to shrink as NPG catalysts themselves are further improved, minimising the trade-offs between operating and capital costs¹⁴.

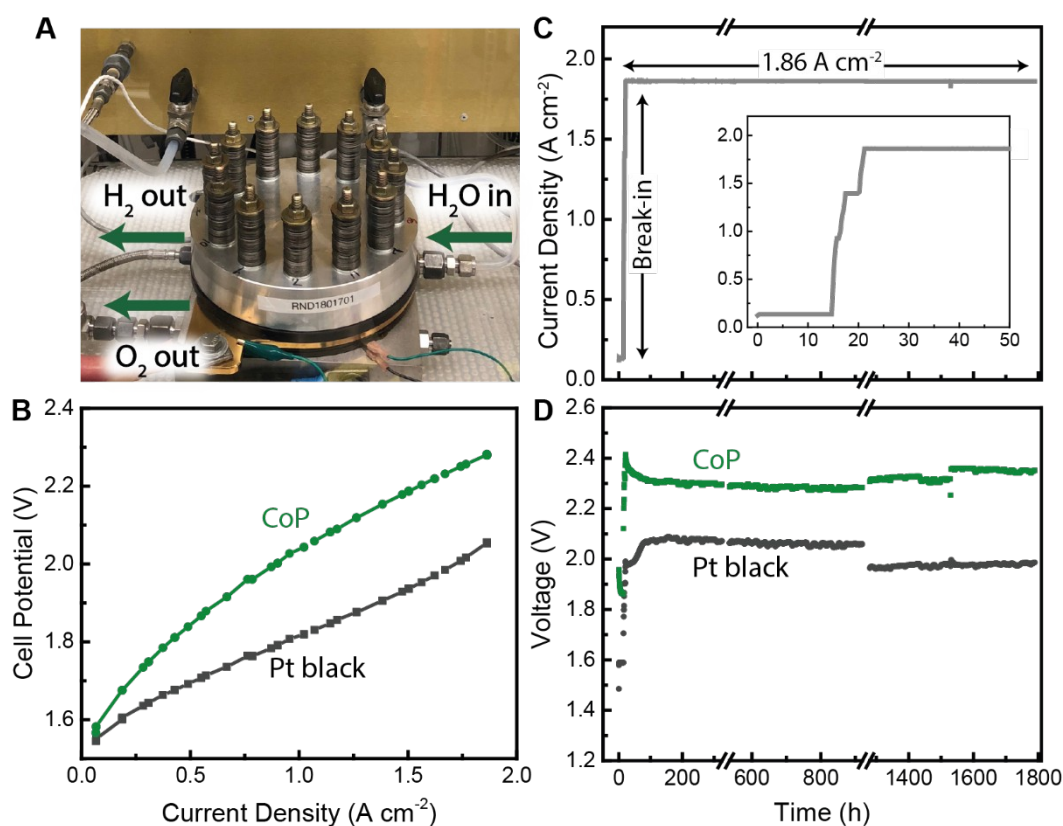


Fig. 2. Polymer electrolyte membrane electrolyser performance. (A) Photograph of the 86 cm² electrolyser test station. (B) Polarisation curve. (C) Current density profile for the

durability protocol. The inset shows the current density profile for the break-in period only. (D) Durability voltage-time plots for the PEM electrolyser prepared with $1.0 \text{ mg}_{\text{CoP}}.\text{cm}^{-2}$ loading while operating at $50 \text{ }^{\circ}\text{C}$ and 400 psi. Voltage discontinuities result from power outage-induced restarts. CoP data is shown in green; Pt black data is shown in black.

The CoP and Pt-based MEA durability tests were also conducted in the 2-cell stack following the polarisation studies. The differences in operating conditions between the 2-electrode and 3-electrode stability measurements are noted in Supplementary Table 3. The tests were initiated at $50 \text{ }^{\circ}\text{C}$ and held at $0.135 \text{ A}.\text{cm}^{-2}$ for $\sim 20 \text{ h}$ (Fig. 2C and 2D). After 20 h of operation, the temperature was ramped to $55 \text{ }^{\circ}\text{C}$ and the current was increased to $1.86 \text{ A}.\text{cm}^{-2}$ over 6 h. The current density was subsequently held at $1.86 \text{ A}.\text{cm}^{-2}$ for the remaining 1763 h of testing. During the durability measurement, the CoP MEA stabilised within 50 h to provide steady operation at 2.30 V for $>900 \text{ h}$ with energy consumption of $60.4 \text{ kWh}.\text{kg}_{\text{H}_2}^{-1}$. The Pt-based MEA operated under the same conditions ($1.86 \text{ A}.\text{cm}^{-2}$, $55 \text{ }^{\circ}\text{C}$, 400 psi) at 2.06 V as expected without degradation, corresponding to energy consumption of $54.5 \text{ kWh}.\text{kg}_{\text{H}_2}^{-1}$. Transient behaviour in the break-in phase is discussed in the supplementary information.

After 922 h of continuous testing, the 2-cell stack (CoP and Pt MEAs) lost power briefly ($<1 \text{ min}$) and was restarted. The reset resulted in an increase ($\sim 50 \text{ mV}$) in cell potential for the CoP MEA and a slightly reduced potential for the Pt MEA ($\sim 6 \text{ mV}$). A second, small abrupt increase in potential was observed after 1550 h of operation, likely due to a second disruption in the applied potential. Duplicate CoP and Pt MEAs were fabricated and tested with a similar protocol and were shown to be extremely stable with comparable cell potentials (Supplementary Fig. 6). Discussion of the MEA restarts and characterisation of the CoP GDE after the 1700 h durability test are provided in the supplementary information (Supplementary Fig. 7). Analogous to the fuel cell literature, it is important to note that Pt-based commercial PEM electrolysers are also known to degrade on start-up and shut-down cycling and hence this challenge is relevant for all known catalysts, precious metal and non-PGMs alike ²⁶.

In a 3-electrode lab-scale configuration, it has been reported that non-precious metal ionic compound catalysts such as transition metal phosphides dissolve at higher rates under open circuit potential conditions, but are stable when evolving hydrogen, even when cycling from low to high production rates ^{27,28}. This report is consistent with our lab-scale durability

measurements of CoP dissolution during electrochemical testing (Supplementary Figs. 8-9). We therefore postulate that CoP dissolution occurred when the MEA lost power briefly after 922 h and 1550 h of operation leading to the increased cell potential. Furthermore, we propose operating procedures that maintain a small operating current could prevent this degradation mechanism.

The CoP MEA produced a total of 10.1 kg of H₂ (912 L at standard temperature and pressure), and we conservatively estimate a turnover number of 5.3×10^6 H₂ molecules produced per CoP site assuming all CoP units are active thus evidencing the high stability of the catalyst. Details of the calculations are shown in the supplementary information. The CoP MEA requires 12 – 18 % greater power density than the Pt baseline MEA, a potentially attractive trade-off between electricity consumption and electrolyser capital cost depending on the application and the local cost of electricity. While this work highlights a significant step towards non-PGM catalyst incorporation in commercial electrolysers, the difference in performance between CoP and Pt is still too substantial for wide-scale commercial deployment, motivating continued research and development of non-PGM catalysts.

Analyses show that the levelised cost of hydrogen from water electrolysis is currently dominated by the cost of electricity^{29,30}. However, as society follows a path towards increased electrification and electricity prices drop, the capital cost of electrolysers will begin to dominate.³¹ Utilisation of durable, low-cost NPG catalysts that can replace expensive and price inelastic precious metals is one critical step towards reducing the overall capital cost of PEM electrolysis (Supplementary Table 4). While the result presented here is a significant achievement, we note that cost reductions across all system components are needed for TW-scale deployment of PEM electrolysers. A full techno-economic analysis on the implications of this report is outside the scope and will be the subject of future investigations.

Conclusions. Our initial demonstration of an active and highly stable NPG HER catalyst in a commercial-scale PEM electrolyser highlights the practical relevance of NPG systems. By extending our lab-scale stability study from liquid electrolyte and 1 cm² electrode area to an 86 cm² commercial PEM electrolyser with >1700 h of stable operation at elevated temperature and pressure, we demonstrate the commercial relevance of NPG catalysts. Compared to a Pt-based PEM, we found the CoP PEM to pay a 12 – 18 % power penalty under the operating conditions, but to provide a significant improvement in material cost over

the commercial Pt catalyst. We believe that the results represent a possible entry point for NPG catalyst utilisation in commercial water electrolyzers. Continued research efforts between industry and academia enables pathways to lowering the capital investment costs of PEM electrolyzers while maintaining high operating efficiencies to implement grid-scale energy storage.

References

1. Bertuccioli, L. *et al.* *Development of Water Electrolysis in the European Union.* (2014).
2. Vesborg, P. C. K. & Jaramillo, T. F. Addressing the terawatt challenge: Scalability in the supply of chemical elements for renewable energy. *RSC Adv.* **2**, 7933–7947 (2012).
3. Hinnemann, B. *et al.* Biomimetic Hydrogen Evolution: MoS₂ Nanoparticles as Catalyst for Hydrogen Evolution. *J Am Chem Soc* **36**, 5308–5309 (2005).
4. Jaramillo, T. F. *et al.* Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nanocatalysts. *Science (80-.)*. **317**, 100–102 (2007).
5. Callejas, J. F., Read, C. G., Roske, C. W., Lewis, N. S. & Schaak, R. E. Synthesis, Characterization, and Properties of Metal Phosphide Catalysts for the Hydrogen-Evolution Reaction. *Chem. Mater.* **28**, 6017–6044 (2016).
6. Shi, Y. & Zhang, B. Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. *Chem. Soc. Rev.* **45**, 1529–1541 (2016).
7. Kibsgaard, J. & Jaramillo, T. F. Molybdenum phosphosulfide: An active, acid-stable, earth-Abundant catalyst for the hydrogen evolution reaction. *Angew. Chemie - Int. Ed.* **53**, 14433–14437 (2014).
8. Mccrory, C. C. L. *et al.* Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **137**, 4347–57 (2015).
9. Corrales-Sánchez, T., Ampurdanés, J. & Urakawa, A. MoS₂-based materials as alternative cathode catalyst for PEM electrolysis. *Int. J. Hydrogen Energy* **39**, 20837–20843 (2014).
10. Ng, J. W. D. *et al.* Polymer Electrolyte Membrane Electrolyzers Utilizing Non-precious Mo-based Hydrogen Evolution Catalysts. *ChemSusChem* **8**, 3512–3519 (2015).
11. Di Giovanni, C. *et al.* Low-Cost Nanostructured Iron Sulfide Electrocatalysts for PEM Water Electrolysis. *ACS Catal.* **6**, 2626–2631 (2016).
12. Sun, X. *et al.* Earth-Abundant Electrocatalysts in Proton Exchange Membrane Electrolyzers. *Catalysts* **8**, 657 (2018).
13. Anantharaj, S. *et al.* Recent Trends and Perspectives in Electrochemical Water Splitting with an Emphasis on Sulfide, Selenide, and Phosphide Catalysts of Fe, Co, and Ni: A Review. *ACS Catal.* **6**, 8069–8097 (2016).
14. Xiao, P., Chen, W. & Wang, X. A Review of Phosphide-Based Materials for Electrocatalytic Hydrogen Evolution. *Adv. Energy Mater.* **5**, 1–13 (2015).

15. Liu, W. *et al.* A highly active and stable hydrogen evolution catalyst based on pyrite-structured cobalt phosphosulfide. *Nat. Commun.* **7**, 1–9 (2016).
16. Popczun, E. J., Read, C. G., Roske, C. W., Lewis, N. S. & Schaak, R. E. Highly active electrocatalysis of the hydrogen evolution reaction by cobalt phosphide nanoparticles. *Angew. Chemie - Int. Ed.* **53**, 5427–5430 (2014).
17. Kibsgaard, J. *et al.* Designing an improved transition metal phosphide catalyst for hydrogen evolution using experimental and theoretical trends. *Energy Environ. Sci.* **8**, 3022–3029 (2015).
18. Hellstern, T. R., Benck, J. D., Kibsgaard, J., Hahn, C. & Jaramillo, T. F. Engineering Cobalt Phosphide (CoP) Thin Film Catalysts for Enhanced Hydrogen Evolution Activity on Silicon Photocathodes. *Adv. Energy Mater.* **6**, 1501758 (2016).
19. Wu, Z., Huang, L., Liu, H. & Wang, H. Element-Specific Restructuring of Anion- and Cation-Substituted Cobalt Phosphide Nanoparticles under Electrochemical Water-Splitting Conditions. *ACS Catal.* **9**, 2956–2961 (2019).
20. Saadi, F. H. *et al.* Operando Spectroscopic Analysis of CoP Films Electrocatalyzing the Hydrogen-Evolution Reaction. *J. Am. Chem. Soc.* **139**, 12927–12930 (2017).
21. Yang, H., Zhang, Y., Hu, F. & Wang, Q. Urchin-like CoP Nanocrystals as Hydrogen Evolution Reaction and Oxygen Reduction Reaction Dual-Electrocatalyst with Superior Stability. *Nano Lett.* **15**, 7616–7620 (2015).
22. Zhou, D. *et al.* Interconnected urchin-like cobalt phosphide microspheres film for highly efficient electrochemical hydrogen evolution in both acidic and basic media. *J. Mater. Chem. A* **4**, 10114–10117 (2016).
23. Martens, S. *et al.* A comparison of rotating disc electrode, floating electrode technique and membrane electrode assembly measurements for catalyst testing. *J. Power Sources* **392**, 274–284 (2018).
24. Alia, S. M. *et al.* Activity and Durability of Iridium Nanoparticles in the Oxygen Evolution Reaction. *J. Electrochem. Soc.* **163**, F3105–F3112 (2016).
25. Alia, S. M. & Pivovar, B. S. Iridium-Based Nanowires as Highly Active, Oxygen Evolution Reaction Electrocatalysts. *ACS Catal.* **8**, 2111–2120 (2018).
26. Weiß, A. *et al.* Impact of Intermittent Operation on the Lifetime and Performance of a PEM Water Electrolyzer. *J. Electrochem. Soc.* **166**, 487–497 (2019).
27. Zhang, Y., Gao, L., Hensen, E. J. M. & Hofmann, J. P. Evaluating the Stability of Co₂P Electrocatalysts in the Hydrogen Evolution Reaction for Both Acidic and Alkaline Electrolytes. *ACS Energy Lett.* **3**, 1360–1365 (2018).
28. Ledendecker, M. *et al.* Stability and Activity of Non-Noble-Metal-Based Catalysts Toward the Hydrogen Evolution Reaction. *Angew. Chemie* **129**, 9899–9903 (2017).
29. James, B., Colella, W., Moton, J., Saur, G. & Ramsden, T. *PEM Electrolysis H₂A Production Case Study Documentation*. *PEM Electrolysis H₂A Production Case Study Documentation* (2013).
30. Babic, U., Suermann, M., Büchi, F. N., Gubler, L. & Schmidt, T. J. Critical Review—Identifying Critical Gaps for Polymer Electrolyte Water Electrolysis Development. *J. Electrochem. Soc.* **164**, F387–F399 (2017).
31. National Renewable Energy Laboratory (NREL). *H₂@Scale Workshop Report*. (2017).

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Author contributions:

L.A.K. and M.A.H. contributed equally to this work. L.A.K., M.A.H., and T.R.H. synthesised CoP catalysts. L.A.K. performed x-ray diffraction and scanning electron microscopy characterisation. E.V. performed transmission electron microscopy characterisation. M.A.H. performed electrochemical lab-scale characterisation and testing. C.C., J.M., and N.D. prepared all PEM stack components, assembled and tested the electrolyser, as well as collected all operational data. L.A.K. and M.A.H. contributed to data analysis, including preparation and revision of this manuscript.

Competing interests: The authors declare no competing interests.

Additional information:

Supplementary information is available in the online version of the paper. Reprints and permission information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to T. Jaramillo.

Figure captions:

Fig. 1. Physical and electrochemical characterisation of the CoP catalyst. (A) Powder XRD of the CoP sample (green solid line) and reference pattern (black solid line). (B) TEM

micrograph. Inset shows a higher magnification micrograph of a CoP nanoparticle. (C) Linear sweep voltammograms (LSVs) (iR-corrected) of the CoP catalyst ($0.12 \text{ mg}_{\text{CoP}}\cdot\text{cm}^{-2}$) and commercial Pt catalyst ($0.12 \text{ mg}_{\text{Pt}}\cdot\text{cm}^{-2}$) drop cast onto carbon paper and tested in a 3-electrode electrochemical cell in $0.5 \text{ M H}_2\text{SO}_4$. LSVs are shown for the as-prepared CoP (coloured lines) and commercial Pt (black solid line, cycle 1), as well as after 1,000, 10,000 and 20,000 cycles of accelerated cyclic voltammograms for the CoP catalyst.

Fig. 2. Polymer electrolyte membrane electrolyser performance. (A) Photograph of the 86 cm^2 electrolyser test station. (B) Polarisation curve. (C) Current density profile for the durability protocol. The inset shows the current density profile for the break-in period only. (D) Durability voltage-time plots for the PEM electrolyser prepared with $1.0 \text{ mg}_{\text{CoP}}\cdot\text{cm}^{-2}$ loading while operating at $50 \text{ }^\circ\text{C}$ and 400 psi. Voltage discontinuities result from power outage-induced restarts. CoP data is shown in green; Pt black data is shown in black.)

Data availability statement: The x-ray diffraction reference pattern is available from the Materials Project database under the ID mp-22270. Source data for figures is provided along with the paper as a supplemental file. Additional data that supports the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Methods

Materials and Methods:

Materials. All chemicals and materials were used as received. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 99% pure, Acros Organics) and red phosphorus (powder, 99.99%, Aldrich) were used as catalyst precursors. Vulcan carbon (Vulcan XC 72, Fuel Cell Store) was used as the catalyst support. IPA (99.99%, HPLC grade, Fisher Chemical) and Nafion perfluorinated resin aqueous dispersion (10wt% in H_2O , Sigma-Aldrich) were used to make catalyst inks, which were drop cast onto carbon paper (Toray 120, PTFE treated, Fuel Cells Etc) for the lab scale electrochemistry testing. The $0.5 \text{ M H}_2\text{SO}_4$ electrolyte was prepared from concentrated sulfuric acid (99.999%, Aldrich). A graphite rod (<2 ppm impurities, Ted Pella) was used as the counter electrode during electrochemical testing. Hydrogen gas (99.999%, Airgas) was used during catalyst synthesis and electrochemical testing. A Pt catalyst (20wt% Pt on Vulcan XC-72, Premetek) was tested at the lab-scale for comparison to the CoP catalyst.

CoP Synthesis. The CoP catalyst was prepared via a red phosphorous-based vapour phase phosphidation method, which is a modified version of the method reported by Hellstern *et al.*¹ To prepare the catalyst, wetness impregnation of cobalt nitrate hexahydrate (0.96 g) was performed on Vulcan carbon (1.0 g). The mixture was dried at 90 °C for >2 h and divided between two porcelain boats. The precursors were heated in a three-zone furnace downstream of red phosphorus (0.5 g) in a ceramic boat while flowing 200 sccm of hydrogen gas. Simultaneously, the temperature of the red phosphorous was increased from 25 °C to 375 °C and the temperature of the two boats was increased from 25 to 450 °C in 1 h. The furnace was held at temperature for 4 h and subsequently cooled in 2 h to 25 °C.

Physical Characterisation. Powder x-ray diffraction (XRD) was performed using the D8 Venture (Bruker) with Mo K alpha radiation. Scanning electron microscopy (SEM) was performed with the FEI Magellan 400 XHR simultaneously in both secondary electron and back scattering electron modes. Transmission electron microscopy (TEM) was performed with the FEI Tecnai G2 F20 X-TWIN. Inductively coupled plasma mass spectrometry (ICP-MS) was performed with the Thermo Scientific* XSERIES 2. X-ray photoelectron spectroscopy (XPS) was performed using the PHI Versaprobe 3 with Al K alpha radiation.

Electrochemical Characterisation. The HER activity of the synthesised catalysts was assessed using a three-electrode electrochemical cell with H₂-purged 0.5 M H₂SO₄ as electrolyte, a graphite counter electrode, and a Hg|Hg₂SO₄ reference electrode. Catalyst inks were prepared by sonicating ~10 mg of catalyst (including the carbon) in 3 mL IPA with 6 µL Nafion for >30 min. The working electrodes were prepared by drop casting 0.12 mg of active catalyst (CoP or Pt) from the prepared ink solution onto 1 cm² carbon paper at ~60 °C on a hotplate.

To determine the HER activity of the catalysts, the potential was cycled between -0.05 V and -0.17 V vs. RHE for CoP and between 0 V and -0.05 V vs. RHE for Pt (the potential required for each catalyst to reach a current density of >30 mA.cm⁻²) at 10 mV.s⁻¹. All scans were corrected for the Ohmic resistance of the electrolyte. Catalyst stability was assessed by performing 1,000 potential cycles at 100 mV.s⁻¹ in the same potential window followed by a slow scan at 10 mV.s⁻¹. This was repeated such that the catalyst was cycled 20,000 times at 100 mV.s⁻¹. Degradation was quantified by comparing the difference in applied potential required to achieve -10 mA.cm⁻² for the first and last cyclic voltammograms. Stability was

also probed by chronopotentiometry in which the current was held at -20 mA.cm^{-2} for >180 hours. Slow CV scans (10 mV.s^{-1}) in the range $+0.1 \text{ V}$ to -0.17 V were collected at set intervals during the chronopotentiometry measurements.

Additional square-wave chronopotentiometry tests to simulate variable power supply conditions were conducted. In one experiment, the current density alternated between -100 mA.cm^{-2} and -2 mA.cm^{-2} each for 15-minute intervals for a total of 45 h. In another experiment, the current density alternated between -20 mA.cm^{-2} for 5 h and 0 mA.cm^{-2} for 1 h, for a total of 60 h. Degradation was quantified by the change in potential over time and the amount of Co and P dissolved in the electrolyte.

Electrolyser Setup. The test station used at Proton OnSite followed similar design elements to that of their commercial products to represent the most realistic test conditions. The stand has the capability of simulating relevant operating conditions: up to 80°C , 330 Amps, and 400 psi hydrogen generation pressures. Deionized water flowing at 510 mL.min^{-1} was used for electrolysis and purity was maintained with onboard polishing resins. Fabrication and safety of the test stands followed best practice and is audited annually by the safety committee for continued operation. All data collection was conducted through a proprietary acquisition system configured for monitoring electrochemical device operating parameters. Calibration of the sensors for the data acquisition system was performed as dictated by the manufacturer and can range from every 3-12 months, depending on the device requirements.

Methods Section References

1. Hellstern, T. R., Benck, J. D., Kibsgaard, J., Hahn, C. & Jaramillo, T. F. Engineering Cobalt Phosphide (CoP) Thin Film Catalysts for Enhanced Hydrogen Evolution Activity on Silicon Photocathodes. *Adv. Energy Mater.* **6**, 1501758 (2016).