Transition Metal Phosphide Based Seawater Electrolysis

Subjects: Chemistry, Applied

Contributor: Walid Tahri , Xu Zhou , Rashid Khan , Muhammad Sajid

Large-scale hydrogen (H_2) production is an essential gear in the future bioeconomy. Hydrogen production through electrocatalytic seawater splitting is a crucial technique and has gained considerable attention. The direct seawater electrolysis technique has been designed to use seawater in place of highly purified water, which is essential for electrolysis, since seawater is widely available.

seawater transition metal phosphides (TMPs) electrolysis catalysts

1. Introduction

Since high-purity water is required for electrolysis and seawater is widely available for hydrogen (H_2) production, extensive research has been performed to create direct seawater electrolysis technology. The quest for pure, renewable, and affordable energy has become essential to ensuring worldwide socioeconomic growth in light of the energy shortage and the need to protect the ecosystem [1][2][3][4]. Although freshwater makes up only 3.5% of the world's water resources, freshwater electrocatalytic splitting is regarded as a safe and effective way to generate adulterated H_2 [5]. Therefore, piezoelectric catalytic wastewater degradation may be achieved by utilizing the energy generated by water flow and low-frequency mechanical energy [6][7]. Several approaches for H_2 production and H_2 chemical materials storage have been established, but discovering an effective and secure method for H_2 production is still required. Asim et al. [8] developed the solid material ammonia borane (NH3BH3) as the most promising H_2 storage material. The same authors developed an amalgamation of gold nanoparticles with metal phosphides and speculated them to be effective catalysts (e.g., Au/Ni_2P and Au/CoP) to improve the H_2 evolution rate [9]. Moreover, in the long-term, the electrolysis of water processes that lead to H_2 generation may increase the likelihood of seawater electrolysis [10]. Simultaneously, seawater electrolysis encounters obstacles from the chlorine evolving reaction (CER) and the kinetically slow evolution reaction of oxygen (OER) when the total salinity is typically 3.5 weight percent and the pH is around 8 [11].

In addition, there are highly promising opportunities for developing inexpensive, effective, and efficient transition metals and their compounds to substitute for catalysts, based on noble metals. In particular, several transition metals, including transition metal phosphides (TMPs), transition metal oxides (TMOs), transition metal dihalides (TMDs), transition metal carbides (TMCs), and transition metal nitrides (TMNs), have shown high activity and stability. TMPs are considered a good alternative to rare metals because of their high electrical conductivity, strong durability against corrosion, as well as substantial catalytic activity. Therefore, due to their distinctive physicochemical properties, TMPs are one of the most intriguing potential electrocatalysts that break through the limits of being suitable. They have been extensively employed in numerous catalytic reactions in the fields of energy transformation and catalysis, such as photocatalytic hydrogen evolution [12]. Because of the availability of natural resources and their excellent conductivity, stability, and metal atom coordination effects, TMPs have received much attention recently [13][14]. Nevertheless, the working efficiency of TMP-based hydrogen evolution reaction (HER) catalysts continues to be impaired by some challenging and unresolved issues. It is still unclear whether active dopants deliver more active sites to enhance the activity of TMPs' occupant sites [15]. Recent research has revealed that seawater electrolysis has good characteristics and stability [16]. For instance, Wu et al. [11] and Liu et al. [16] constructed catalysts that showed outstanding activity and stability, such as (Ni_2P-Fe_2P). The same authors developed a CoPx@FeOOH catalyst, which was also stable for 80 hours at a high-level current of about 500 mA/cm^2 in 1.0 M KOH seawater with an overpotential of 283 mV for 100 mA/cm^2. Chang et al. [17] developed a Fe, P-$NiSe_2$ NF catalyst for gas phase chemical deposition, which displayed stability over eight days with a significant current density of about 800 mA/cm^2 at 1.8 V. Moreover, during unrestricted seawater circumstances, the open-circuit voltage for HER at 10 mA/cm^2 was 290 mV for the CoNiP/CoxP/NF catalyst [18].

Furthermore, TMPs are also potentially useful, non-noble electrochemical catalysts for the evolution reaction of H_2. Due to their excellent HER electrocatalytic efficiency, high conductivity, and durability against corrosion, TMPs have sparked great interest. TMPs are recognized as desirable HER catalyst components compared to other transition metal elements (e.g., metal sulfides) because of their abundant reserves, unique framework, variable composition, and outstanding electrical conductivity [15]. Recent studies have found that transition metal phosphides have exceptional stability and activity in seawater electrolysis. **Table 1** provides a quick overview of the characteristics of various recently developed TMP-based electrocatalysts. Although extensive work has been performed, there is still vast room to develop a stable, high-potential catalyst in order to produce sustainable hydrogen from seawater in the long-term.

Table 1. Transition metal-based electrocatalysts.

Type	Characteristics	References
Phosphides (TMPs)	The metal and P sites in TMPs function as hydride acceptors and proton acceptor centers. Metal phosphides exhibit excellent electrical conductivity when the right quantities and ratios of metal and phosphorus atoms are used. TMPs can also be produced by the use of elemental phosphorus at temperatures above 600 °C. TMPs demonstrated substantial activity and stability in seawater electrolysis. The electrochemical stability was greatly improved by the synergistic contribution of 3D pore structures, electronic effects, and conductive substrates.	[17][19][20][21]
Oxides (TMOs)	TMOs are regarded as effective HER catalysts due to their diverse crystal structures, resources, and significant catalytic activity, which may lead to Pt-like performance in HER. The amorphous structure offers more active sites for electrocatalytic reactions.	[22]
	The structure of metal oxide materials influences electrocatalytic performance as well. The amorphous material's atom arrangement can result in a large number of exposed surfaces and defects.	[23][24][25][26][27]

Type	Characteristics	References
	Due to their low activity and poor conductivity, they perform poorly when compared with comparable electrocatalysts. Defect engineering is a more promising approach for improving HER performance by making the edge sites available. It has been exploited by many researchers in diverse research fields, such as photocatalytic materials, rational design of NH3 semiconductor photocatalysts, and developments in SERS material design based on semiconductors. It can also be used to enhance the catalytic performance of 2D TMOs (e.g., 2D CeO_2)	
Dihalides (TMDs)	Can outperform other noble metal catalysts due to their high degree of chemical stability and adaptability across a wide range of pH values. The HER activity of TMDs can be increased by doping with both metallic atoms (e.g., Fe, Co, Ni) and non-metallic atoms (e.g., B, N, O), according to experiments and DFT calculations. They have great potential in ECR applications.	[28][29][30]
Carbides (TMCs)	The disordered structure, which provides a significant number of uncharged sulfur atoms as active sites for HER and a quasiperiodic arrangement of nanodomains for fast interdomain electron transport, is attributed to the excellent HER electrocatalytic activity (e.g., commercial Mo_2C in both acid/basic media). Aside from their high electrical conductivity, their properties of H_2 adsorption and d-band electronic density state (similar to Pt) show an optimal combination, which is thought to be the main factor for the observed high HER activity.	[31][32]
Nitrite (TMNs)	Very good at conducting electricity and resisting corrosion. Stable for seawater splitting. The vast majority of bulk TMNs that have been reported have HER activity that is listed below expectations due to a lack of hydrogen bonding energy.	[33][34][35]

2 [36] ions. The ion metal tellurides (TMTs) and phosphides (TMPs) for HER.

2. A synopsis of TMPs

Structure: Fundamental Concepts

Phosphides are the products created when phosphorus is combined with any d- (such as nickel (Ni), molybdenum (Mo), tungsten (W), cobalt (Co), and iron (Fe)) or f-metal. TMPs are resistant metallic substances with acidic as well as metallic sites [37][38]. The metal phosphides react quickly with water and moisture in the air or stored grain to form phosphine gas. Additionally, these materials have complicated structural characteristics and special chemical, physical, and electrical properties because of the crystal lattice interactions between the metal and phosphorus. Previous research on TMP structures can be found in the literature, as reported by [39][40].

TMPs have diverse characteristics that are influenced by several important criteria, including preparation method, P source, capping agent, heating rate, and so on, in addition to their morphology and particle size. TMPs have been used in a wide variety of catalytic reactions because of the versatile nature of their structures [41]. There are numerous methods for synthesizing TMPs outlined in the literature. These methods have been grouped into four different groups: (i) P solvothermal reactions, (ii) solution-phase reactions, (iii) gas–solid reactions, and (iv) other methods [42]. As described by Bhunia et al. [43], different TMP synthesis methods have distinct benefits and drawbacks based on various comparison criteria, including electrocatalyst surface area, TMP conductivity, and other parameters, as shown in **Table 2**.

Table 2. A brief review of the latest and most recent advanced methods for synthesizing transition metal phosphide-based catalysts.

Method of TMPs Synthesis	Advantages	Disadvantages	References
Metal Organic Framework (MOF)-derived methods	Control of morphology High surface area Composition control Doped carbon layer formation	Two steps with lab-scale synthesis methods	[43]
Wet chemical methods	Monodispersed particles Composition control Single-step methods	Difficult to control the reaction conditions as highly volatile solvent required	
Bulk conversion	Large-scale synthesis Composition control	Bulk microstructure Poisonous byproduct gas formation	
Phytic acid-derived methods	Large-scale synthesis Composition control Doped carbon layer formation	Microstructure optimization	

tal, which inhibits electron dispersion around the metal atom while enhancing metal-to-P electron transport. The difference between the M–P electronegativity and the M:P ratio determines the properties of the metal phosphide. TMPs, on the other hand, display a mix of covalent and ionic nature bonds due to minor differences in electronegativity. This results in a little positive charge (+) for the metal and a tiny negative charge (−) for the phosphorus. As a result, this unique bond has exceptional thermal and chemical stability as well as strength [44]. On the other hand, TMPs have high activities and good stability due to their earth-abundant resources [45][46][47].

Due to the stoichiometric ratio of metal to phosphorus in their chemical formula (metal-rich phosphides such as M_3P and M_2P, mono-metal phosphides such as MP, and phosphorus-rich metal phosphides such as MP_2 and MP_3), an additional approach to classifying TMPs is to split them into three categories: binary, ternary, and supported types [48], as shown in **Table 3**. In the open-source literature, several different nanostructures of binary TMPs have been discovered, involving CoP in the form of nanotubes, nanoparticles, nanosheets, and nanorods [49][50]; Co_2P in the form of nanoflowers, nanoparticles, and nanosheets [51][52]; Cu_3P in the form of nanoarrays and nanowires [53][54]; and MoP in the form of nanoflakes and nanoparticles [55][56]. Ternary phosphides are outstanding catalysts for various chemical reactions and exhibit interesting structures. They might be present in the form of nanowires $NiCo_2Px$ [57][58], porous NiCu-P [59][60][61], and core–shell CoMoP [62]. Several studies have addressed the use of supported TMPs and the difficulties associated with their chemistry in their use. These catalysts can behave in diverse forms, for example, alumina, silica, and carbon [63][64][65].

Table 3. Other Classifications of TMPs with their Performances.

Catalysts	Forms	Outcomes	References
		Binary phosphides	
CoP	Nanotube, nanoparticles, nanosheets, nanorods	Improved catalyst activity and stability through the synergetic effect of the bimetal. Has a rounded shape after phosphorization.	[49][50]
Co_2P	Nanoflowers, nanoparticles, nanosheets	Enhanced electrochemical performance. Highly active HER electrocatalyst. High redox reactivity in an alkaline system.	[51][52]
Cu_3P	Nanoarrays, nanowires	Much higher surface roughness and exposes more active sites. Acted as an energy-efficient, bifunctional catalyst electrode with high activity.	[53][54]
MoP	Nanoflakes, nanoparticles	The resulting electrode worked as an active catalyst for both OER and HER in an alkaline electrolyte. Contributes significantly to the high activity of the catalyst.	[55][56]
		Ternary phosphides	
$NiCo_2Px$	Nanowires	Interesting morphologies and catalytic performance may reveal long-term stability in all pH conditions. Exhibited impressive universal pH catalytic performance.	[57][58]
Ni–Fe–P	Nanocubes	At 350 °C, the catalyst displayed a distinctive porous nanocube morphology with a loose and uneven surface. It demonstrated excellent HER and OER activities as well as exceptional long-term stability. Exposed a greater number of active sites and ensured adequate contact between catalyst and electrolyte.	[66]
CoMoP NiCu-P	Core-shell, Porous	With a Faradaic efficiency (FE) of 92.5%, it demonstrated superior stability and HER performance in real seawater. The carbon shell’s high proton ability to absorb effectively raises HER performance.	[62]
NaH_2PO_2, TOP, Red P	Plethora of P sources	The electrode showed outstanding electrochemical stability, regardless of electrolyte pH, and high HER activity in a wide pH range.	[59][60][61]

Catalysts	Forms	Outcomes	References
Supported phosphides			
Alumina, silica	Alumina, silica	Al_2O_3 has a high water content of 30%, which causes the intrinsic oxidation of the metal and P in the TMPs.	[65]
Activated carbon	Activated carbon	Presence of micropores with poor mechanical stability. It can be modified through the electric potential to remove biogas such as H_eS. [22][27][37][46]	[63][64][67]
MCM-41, SBA-15	Mesoporous silica	High surface area and acid site density.	[68]

seawater electrolysis and achieve high-efficiency hydrogen production. Notably, the significant water electrolysis reaction is formed by two half-cell reactions, the evolution reaction of hydrogen (HER) and the evolution reaction of oxygen (OER) [69][70], and both depend on the electrolyte's pH [71]. This means that OER refers to oxidizing water at the anode, while HER refers to reducing water at the cathode to yield H_2. Additionally, water electrolysis, a thermodynamic chemical process, has an overall Gibbs free energy for hydrogen adsorption (ΔG_H*) value of about 237.2 Kj mol^{-1} [72].

In different pH environments, water decomposes according to Equations (1)–(4).

In acidic pH:

$$\text{Anode: } 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \qquad (2)$$

In basic pH:

$$\text{Anode: } 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad (3)$$

$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (4)$$

3.1. Characteristics of Seawater Catalytic Reaction

Seawater is generally rich in salts compared to freshwater, which complicates the electrolytic process [10][73]. The effects of different chemical elements (anions and cations) present in seawater on water electrolysis are discussed in the following paragraphs.

3.2. Complementary Effects of Complex Ions

Due to the presence of up to 3.5 wt% salts, seawater has strong ionic conductivity [74]. In seawater, ions of magnesium, sodium, chloride, potassium, calcium, and sulfate account for >99% of the total seawater ion content [75][76]. It is also estimated that artificial seawater has a dissolved solids content totaling approx. 35,000 ppm, of which sodium chloride (NaCl) makes up about 30,000 ppm. The composition of seawater is presented in **Table 4** [77][78].

Table 4. Main components (in ppm) of seawater.

Magnesium (Mg^{2+})	Chloride (Cl^{-})	Sodium (Na^{+})	Sulfate (SO_4^{2-})	Calcium (Ca^{2+})	Total Dissolved Salts (TDS)
1295	19,345	10,752	2710	416	35,000

Nevertheless, to simulate real seawater, it has also reportedly been claimed that some Mg^{2+}, Ca^{2+}, K^{+}, and SO_4^{2-} are added. Seawater's complex ion composition can boost its ionic conductivity, making seawater electrolysis more challenging. As the H^{+} is depleted, for example, the resultant OH combines with both cations (Ca^{2+} and Mg^{2+}) to produce insoluble precipitates of calcium oxide and magnesium oxide, respectively. These insoluble precipitates on the electrode surface could obstruct the reaction sites [71][79][80].

3.3. Effects of Complex Ions

Chloride ions can damage both anodes and cathodes in seawater. The active cores of the cathode side's catalysts are inhibited by chloride ions, slowing down the reaction and hastening the catalysts' deterioration [81]. However, because the chloride ions may take part in reduction events that are harmful to OER, considerable amounts of chlorine or hypochlorite may develop on the anode side [82]. The reduction processes of Cl^{-} at the anode side are described by Equations (5) and (6) [82][83].

$$\text{In acid pH medium: } 2Cl^{-} \rightarrow Cl_2 + 2e^{-} \qquad (5)$$

$$\text{In basic pH medium: } Cl^{-} + 2OH^{-} \rightarrow ClO^{-} + H_2O + 2e^{-} \qquad (6)$$

On the other hand, OER is more beneficial kinetically than CER [84]. The volt differential between CER and OER in the basic environment (blue area) is 0.490 V in the pH range of 7.5 to 14, but it decreases under acidic conditions. In these circumstances, OER should have an overpotential in an alkaline medium significantly lower than 0.49 V in an attempt to develop O_2 and prevent CER from producing hypochlorite ions (ClO^{-}).

References

1. Tian, X. Engineering bunched Pt-Ni alloy nanocages for efficient oxygen reduction in practical fuel cells. Science 2019, 366, 850–856.
2. Tian, X.; Lu, X.F.; Xia, B.Y.; Lou, X.W.D. Advanced electrocatalysts for the oxygen reduction reaction in energy conversion technologies. Joule 2020, 4, 45–68.
3. Yang, Y.; Yu, Y.; Li, J.; Chen, Q.; Du, Y.; Rao, P.; Li, R.; Jia, C.; Kang, Z.; Deng, P. Engineering ruthenium-based electrocatalysts for effective hydrogen evolution reaction. Nanomicro Lett. 2021, 13, 160.
4. Yu, Y.; Chen, Q.; Li, J.; Rao, P.; Li, R.; Du, Y.; Jia, C.; Huang, W.; Luo, J.; Deng, P.J. Progress in the development of heteroatom-doped nickel phosphates for electrocatalytic water splitting. J.

Colloid. Interface Sci. 2022, 607, 1091–1102.

5. Feng, S.; Yu, Y.; Li, J.; Luo, J.; Deng, P.; Jia, C.; Shen, Y.; Tian, X. Recent progress in seawater electrolysis for hydrogen evolution by transition metal phosphides. Catal. Commun. 2022, 162, 106382.
6. Wang, J.; Zhou, X.; Hao, J.; Wang, Z.; Huo, B.; Qi, J.; Wang, Y.; Meng, F. Sustainable self-powered degradation of antibiotics using Fe3O4@MoS2/PVDF modified pipe with superior piezoelectric activity: Mechanism insight, toxicity assessment and energy consumption. Appl. Catal. B 2023, 331, 122655.
7. Wang, Z.; Xiang, M.; Huo, B.; Wang, J.; Yang, L.; Ma, W.; Qi, J.; Wang, Y.; Zhu, Z.; Meng, F. A novel ZnO/CQDs/PVDF piezoelectric system for efficiently degradation of antibiotics by using water flow energy in pipeline: Performance and mechanism. Nano Energy 2023, 107, 108162.
8. Asim, M.; Zhang, S.; Wang, Y.; Maryam, B.; Sajid, M.; Shi, C.; Pan, L.; Zhang, X.; Zou, J.-J. Self-supporting NiCoP for hydrogen generation via hydrolysis of ammonia borane. Fuel 2022, 318, 123544.
9. Asim, M.; Maryam, B.; Zhang, S.; Sajid, M.; Kurbanov, A.; Pan, L.; Zou, J.-J. Synergetic effect of Au nanoparticles and transition metal phosphides for enhanced hydrogen evolution from ammonia-borane. J. Colloid. Interface Sci. 2023, 638, 14–25.
10. Dresp, S.R.; Dionigi, F.; Klingenhof, M.; Strasser, P. Direct electrolytic splitting of seawater: Opportunities and challenges. ACS Energy Lett. 2019, 4, 933–942.
11. Wu, L.; Yu, L.; Zhang, F.; McElhenny, B.; Luo, D.; Karim, A.; Chen, S.; Ren, Z. Heterogeneous bimetallic phosphide Ni2P-Fe2P as an efficient bifunctional catalyst for water/seawater splitting. Adv. Funct. Mater. 2021, 31, 2006484.
12. Hong, L.F.; Guo, R.T.; Yuan, Y.; Ji, X.Y.; Lin, Z.D.; Li, Z.S.; Pan, W.G. Recent progress of transition metal phosphides for photocatalytic hydrogen evolution. ChemSusChem 2021, 14, 539–557.
13. Wang, Y.; Kong, B.; Zhao, D.; Wang, H.; Selomulya, C. Strategies for developing transition metal phosphides as heterogeneous electrocatalysts for water splitting. Nano Today 2017, 15, 26–55.
14. Yu, F.; Zhou, H.; Huang, Y.; Sun, J.; Qin, F.; Bao, J.; Goddard, W.A., III; Chen, S.; Ren, Z. High-performance bifunctional porous non-noble metal phosphide catalyst for overall water splitting. Nat. Commun. 2018, 9, 2551.
15. Liu, D.; Xu, G.; Yang, H.; Wang, H.; Xia, B.Y. Rational Design of Transition Metal Phosphide-Based Electrocatalysts for Hydrogen Evolution. Adv. Funct. Mater. 2023, 33, 2208358.
16. Liu, D.; Ai, H.; Chen, M.; Zhou, P.; Li, B.; Liu, D.; Du, X.; Lo, K.H.; Ng, K.W.; Wang, S.P. Multi-phase heterostructure of CoNiP/CoxP for enhanced hydrogen evolution under alkaline and

seawater conditions by promoting H2O dissociation. Small 2021, 17, 2007557.

17. Chang, J.; Wang, G.; Yang, Z.; Li, B.; Wang, Q.; Kuliiev, R.; Orlovskaya, N.; Gu, M.; Du, Y.; Wang, G. Dual-doping and synergism toward high-performance seawater electrolysis. J. Adv. Mater. 2021, 33, 2101425.
18. Wu, L.; Yu, L.; McElhenny, B.; Xing, X.; Luo, D.; Zhang, F.; Bao, J.; Chen, S.; Ren, Z. Rational design of core-shell-structured CoPx@FeOOH for efficient seawater electrolysis. Appl. Catal. B 2021, 294, 120256.
19. Han, L.; Dong, S.; Wang, E. Transition-metal (Co, Ni and Fe)-based electrocatalysts for the water oxidation reaction. J. Adv. Mater. 2016, 28, 9266–9291.
20. Liu, G.; Wang, M.; Xu, Y.; Wang, X.; Li, X.; Liu, J.; Cui, X.; Jiang, L. Porous CoP/Co2P heterostructure for efficient hydrogen evolution and application in magnesium/seawater battery. J. Power Source 2021, 486, 229351.
21. Weng, C.C.; Ren, J.T.; Yuan, Z.Y. Transition metal phosphide-based materials for efficient electrochemical hydrogen evolution: A critical review. J. Catal. 2020, 13, 3357–3375.
22. Yang, T.; Xu, Y.; Lv, H.; Wang, M.; Cui, X.; Liu, G.; Jiang, L.J. Triggering the intrinsic catalytic activity of Ni-doped molybdenum oxides via phase engineering for hydrogen evolution and application in Mg/seawater batteries. ACS Sustain. Chem. Eng. 2021, 9, 13106–13113.
23. Anantharaj, S.; Noda, S. Amorphous catalysts and electrochemical water splitting: An untold story of harmony. Small 2020, 16, 1905779.
24. Bai, S.; Zhang, N.; Gao, C.; Xiong, Y. Defect engineering in photocatalytic materials. Nano Energy 2018, 53, 296–336.
25. Shi, R.; Zhao, Y.; Waterhouse, G.I.; Zhang, S.; Zhang, T. Defect engineering in photocatalytic nitrogen fixation. ACS Catal. 2019, 9, 9739–9750.
26. Song, G.; Cong, S.; Zhao, Z. Defect engineering in semiconductor-based SERS. J. Chem. Eng. 2022, 13, 1210–1224.
27. Jin, H.; Guo, C.; Liu, X.; Liu, J.; Vasileff, A.; Jiao, Y.; Zheng, Y.; Qiao, S.-Z. Emerging two-dimensional nanomaterials for electrocatalysis. Chem. Rev. 2018, 118, 6337–6408.
28. Deng, J.; Li, H.; Xiao, J.; Tu, Y.; Deng, D.; Yang, H.; Tian, H.; Li, J.; Ren, P.; Bao, X. Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS2 surface via single-atom metal doping. Energy Environ. Sci. 2015, 8, 1594–1601.
29. Hinnemann, B.; Moses, P.G.; Bonde, J.; Jørgensen, K.P.; Nielsen, J.H.; Horch, S.; Chorkendorff, I.; Nørskov, J.K. Biomimetic hydrogen evolution: MoS2 nanoparticles as catalyst for hydrogen evolution. J. Am. Chem. Soc. 2005, 127, 5308–5309.

30. Liu, X.; Xiao, J.; Peng, H.; Hong, X.; Chan, K.; Nørskov, J.K. Understanding trends in electrochemical carbon dioxide reduction rates. Nat. Commun. 2017, 8, 15438.
31. Zhang, X.; Huang, L.; Han, Y.; Xu, M.; Dong, S. Nitrogen-doped carbon encapsulating γ-MoC/Ni heterostructures for efficient oxygen evolution electrocatalysts. Nanoscale 2017, 9, 5583–5588.
32. Vrubel, H.; Hu, X. Molybdenum boride and carbide catalyze hydrogen evolution in both acidic and basic solutions. Angew. Chem. Int. Ed. Engl. 2012, 51, 12703–12706.
33. Tian, X.; Luo, J.; Nan, H.; Zou, H.; Chen, R.; Shu, T.; Li, X.; Li, Y.; Song, H.; Liao, S. Transition metal nitride coated with atomic layers of Pt as a low-cost, highly stable electrocatalyst for the oxygen reduction reaction. J. Am. Chem. Soc. 2016, 138, 1575–1583.
34. Tian, X.; Tang, H.; Luo, J.; Nan, H.; Shu, T.; Du, L.; Zeng, J.; Liao, S.; Adzic, R.R. High-performance core–shell catalyst with nitride nanoparticles as a core: Well-defined titanium copper nitride coated with an atomic Pt layer for the oxygen reduction reaction. ACS Catal. 2017, 7, 3810–3817.
35. Jin, H.; Liu, X.; Vasileff, A.; Jiao, Y.; Zhao, Y.; Zheng, Y.; Qiao, S.-Z. Single-crystal nitrogen-rich two-dimensional Mo5N6 nanosheets for efficient and stable seawater splitting. ACS Nano 2018, 12, 12761–12769.
36. Shah, S.S.A.; Khan, N.A.; Imran, M.; Rashid, M.; Tufail, M.K.; Rehman, A.U.; Balkourani, G.; Sohail, M.; Najam, T.; Tsiakaras, P. Recent Advances in Transition Metal Tellurides (TMTs) and Phosphides (TMPs) for Hydrogen Evolution Electrocatalysis. Menbranes 2023, 13, 113.
37. Ren, T.; Li, M.; Chu, Y.; Chen, J. Thioetherification of isoprene and butanethiol on transition metal phosphides. J. Energy Chem. 2018, 27, 930–939.
38. Lee, Y.-K.; Oyama, S.T. Bifunctional nature of a SiO2-supported Ni2P catalyst for hydrotreating: EXAFS and FTIR studies. J. Catal. 2006, 239, 376–389.
39. Bussell, M.E. New methods for the preparation of nanoscale nickel phosphide catalysts for heteroatom removal reactions. React. Chem. Eng. 2017, 2, 628–635.
40. Golubeva, M.; Zakharyan, E.; Maximov, A. Transition metal phosphides (Ni, Co, Mo, W) for hydrodeoxygenation of biorefinery products (a review). Pet. Chem. 2020, 60, 1109–1128.
41. Pu, Z.; Liu, T.; Amiinu, I.S.; Cheng, R.; Wang, P.; Zhang, C.; Ji, P.; Hu, W.; Liu, J.; Mu, S. Transition-metal phosphides: Activity origin, energy-related electrocatalysis applications, and synthetic strategies. Adv. Funct. Mater. 2020, 30, 2004009.
42. Alvarez-Galvan, M.C.; Campos-Martin, J.M.; Fierro, J. Transition metal phosphides for the catalytic hydrodeoxygenation of waste oils into green diesel. J. Catal. 2019, 9, 293.
43. Bhunia, K.; Chandra, M.; Sharma, S.K.; Pradhan, D.; Kim, S.-J. A critical review on transition metal phosphide based catalyst for electrochemical hydrogen evolution reaction: Gibbs free

energy, composition, stability, and true identity of active site. Coord. Chem. Rev. 2023, 478, 214956.

44. Shi, Y.; Li, M.; Yu, Y.; Zhang, B. Recent advances in nanostructured transition metal phosphides: Synthesis and energy-related applications. Energy Environ. Sci. 2020, 13, 4564–4582.
45. Huang, Y.; Hu, L.; Liu, R.; Hu, Y.; Xiong, T.; Qiu, W.; Balogun, M.-S.J.T.; Pan, A.; Tong, Y. Nitrogen treatment generates tunable nanohybridization of Ni5P4 nanosheets with nickel hydr (oxy) oxides for efficient hydrogen production in alkaline, seawater and acidic media. Appl. Catal. B 2019, 251, 181–194.
46. Liu, T.; Liu, H.; Wu, X.; Niu, Y.; Feng, B.; Li, W.; Hu, W.; Li, C. Molybdenum carbide/phosphide hybrid nanoparticles embedded P, N co-doped carbon nanofibers for highly efficient hydrogen production in acidic, alkaline solution and seawater. Electrochim. Acta 2018, 281, 710–716.
47. Lu, X.; Pan, J.; Lovell, E.; Tan, T.H.; Ng, Y.H.; Amal, R. A sea-change: Manganese doped nickel/nickel oxide electrocatalysts for hydrogen generation from seawater. Energy Environ. Sci. 2018, 11, 1898–1910.
48. Pei, Y.; Cheng, Y.; Chen, J.; Smith, W.; Dong, P.; Ajayan, P.M.; Ye, M.; Shen, J. Recent developments of transition metal phosphides as catalysts in the energy conversion field. J. Mater. Chem. 2018, 6, 23220–23243.
49. Yu, S.H.; Chua, D.H. Toward high-performance and low-cost hydrogen evolution reaction electrocatalysts: Nanostructuring cobalt phosphide (CoP) particles on carbon fiber paper. ACS Appl. Mater. Interfaces 2018, 10, 14777–14785.
50. Zeng, Y.; Wang, Y.; Huang, G.; Chen, C.; Huang, L.; Chen, R.; Wang, S. Porous CoP nanosheets converted from layered double hydroxides with superior electrochemical activity for hydrogen evolution reactions at wide pH ranges. Chem. Commun. 2018, 54, 1465–1468.
51. Huang, H.-B.; Luo, S.-H.; Liu, C.-L.; Yi, T.-F.; Zhai, Y.-C. High-surface-area and porous Co2P nanosheets as cost-effective cathode catalysts for Li–O2 batteries. ACS Appl. Mater. Interfaces 2018, 10, 21281–21290.
52. Ye, C.; Wang, M.Q.; Chen, G.; Deng, Y.H.; Li, L.J.; Luo, H.Q.; Li, N.B. One-step CVD synthesis of carbon framework wrapped Co2P as a flexible electrocatalyst for efficient hydrogen evolution. J. Mater. Chem. 2017, 5, 7791–7795.
53. Fan, M.; Chen, Y.; Xie, Y.; Yang, T.; Shen, X.; Xu, N.; Yu, H.; Yan, C. Half-cell and full-cell applications of highly stable and binder-free sodium ion batteries based on Cu3P nanowire anodes. Adv. Funct. Mater. 2016, 26, 5019–5027.
54. Liu, M.; Zhang, R.; Zhang, L.; Liu, D.; Hao, S.; Du, G.; Asiri, A.M.; Kong, R.; Sun, X. Energy-efficient electrolytic hydrogen generation using a Cu3P nanoarray as a bifunctional catalyst for hydrazine oxidation and water reduction. Inorg. Chem. Front. 2017, 4, 420–423.

55. Jiang, Y.; Lu, Y.; Lin, J.; Wang, X.; Shen, Z. A hierarchical MoP nanoflake array supported on Ni foam: A bifunctional electrocatalyst for overall water splitting. Small Methods 2018, 2, 1700369.
56. Lan, K.; Wang, X.; Yang, H.; Iqbal, K.; Zhu, Y.; Jiang, P.; Tang, Y.; Yang, Y.; Gao, W.; Li, R. Ultrafine MoP nanoparticles well embedded in carbon nanosheets as electrocatalyst with high active site density for hydrogen evolution. ChemElectroChem 2018, 5, 2256–2262.
57. Zhang, R.; Wang, X.; Yu, S.; Wen, T.; Zhu, X.; Yang, F.; Sun, X.; Wang, X.; Hu, W. Ternary NiCo2Px nanowires as pH-universal electrocatalysts for highly efficient hydrogen evolution reaction. J. Adv. Mater. 2017, 29, 1605502.
58. Liu, C.; Zhang, G.; Yu, L.; Qu, J.; Liu, H. Oxygen doping to optimize atomic hydrogen binding energy on NiCoP for highly efficient hydrogen evolution. Small 2018, 14, 1800421.
59. Asnavandi, M.; Suryanto, B.H.; Yang, W.; Bo, X.; Zhao, C. Engineering, Dynamic hydrogen bubble templated NiCu phosphide electrodes for pH-insensitive hydrogen evolution reactions. ACS Sustain. Chem. Eng. 2018, 6, 2866–2871.
60. Guan, Q.; Sun, C.; Li, R.; Li, W. The synthesis and investigation of ruthenium phosphide catalysts. Catal. Commun. 2011, 14, 114–117.
61. Park, J.; Koo, B.; Yoon, K.Y.; Hwang, Y.; Kang, M.; Park, J.-G.; Hyeon, T.J. Generalized synthesis of metal phosphide nanorods via thermal decomposition of continuously delivered metal−phosphine complexes using a syringe pump. J. Am. Chem. Soc. 2005, 127, 8433–8440.
62. Ma, Y.-Y.; Wu, C.-X.; Feng, X.-J.; Tan, H.-Q.; Yan, L.-K.; Liu, Y.; Kang, Z.-H.; Wang, E.-B.; Li, Y.-G. Highly efficient hydrogen evolution from seawater by a low-cost and stable CoMoP@C electrocatalyst superior to Pt/C. Energy Environ. Sci. 2017, 10, 788–798.
63. Berenguer, A.; Sankaranarayanan, T.; Gómez, G.; Moreno, I.; Coronado, J.; Pizarro, P.; Serrano, D. Evaluation of transition metal phosphides supported on ordered mesoporous materials as catalysts for phenol hydrodeoxygenation. Green. Chem. 2016, 18, 1938–1951.
64. Korányi, T.I.; Vít, Z.; Poduval, D.G.; Ryoo, R.; Kim, H.S.; Hensen, E.J. SBA-15-supported nickel phosphide hydrotreating catalysts. J. Catal. 2008, 253, 119–131.
65. Moon, J.-S.; Lee, Y.-K. Support effects of Ni2P catalysts on the hydrodeoxygenation of guaiacol: In situ XAFS studies. Top. Catal. 2015, 58, 211–218.
66. Xuan, C.; Wang, J.; Xia, W.; Peng, Z.; Wu, Z.; Lei, W.; Xia, K.; Xin, H.L.; Wang, D. Porous structured Ni–Fe–P nanocubes derived from a prussian blue analogue as an electrocatalyst for efficient overall water splitting. ACS Appl. Mater. Interfaces 2017, 9, 26134–26142.
67. Farooq, M. In-situ regeneration of activated carbon using electric potential swing desorption (EPSD) for carbon dioxide and hydrogen sulphide removal from biogas. Eng. Phys. Sci. Bioresour. Technol. 2018, 249, 125–131.

68. Wu, S.-K.; Lai, P.-C.; Lin, Y.-C.; Wan, H.-P.; Lee, H.-T.; Chang, Y.-H. Atmospheric hydrodeoxygenation of guaiacol over alumina-, zirconia-, and silica-supported nickel phosphide catalysts. ACS Sustain. Chem. Eng. 2013, 1, 349–358.
69. Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S.Z. Design of electrocatalysts for oxygen-and hydrogen-involving energy conversion reactions. Chem. Soc. Rev. 2015, 44, 2060–2086.
70. Lee, K.-G.; Balamurugan, M.; Park, S.; Ha, H.; Jin, K.; Seo, H.; Nam, K.T. Importance of entropic contribution to electrochemical water oxidation catalysis. ACS Energy Lett. 2019, 4, 1918–1929.
71. Yao, Y.; Gao, X.; Meng, X. Recent advances on electrocatalytic and photocatalytic seawater splitting for hydrogen evolution. Int. J. Hydrogen Energy 2021, 46, 9087–9100.
72. Morales-Guio, C.G.; Stern, L.-A.; Hu, X. Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. Chem. Soc. Rev. 2014, 43, 6555–6569.
73. Tong, W.; Forster, M.; Dionigi, F.; Dresp, S.; Sadeghi Erami, R.; Strasser, P.; Cowan, A.J.; Farràs, P. Electrolysis of low-grade and saline surface water. Nat. Energy 2020, 5, 367–377.
74. Niu, X.; Tang, Q.; He, B.; Yang, P. Robust and stable ruthenium alloy electrocatalysts for hydrogen evolution by seawater splitting. Electrochim. Acta 2016, 208, 180–187.
75. Ayyub, M.M.; Chhetri, M.; Gupta, U.; Roy, A.; Rao, C. Photochemical and photoelectrochemical hydrogen generation by splitting seawater. Chem. Eur. J. 2018, 24, 18455–18462.
76. Millero, F.J.; Feistel, R.; Wright, D.G.; McDougall, T.J. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. Deep Sea Res. I. Oceanogr. Res. Pap. 2008, 55, 50–72.
77. Esmaeilion, F. Hybrid renewable energy systems for desalination. Appl. Water Sci. 2020, 10, 84.
78. Kucera, J. Desalination: Water from Water; John Wiley & Sons: Hoboken, NJ, USA, 2019; Available online: https://www.perlego.com/book/992822/desalination-water-from-water-pdf (accessed on 22 May 2023).
79. Luo, W.; Yang, Z.; Li, Z.; Zhang, J.; Liu, J.; Zhao, Z.; Wang, Z.; Yan, S.; Yu, T.; Zou, Z. Solar hydrogen generation from seawater with a modified BiVO4 photoanode. Energy Environ. Sci. 2011, 4, 4046–4051.
80. Wang, C.; Shang, H.; Jin, L.; Xu, H.; Du, Y. Advances in hydrogen production from electrocatalytic seawater splitting. Nanoscale 2021, 13, 7897–7912.
81. Dionigi, F.; Reier, T.; Pawolek, Z.; Gliech, M.; Strasser, P. Design criteria, operating conditions, and nickel–iron hydroxide catalyst materials for selective seawater electrolysis. ChemSusChem 2016, 9, 962–972.

82. Khatun, S.; Hirani, H.; Roy, P. Seawater electrocatalysis: Activity and selectivity. J. Mater. Chem. 2021, 9, 74–86.
83. Okada, T.; Abe, H.; Murakami, A.; Shimizu, T.; Fujii, K.; Wakabayashi, T.; Nakayama, M. A bilayer structure composed of Mg|Co-MnO2 deposited on a Co(OH)2 film to realize selective oxygen evolution from chloride-containing water. Langmuir 2020, 36, 5227–5235.
84. Cook, T.R.; Dogutan, D.K.; Reece, S.Y.; Surendranath, Y.; Teets, T.S.; Nocera, D.G. Solar energy supply and storage for the legacy and nonlegacy worlds. Chem. Rev. 2010, 110, 6474–6502.

Retrieved from https://encyclopedia.pub/entry/history/show/114030