The Key Role of MOFs in Hydrogen Production from Seawater sing Alkaline Electrolysis: Mini Review

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Abstract:

Seawater electrolysis is an environmentally friendly and effective strategy for producing green hydrogen. However, a major drawback of electrochemical systems is that they are susceptible to damage from the aggressiveness of salty seawater. Therefore, a key parameter affecting the performance of the electrode is its resistance to this aggressive seawater. The development of metal-organic framework (MOF) electrocatalysts is a promising approach to solve the problems associated with direct alkaline seawater electrolysis. The use of Mg, Mo, Ni, and Ti in MOF-based catalysts can increase operational efficiency and reduce the cost of electrode materials for hydrogen production on an industrial scale. Thus, MOFs can be said to be an alternative to critical, expensive materials. In this review, we reviewed scientific literature between 2021 and 2026 on the use of MOFs in alkaline seawater electrolysis systems.

Keywords:

Metal–organic frameworks (MOFs); Alkaline seawater electrolysis; Electrocatalysts; Hydrogen production.

1. Introduction

Hydrogen generated by water electrolysis provides a clean energy carrier and high energy density, unlike conventional production from fossil fuels [1, 2]. The dependence of traditional electrolysis technologies on purified water, which is a limited resource, accounting for less than 1% of the planet's water supply, is an obstacle to their widespread application. Seawater electrolysis is emerging as a substitute in this situation, utilizing the most abundant water source in the world [3]. The complex chemistry of the marine environment poses significant technological obstacles to direct seawater electrolysis, despite its great potential. High concentrations of chloride ions, which feed the competing chlorine evolution reaction (ClER) at the anode, are the main barrier. In addition to producing hazardous byproducts and severely corroding electrode materials, ClER reduces the Faraday efficiency of the intended oxygen evolution reaction (OER). Furthermore, in alkaline systems, calcium and magnesium ions precipitate as insoluble hydroxides, such as Mg(OH)2 and Ca(OH)2. The life of the electrolyzer is significantly reduced as a result of the rapid deposition and blocking of catalytically active sites [4]. Although electrocatalysts are known to have high activity, they lack the required stability and selectivity. This is necessary for seawater separation, especially those based on noble metals such as ruthenium (Ru), iridium (Ir) and platinum (Pt). These metals are not applicable for industrial applications due to their high cost and limited availability. As a result, current research is focused on the creation of complex base metal catalysts that can support high current densities while withstanding the harsh conditions of saline electrolytes [5-7]. Due to their special structural characteristics, metal-organic frameworks (MOFs) have recently emerged as a revolutionary class of materials for seawater electrolysis. Due to their incredibly large surface areas, highly structured crystal structures, and variable porosity, MOFs allow for precise molecular engineering. To inhibit ClER and improve OER selectivity, their porous architectures can be carefully designed to preferentially pass water molecules while resisting hazardous ions such as chlorine. Furthermore, the synergistic effects between organic linkers and metal centers (such as Fe, Ni, Co, Mg, and Mo) offer a solid basis for the development of stable, multifunctional electrocatalysts that are economical and efficient [8-10].This mini review's objective is to examine the advancements in MOF-based electrocatalysts for alkaline seawater electrolysis throughout the previous five years. We discuss over MOFs as electrocatalyst, challenges to producing hydrogen from seawater via alkaline electrolysis, and future directions. The purpose of this work is to emphasize how important MOFs are to electrochemical alkaline seawater electrolysis systems.

2. MOFs as electrocatalyst for hydrogen production from seawater electrolysis

MOFs are a promising class of electrocatalysts that bridge the gap between homogeneous and heterogeneous catalysis. Their special crystal structure, which is composed of organic linkers coordinating metal nodes, offers a flexible structure to enhance the complex reactions involved in seawater splitting [11].

2.1. Structural advantages for seawater electrolysis

MOFs, due to their large electrochemically active surface area and high intrinsic porosity, are attractive for seawater electrolysis. The tunable pore size of MOFs can function as a “molecular sieve,” unlike bulky metal oxides. It is possible to sterically confine or repel larger or deleterious ions, including sulfates and chlorides, while facilitating the flow of water molecules and hydroxide ions to the active sites by careful design of the framework. To achieve high current densities at low overpotentials, these features offer a high density and accessible active sites [12].

2.2. Increasing selectivity and suppressing ClER

The competition between the OER and the ClER is the most significant barrier in alkaline seawater electrolysis (Figure 1). MOF electrocatalysts improve the efficiency of the reaction by modifying the electronic structure [13]. To promote the adsorption of OER intermediates, the coordination environment around the metal sites (such as Ni, Fe, and Co) can be controlled. According to recent studies, the addition of certain metals, such as titanium (Ti) or molybdenum (Mo), to the MOF lattice creates a protective barrier or negatively charged surface layer that electrostatically repels chlorine ions, resulting in an increased OER selectivity [14-15].

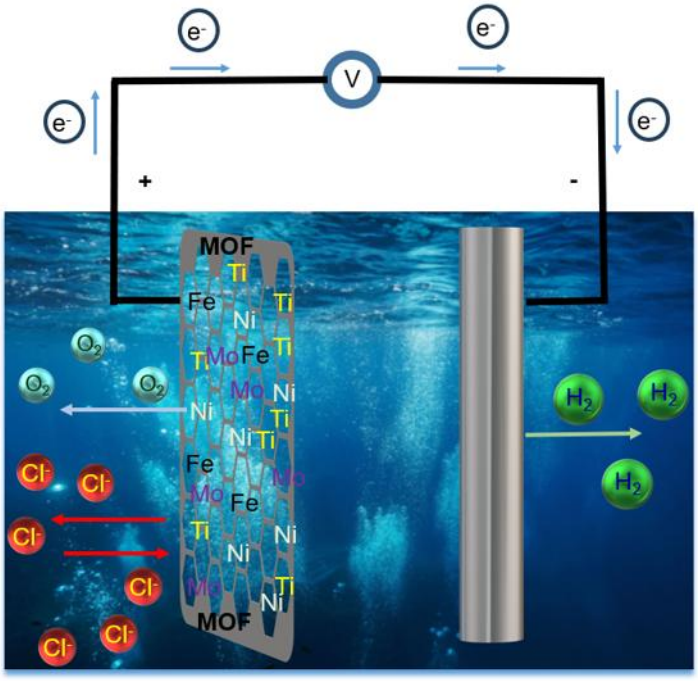

Figure 1. *Direct alkaline seawater electrolysis cell. The anode is functionalized with a multi-metal MOFs (Ni, Fe, Ti, Mo).*

2.3. MOF-Derived Electrocatalysts

It is important to note that many high-performance electrocatalysts are derived from MOFs. Thay can be transformed into metal phosphides, sulfides, or carbon-encapsulated metal nanoparticles by carefully regulated pyrolysis or phosphorization. These derivatives (Table 1) frequently have exceptional mechanical strength and electrical conductivity, both of which are necessary for long-term stability in the corrosive marine environment [16-17].

Table 1. *Examples of MOF electrocatalysts studied in the period 2021-2026.*

MOFs	Example	Reaction	Overpotential η mV	Advantage	Ref.
Pristine 2D	2D Ni/MOF	OER HER	70 – 350 mV	Maximum Atomic Utilization; Highly Tunable Electronic Structure; Rapid Mass and Charge Transport; Structural Flexibility for Composites; Defined Periodic Structure; Synergistic Bimetallic Effects.	[18]
Bimetallic	$NixFe_{1}–xSe_{2}$	Overall Water Splitting	OER - 310 mV / 100 mA cm^{-2} ; 390 mV / 500 mA cm^{-2} HER 189 mV / 100 mA cm^{-2} ; 315 mV / 500 mA cm^{-2}	Dual functionality; High current density; Optimized adsorption; Long-lasting durability.	[19]
MOF-Derived Phosphides	CoP/Fe_2P	Overall Water Splitting	HER 259/500 mA cm^{-2} OER 307 mV/500 mA cm^{-2}	*p-d* orbital coupling	[20]
MOF-Derived Sulfides	Mo–CuS/NiS/NF	HER	78 mV/ 10 mA cm^{-2}	Enhanced performance. Stability.	[21]
Hybrid Composites	$Ni_2P@CeO_2$	HER	HER 62 mV/10 mA/cm^{-2} OER 229 mV/10 mA/cm^{-2}	Stability in alkaline natural seawater over 100 h	[22]

3. Challenges to producing hydrogen from seawater via alkaline electrolysis

MOF-based electrocatalysts hold great promise for the large-scale commercialization of hydrogen generation from seawater, but several important challenges need to be addressed.

3.1. Anodic competition and chlorine evolution reaction

The key challenge is the kinetic and thermodynamic competition between the ClER and the OER [4]. The high concentration of chloride ions in seawater induces the formation of hypochlorite, which is extremely corrosive, although alkaline conditions theoretically promote OER. Catalyst degradation and reduced Faraday efficiency result from the continued inability of most MOFs to maintain 100% selectivity for extended periods of time [23-24].

3.2. Surface scaling and membrane fouling

Alkaline electrolysis leads to natural precipitation of insoluble hydroxides, primarily $Ca(OH)_2$ and $Mg(OH)_2$ as well. As physical barriers, these solids:

- Blocking of the active catalytic sites of the MOFs [25].
- Increasing the ohmic resistance of the cell [26].
- Obstruction of ion exchange membranes [27].

One significant engineering challenge is controlling this "scaling" effect without costly desalination or ongoing chemical cleaning.

3.3. Long-term stability of MOF structures

Research efforts have focused on the low stability of MOF electrocatalysts in saline conditions. The structure of the electrocatalyst used in alkaline seawater electrolysis must be able to chemically attack Cl^- ions and high pH. The rapid release of H_2 and O_2 bubbles can cause mechanical stress that can detach the MOF layers from the conductive support (such as nickel foam). It is still a challenge to develop MOF electrocatalysts that can withstand industrial current densities and retain their crystalline structure for thousands of hours [28].

4. Future directions

To move towards industrial implementation of seawater electrolysis based on MOF electrocatalysts, several strategic directions must be considered.

4.1. Innovative surface protection strategies

Improved surface engineering of MOF electrocatalysts is needed to counteract the formation of Mg/Ca precipitates and the corrosive behaviour of chloride ions. The rapid release of gas bubbles can be facilitated by designing hydrophobic/aerophilic surfaces that protect the MOF from physical damage. Furthermore, the creation of MOFs with specific “ion filter” shells or negatively charged functional groups could successfully repel Cl^- ions and prevent the accumulation of solid hydroxides on the catalytic surface [29-30].

4.2. Green and scalable synthesis

The development of solvent-free or water-based MOF synthesis techniques is necessary for the shift to industrial scale to lower costs and lessen environmental effect. To create large-area, economical electrodes, research into continuous flow manufacturing and electrochemical deposition of MOFs directly onto industrial substrates (such as nickel mesh or stainless steel) would be crucial [31].

4.3. Connecting Renewable Energy Sources

Future research should evaluate the efficiency of MOF electrocatalysts under variable power inputs, typical of wind and solar power, as saltwater electrolysis is often envisioned for non-grit supplies. A key initial step toward working “energy-to-hydrogen” solutions is to ensure that MOF-based systems can withstand non-uniform loads without deterioration in quality [32].

5. Conclusion

A key initial step towards a sustainable green hydrogen economy is the development of efficient and long-lasting electrocatalysts for alkaline seawater electrolysis. The emerging potential of MOFs as a flexible electrocatalyst platform is highlighted in this mini review. MOF electrocatalysts offer a rare opportunity to achieve high OER selectivity while suppressing the chlorine evolution side reaction due to their large surface area, tunable porosity, and capacity to accommodate several active metal sites, including Ni, Fe, Co, and Mo. That being said, there are several barriers that need to be overcome before laboratory prototypes can be used in industrial settings. Still, efforts of scientists need to be focused on long-term structural stability and durability. In conclusion, strategic engineering of MOF electrocatalysts offers one of the most promising technologies in the quest for clean, unlimited energy from seawater, despite the ongoing challenges.

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References

[1] Boretti A., Pollet B.G., Hydrogen economy: Paving the path to a sustainable, low-carbon future. International Journal of Hydrogen Energy 2024; 93: 307-19. https://doi.org/10.1016/j.ijhydene.2024.10.350.

[2] Elazab M.A., Elgohr A.T., Bassyouni M., Kabeel A.E., Attia M.E.H., Elshaarawy M.K., Hamed A.K., Alzahrani H.A.H., Green Hydrogen: Unleashing the Potential for Sustainable Energy Generation. Results in Engineering 2025;27:106031https://doi.org/10.1016/j.rineng.2025.106031.

[3] Gao F.Y., Yu P.C., Gao M.R., Seawater electrolysis technologies for green hydrogen production: challenges and opportunities. Current Opinion in Chemical Engineering 2022;36:100827. https://doi.org/10.1016/j.coche.2022.100827.

[4] Raza N., Challenges and solutions in suppressing chlorine evolution reaction in seawater electrolysis. Journal of Power Sources 2025;659:238331. https://doi.org/10.1016/j.jpowsour.2025.238331.

[5] Kumar N., Aepuru R., Lee S.Y., Park S.J., Advances in Catalysts for Hydrogen Production: A Comprehensive Review of Materials and Mechanisms. Nanomaterials 2025;15(2):256. https://doi.org/10.3390/nano15040256

[6] Ramírez A.M.R., Heidari S., Vergara A., Aguilera M.V., Preuss P., Camarada M.B., Fischer A., Rhenium-Based Electrocatalysts for Water Splitting. ACS Materials Au 2023;3(3):177-200.DOI: 10.1021/acsmaterialsau.2c00077

[7] Jamadar A.S., Sutar R., Patil S., Khandekar R., Yadav J.B., Progress in metal oxide-based electrocatalysts for sustainable water splitting. Materials Reports: Energy 2024;4(3):100283. https://doi.org/10.1016/j.matre.2024.100283.

[8] Tsacheva I., Yazici M.S., Mahadi A.H., Uzunoglu A., Uzun D., Metal–Organic Frameworks for Seawater Electrolysis and Hydrogen Production: A Review. Electrochem 2025;6(1):37. https://doi.org/10.3390/electrochem6040037

[9] El Hanafi M., BaQais A., Saadi M., Ahsaine H.A., Advances and Outlook of Metal–Organic Frameworks as High-Performance Electrocatalysts for Hydrogen Evolution Reaction: A Minireview. Energy & Fuels 2023;37(15):10869-85. DOI: 10.1021/acs.energyfuels.3c01533

[10] Xu Z., Yeh C.L., Chen J.L., Lin J.T., Ho K.C., Lin R.Y.Y., Metal–Organic Framework-Derived 2D NiCoP Nanoflakes from Layered Double Hydroxide Nanosheets for Efficient Electrocatalytic Water Splitting at High Current Densities. ACS Sustainable Chemistry & Engineering 2022;10(35):11577-86. https://doi.org/10.1021/acssuschemeng.2c03250

[11] Yang T., Zhang H., Pang B., Wong J.W.C., Recent Advances in Transition Metal-Based Metal-Organic Frameworks for Hydrogen Production. Small Sci 2025;5(1):2400446. https://doi.org/10.1002/smsc.202400446

[12] Sana Fathima T.K., Ghosh A., Ramaprabhu S., Efficient, chlorine-free, and durable alkaline seawater electrolysis enabled by MOF-derived nanocatalysts. International Journal of Hydrogen Energy 2024;90:546-56. https://doi.org/10.1016/j.ijhydene.2024.09.437.

[13] Chen Y., Shen L., Wang C., Feng S., Zhang N., Zhang K., Yang B., Utilizing tannic acid and polypyrrole to induce reconstruction to optimize the activity of MOF-derived electrocatalyst for water oxidation in seawater. Chemical Engineering Journal 2022;430:132632. https://doi.org/10.1016/j.cej.2021.132632.

[14] Shyam M., Arooj M., ul Haq T., Identification and mechanistic understanding of active sites in bimetallic catalysts for electrochemical water splitting. Sustainable Energy & Fuels 2026;10:488-530. https://doi.org/10.1039/D5SE01497B

[15] Bhardwaj A.A., Vos J.G., Beatty M.E.S., Baxter A.F., Koper M.T.M., Yip N.Y., Esposito D.V., Ultrathin Silicon Oxide Overlayers Enable Selective Oxygen Evolution from Acidic and Unbuffered pH-Neutral Seawater. ACS Catalysis 2021;11(3):1316-30. DOI: 10.1021/acscatal.0c04343

[16] Xiao W., Cheng M., Liu Y., Wang J., Zhang G., Wei Z., Li L., Du L., Wang G., Liu H., Functional Metal/Carbon Composites Derived from Metal–Organic Frameworks: Insight into Structures,

Properties, Performances, and Mechanisms. ACS Catalysis 2023;13(3):1759-90. DOI: 10.1021/acscatal.2c04807

[17] Pan T., Wang Y., Zhang S., Wang D., Li Q., Pang H., MOF-Based Electrocatalysts for Water Electrolysis, Energy Storage, and Sensing: Progress and Insights. Chem Rec 2025;25(2):e202400253. https://doi.org/10.1002/tcr.202400253

[18] Salman M., Zhou H., Ahmed S., et al. 2D metal-organic frameworks and their composites for water splitting: Catalytic insights, synthesis pathways, and structural engineering strategies. Coord Chem Rev 2025;544:216985. https://doi.org/10.1016/j.ccr.2025.216985.

[19] Muthurasu A., Natarajan L., Kim T.W., et al. Engineering Efficient Bifunctional Electrocatalyst of Ruthenium Nanocluster Heterointerface Integrated Nickel–Iron Diselenide for Alkaline Freshwater and Seawater Electrolysis. ACS Appl Mater Interfaces 2025;17(17):25237-52.DOI: 10.1021/acsami.4c22733

[20] Liu E., Guo Y., Zhao J., et al. p-d Orbital hybridization enhanced MOF-on-MOF derived CoP/Fe2P bimetallic phosphide electrocatalyst for stable water electrolysis. J Energy Chem 2026;112:198-207. https://doi.org/10.1016/j.jechem.2025.08.044.

[21] Zeb Z., Liu Y., Khan N., et al. Engineering Mo-Doped Sulfide Heterointerfaces from POM-MOFs for Enhanced Alkaline Seawater Hydrogen Evolution. Inorg Chem 2025;64(50):24601–14. https://doi.org/10.1021/acs.inorgchem.5c04190

[22] Lyu C., Cheng J., Wang H., et al., Construction of interface-engineered coral-like nickel phosphide@cerium oxide hybrid nanoarrays to boost electrocatalytic hydrogen evolution performance in alkaline water/seawater electrolytes. Adv Compos Hybrid Mater 2023;6:175. https://doi.org/10.1007/s42114-023-00750-0

[23] Ekerenam O.O., Ikeuba A.I., Njoku C.N., Njoku D.I., Emori W., Nwokolo I.K., Etim I.I.N., Okonkwo B.O., Udoh I.I., Daniel E.F., Uzoma P.C., Awonusi B.O., Kolawole S.K., Etim I.P., Olanrele O.S., Advancements in corrosion studies and protective measures for copper and copper-based alloys in varied environmental conditions. Results in Engineering 2025;26:105257. https://doi.org/10.1016/j.rineng.2025.105257.

[24] Liang X., Wang S., Feng J., Xu Z., Guo Z., Luo H., Zhang F., Wen C., Feng L., Wan C., Titirici M.M., Structural transformation of metal–organic frameworks and identification of electrocatalytically active species during the oxygen evolution reaction under neutral conditions. Inorganic Chemistry Frontiers 2023;10(10):2961-77. https://doi.org/10.1039/D2QI02436E

[25] Zeng T., Liao L., Li C., Zhou D., Li G., Yao X., Recent Advances and Design Strategies of Metal-Organic Framework-Based Materials for High Current Density Alkaline Water Electrolysis. Carbon Neutralization 2026;5:1-33. https://doi.org/10.1002/cnl2.70113.

[26] Yu L., Ning M., Wang Y., et al. Direct seawater electrolysis for hydrogen production. Nat Rev Mater 2025;10:857-73. https://doi.org/10.1038/s41578-025-00826-x

[27] Liu Y., Wang Y., Fornasiero P., Tian G., Strasser P., Yang X.Y., Long-term Durability of Seawater Electrolysis for Hydrogen: From Catalysts to Systems. Angewandte Chemie International Edition 2024;63:e202412087https://doi.org/10.1002/anie.202412087

[28] Zhang B., Zheng Y.J., Ma T., Yang C.D., Peng Y.F., Zhou Z.H., Zhou M., Li S., Wang Y.H., Cheng C., Designing MOF Nanoarchitectures for Electrochemical Water Splitting. Advanced Materials 2021;33(26):2006042.. https://doi.org/10.1002/adma.202006042

[29] An Y., Lv X., Jiang W., Wang L., Shi Y., Hang X., Pang H., The stability of MOFs in aqueous solutions—research progress and prospects. Green Chemical Engineering 2024;5(2):187-204. https://doi.org/10.1016/j.gce.2023.07.004.

[30] Li S., Li J., Ma Q., Enhancing water resistance of metal-organic frameworks. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2025;707:135817. https://doi.org/10.1016/j.colsurfa.2024.135817.

[31] Xu Z., Wu Z.S., Scalable production of high-performance electrocatalysts for electrochemical water splitting at large current densities. eScience 2025;5(4):100334. https://doi.org/10.1016/j.esci.2024.100334.

[32] Sowbakkiyavathi E.S., Dhandapani P., Ramasamy S., Oh J.H., In I., Lee S.J., Subramania A., Recent advances in MOFs, MOF-derived materials and their composites as electrocatalysts for hydrogen production. RSC Sustainability 2025;3(9):3628-51. https://doi.org/10.1039/D5SU00199D