

Bipolar Membrane Seawater Splitting for Hydrogen Production: A Review

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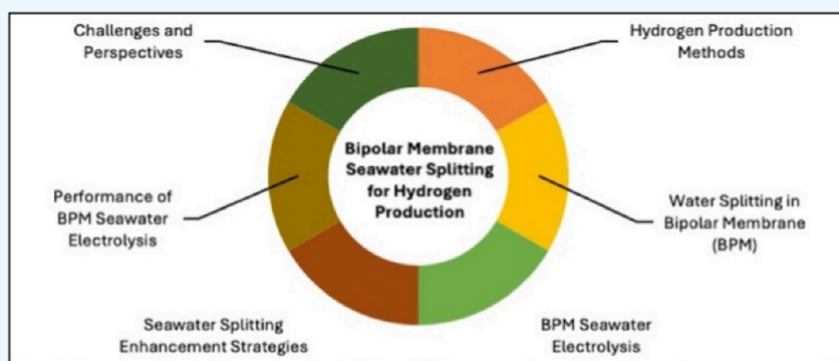
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ABSTRACT: The growing demand for clean energy has spurred the quest for sustainable alternatives to fossil fuels. Hydrogen has emerged as a promising candidate with its exceptional heating value and zero emissions upon combustion. However, conventional hydrogen production methods contribute to CO₂ emissions, necessitating environmentally friendly alternatives. With its vast potential, seawater has garnered attention as a valuable resource for hydrogen production, especially in arid coastal regions with surplus renewable energy. Direct seawater electrolysis presents a viable option, although it faces challenges such as corrosion, competing reactions, and the presence of various impurities. To enhance the seawater electrolysis efficiency and overcome these challenges, researchers have turned to bipolar membranes (BPMs). These membranes create two distinct pH environments and selectively facilitate water dissociation by allowing the passage of protons and hydroxide ions, while acting as a barrier to cations and anions. Moreover, the presence of catalysts at the BPM junction or interface can further accelerate water dissociation. Alongside the thermodynamic potential, the efficiency of the system is significantly influenced by the water dissociation potential of BPMs. By exploiting these unique properties, BPMs offer a promising solution to improve the overall efficiency of seawater electrolysis processes. This paper reviews BPM electrolysis, including the water dissociation mechanism, recent advancements in BPM synthesis, and the challenges encountered in seawater electrolysis. Furthermore, it explores promising strategies to optimize the water dissociation reaction in BPMs, paving the way for sustainable hydrogen production from seawater.

1. INTRODUCTION

The increasing global demand for sustainable and eco-friendly fuels has posed a critical challenge in recent decades. Although fossil fuels have long been relied upon as a cost-effective and versatile energy source, their significant drawbacks, such as greenhouse gas emissions, acid rain, and rapid depletion, have limited their use in various industries.^{1,2} As a result, there is an urgent need to explore alternative, clean, and efficient energy options. Hydrogen or H₂ has emerged as a promising solution, serving as a critical industrial raw material with wide-ranging applications in power generation, transportation, synthetic fuels, and industrial processes.³ Its exceptional gravimetric heating value, reaching up to 141.9 MJ/kg, surpasses those of methane, gasoline, diesel, and methanol,⁴ making it highly appealing.

Additionally, hydrogen offers the distinct advantage of emitting zero emissions when utilized for combustion.⁵

The production method of hydrogen determines its environmental impact and carbon neutrality. When hydrogen is obtained from fossil fuels like oil and coal, known as “gray hydrogen”, it releases carbon dioxide or CO₂ when burned.⁶ On the other hand, “blue hydrogen”, which is produced similarly but

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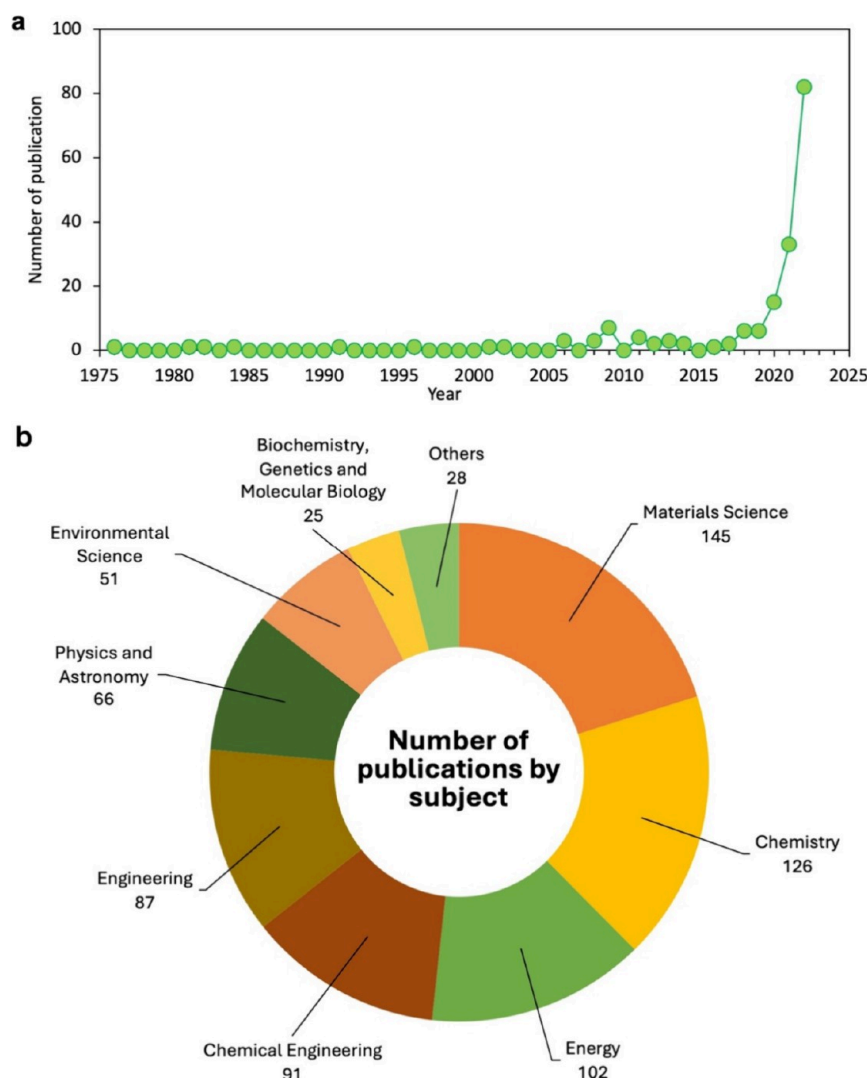


Figure 1. Publications related to hydrogen production from seawater electrolysis. (a) Annual publications. (b) Publication by subject. Data were retrieved from SCOPUS on June 4, 2023.

incorporates carbon capture technology, prevents CO₂ emissions by securely storing the captured carbon or utilizing it in industrial processes.⁷ The cleanest form of hydrogen, called “green hydrogen”, is derived from renewable energy sources and does not generate any carbon emissions.⁸ Conventional techniques for hydrogen production, such as coal-based water-gas-shift and fossil fuel reformation processes, contribute significantly to CO₂ emissions. However, there is now an established industrial system for electrocatalytic hydrogen production through water splitting, which provides a more environmentally friendly alternative.^{8,9}

Currently, the production of green hydrogen using commercial water electrolyzers heavily relies on the availability of high-purity fresh water.^{10,11} However, freshwater scarcity presents a significant challenge in many regions, with more than 80% of the global population experiencing high-risk water security.¹² In contrast, seawater represents an abundant and nearly limitless resource, accounting for over 96% of the world’s water storage and about 71% of the Earth’s surface.¹⁰ Hence, a growing body of research in seawater electrolysis encompasses various subjects, as illustrated in Figure 1.

Figure 1a illustrates annual publications pertaining to the process of seawater electrolysis for hydrogen production. The

initial scholarly interest in this subject can be traced back to the 1970s and 1980s, indicating a fundamental fascination with the utilization of hydrogen derived from seawater as an alternative source of energy. However, the limited number of publications in the subsequent decades suggests that the field may have been in its early stages or undergoing exploration. It is evident that in recent years, there has been a significant increase in research activity. This surge in recent years emphasizes a renewed or potentially intensified focus on the potential of seawater electrolysis for the sustainable production of hydrogen. This can be attributed to advancements in technology, the heightened global emphasis on renewable energy, or the search for efficient and environmentally friendly alternatives to conventional energy sources. The data present a depiction of a field that, after years of establishing its foundation, is now rapidly progressing and expanding, indicating its growing significance in the scientific and energy sectors.

Figure 1b presents an all-inclusive representation of the dissemination of investigations in seawater electrolysis. The areas of Materials Science and Chemistry arise as preeminent fields, signifying a pronounced emphasis on the innovation of novel materials and the examination of electrochemical dynamics. The noteworthy presence of Energy and Engineering

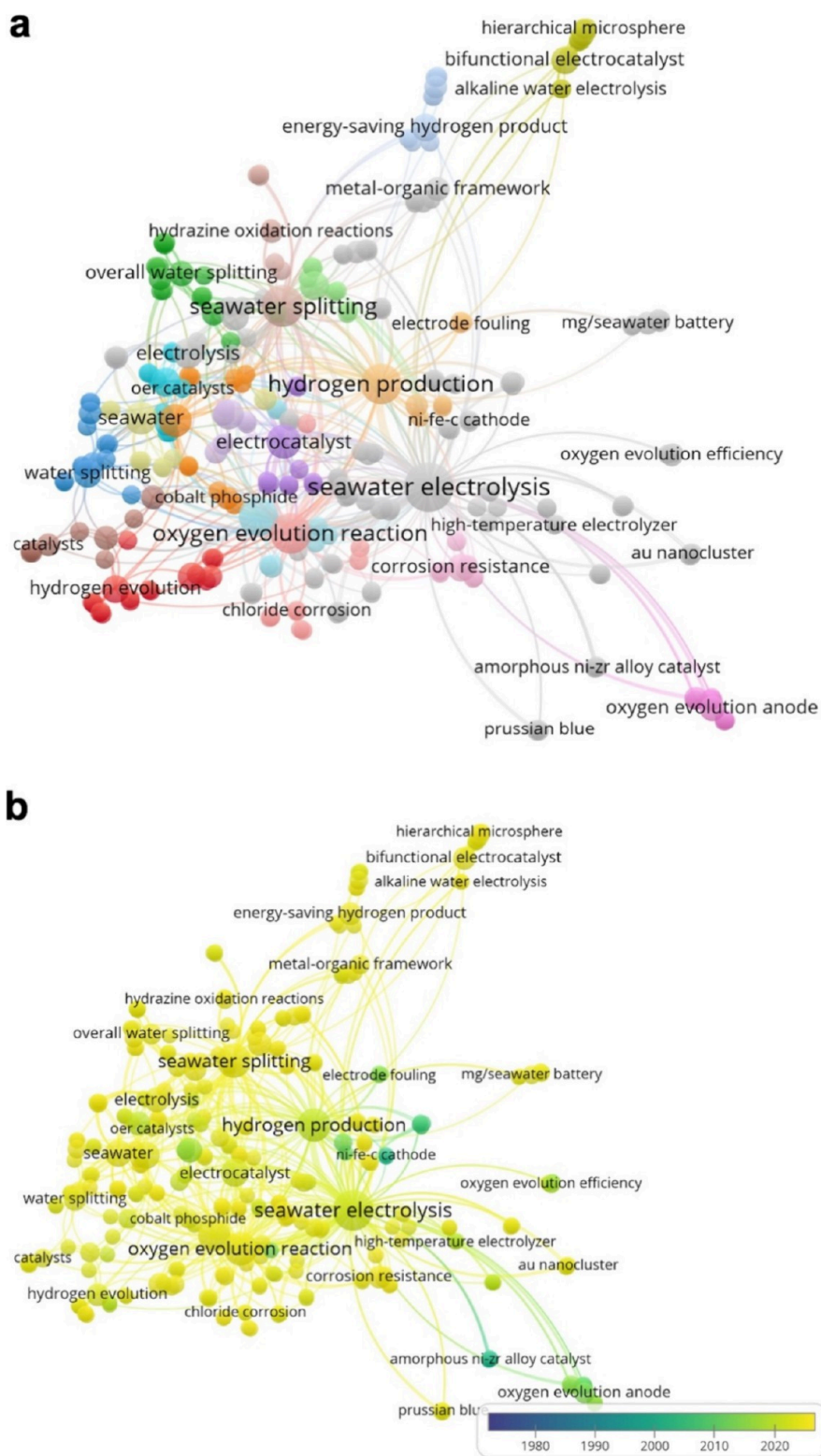


Figure 2. Keyword network and overlay of research related to seawater electrolysis for hydrogen production. These images are generated by using VOSViewer. Data were retrieved on June 4, 2023.

fields implies that the technique employed in this investigation holds the potential to be implemented in sustainable energy systems. The extensive range of data, spanning from Physics to Biochemistry and even Computer Science, suggests that this research is founded on a diverse basis and can be employed in a

multitude of ways, ranging from the exploration of environmental implications to the creation of computational models.

Figure 2a,b present a comprehensive analysis of the evolving research landscape surrounding hydrogen production from seawater electrolysis. These visualizations utilize color coding to represent publication years, highlighting the temporal pro-

gression of research milestones. The key themes of “seawater electrolysis”, “hydrogen production”, and “oxygen evolution reaction” consistently anchor the depicted research continuum. Notably, recent changes in the color spectrum emphasize the growing importance of “electrolysis”, “water splitting”, and “electrocatalyst”, suggesting rapid advancements in these areas, particularly in the field of material sciences. The emergence of terms like “metal–organic framework”, “hierarchical microsphere”, and “bifunctional electrocatalyst” indicates a shift toward novel material explorations aimed at optimizing electrolysis efficiency.

In contrast, the connection between “corrosion resistance”, “electrode fouling”, and related terms highlights the ongoing challenges in this field, underscoring the need to improve system longevity and efficiency. These comprehensive visualizations not only showcase the foundational aspects of the research but also demonstrate the depth and breadth of interdisciplinary efforts, encompassing the understanding of core chemical processes, the development of advanced materials, and the resolution of inherent challenges. Thus, this synthesis provides a comprehensive overview of the complex and multidimensional endeavors within seawater electrolysis for hydrogen production.

Two primary methods, one-step seawater electrolysis and two-step seawater electrolysis, have been investigated as potential approaches for producing green hydrogen through seawater electrolysis.^{10,13,14} While some researchers support the idea of direct seawater electrolysis and the development of electrolyzers that can utilize seawater as a water source, others argue that direct seawater splitting may not be cost-effective when considering the capital and operational expenses associated with initial seawater purification.^{15–17} These proponents suggest that the cost of purification, which currently represents a small portion of the price of green hydrogen (<0.1\$ per kg H₂) due to the utilization of small-scale reverse osmosis seawater purification technology, would significantly rise with widespread implementation and the integration of renewable energy for seawater purification.¹¹ Dry coastal areas, including the Middle East, South Africa, the west coast of the Americas, and coastal areas of Australia, face a shortage of freshwater but possess ample seawater resources and abundant wind and solar energy.¹⁰ Therefore, it is feasible to harness surplus renewable electricity in arid desert zones near ocean coastlines to carry out seawater electrolysis and produce hydrogen.¹⁰

However, direct seawater electrolysis encounters various fundamental and engineering challenges that must be tackled. One of these challenges involves addressing the corrosion issue, as the stability of both the anode and cathode is compromised by chlorine gas and chloride ions.^{18,19} The presence of salts in seawater, with concentrations of up to 3.5 wt % and various metal ions, poses challenges by participating in competing electrochemical reactions during the hydrogen evolution reaction (HER) at the cathode, thereby limiting the efficiency of water electrolysis.²⁰ Additionally, the presence of bacteria and microorganisms in natural seawater can lead to the formation of insoluble precipitates on the catalyst surface, potentially impacting the HER performance.²¹ Moreover, the high concentration of chloride ions can hinder the activity of catalysts by blocking their active centers.²² Furthermore, the chlorine evolution reaction (CIER) can act as a competing reaction to the oxygen evolution reaction (OER) at the anode.²³ Extensive research has been conducted on a wide range of catalysts for seawater electrolysis. Noteworthy catalysts employed for the OER in seawater include metal (hydrogen) oxides, nitrides,

phosphides, borides, and hybrid catalysts.^{24–27} In addition to these OER catalysts, noble metal alloys, noble metals supported on carbon, MXene-based complexes, and hybrid materials with diverse composites or structures have been utilized as catalysts for the HER in seawater.^{25,28} Each of these catalysts exhibits its own set of advantages and disadvantages when applied in the context of seawater electrolysis.

The electrolysis process is composed of two half-reactions, i.e., the OER at the anode and the HER at the cathode. To ensure the production of high-purity hydrogen, ion exchange membranes are used to separate the reactions at the two electrodes. However, the current use of proton-exchange membranes or anion-exchange membrane integrated systems in this process restricts the pH environment to either acidic or alkaline, posing significant limitations on the overall performance of the electrodes and the feasibility of the technique.^{25,26} Additionally, proton exchange membrane (PEM) electrolyzer systems hinder the use of non-noble metal catalysts and contribute to high costs.^{25,29} To overcome this challenge, researchers have been actively investigating the use of bipolar membranes (BPMs) in water electrolysis.²⁹ BPMs consist of a cation-exchange membrane layer (CEL) and an anion-exchange membrane layer (AEL). By applying a reverse bias (CEL facing the cathode and AEL facing the anode), the ions at a bipolar or junction or interfacial layer, which is the junction of CEL and AEL, initially migrate to the bulk solution.³⁰ Subsequently, as the ions become depleted, water molecules at the interfacial layer undergo polarization and dissociation, generating H⁺ and OH⁻ ions.³¹ These ions then move into adjacent solution compartments, creating an acidic and basic environment. Leveraging the unique water dissociation characteristics of the interfacial layer, the incorporation of BPMs in the electrochemical configuration allows for the maintenance of two distinct pH environments.³² In contrast to traditional configurations, which must optimize electrode stability, catalyst activity, and cost at both the cathode and anode for a single pH, the BPM permits electrochemical devices in which optimum pH conditions can be determined individually for each half-reaction.³³ BPM allows hydrogen and oxygen evolution processes under appropriate pH conditions, reducing overall cell voltage for the water dissociation reaction.³⁴ The strong electric field at the interface and the presence of catalysts in the junction or interface of BPM are responsible for the acceleration of water dissociation.³⁰ Alongside the thermodynamic potential, the water dissociation potential of BPMs significantly impacts the system efficiency.³⁰ Recent research has shown that energy-saving hydrogen production by seawater electrolysis employing BPM results in low cell voltages and lower electricity use.³⁵

This paper comprehensively discusses the production of hydrogen from seawater by using BPMs. The discussion begins with an overview of various hydrogen production methods. It then delves into the mechanism of water splitting using bipolar membranes and the recent advancements in their fabrication. The final part of the discussion focuses on the BPM electrolysis performance in hydrogen production from seawater, limitations, and enhancement strategies. Then, the challenges and perspectives in this field are pointed out.

2. COMPARATIVE ANALYSIS OF HYDROGEN PRODUCTION METHODS

There are several methods available for hydrogen production. Details of each method can be found in refs 36 and 37. Steam reforming is currently the dominant method for hydrogen

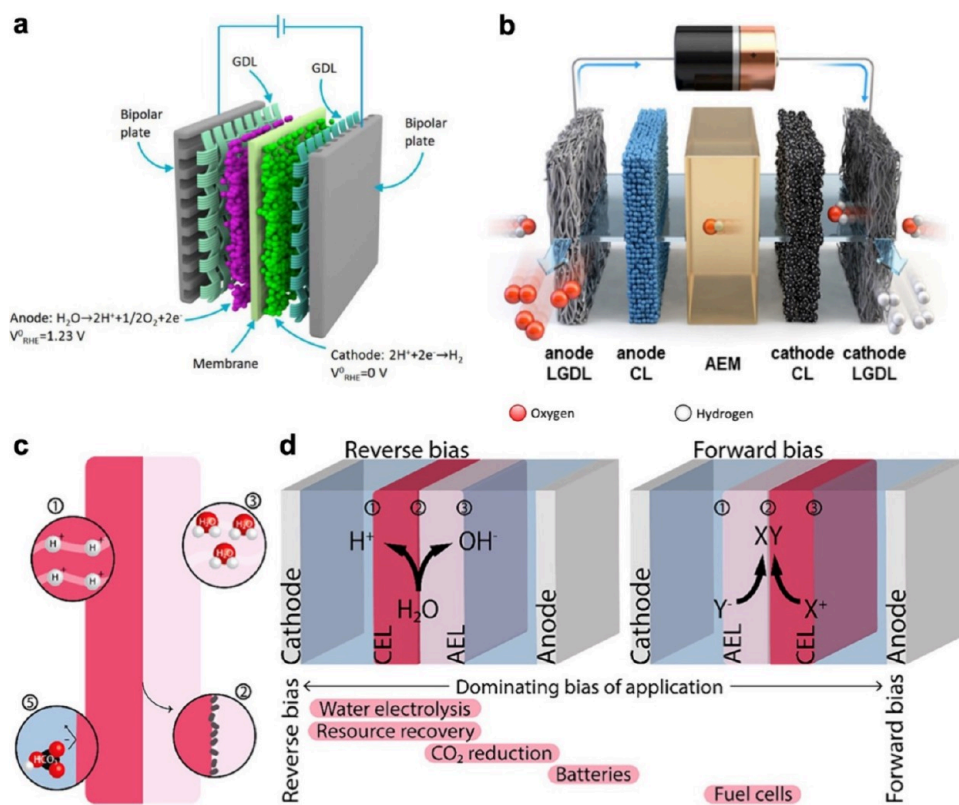


Figure 3. Membrane-based water electrolysis. (a) Proton exchange membrane electrolysis. Reprinted with permission from ref 50. (b) Anion exchange membrane electrolysis. Reprinted with permission from ref 51. (c) Bipolar membrane and important characteristics. (d) Bipolar membrane electrolysis in reverse and forward bias modes. (c) and (d) are reprinted with permission from ref 52 under a Creative Commons license, <https://creativecommons.org/licenses/by-nc-nd/4.0>.

production, accounting for the majority of global output.³⁸ It involves the combination of methane and steam in high-temperature reactors, resulting in the production of hydrogen, carbon monoxide, and some carbon dioxide. However, steam methane reforming has environmental drawbacks due to the emission of greenhouse gases.⁷ Efforts are being made to address these issues through the implementation of carbon capture and storage technologies, which can effectively reduce CO_2 emissions.³⁹ Studies are also focused on improving catalyst performance and exploring the integration of renewable energy sources to enhance process efficiency and sustainability.^{40–44} To overcome the sensitivity of steam methane reforming catalysts to carbon deposition and sulfur poisoning, researchers have explored the use of bimetallic catalysts, such as nickel-based catalysts supported on alumina–zirconia.^{45,46} Moreover, alternative feedstocks like ethanol are being investigated for steam reforming due to their advantages, such as favorable characteristics, including easy transportability, biodegradability, low toxicity, and the ability to yield significant amounts of hydrogen at lower temperatures.^{47,48} The integration of concentrated solar systems with steam methane reforming plants has shown promise in reducing energy costs and CO_2 emissions.⁴⁹

Coal gasification offers a potential alternative to steam methane reforming, utilizing cheaper feedstocks and reducing dependence on oil and gas imports. This method enables the production of green hydrogen, which supports the transition to sustainable energy systems. Through coal gasification, coal is converted to a mixture of gases, primarily carbon monoxide and hydrogen, through reactions with steam or carbon dioxide. The

water-gas-shift reaction plays a crucial role in increasing the hydrogen concentration in the produced syngas.⁵³ Coal gasification provides advantages such as low cost and abundant domestic resources, efficient CO_2 capture, and reduced carbon footprint.⁵⁴

Various gasification technologies, including conventional and new approaches, are employed in coal gasification. Established technologies like fixed bed, fluidized bed, and entrained flow bed have achieved large-scale applications.⁵⁵ Newer technologies aim to enhance the energy conversion efficiency, obtain hydrogen-rich syngas, and reduce CO_2 emissions. Examples of these newer technologies include supercritical water gasification, plasma gasification, and chemical-looping gasification. Another notable approach is underground coal gasification (UCG), which offers flexibility in gas production and utilization while utilizing unmineable coal reserves and minimizing environmental impact.⁵⁶ However, challenges for coal gasification include high operational and capital costs, the need for advanced infrastructure, and proper management of CO_2 emissions and solid waste products generated during the process.^{57–59}

Water electrolysis is a versatile hydrogen production method that employs various electrolyzers. Unlike other processes, water electrolysis is eco-friendly, producing only oxygen as a byproduct. Figure 3a–c showcases several membrane-based electrolyzers. A proton exchange membrane (PEM) electrolyzer (Figure 3a) operates at lower temperatures, providing excellent current densities, fast response times, and high energy efficiency.^{60–63} However, PEM electrolysis technology demands costly catalysts, perfluorinated membranes, and specialized materials due to its acidic environment, making it more

Table 1. Principal Processes, Advantages, and Disadvantages of Hydrogen Production Methods^{88–90}

method	principal process	advantages	disadvantages
steam methane reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	high efficiency, low cost	high greenhouse gas emissions, nonrenewable
coal gasification	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	abundant feedstock, low cost	high greenhouse gas emissions, nonrenewable
electrolysis of water	$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$	renewable, no greenhouse gas emissions	high energy consumption, high cost
photoelectrochemical water splitting	$\text{H}_2\text{O} + \text{photons} \rightarrow \text{H}_2 + \text{O}_2$	renewable, no greenhouse gas emissions	low efficiency, high cost
biological processes	various	renewable, low energy consumption	low efficiency, slow reaction rate

expensive than other methods.^{60–63} Anion exchange membrane (AEM) electrolysis combines the benefits of PEM and alkaline electrolysis (Figure 3b). It utilizes a thin, dense, nonporous polymer membrane to separate the electrode chambers, transferring charges via hydroxide ions, similar to alkaline water electrolysis.⁶⁴ AEM electrolysis has advantages, including cost-effective transition-metal catalysts and more affordable AEM membranes than Nafion-based ones used in PEM electrolysis.^{65,66} It can also replace high-cost porous transport layers and bipolar plates with cost-effective stainless-steel alternatives.^{65,66} However, AEM electrolysis needs to improve its performance and durability, hindering its full commercial potential.⁶⁷ Challenges include efficiency and productivity issues and membrane degradation for AEMs based on specific materials.⁶⁸ Further research is required to optimize its performance. Another membrane-based electrolysis technology is the BPM electrolyzer (Figure 3c,d). It utilizes a specialized BPM with AEL and CEL. This bipolar layer or interface layer facilitates the splitting of water molecules. An ideal BPM should possess several desirable features including high conductivity of the individual bulk layers, fast chemical kinetics at the interface, high water permeability, long operational lifetime under current densities, and low parasitic ion crossover (refer to Figure 3c, nos. 1–3 and 5; no. 4 is not shown). The advantages of BPM electrolysis include accelerated water dissociation and independent optimization of environments and catalysts.⁶⁹ This technology is discussed in the next section.

The second type of electrolysis does not use a membrane as a separator. Alkaline electrolysis, using an alkaline electrolyte solution, proves cost-effective for large-scale applications but has lower energy efficiency and slower loading response.^{70–72} It faces limitations for mass production due to low operating pressure and restricted current densities.⁵⁸ Another non-membrane electrolyzer is the solid oxide electrolysis cell (SOEC). The SOEC operates at higher temperatures,⁷³ but it offers high energy efficiency.⁷⁴ However, the SOEC faces challenges of stability and degradation at high temperatures, making it less suitable for large-scale implementation.⁷⁵ Each electrolysis technology has its own limitations and considerations, including cost, efficiency, operating pressure, and material requirements, which must be carefully evaluated for specific applications.

Another alternative process for hydrogen production is photoelectrochemical (PEC) water splitting. PEC water splitting is a promising approach that combines photochemistry and electrochemistry to directly convert solar energy into hydrogen and oxygen. It utilizes semiconductor materials as photoelectrodes to absorb light and generate charge carriers, which drive the water splitting reaction.⁷⁶ The photoanode facilitates the reduction of water molecules, producing oxygen gas through the oxygen evolution reaction, while the holes on the surface of the photoanode oxidize water molecules to form protons.⁷⁷ These protons then migrate to the cathode through the electrolyte, where they combine with electrons from the

external circuit to generate hydrogen gas. PEC water splitting offers significant advantages, as it harnesses abundant and renewable solar energy for sustainable hydrogen production. It enables efficient solar-to-chemical energy conversion, directly converting absorbed photons into chemical fuels. PEC cells can also be integrated with other renewable energy sources to create hybrid energy systems. However, there are challenges to overcome, including improving efficiency, stability, and scalability.⁷⁸ Ongoing research focuses on enhancing the kinetics of the oxygen and hydrogen evolution reactions to minimize energy losses and increase reaction rates.⁷⁷ Despite these challenges, PEC water splitting holds great potential for clean and renewable hydrogen production.

Biological processes for hydrogen production involve the utilization of microorganisms or enzymes to facilitate reactions. Compared to other methods, biological processes offer unique advantages such as compatibility with diverse feedstocks and potential for decentralized production.^{79,80} Dark fermentation is a simple anaerobic process in which anaerobic bacteria break down organic matter to produce hydrogen along with byproducts like acetic and butyric acids.⁸¹ It offers sustainability and lower energy requirements compared with conventional methods, and a wide range of feedstocks can be used. However, challenges such as low yields and sensitivity to operating conditions need to be addressed.⁷⁹

Photofermentation is another biological process that utilizes photosynthetic bacteria to trigger anaerobic fermentation.^{82,83} It is more effective in hydrogen production compared to dark fermentation and offers renewable energy and waste reduction benefits.⁸⁴ The produced hydrogen is of high purity, reducing the need for purification.^{82,83} However, photofermentation requires light energy and has low light conversion efficiencies, limiting its application in certain conditions and resulting in lower energy efficiency.⁸⁵ Dark–photo cofermentation is a two-step process that combines the advantages of dark and photo fermentation.⁸⁶ Organic wastes are first dark fermented, producing hydrogen and organic acids, which then serve as electron donors for hydrogen synthesis in the subsequent photo fermentation phase. Dark–photo cofermentation significantly enhances overall hydrogen generation by merging the benefits of both processes.⁸⁷ It offers a promising approach to improve hydrogen production efficiency compared to standalone dark or photofermentation methods.

Hydrogen production methods encompass various technologies continually being improved to enhance efficiency, sustainability, and environmental friendliness. Steam reforming remains the dominant method due to its high global output, but efforts are underway to address its environmental drawbacks through carbon capture and the exploration of alternative feedstocks. Coal gasification offers potential for energy independence and green hydrogen production. However, it also poses challenges regarding carbon emissions and the need for advanced carbon capture technologies. Water electrolysis provides a versatile and environmentally friendly approach, with

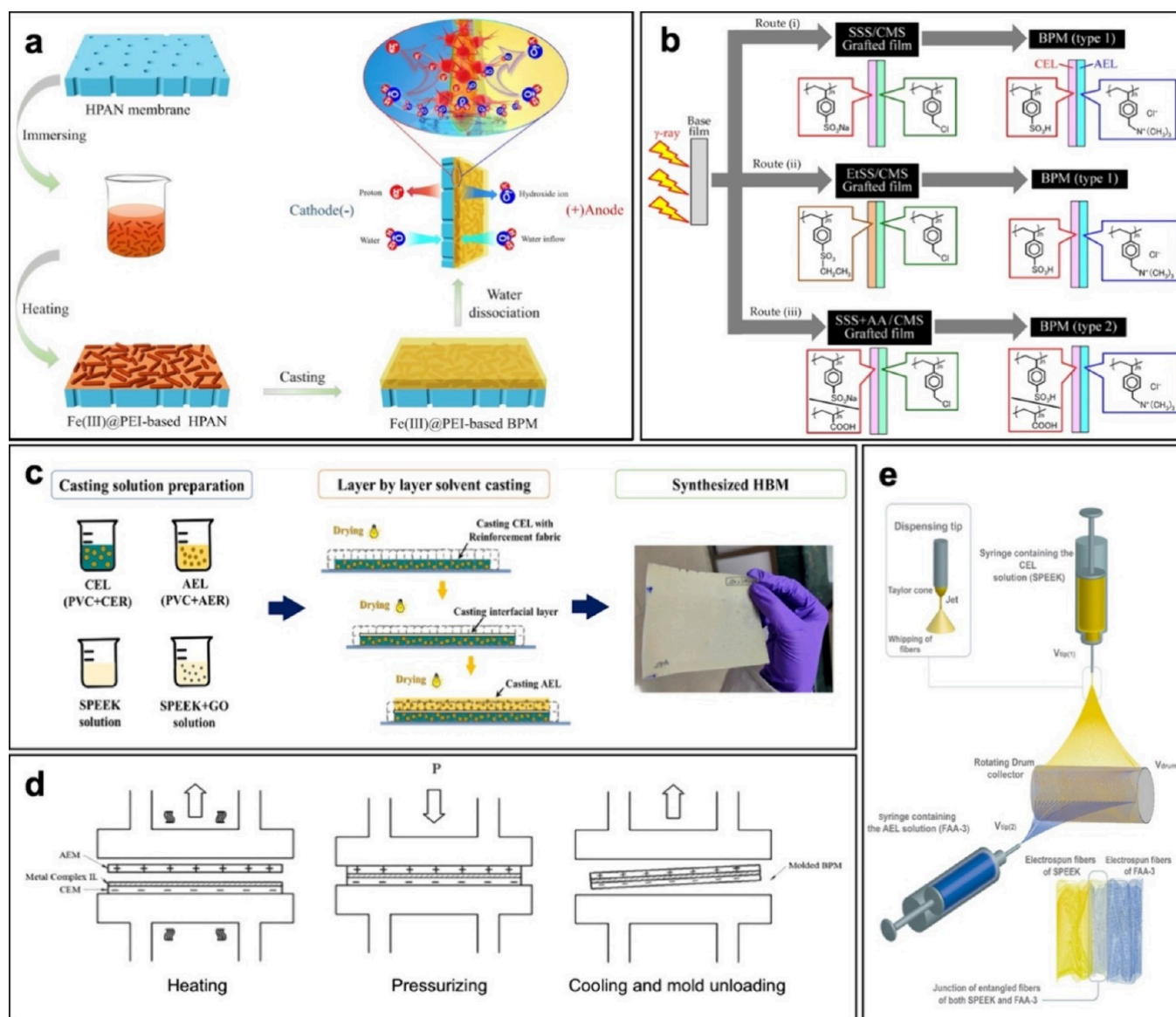


Figure 4. Several preparation methods of bipolar membranes. (a) Solution casting. Reprinted with permission from ref 96. (b) Grafting polymerization-based techniques.⁹⁷ Used under a Creative Commons license, <http://creativecommons.org/licenses/by/4.0>. (c) Layer-by-layer assembly. Reprinted with permission from ref 98. (d) Hot-pressing method. Reprinted with permission from ref 99. (e) Electrospinning.⁹⁷ Used under a Creative Commons license, <https://creativecommons.org/licenses/by-nc-nd/4.0>.

different electrolyzer types catering to specific needs. However, this method requires a significant amount of electricity to produce hydrogen. Additionally, advancements in electrolyzer technology are needed to improve the efficiency and reduce costs for widespread adoption. PEC water splitting harnesses abundant solar energy to convert photons directly to chemical fuels, holding great promise for clean and renewable hydrogen production. However, there are still challenges to overcome the scalability and commercial viability. Biological processes, such as dark fermentation, photo fermentation, and dark-photo cofermentation, offer alternative pathways that leverage microorganisms and enzymes, offering sustainability and compatibility with diverse feedstocks. However, these processes still need to be improved in efficiency and cost-effectiveness. Each method has advantages, limitations, and considerations, which must be carefully evaluated based on specific application requirements (Table 1). Ongoing research and technological advancements

aim to improve efficiency, stability, scalability, and cost-effectiveness across all hydrogen production methods.

Bipolar membrane electrolysis is an interesting option for producing green hydrogen through water electrolysis, as discussed earlier. To enhance the performance of bipolar membrane electrolysis, one approach is to develop fabrication methods to obtain membranes with excellent performance, durability, and cost-effectiveness. The fabrication methods for bipolar membranes are discussed in the following section.

3. BIPOLAR MEMBRANE AND ITS WATER SPLITTING MECHANISM

Various techniques, such as solution casting, grafting polymerization, layer-by-layer assembly, hot or cold pressing, and electrospinning, have been employed to synthesize BPMs. Furthermore, significant research has been dedicated to exploring the impact of integrating nanomaterials, such as

Table 2. Bipolar Membrane Preparation Methods^a

method	CEL	AEL	water uptake (%)	thickness (μm)	membrane conductivity (mS cm^{-1})	ref
solution casting	cation exchange resin powder and polystyrene	commercial anion exchange membrane	52	1,006	3.29	100
solution casting	anion exchange resin powder and polystyrene	commercial cation exchange membrane	55	1,087	3.48	100
solution casting	cation exchange resin powder and polyvinyl chloride; sulfonated polyether ether ketone and graphene oxide for interlayer	anion exchange resin powder and polyvinyl chloride	40	212		104
radiation-induced grafting	sodium <i>p</i> -styrenesulfonate + acrylic acid/water (grafted on poly(ethylene-co-tetrafluoroethylene film))	chloromethyl styrene/xylene (grafted on poly(ethylene-co-tetrafluoroethylene film))	76.1	86		107
layer-by-layer	sulfonated polyether sulfone (exfoliated nano-MoS ₂ as inter layer)	IONSEP-HC-A anion exchange membrane	52.6	600	30.84	110
hot pressing	dual-sulfonated poly(arylene ether ketone)	butyl-N ₃ -substituted imidazolium-functionalized poly(arylene ether ketone)	~35	175–190		34
electrospinning	sulfonated poly(ether ether ketone)	quaternized poly(phenylene oxide)		45		111
electrospinning	sulfonated poly(2,6-dimethyl-1,4-phenylene oxide), polyethylene glycol as interlayer	quaternized poly(2,6-dimethyl-1,4-phenylene oxide)	82.3	15–20		112

^aCEL, cation exchange layer; AEL, anion exchange layer.

metal oxides/hydroxides and graphene oxide, to enhance membrane efficiency and improve ion transport. Gaining a thorough understanding of the water-splitting mechanisms within these BPMs is essential for optimizing their performance and unlocking their potential in various fields, including water electrolysis.

3.1. Recent Advances in Bipolar Membrane Synthesis.

The synthesis of a bipolar membrane involves the creation of the three layers that make up the membrane: the anion exchange membrane (AEM), the cation exchange membrane (CEM), and the bipolar layer in between. In general, the synthesis of bipolar membranes can create two types of membranes, namely homogeneous and heterogeneous membranes, just similar to monopolar ion exchange membranes.^{91,92} Ion exchange with a homogeneous structure consists of a polymer matrix with fixed ions and mobile counterions. In addition, there are several cations that are kept as limited as possible to produce high permselectivity through the membrane.⁹³ In a heterogeneous membrane there are ion exchange resin particles embedded in a hydrophobic polymer structure.^{94,95} Hydrophobic polymers are generally impermeable to ions; therefore, the pathways of ions are directed through the ion exchange particles. Thus, the pathways of ions in the heterogeneous membrane are longer than in the homogeneous membrane. Hence, BPM with a homogeneous structure is preferable due to its more evenly distributed ionic groups and the absence of inert binder.⁹¹

In current years, several synthesis methods have been employed to fabricate bipolar membranes, including solution casting, grafting polymerization, layer-by-layer assembly, hot or cold pressing, incorporation of nanomaterials, and electrospinning as presented in Figure 4 and Table 2. The solution casting method involves dissolving the respective polymer materials for the AEM and CEM in separate solvents (Figure 4a). The solutions are then cast onto a substrate, such as a glass plate, using various techniques like spin coating, doctor-blade coating, spray coating, or dip coating.^{91,100–103} The two cast layers are then brought into contact to form the bipolar layer. The composite membrane is then dried, and subsequent treatments, such as hot pressing or chemical cross-linking, can be applied to improve its performance.^{100,104} A casting method has been considered as the simplest technique to synthesize

BPM, and the membranes produced are usually heterogeneous membranes.¹⁰⁵ Bhadja et al.¹⁰⁰ prepared two different heterogeneous BPMs. The first membrane was fabricated by dispersing cation exchange resin powder in polystyrene solution and then cast on a commercial anion exchange membrane. The second BPM membrane was synthesized by the mixing of anion exchange resin powder with polystyrene solution, followed by casting the mixture on a commercially available cation exchange membrane. The BPMs produced good mechanical stability and electrochemical properties for use in a bipolar electro dialysis process. The cation layer, anion layer, and bipolar membranes were separately prepared, and their properties were evaluated. Both the BPMs were used to study the hydrolysis of inorganic and organic salts into their corresponding acid and alkali by a bipolar electro dialysis technique.¹⁰⁰ Another experiment was conducted by Eswaraswamy et al.¹⁰⁴ Heterogeneous BPMs were also successfully synthesized in this study. To improve the mechanical strength of the membrane during the fabrication process, nylon-based woven fabric was employed as a reinforcer. The casting solution was prepared by dissolving resin powder in PVC solution, and then the dispersion was cast over woven fabric and dried. Membranes with different thicknesses were also prepared in this study by employing layer-by-layer casting of the casting solution. Membranes produced from the study could produce acid and base under a constant current density. In addition, the BPM-based electro dialysis system produced a water dissociation rate of up to $0.0042 \text{ mol m}^{-2} \text{ s}^{-1}$, a current efficiency of 81.4%, and energy consumption up to 11 kWh kg^{-1} , respectively.¹⁰⁴

Grafting polymerization based techniques are other techniques that have been employed to synthesize BPMs (Figure 4b). The grafting polymerization technique and its variations, including plasma-induced grafting polymerization and irradiation-induced grafting polymerization, have been successfully applied to produce different types of BPMs.^{106–108} This method involves the deposition of a thin polymer layer onto a substrate through activation of the surface using plasma, followed by grafting of monomers onto the activated surface. The grafted polymer layer can be selectively modified to create the anion-selective and cation-selective regions of the bipolar membrane.^{106,109} In general, the process of plasma-induced grafting

polymerization for synthesizing bipolar membranes typically includes the following procedures.^{107,109} (a) A substrate activation process is used, where the substrate surface is exposed to a low-temperature plasma, which generates highly reactive species. This plasma treatment activates the surface by creating functional groups and providing sites for subsequent grafting reaction, (b) A monomer grafting process is used, where the substrate is immersed in a monomer solution containing both anion-selective and cation-selective monomers. The reactive species created by the plasma treatment facilitate the grafting of the monomers onto the activated surface. (c) A selective modification process is used to create anion-selective and cation-selective regions. This can be achieved through various methods such as postgrafting functionalization or by using a combination of different monomers during the grafting process. (d) Cross-linking and polymerization are used to provide mechanical stability and enhance the performance of the bipolar membrane. The grafted polymer layer is often cross-linked and polymerized. This step can be achieved through thermal or chemical methods depending on the specific polymer system.

In the radiation-induced grafting polymerization technique, a base polymer film is irradiated by a γ -ray or electron beam, and then the film is immersed in a monomer solution. Graft polymerization of monomers begins at the polymer backbones of the film from both sides of the surfaces and gradually propagates deep inside to extend the grafted regions. This polymerization mechanism is then able to produce a homogeneous distribution of graft chains throughout the film. Finally, graft chains are chemically transformed to functional polymers to obtain the required membranes.¹⁰⁷ A BPM using base ethylene-*co*-tetrafluoroethylene film was successfully fabricated using this technique. Sodium *p*-styrenesulfonate and acrylic acid in water were cograftered from one side of the base film, while on the other side chloromethylstyrene in xylene was grafted. Finally, chloromethylstyrene units were quaternized to produce the BPM intended for fuel cell applications.¹⁰⁷

The third method to produce BPM is layer-by-layer assembly (Figure 4c). This method involves the sequential deposition of multiple alternating layers of anion- and cation-selective materials until the desired thickness is achieved.^{104,113} It utilizes electrostatic interactions between oppositely charged polymers and their precursors. Typically, a substrate is initially coated with a positively charged layer followed by a negatively charged layer, and the process is repeated to build up the multilayer structure. The final layer is often cross-linked or treated to enhance its stability.¹⁰⁴ The layer-by-layer synthesis technique is usually combined with a casting technique.¹¹⁴ A heterogeneous BPM based on resin and polyvinyl chloride (PVC) has been fabricated using this technique. The casting solution consisting of resin, PVC, and montmorillonite (MMT) were casted layer-by-layer begun with an anion exchange layer and then followed by an interfacial catalyst layer and cation exchange layer. Prior to casting the next layer, the previous layer dried completely.¹¹⁴ The BPM from this study enhanced the acid-alkali production capacity of the BPM due to the presence of MMT as a catalyst at the interfacial layer. Successful production of acid and alkali from salt using BPM produced by a layer-by-layer technique was also demonstrated by Rathod et al.¹¹⁰ The BPM in this study consisted of a commercial IONSEP-HC-A anion exchange membrane, polyether sulfone based cation exchange membrane, and nanomolybdenum disulfide (MoS_2) particles. The BPM with the highest content of MoS_2 produced a significant enhancement in the membrane properties, including higher ion

exchange capacity and higher ionic conductivity, than the membrane with no particles. In addition, the presence of an interfacial layer filled with MoS_2 particles could improve the acid-alkali production and water splitting efficiency.¹¹⁰

Another fabrication technique of BPM is the application of hot or cold pressing.^{34,115} In this technique, after separately preparing the AEM and CEM layers using various methods (e.g., solution casting or interfacial polymerization), the two layers can be directly bonded together using heat and pressure or a lamination process (Figure 4d). This technique involves placing the two membranes in contact and subjecting them to elevated temperatures and pressure to promote intermolecular adhesion between the layers. Hot pressing helps create a strong and continuous bipolar layer.^{34,91} In the cold pressing process, the production of the BPM membrane is conducted by pressing together at ambient temperature.¹¹⁵ In a present study, poly(arylene ether ketone) or PAEK-based BPMs with no catalyst for water splitting were synthesized by a simple hot pressing technique. As the anion exchange layer, N3-butyl-substituted imidazolium-based PAEK or PAEK-APBI was employed, while a pendant dual-sulfonated PAEK or PAEK-SDPA membrane was used as the proton exchange membrane. The anion exchange and proton exchange membranes were first prepared by a solution casting technique. Then the two membranes were hot pressed for 5 min at 100 °C under 10 MPa. The thicknesses of the produced membranes after hot pressing were more than 150 nm. The BPMs showed very high chemical stability in acids and base. In addition, the membranes could dissociate water without any water splitting catalyst, which showed their potential to be applied in water electrolysis process to produce hydrogen energy.³⁴

An electrospinning synthesis technique is also applied to synthesize BPMs. Electrospinning involves the formation of ultrafine fibers through the application of an electric field to a polymer solution (Figure 4e). This technique has been employed to fabricate BPMs with high porosity, large surface area, and a uniform structure. Electrostatic assembly, on the other hand, utilizes the attraction between oppositely charged particles to deposit polymer layers and nanomaterials onto a substrate, enabling the creation of layered bipolar membranes with precise control over the composition and thickness of each layer.¹¹¹ In a recent study, BPM was fabricated by an electrospinning experiment. For the cation exchange polymer, sulfonated poly(ether ether ketone) was applied, while quaternized poly(phenylene oxide) (QPPO, with trimethylammonium fixed-charge sites) was employed as the anion exchange polymer.¹¹¹ The electrospinning process was conducted by employing two-spinneret equipment with a rotating and oscillating drum collector. The spinning process was initiated by spinning a SPEEK fiber mat, followed by dual fiber SPEEK/QPPO and $\text{Al}(\text{OH})_3$ nanoparticles for the catalyst in the interfacial layer. As the top layer, a QPPO fiber mat was applied. The produced membranes possessed a high interfacial area and high selectivity. The BPMs were also able to be operated at high current densities with a low drop in voltage. This is an indication that the BPMs fabricated by this technique have great potential for many applications including electrodialysis separations, electrochemical hydrogen generation, and fuel cells.

In addition to the synthesis of AEL and CEL layers, the role of a junction inside BPM has been the focus of research to enhance the water dissociation ability of BPM.¹¹⁶ Hence, the synthesis of the interface or junction is critical to ensure the good performance of a BPM. One of the recent approaches to

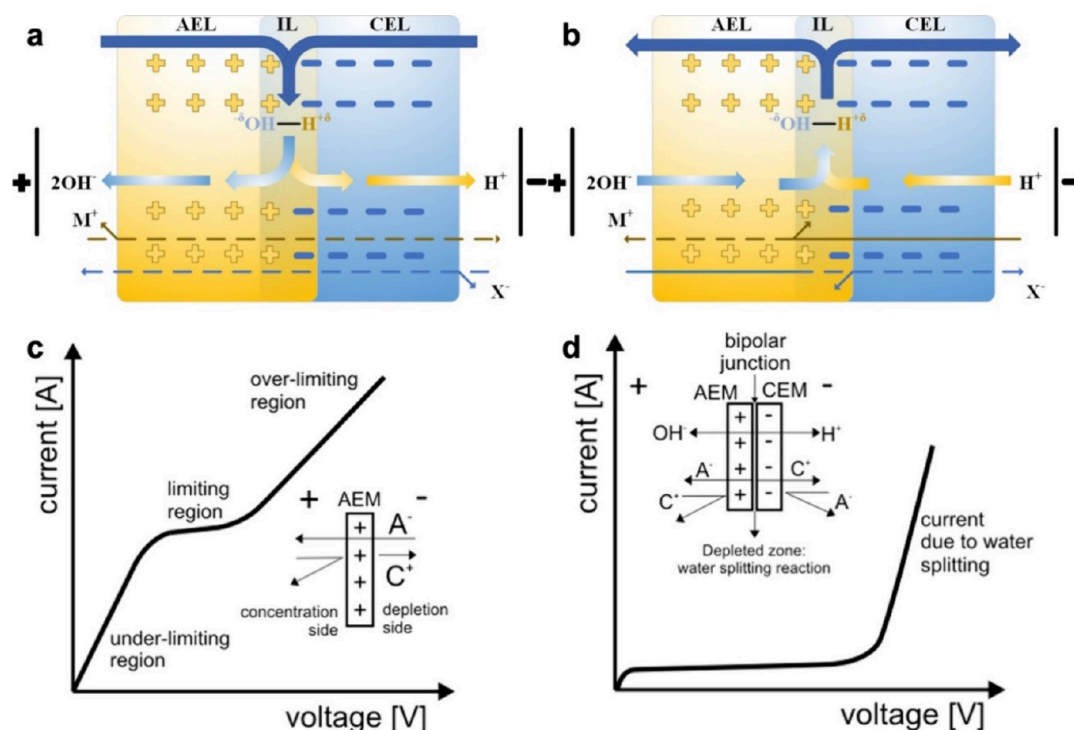


Figure 5. Water splitting in a bipolar membrane. (a) Water splitting or water dissociation in a reverse bias mode. (b) Water recombination in a BPM-based system. (a) and (b) are adapted from ref 91. (c) Typical current–voltage curve of an anion exchange membrane. (d) Typical current–voltage curve of BPM. (c) and (d) are reprinted with permission from ref 127.

improving the performance of BPMs is the incorporation of nanomaterials. Nanoparticles have been incorporated into the polymer matrix to enhance the ion transport, mechanical strength, and chemical stability of the membranes. These nanomaterials provide a high surface area and facilitate the creation of nanochannels, improving the conductivity of the membranes.¹¹⁶ Recently, inorganic catalysts containing metal elements have been the main trend of research, such as metal oxides/hydroxides ($\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$) and metal ion complexes.⁹⁶ The dissociation of water on metal oxides and hydroxides occurs by adsorption of water onto the surface, followed by transfer of protons from the water to neighboring oxygen atoms, resulting in hydroxide ions. However, in the actual electrolysis process, the catalyst containing metal ions has the disadvantage that the metal ions are easily lost due to their small size, and an effective method is to immobilize the metal ions.^{102,116} In addition, other materials, such as graphene oxide (GO),^{117,118} molybdenum disulfide (MoS_2),¹¹⁶ montmorillonite (MMT) nanoclay,¹¹⁴ and dipicolinic acid.¹¹⁹

It is important to note that the choice of synthesis technique depends on factors such as the desired properties of the bipolar membrane, ease of scalability, and specific application requirements. Each technique has its advantages and limitations, and researchers continue to explore and develop new methods for synthesizing bipolar membranes with enhanced performance and efficiency.

3.2. Water Splitting Mechanisms in Bipolar Membrane. BPM has emerged as a promising technology for efficient water splitting or water dissociation due to its unique structure and ion exchange capabilities. For hydrogen production, water splitting or water dissociation is crucial, as this is the process of separating water into its constituent elements.^{120–123} A BPM consists of three layers, namely a strong acid cation-exchange layer (CEL), a strong base anion-exchange

layer (AEL), and a bipolar or junction or interfacial layer in between, which usually contains a catalyst that promotes water dissociation.^{117,124} The AEL selectively allows the passage of anions, while the CEL allows the passage of cations. The junction layer is a combination of a cationic and an anionic polymer that acts as a barrier and facilitates ion exchange. According to the Donnan exclusion principle, BPM is impermeable to cations and anions, but at the same time, the BPM is a strong emitter of ions in the form of protons (i.e., usually in the form of H^+ ion) and hydroxide (OH^-) ions from enhanced water dissociation.¹²¹ The water splitting or water dissociation mechanism that occurs inside BPM is very important to understand before the BPM can be applied in various applications. Hence, this section of this paper critically summarizes the mechanism based on previous studies on the water splitting or water dissociation mechanism.^{117,121,124–126}

Compared to conventional ion exchange membranes, such as anion exchange membranes (AEMs) and cation exchange membranes (CEMs), which are commonly used for ion exchange purposes, BPMs are not synthesized mainly for bridging the ion transport across the BPMs. In many applications, such as for acid and base production¹²⁸ and water electrolysis,^{34,129,130} the main role of BPMs is to promote water splitting or water dissociation, where the protons and hydroxide ions are produced from water dissociation inside the BPMs. Unlike an electrolysis process, the water splitting or water dissociation in BPMs does not produce any gas.⁹¹ In other applications, such as in fuel cell and flow batteries,¹³¹ the capability of BPMs to recombine water or the opposite of water dissociation has also been studied.

The BPM abilities to either dissociate or recombine water molecules can be explained by using an analogy of BPM system as a p–n (positive–negative) junction in a solid semiconductor.^{120–122} In a p–n junction, the working condition

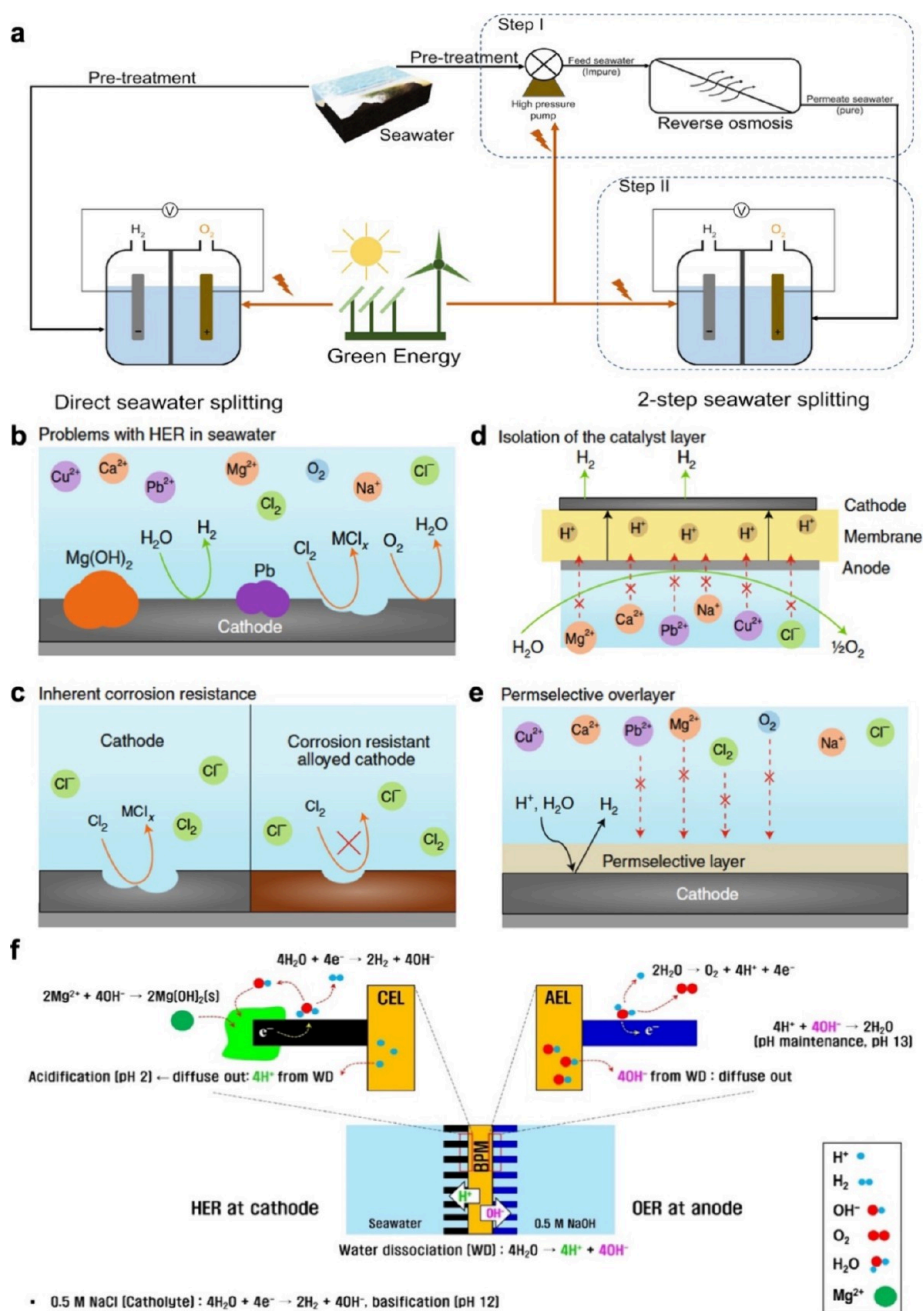


Figure 6. Seawater electrolysis. (a) Indirect and direct seawater electrolysis.¹³⁶ Used under a Creative Commons license, <https://creativecommons.org/licenses/by/4.0>. (b–e) Challenges for designing seawater-based electrolysis. Reprinted with permission from ref 149. Copyright 2023 Springer Nature Limited. (f) Scaling formation in electrode of BPM electrolyzer. Reprinted with permission from ref 150.

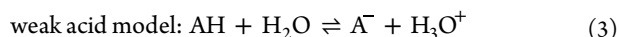
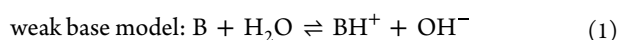
can be adjusted either as “reverse bias” or “forward bias” modes of operation as shown in Figure 5a,b. In reverse bias mode, the CEL of the system is located near the negative electrode or cathode, and the AEL is placed near the anode. Whereas in forward bias mode, the polarities of the layer and electrode are positioned in the reverse direction compared to that in the reverse mode of operation. Water dissociation occurs when the reverse mode is applied. When current is applied across a BPM, the ionic current through the membrane cannot be kept by ions in the bulk solution. This is mainly because both cations and anions cannot pass both layers of a BPM. To compensate for the phenomenon, water dissociation at the membrane interface occurs to produce H⁺ and OH⁻ ions that carry the ionic current. The H⁺ ions then pass through the CEL and the OH⁻ ions leave

the membrane through AEL. Both ions produce an acid and a base environment on opposite sides of the membrane, consequently creating a pH gradient over the BPM.^{128,132} In contrast to reverse bias, in the forward bias mode of operation H⁺ and OH⁻ ions migrate from the outer solutions toward the bipolar junction, where they recombine into water. Water permeates out of the junction through CEL and AEL, thus leading to the acid–base neutralization. In forward bias mode, the membrane has low resistance due to ion accumulation at the junction, while under reverse bias, initially the BPM shows high electrical resistance followed by the water dissociation mechanism that leads to the increase in current associated with the increase in voltage as presented in a typical current–voltage curve in Figure 5d (which is different from those in anion

exchange membrane electrolysis (Figure 5c)). This water dissociation mechanism is usually explained by the second Wien effect, which describes the influence of strong electric fields on weak electrolytes. In this case, the dissociation degree and ion mobility of electrolytes increase at high electrical field.⁹¹ However, the second Wien effect assumes that the applied electric field is the sole cause of water dissociation. This assumption will need unrealistically high values of electric field at the junction^{108,133} and also neglect the additional results when high electric fields are applied.

In addition to the second Wien effect, in current years, several publications explained the water dissociation or water splitting phenomenon in a BPM using catalytic process via protonation–deprotonation reactions at the BPM interface facilitated by the membrane ionic headgroups.^{126,129,130,134} The protonation–deprotonation mechanism was first proposed by Simon and Khanarian in 1978 to explain the water dissociation mechanism in BPM.¹²⁰ The theory basically claims the possibility of H⁺ and OH[−] ions production in proton-transfer reactions between water and fixed charged groups^{91,134,135} with the presence of a catalyst in water splitting. Hence, in contrast to the second Wien effect that assumes similar water-dissociating properties for both CEL and AEL layers, the protonation–deprotonation mechanism explains that the water dissociation rate depends on the type of fixed groups in CEL and AEL, where both layers might provide different catalytic activities.¹¹⁶

In general, the protonation–deprotonation mechanism proposes that the weakly basic or acidic headgroups of the ionomers in the BPM dissociates water in the interface layer in a two-step reaction as^{91,121,124,125,133}



where BH⁺ is the fixed charged group attached on AEL that acts as the catalytic center. In the weak acid mode, the catalytic center is dominated by A[−]. Hence, combining eqs 1 and 2 as well as eqs 3 and 4, the water splitting/water dissociation and water recombination reactions can be written as



4. BIPOLAR MEMBRANE SEAWATER ELECTROLYSIS

The production of hydrogen via seawater electrolysis presents a promising avenue for addressing the challenges of energy sources and supply. There are two distinct approaches to seawater electrolysis, namely, indirect and direct methods. Indirect seawater electrolysis requires an initial stage of desalination whereby freshwater is produced and subsequently used as the feedstock for conventional water electrolysis to generate hydrogen (Figure 6a). This approach circumvents the negative impacts of high salinity on the electrolysis process, but it necessitates an additional desalination step, thereby increasing the overall energy consumption and cost.^{136–139} Conversely, direct seawater electrolysis involves the direct splitting of seawater into hydrogen and oxygen, without the requirement for a separate desalination stage (Figure 6a), making it more energy-efficient and cost-effective.^{137–139}

However, direct seawater electrolysis poses its own set of challenges (Figure 6b–e). The high concentration of salts in seawater can cause mineral scales to form on the electrode surfaces, which can impede the efficiency of the electrolysis process and hinder hydrogen production (Figure 6b). This may necessitate frequent cleaning or replacement of the electrodes, leading to operational disruptions and higher costs. The presence of corrosive species such as chloride ions in seawater leads to significant corrosion of the electrodes and other electrolysis components, which results in reduced equipment lifespan and increased maintenance costs.^{140,141} Additionally, the formation of hypochlorite ions during electrolysis can exacerbate the corrosion issues (Figure 6c). Seawater has lower ion conductivity compared to freshwater or low-salinity water, which adversely impacts the overall electrolysis efficiency.^{140,142} The higher resistance to ion transport necessitates higher electrical potentials, which can lead to an increased energy consumption. The generation of hydrogen and oxygen gas during electrolysis can also result in gas bubble accumulation on the electrode surfaces, further reducing the efficiency and potentially causing electrode fouling. Proper gas bubble management strategies are therefore crucial for maintaining stable operation.^{143,144}

While the use of PEM electrolysis is widespread in freshwater electrolysis due to its high efficiency and rapid response, it faces challenges in seawater electrolysis. The PEM electrolysis membrane is vulnerable to degradation in the presence of high salinity and impurities in seawater, resulting in decreased performance and increased costs. To make PEM electrolysis more appropriate for seawater applications, specialized and costly materials are required.^{145,146} AEM electrolysis has superior tolerance to high salinity than PEM electrolysis and can operate at lower temperatures, thereby conserving energy.^{143,147} Nonetheless, AEM technology still has limitations with respect to stability and selectivity under the harsh conditions of seawater electrolysis. Research is ongoing to enhance the performance and durability of AEMs in seawater electrolysis systems. Alkaline electrolysis is one of the earliest electrolysis technologies, but it is not suited for seawater electrolysis due to the presence of carbonate ions in seawater.^{143,148} These ions can cause carbonates to precipitate, resulting in scaling and a decreased overall efficiency. Additionally, alkaline electrolysis usually necessitates high operating temperatures, which can lead to increased energy consumption.¹⁴⁸

BPM electrolysis offers a potential solution to the challenges faced by other water electrolysis technologies in seawater electrolysis. When an electrical field is applied, BPM facilitates the transport of protons from the anode to the cathode while simultaneously generating hydroxide ions, resulting in localized pH changes.^{151,152} The localized pH changes at the BPM help prevent scaling, enhancing the overall system efficiency (Figure 6f). The hydroxide ions produced at the cathode can react with the acidic components in seawater, reducing the likelihood of scale formation.^{150,153} BPM electrolysis can help manage gas bubble formation more effectively, reducing the risk of electrode fouling. The localized pH changes can facilitate the release of gas bubbles, preventing their accumulation on the electrode surfaces.¹⁵³ The water dissociation reaction, being the crucial aspect of BPM performance, necessitates further development with respect to the reaction rate. Therefore, the present discourse expounds on the strategies to enhance the water

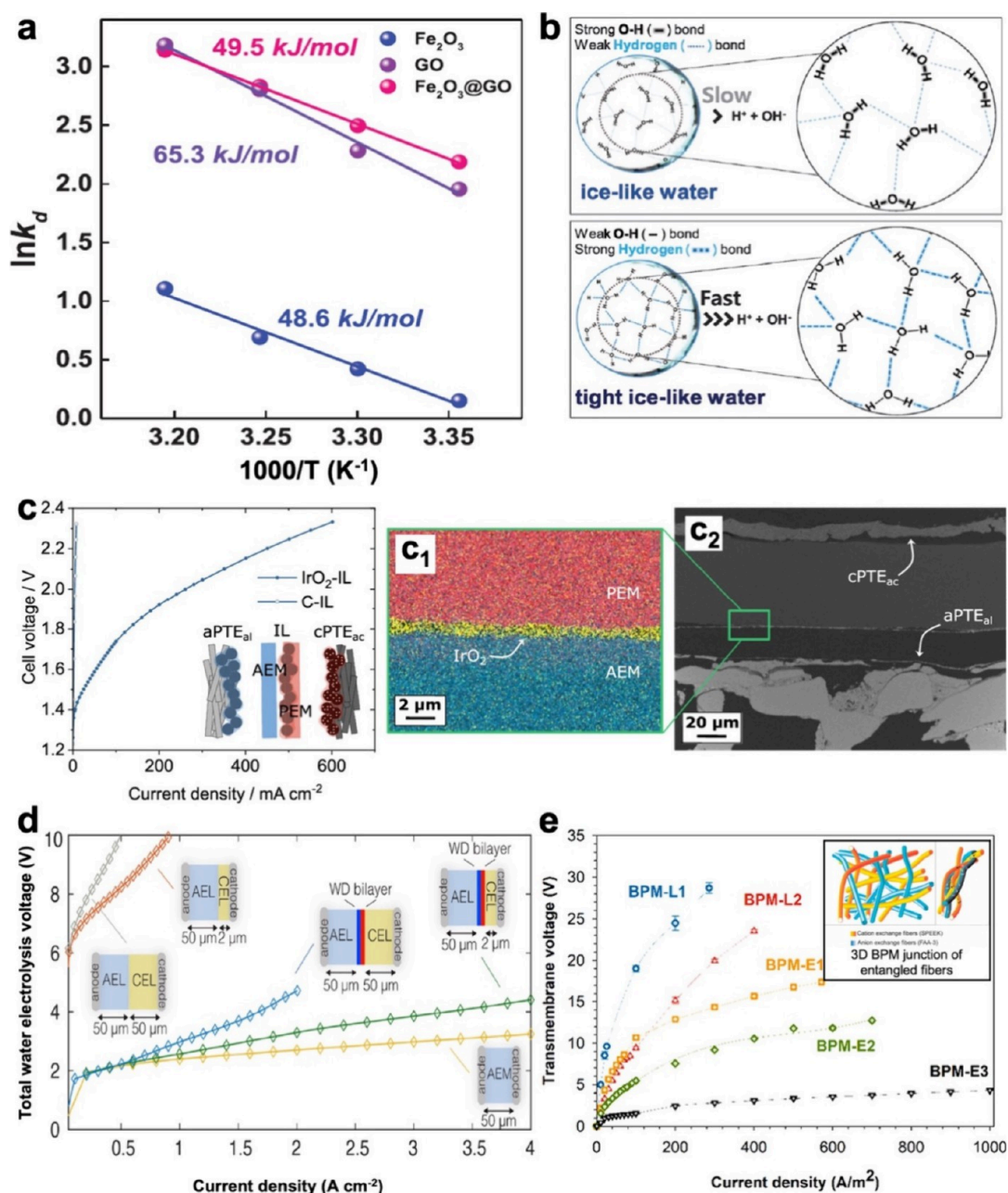


Figure 7. Several reported strategies to improve BPM performance. (a) Arrhenius plots for the WDR rate constant employing several types of catalysts (at a reverse bias of -0.88 V). (b) Schematic illustration of the impact of tight ice-like water and ice-like water on the water dissociation rate. (a) and (b) are reprinted with permission from ref 157. (c) BPM electrolyzer with IrO₂-IL. (c₁) EDX map of the membrane cross section. (c₂) SEM of the membrane cross section. (c), (c₁), and (c₂) are reprinted from ref 161 under a Creative Commons license, <https://creativecommons.org/licenses/by-nc-nd/4.0>. (d) Voltage–current curve of electrolysis using various BPM types. Reprinted with permission from ref 162. (e) Current–voltage curve BPMs with a laminated 2D junction (BPM-L) and a 3D electrospun entangled junction (BPM-E).⁹⁷ Used under a Creative Commons license, <https://creativecommons.org/licenses/by-nc-nd/4.0>.

dissociation reaction in BPM seawater electrolysis in a subsequent section.

5. ENHANCEMENT STRATEGIES OF SEAWATER SPLITTING USING BIPOLAR MEMBRANE

To further improve the seawater dissociation reaction in BPMs, a combination of catalyst selection, membrane design optimization, implementation of advanced materials and surface modifications, and optimization of operational parameters can be employed. Catalyst selection involves choosing high-activity and -concentration catalysts to enhance the water dissociation

process. Chemicals like amphiprotic hydroxide compounds, weak polymeric acids and bases, and other suitable catalysts have been studied to determine their effectiveness in catalyzing seawater dissociation.^{28,154–156} For instance, the Fe₂O₃@GO catalyst, which comprises highly Lewis acidic Fe atoms, produces partially dissociated bound water.¹⁵⁷ This form of water contributes to the compactness of “ice-like water,” resulting in weaker O–H interactions between water molecules. As a result, the activation barriers are reduced, which improves the water dissociation reaction rate dramatically (Figure 7a,b). In another study, the utilization of Fe-MIL-101-NH₂ as the

interfacial layer was found to enhance water splitting.¹⁵⁸ The membrane performance was notably influenced by the loading concentration of Fe-MIL-101-NH₂, with an optimal 0.1 g/L concentration. Fe-MIL-101-NH₂, containing weak acid and metallic groups, served as an effective catalyst for water dissociation. The modified BPM demonstrated improved efficiency in water dissociation due to the presence of amino groups, iron ions, and the material porous structure.¹⁵⁸ A novel approach for creating shielded catalytic bipolar membranes utilizing an earth-abundant goethite Fe³⁺O(OH) catalyst has been introduced.¹⁵⁹ This strategy effectively reduces the activation energy barrier, resulting in energy efficiency and cost effectiveness. The membranes displayed low water dissociation voltages, exceptional cyclic stability, long-term electrostability, and rapid acid–base generation. Polyethylene glycol, a hydrophilic polymer, has improved the water dissociation reaction in BPM.¹⁶⁰ A layer-by-layer solution casting method with varied molecular weights of PEG as the interface layer was used to construct various BPMs. The experimental results emphasized outstanding PEG catalytic activity in water dissociation, with increased molecular weights resulting in better performance.¹⁶⁰ Mayerhöfer et al. investigated the incorporation of an IrO₂ interlayer between anion exchange membrane and the proton exchange membrane (Figure 7c,c₁,c₂) for improving the efficacy of a water dissociation reaction in BPM.¹⁶¹ The incorporation of an IrO₂ interlayer resulted in a significant increase in the catalytic activity for water dissociation, leading to a noteworthy surge in current density from 5 mA cm⁻² to 450 mA cm⁻² at 2.2 V (Figure 7c). This augmentation was ascribed to the catalytic activity of IrO₂, as opposed to an increase in surface area, which was demonstrated by the integration of nanoparticles into the interfacial layer. Nevertheless, the study also brought to the fore complications associated with long-term stability, as the membrane configuration underwent significant and irreversible performance degradation after 10 h of operation.

Membrane design optimization is another strategy to improve seawater dissociation in BPM. Transporting water molecules against the flow of hydrated H⁺ and OH⁻ in the AEL and CEL poses a challenge for water dissociation in BPMs, limiting their operation at current densities above 0.5 A cm⁻².¹⁶² A recent study successfully demonstrated a thin-CEL BPM configuration that maintained a significant pH difference between the anode and cathode, even at high current densities of up to 3.4 A cm⁻².¹⁶² This BPM achieved efficient water dissociation with a low total electrolysis voltage and an estimated overpotential (Figure 7d). The ability to operate at high current densities is vital for emerging BPM applications, particularly water electrolysis. A study investigated the impact of the fixed charge density at the bipolar junction on water splitting.¹⁶³ The results showed a strong dependence of water-splitting properties on both the fixed charge density at the bipolar junction and the degree of cross-linking in the AEL. In order to enhance water splitting efficiency, an alkali-treated polyacrylonitrile layer was introduced as an active junction material using a spin coating technique.¹⁶³ This modification led to a significant improvement in water splitting efficiency.¹⁶³ In addition to fixed charge density, the water content significantly impacts the water dissociation reaction. A study has compared two types of heterogeneous bipolar ion exchange membranes made of powdered ion-exchange resin with varying water contents.¹⁶⁴ The findings revealed that the membranes with a higher water content exhibited approximately 25% higher performance at the

stack. Using nanoporous membranes is another strategy to facilitate efficient water dissociation. Nanoporous membranes with a large surface area can improve ion transport and promote water dissociation. One study showed that shielded goethite catalysts allow quick water dissociation in bipolar membranes.¹⁵⁹

Another approach to enhancing seawater dissociation was proposed through membrane structure engineering. A benzimidazolium-based anion exchange membrane was used to create BPMs in combination with a Nafion membrane.¹⁶⁵ The process involved laminating the anion exchange membrane with a Nafion NR-211 membrane without any interface modification. As a result, the fabricated bipolar membranes displayed an average thickness of 90 μm, with enhanced water splitting. The key factor contributing to improved water dissociation lies in the sharp hydrophilic interface formed by the two membranes with a space charge region spanning just a few nanometers. This arrangement generates a substantial electric field at the interface, effectively enhancing water dissociation.¹⁶⁵ The dimension of the bipolar junction is also an important factor. A study has explored the impact of combining anion and cation exchange nanofibers at the junction of BPM on the rate of water dissociation.⁹⁷ Two types of bipolar membranes were compared: one with a 2D laminated junction and another with a 3D electrospun entangled junction (Figure 7e). The results showed that BPMs with the 3D entangled junction exhibit a higher water dissociation rate, as indicated by the reduced BPM potential, than the 2D laminated junction (Figure 7e). The entangled junction provides a larger surface area for the reaction to occur, which increases the efficiency of the water dissociation process.

An alternative approach to enhance seawater splitting in BPM is introduction of electronically conducting materials along with a traditional catalyst in the interlayer.¹⁶⁶ Electronic conducting substances like graphene, carbon nanotubes, and graphene oxide have been successfully employed to create BPM interlayers.¹⁶⁶ The results displayed a significant reduction in voltages required for water splitting in BPMs with these interlayer materials compared to BPMs without interlayer material. The inclusion of electronically conducting interlayer materials in BPMs intensifies the electric field within the mobile ion-depleted region. This increased electric field intensity plays a pivotal role in facilitating the dissociation of water into hydronium and hydroxide ions, offering promising prospects for advancing water splitting.¹⁶⁶ A similar approach has been reported in a study.¹¹⁸ BPMs were synthesized by integrating phosphorylated graphene oxide (PGO), quaternized graphene oxide (QGO), and a combination of PGO/QGO. BPM with PGO/QGO showed high current efficiency and reduced energy consumption compared with other examined BPMs. The BPM with PGO/QGO also showed an enhanced water-splitting performance, notable resistance reduction, and exceptional permselectivity across more than ten experimental cycles.

Various approaches have been explored to enhance the chemical stability of the BPMs. One such approach involves employing chemically stable materials. The alkaline stability of two novel aminated polyphenylene-based polymers used as anion exchange layers in BPMs was investigated in a study.¹⁶⁷ The custom-made BPMs were then compared with commercially available membranes. The findings revealed that the polyphenylene-based membranes exhibited significantly higher stability against backbone cleavage than the commercially used polysulfone-based anion exchange membranes. The custom-

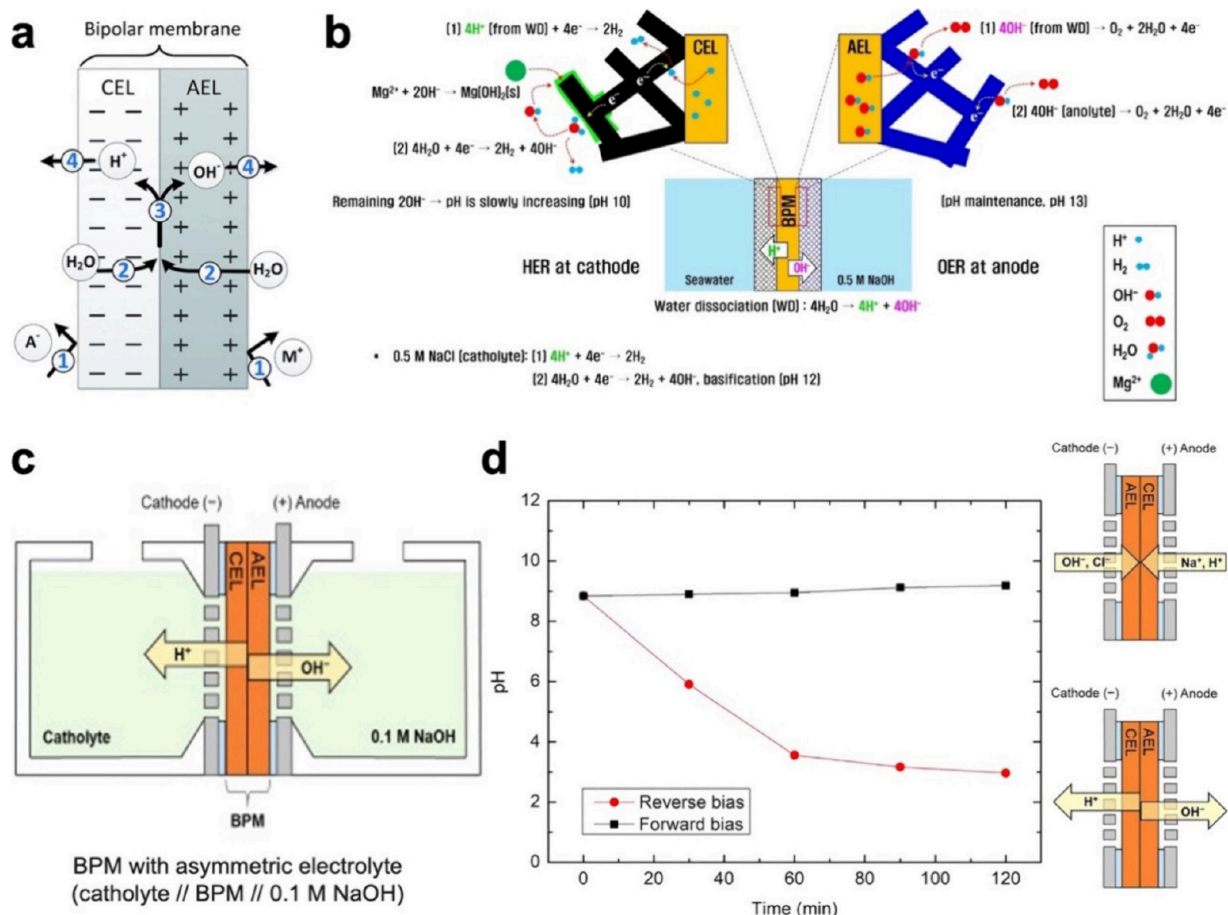


Figure 8. (a) The operational mechanism of a bipolar membrane is described as follows: cations (M^+) are barred from the AEL, and anions (A^-) are prevented from entering CEL (1). This restriction causes water molecules to dissociate at the boundary between these two layers (3), a process facilitated by the diffusion of water (2). Consequently, this leads to the movement of H^+ and OH^- ions (4). Reprinted from ref 174. (b) Various reactions occur during seawater electrolysis. Reprinted from ref 150. (c) BPM electrolyzer with asymmetric electrolyte. (d) Effect of BPM electrolysis mode on solution pH. (c) and (d) are reprinted with permission from ref 153.

made membrane, containing a quaternary ammonium-tethered poly(biphenylalkylene) (PBPA) AEL, displayed exceptional performance stability in both tests. Further stability tests and DFT calculations confirmed that the PBPA polymer outperformed others, showcasing the highest level of stability.¹⁶⁷ Poly(arylene ether ketone) (PAEK) is another chemically stable polymer widely used in the preparation of BPMs. A synthesized BPM was fabricated by incorporating dual-sulfonated poly(arylene ether ketone) as the CEL and butyl- N_3 -substituted imidazolium-functionalized poly(arylene ether ketone) as the AEL.³⁴ This BPM was effectively employed as a separator in an acid-alkaline dual-electrolyte water electrolysis system to prevent bulk neutralization. The BPM showed remarkable chemical stability with a minimal weight loss of less than 3.4% after being subjected to both strong acids and bases for 28 days. Such exceptional stability can be attributed to PAEK's inherent properties, specifically the rigid aromatic ring present in its chemical structure, which contributes to its high resistance to chemical degradation. Numerous works have exerted substantial endeavors to amplify the rate of water dissociation in BPM electrolyzers.^{168–171} Nevertheless, the utilization of the BPM electrolyzer in seawater electrolysis is relatively limited. The efficacy of BPM electrolyzers in seawater electrolysis is discussed further in the next section.

6. PERFORMANCE EVALUATION OF BIPOLAR MEMBRANE SEAWATER SPLITTING SYSTEM

The working principle of a BPM highlights the selective permeability of its layers: cations (M^+) are barred from entering the AEL, and anions (A^-) cannot enter the CEL (Figure 8a). This specificity results in water molecules diffusing to the interface between these two layers, where they undergo dissociation into hydrogen ions (H^+) and hydroxide ions (OH^-). This process is crucial for electrolysis, as it supplies the necessary ions for the hydrogen evolution reaction (HER) at the cathode and potentially for the oxygen evolution reaction (OER) at the anode, depending on the conditions. The mechanism by which water reaches this interface is through diffusion, driven by concentration gradients across the membrane. This diffusion is essential for maintaining a continuous supply of water to the interface, ensuring that the electrolysis process can proceed efficiently. The BPM's design facilitates this by creating a physical and chemical environment conducive to water molecule movement and dissociation, effectively separating the generation of H^+ and OH^- ions and directing them toward their respective electrodes.^{170,172,173}

The interplay between the OER and chlorine evolution reaction (CER) poses a significant challenge in seawater electrolysis, particularly due to seawater's high chloride ion

concentration which favors ClER at the anode, risking corrosive damage to electrolyzer components. A BPM electrolyzer, utilizing porous electrodes, enhances the charge-transfer reaction efficiency, supported by the confinement effect of the porous structure that extends the interaction of generated protons and hydroxide ions with the electrode surface, facilitating efficient electron transfer (Figure 8b). The acidification of seawater, driven by proton diffusion from BPM's water dissociation into the catholyte, allows proton reduction without significantly altering seawater's pH, thus supporting hydrogen production amidst increasing pH and inorganic precipitate formation. Magnesium ions in seawater capture hydroxide ions from the HER, preventing catholyte basification and contributing to seawater acidification alongside BPM's proton supply.¹⁵⁰

Figure 8c,d reveals how proton flux influences seawater acidification in a bipolar membrane (BPM) system, highlighting the directional migration of cations and anions under a unidirectional electric field. Forward bias leads to the accumulation of Na^+ and Cl^- at the CEL/AEL interface, migrating through the BPM with minimal resistance, which inhibits water dissociation (WD) and results in a slightly alkaline solution (around pH 9). Conversely, the reverse bias induces acidification of the catholyte, pinpointing protons from WD as the acidifying agents. This illustrates that hydroxide precipitation and WD under reverse bias collectively acidify the catholyte, showcasing the BPM's crucial role in pH modulation based on the electric bias direction. This process aids in the disintegration of inorganic precipitate films, facilitated by the Pt-mesh cathode, as evidenced by reduced magnesium and calcium ion concentrations upon continuous operation. Substituting the BPM with an anion exchange membrane shifts the solution toward strong alkalinity due to a stark magnesium ion reduction, emphasizing the BPM's essential function in maintaining pH balance. Thus, this BPM-mediated acidification mechanism during direct seawater electrolysis is pivotal for reducing energy consumption, suppressing ClER, and enhancing OER selectivity.¹⁵³

Several investigations have been conducted on the efficacy of BPM electrolyzers in seawater electrolysis. One such study involved a comparative analysis with proton exchange membrane electrolyzers, utilizing 0.5 M NaCl as the cathode feed.¹⁴² In comparison to symmetric deionized water-fed conditions, both electrolyzers displayed an elevated total cell voltage. The presence of NaCl caused alterations in H^+ and Na^+ ion concentrations at the cathode interface, thereby influencing the cell voltage. The BPM water electrolyzer was found to be more susceptible to NaCl effects than the proton exchange membrane water electrolyzer, leading to potential losses in the water dissociation layer and the AEL-anode catalyst interface. Cl^- or Na^+ ions that reach the BPM junction may also hinder water dissociation or WD catalyst active sites, culminating in increased resistance in the water dissociation process. However, the BPM water electrolyzer demonstrated superior chlorine (Cl^-) oxidation mitigation at the anode, resulting in a significantly higher Faradaic efficiency (FE) for H_2 production. Specifically, a BPM water electrolyzer (BPMWE) limited Cl^- oxidation to corrosive OCl^- with an FE of only 0.005%, while a PEM water electrolyzer (PEMWE) achieved up to 10% FE for Cl^- oxidation (Figure 9a). This advantageous property of BPMWEs enables longer-term seawater electrolysis, outperforming PEMWEs by 140 times in this context. In contrast, the PEMWE experienced a rapid increase in voltage and failure

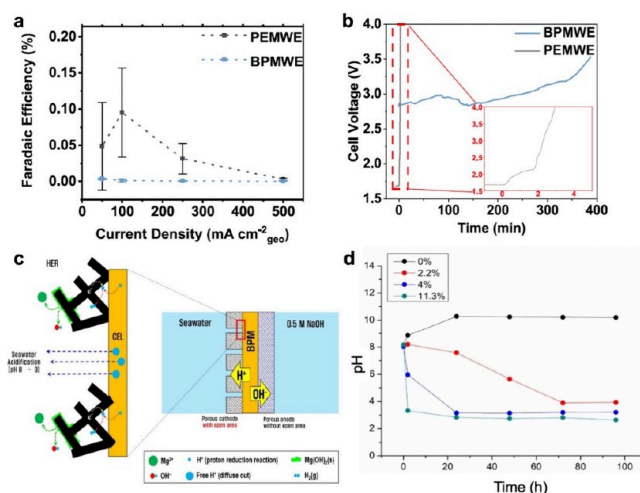


Figure 9. Bipolar membrane seawater electrolysis. (a) Faradaic efficiency of Cl^- oxidation during the electrolysis of 0.5 M NaCl solution. PEMWE: proton exchange membrane electrolysis. (b) Cell voltage–time profile during real water electrolysis. BPMWE: bipolar membrane water electrolysis. (a) and (b) are reprinted with permission from ref 142. (c) The process of seawater acidification occurs as a result of the diffusion of free protons, which emanate from the open area of a porous cathode. (d) Variability in the pH levels of the bulk seawater. (c) and (d) are reprinted with permission from ref 150.

within 3 min of operation due to the generation of corrosive free chlorine species in its acidic anode-CEL environment (Figure 9b).

Han¹⁵⁰ conducted a study on optimizing the interface between a porous electrode and a BPM in zero-gap seawater electrolyzers to improve the performance of direct seawater electrolysis. The study implemented an asymmetric hydrogen evolution reaction at the porous cathode and created a locally acidic environment through proton flux from the BPM-induced water dissociation. This resulted in stable hydrogen production with a lower overpotential and improved stability compared to traditional mesh electrodes. The introduction of a small open area in the BPM allowed for free protons to diffuse out and acidify the seawater, further mitigating inorganic scaling on the cathode's front side (Figure 9c,d). These findings hold promise for minimizing inorganic scaling and improving interfacial phenomena in direct seawater electrolysis and related electrochemical systems using natural seawater as the catholyte. The study also investigated the effect of the open area of the electrode on the seawater pH and cell potential in direct seawater electrolysis. A larger open area resulted in faster seawater acidification, which had an impact on the cathode potential and overall cell potential. The study provided valuable insights into this relationship, but further exploration of the underlying mechanisms and broader implications is necessary to enhance its practical relevance and contribution to the field.

In a separate investigation, Han et al.¹⁵³ employed a technique known as synergistic acidification by inorganic precipitation, combined with proton flux from a bipolar membrane, in the process of direct seawater electrolysis. The pH level of seawater was effectively decreased to 2, with hydroxide ions being produced at the cathode through the process of HER. The acidification process was accomplished by the cooperative impact of hydroxide ions that were trapped by inorganic precipitation at the cathode and proton flux from the

Table 3. BPM Seawater Electrolysis^a

BPM	electrode		electrolyte	performance	ref
	cathode	anode			
homemade	Pt black on carbon paper PTL	IrOx nanoparticles on a stainless-steel PTL	seawater for both electrolytes	total cell voltage increased by 0.90 V (>6 h operation; 250 mA/cm ²)	142
CEL: Nafion 212 AEL: PiperION TP-85 IL: TiO ₂ nanoparticles free chlorine was undetected					
commercial BPM (Astom, Corp. Japan)	porous Pt	porous Pt	catholyte, seawater; anolyte, NaOH solution (0.5 M)	cell voltage was stable at -2.3 V (100 h; 20 mA/cm ²) inorganic scaling on electrode was successfully minimized	150
commercial BPM (Astom, Corp. Japan) with Fe catalyst	Pt-coated Ti mesh	Pt-coated Ti mesh	catholyte, sea salt solution; anolyte, NaOH solution (0.1 M)	cell voltage was changed from -3.0 to -3.5 V (100 h; 10 mA/cm ²) electrolyte crossover was effectively blocked CIER was suppressed, selectivity for OER was maximized	153
commercial BPM (Fumasep FBM, FuMA-Tech)	NiMo	NiFe-LDH	artificial seawater (36 g/L salinity) as electrolyte in desalination cell anolyte, 1 M KOH; catholyte, 1 M H ₂ SO ₄	BPM electrolysis was coupled with desalination cell. Faradaic efficiencies for O ₂ and H ₂ production >95% (at <i>j</i> = 100 mA cm ⁻² , 20 h)	175

^aPTL: porous transport layer.

dissociation of water in a separator that was acted upon by a bipolar membrane. The process of acidification that was used in the proposed direct seawater electrolysis system with a BPM played a key role in reducing cathode passivation, eliminating the requirement of additional inorganic precipitate treatment and lowering the necessary cathode potential for the HER. This, in turn, allowed for stable and long-term direct seawater electrolysis. The BPM played a critical part in sustaining the optimal electrolyte concentration, suppressing the CIER, and optimizing the efficiency of the OER.

Kim et al.¹⁷⁵ conducted a study on an electrolyzer design that is a combination of desalination and electrolysis. The design utilized a Ni- and Fe-layered double hydroxide (NiFe-LDH) anode and a binary NiMo cathode for overall water splitting, coupled with desalination of saline water and production of value-added chemicals. Remarkably low overpotentials were demonstrated by the electrode pairs for the OER and HER in 1 M KOH and 1 M H₂SO₄ solutions, respectively, which were comparable to those of noble metal catalysts. The electrode pairs were separated by a BPM. By employing anion- and cation-exchange membranes with BPMs in specific configurations (NiFe-LDH/BPM/[AEM/CEM]_{*n*}/BPM/NiMo; *n* = 1 or 5), the system efficiently desalinated brackish water and seawater with a specific energy consumption of 1.8 kWh m⁻³. The system also produced HCl and NaOH at high Faradaic efficiencies (>95%) for O₂ and H₂ production at 100 mA cm⁻² over 20 h, without altering the initial pH values of the anolyte and catholyte. The electrode pairs exhibited excellent stability, which makes the proposed multifunctional electrolyzer a highly promising solution for green hydrogen production, saline water desalination, and value-added chemical synthesis.

While the utilization of a BPM electrolyzer for seawater electrolysis displays promise, as demonstrated by several studies (Table 3), there remain substantial areas of research and development that necessitate attention, notably pertaining to the BPM itself, in order to further decrease the energy required for water dissociation. It is imperative to conduct further

analyses and improvements in BPM technology to fully realize its applicability and optimize its effectiveness in direct seawater electrolysis.

The implementation of direct seawater electrolysis using BPM electrolyzer faces numerous obstacles impacting its industrial deployment and economic viability. Corrosion, primarily due to high chloride concentration in seawater, affects the longevity of components like electrodes and BPM, necessitating corrosion-resistant materials and coatings for system stability.^{17,153,176} Inorganic scaling, resulting from various compounds in seawater, leads to scaling on electrode surfaces, blocking catalyst sites, reducing efficiency, and increasing cell voltage, requiring effective mitigation strategies like novel electrode designs or water pretreatment processes.¹⁵⁰ The high cost of materials such as iridium for electrodes and corrosion-resistant components for BPMs also poses financial challenges, driving the need for more cost-effective materials or optimized usage.¹⁴² Additionally, commercial BPMs may not be sufficiently optimized for large-scale seawater electrolysis in terms of water dissociation kinetics and durability in harsh conditions, necessitating research into advanced BPMs that are more efficient and cost-effective.⁵² Addressing these challenges is essential for the widespread industrial application and economic viability of direct seawater electrolysis using BPM technology, with research efforts focused on overcoming corrosion, scaling, and cost barriers, as well as enhancing BPM performance for efficient and sustainable seawater electrolysis.¹⁷⁷

The effectiveness of catalysts in BPM electrolyzers has been a focal point in enhancing water dissociation. High-activity catalysts, such as amphoteric hydroxide compounds and weak polymeric acids and bases, have shown promise in improving the seawater dissociation efficiency. Notably, the Fe₂O₃@GO catalyst, which features Lewis-acidic Fe atoms, aids in producing partially dissociated bound water. This catalyst structure leads to reduced activation barriers, thereby significantly enhancing the rate of the water dissociation reaction.¹⁵⁷ Further research in this

area, exploring a variety of catalysts, could yield substantial improvements in the efficiency of BPM electrolyzers.

The design and composition of BPMs are critical in determining their efficiency. Research has indicated that factors such as fixed charge density at the bipolar junction and water content within the membranes significantly influence the water splitting efficiency. For instance, membranes with higher water content have demonstrated superior performance, highlighting the importance of membrane hydration in BPM functionality.¹⁶⁴ Moreover, the use of nanoporous membranes, which offer enhanced ion transport and promote water dissociation, represents a promising avenue for design optimization.¹⁵⁹

Engineering the structure of BPMs by combining different types of membranes can lead to improved water dissociation. For example, the use of a benzimidazolium-based anion exchange membrane in combination with a Nafion membrane has shown potential for enhancing water splitting. This combination creates a sharp hydrophilic interface and a substantial electric field at the junction, which effectively promotes water dissociation.¹⁶⁵ Exploring various combinations and configurations of membranes could provide further insights into optimizing the BPM design for enhanced performance.

Introducing electronically conducting materials such as graphene, carbon nanotubes, and graphene oxide into BPM (bipolar membrane) interlayers has significantly reduced the voltage required for water splitting.¹⁶⁶ These materials enhance the electric field in the ion-depleted region, aiding the dissociation of water into hydronium and hydroxide ions and thereby improving the efficiency of BPM electrolyzers in seawater electrolysis. This innovation is complemented by recent advancements in transition metal oxide (TMO)-based OER electrocatalysts for seawater splitting.¹⁷⁸ These advancements include the development of noble metal oxides, non-noble metal oxides, and compound oxides, offering advantages such as low cost, easy synthesis, and good stability. However, a challenge remains, as most of these catalysts display insufficient efficiency, primarily due to their high overpotentials and limited stability. This combination of electronically conducting materials in BPM interlayers and novel TMO-based electrocatalysts presents a promising direction for enhancing the overall efficiency and effectiveness of seawater electrolysis systems.

Employing chemically stable materials in the construction of BPMs is essential for their longevity and performance stability, particularly in the challenging conditions of seawater electrolysis. Studies have investigated the use of polyphenylene-based polymers and poly(arylene ether ketone) for their high stability against chemical degradation. Such materials have shown increased resistance to backbone cleavage compared to traditional polymers used in BPMs.¹⁶⁷ Continued research in this area is crucial for developing BPMs that can withstand the harsh conditions of seawater electrolysis over extended periods.

7. CHALLENGES AND PERSPECTIVES

The global demand for clean energy sources has highlighted the limitations of fossil fuels, leading to the urgent need for alternative options. Hydrogen has emerged as a viable candidate with its exceptional heating value and zero emissions when it is utilized for combustion. However, hydrogen production methods determine its environmental impact, and conventional techniques contribute significantly to CO₂ emissions. The use of seawater as a resource for hydrogen production presents an abundant and nearly limitless opportunity, especially in dry coastal areas with abundant seawater resources and surplus

renewable energy. Direct seawater electrolysis has been explored as a potential approach, but it faces challenges such as corrosion, competing electrochemical reactions, and the presence of bacteria and microorganisms. To overcome these obstacles, researchers have investigated the use of bipolar membranes, which allow for two distinct pH environments and optimization of electrode stability, catalyst activity, and cost for each half-reaction. This innovative approach could improve the efficiency and energy-saving aspects of seawater electrolysis, making it a promising avenue for hydrogen production from seawater.

With their unique structure and ion exchange capabilities, BPMs promote water dissociation by selectively allowing the passage of protons and hydroxide ions while acting as a barrier to cations and anions. The mechanism of water splitting or dissociation in BPMs involves the application of reverse bias mode, leading to the production of H⁺ and OH⁻ ions that carry the ionic current. Conversely, in forward bias mode, the ions migrate toward the bipolar junction and recombine into water, resulting in acid–base neutralization. The water dissociation phenomenon can be explained through the second Wien effect or catalytic processes facilitated by the membrane's ionic headgroups. The protonation–deprotonation mechanism proposes involving fixed charged groups in the CEL and AEL layers, which may exhibit different catalytic activities. Overall, understanding the water-splitting mechanism in BPMs is crucial for their application in various fields, including water electrolysis.

The synthesis of BPMs has seen significant advancements in recent years, with various methods being employed to fabricate these membranes. The choice of synthesis technique depends on the desired properties of the BPM, the scalability, and specific application requirements. Each method has advantages and limitations, and ongoing research aims to develop new techniques for synthesizing BPMs with an enhanced performance and efficiency. The incorporation of nanomaterials, such as metal oxides/hydroxides, graphene oxide, molybdenum disulfide, and montmorillonite nano clay, has been explored to enhance the properties of BPMs, including ion transport, mechanical strength, and chemical stability. Inorganic catalysts containing metal elements have shown promise in improving water dissociation ability, although the immobilization of metal ions is necessary to prevent their loss during electrolysis.

The utilization of seawater electrolysis for hydrogen production presents a promising solution to the challenges surrounding energy sources and supply. Compared with indirect methods that necessitate an additional desalination step, direct seawater electrolysis proves to be more energy-efficient and cost-effective. Nevertheless, direct seawater electrolysis encounters certain obstacles, such as the development of mineral scales on electrode surfaces, corrosion concerns, lower ion conductivity, gas bubble accumulation, and electrode fouling. BPM electrolysis holds potential, as it enables the transportation of protons and hydroxide ions, leading to localized pH changes that impede scaling and enhance system efficiency. Additionally, BPM technology improves gas bubble management and exhibits promise in addressing the challenges faced by other electrolysis technologies.

Various strategies can be employed for the improvement of seawater dissociation in BPM electrolysis. Catalyst selection is a crucial factor that can significantly impact the process. Materials such as Fe₂O₃@GO, Fe-MIL-101-NH₂, and IrO₂ have exhibited promising catalytic activity for water dissociation. Furthermore, membrane design optimization is essential for enhancing the overall efficiency of the process. Recent advancements in thin-

CEL BPM configurations and fixed charge density at the bipolar junction have shown an improved water splitting efficiency. Additionally, nanoporous membranes and membrane structure engineering can offer potential solutions to improve ion transport and create hydrophilic interfaces for efficient water dissociation. Introducing electronically conducting materials in BPM interlayers has also shown a significant reduction in voltage requirements for water splitting. Ensuring the chemical stability of BPMs is another critical aspect that must be taken into consideration. Utilizing chemically stable materials such as aminated polyphenylene-based polymers and poly(arylene ether ketone) has been proven to enhance the overall stability of the process. These research endeavors aim to advance the field of BPM electrolysis and hold promise for achieving efficient and cost-effective seawater dissociation, thereby opening new avenues for sustainable hydrogen production. However, further research and development are necessary to address long-term stability issues and optimize the performance of BPM electrolysis in real-world applications.

The utilization of BPM electrolyzers for seawater electrolysis has exhibited significant potential, as reported performances have indicated. BPMWEs have been found to possess several advantages over PEMWEs, with superior chlorine oxidation mitigation and greater Faradaic efficiency for H₂ production, facilitating longer-term seawater electrolysis. The optimization of the interface between porous electrodes and BPMs has resulted in stable hydrogen production with a reduced overpotential and improved stability, which holds the potential to minimize inorganic scaling. By combining synergistic acidification through inorganic precipitation with proton flux from a bipolar membrane, the seawater pH has been successfully reduced, allowing for stable and long-term direct seawater electrolysis. Moreover, in a BPM-based system, the combination of desalination and electrolysis has efficiently desalinated water, while producing HCl, NaOH, and high Faradaic efficiencies for O₂ and H₂ production. Nevertheless, despite these promising outcomes, further research and development are essential for fully utilizing the potential of BPM electrolyzers for seawater electrolysis. The focus should be on improving BPM technology to decrease the energy required for water dissociation. Addressing long-term stability, electrode scaling, and optimizing BPM design are key areas that require attention. By advancing BPM technology, possibilities for sustainable hydrogen production can be unlocked, paving the way for a greener and more efficient future.

In addition, a detailed investigation of the deposition and separation mechanisms of various substances present in seawater, such as metals, chlorides, sodium, sulfates, sulfites, and organic materials, after electrolysis emerges as a critical avenue for future research. Delving into these mechanisms is not merely an academic exercise; it holds the potential to unravel the fundamental aspects of the electrolysis process, paving the way for the development of more sustainable and efficient methods for harnessing seawater as a resource for electrolysis.

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Notes

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