



Advancements in Membrane Technologies for Enhanced Water Splitting and CO₂ Reduction: A Comprehensive Review

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ABSTRACT:

The global pursuit of sustainable energy and environmental solutions has intensified the focus on water splitting and CO₂ reduction as promising pathways towards a low-carbon future. Membrane technologies have emerged as crucial components in enhancing the efficiency and selectivity of these processes. This comprehensive review explores recent advancements in membrane technologies for water splitting and CO₂ reduction, aiming to provide insights into their fundamental principles, current state-of-the-art developments, and prospects. Various techniques such as electrolysis, electrochemical and photocatalytic CO₂ reduction are discussed, highlighting their respective principles and challenges. Subsequently, the role of membranes in facilitating these processes is examined. Different types of membranes are reviewed in terms of their structure, properties, and recent advancements aimed at improving performance. In the realm of water splitting, membranes play a pivotal role in separating reactants and products, enhancing reactions and enabling efficient utilization of resources. Recent developments in membrane have shown promising results in improving water splitting efficiency and durability. Similarly, in CO₂ reduction processes, membranes are utilized for gas separation, concentration, and selective transport of species, enabling enhanced reaction and product selectivity. Integration of membrane technologies into water splitting and CO₂ reduction systems is another area of focus, with the review examining the advantages and challenges associated with such integration. Integrated membrane systems are presented, showcasing their potential to achieve synergistic effects, and improved overall performance. Despite significant progress, including membrane fouling, stability, and cost-effectiveness, which necessitate further research and development efforts. In conclusion, this review underscores the critical role of membrane technologies in advancing water splitting and CO₂ reduction for sustainable energy and environmental applications. By providing a comprehensive overview of recent advancements, challenges, and prospects, this review aims to stimulate further research and innovation in the field, ultimately contributing to the realization of a cleaner and more sustainable future.

1. Introduction:

In the face of escalating global concerns regarding climate change and the need for sustainable energy solutions, advancements in membrane technologies have emerged as critical components in the quest for enhanced water splitting and CO₂ reduction. These processes hold immense promise in addressing the twin challenges of renewable energy generation and

greenhouse gas mitigation. By harnessing renewable resources and converting CO₂ emissions into valuable products, such as hydrogen fuel and carbon-neutral chemicals, water splitting, and CO₂ reduction offer a pathway towards a low-carbon future. Membrane technologies play a pivotal role in these processes by facilitating the separation, concentration, and selective transport of reactants and products. Through precise



control of mass transfer and ion conductivity, membranes enable the optimization of reaction kinetics and the enhancement of process efficiency. Moreover, membranes offer the potential for integration into scalable and cost-effective systems, thereby paving the way for widespread deployment in industrial and environmental applications. This comprehensive review aims to explore the recent advancements in membrane technologies for enhanced water splitting and CO₂ reduction. By synthesizing the latest research findings and technological innovations, this review seeks to provide a comprehensive understanding of the current state-of-the-art, identify key challenges and opportunities, and outline future research directions in the field. The review begins with an overview of the fundamentals of water splitting and CO₂ reduction, highlighting the importance of these processes in the context of renewable energy and environmental sustainability. Subsequently, the role of membranes in facilitating these processes is examined, encompassing various membrane materials, designs, and functionalities. Recent advancements in membrane materials, including polymeric, ceramic, and composite membranes, are discussed, alongside their implications for enhancing process performance and durability. Furthermore, the review delves into the integration of membrane technologies into water splitting and CO₂ reduction systems, exploring synergistic effects and system-level considerations. Challenges such as membrane fouling, stability, and cost-effectiveness are also addressed, alongside potential strategies for overcoming these barriers. In conclusion, this review underscores the critical role of membrane technologies in advancing water splitting and CO₂ reduction towards sustainable energy and environmental goals. By providing a comprehensive synthesis of recent advancements and future prospects, this review aims to stimulate further research and innovation in the field, ultimately contributing to the realization of a cleaner and more sustainable future.

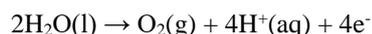
2. Fundamentals of water splitting and CO₂ reduction:

2.1. Water Splitting (Electrolysis of Water):

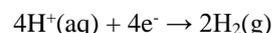
Water splitting is the process of converting water molecules (H₂O) into hydrogen (H₂) and oxygen (O₂) gases via electrochemical processes. This process takes place in an electrolytic cell, which is normally made up of two electrodes (anode and cathode) submerged in an

electrolyte solution, usually water containing dissolved ions to improve conductivity.

Anode Reaction: At the anode (positive electrode), water molecules are oxidized, producing oxygen gas and protons. The anode response can be described as follows:



Water molecules lose electrons (e⁻) and undergo oxidation to form oxygen gas, protons, and electrons. The cathode reaction: Protons from the anode reaction gain electrons at the cathode (negative electrode) and are reduced to produce hydrogen gas. The cathode reaction is expressed as follows:



Protons (H⁺) get electrons (e⁻) and are reduced to produce hydrogen gas (H₂). Overall water splitting reaction: By combining the anode and cathode processes, we obtain the total reaction for water splitting:



This equation represents the conversion of water into hydrogen and oxygen gases through electrolysis.

2.1.1. Role of Membrane:

In the context of water splitting, membranes serve as indispensable components that not only physically separate the cathode and anode compartments but also intricately regulate ion transport, thereby orchestrating the efficient progression of electrochemical reactions. By selectively permitting the passage of ions essential for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) while obstructing the migration of other species, membranes enable the controlled generation of hydrogen gas (H₂) at the cathode and oxygen gas (O₂) at the anode. This selective transport ensures the purity of the generated gases and prevents undesired mixing, safeguarding the integrity and efficiency of the electrolysis process. Furthermore, membranes play a pivotal role in optimizing the kinetics of electrochemical reactions by providing a conduit for ion transport and mitigating electrical losses within the electrolysis cell. Through meticulous optimization of membrane materials and designs, researchers aspire to not only enhance the performance and durability of water splitting technologies but also pave the way for their widespread adoption in sustainable hydrogen production and energy storage applications, thus catalyzing the transition towards a cleaner and more sustainable future.



2.2. CO₂ Reduction (Electrochemical CO₂ Reduction):

Carbon dioxide (CO₂) reduction reactions, occurring within electrochemical cells, involve the conversion of CO₂ into valuable products using electrical energy. The process typically involves a cathode (negative electrode), an anode (positive electrode), and an electrolyte solution. At the cathode, CO₂ molecules undergo reduction by gaining electrons (e⁻), resulting in the formation of various carbon-based compounds such as carbon monoxide (CO), methane (CH₄), and ethylene (C₂H₄). For instance, CO₂ can be reduced to CO with the following reaction:



Simultaneously, oxidation reactions may occur at the anode to balance charge transfer. The overall process utilizes renewable electricity to drive CO₂ conversion, with the application of an electric potential across the cell driving CO₂ reduction at the cathode while complementary oxidation reactions occur at the anode.

2.2.1. Role of Membrane:

Membranes in CO₂ reduction reactions serve crucial functions within electrochemical cells. Firstly, they act as physical barriers, separating the cathode and anode compartments, essential for preventing the mixing of reactants and products, thus ensuring process purity and integrity. Furthermore, membranes facilitate selective ion transport, allowing ions such as protons (H⁺) to move between compartments while maintaining electrical neutrality within the cell. This selective ion transport is critical for enabling the electrochemical reactions to proceed effectively. Additionally, membranes contribute to enhancing reaction kinetics by providing pathways for ion transport and minimizing electrical resistance, ultimately leading to more efficient CO₂ conversion. Membranes can also be integrated with catalysts to create membrane-electrode assemblies (MEAs), promoting efficient CO₂ reduction by allowing direct contact between catalysts and reactants. This integration enhances catalyst utilization, improves reactant distribution, and enhances overall cell performance.

Membranes play a pivotal role in facilitating CO₂ reduction reactions within electrochemical cells by physically separating compartments, facilitating selective ion transport, enhancing reaction kinetics, and integrating with catalysts to improve efficiency and selectivity.

3. Characteristics of good membrane:

A suitable membrane for water splitting and other applications should have certain critical properties to achieve peak performance and efficiency. These qualities include the following:

1. **Selective Permeability:** The membrane should permit the passage of specific ions or molecules while prohibiting others. This selective permeability is critical for separating reactants and products in the electrochemical cell while limiting crossover or mixing.
2. **High Ion Conductivity:** The membrane should be highly conductive for the ions involved in water splitting, such as protons (H⁺) and hydroxide ions (OH⁻). High ion conductivity means that ions are transported efficiently across the membrane, allowing for quick reaction kinetics.
3. **Chemical Stability:** The membrane must be chemically stable under the working circumstances of the water splitting process, which include acidic or alkaline environments, high temperatures, and probable chemical interactions with reactive species. Chemical stability ensures the membrane's longevity and dependability throughout time.
4. **Mechanical Durability:** The membrane must have enough mechanical strength and durability to endure mechanical loads, pressure differentials, and handling during installation and operation. Mechanical durability protects the membrane from deformation, damage, or failure over time.
5. **Thermal Stability:** The membrane's structural integrity and performance should be maintained throughout a wide temperature range while in operation. Thermal stability guarantees that membrane performance remains constant while also preventing deterioration or loss of functioning at high temperatures.
6. **Low Electrical Resistance:** The membrane's electrical resistance should be low in order to reduce ohmic losses and voltage dips across it during ion transport. Low electrical resistance boosts the energy efficiency of the water splitting process.
7. **Chemical Inertness:** The membrane must be chemically inert to the reactants, products, and intermediate species involved in the water splitting process. Chemical inertness eliminates undesired side reactions or membrane breakdown, ensuring that the products produced are pure.
8. **Cost-effectiveness:** The membrane should be inexpensive to produce, install, and maintain, while also



providing comparable performance and endurance when compared to other membrane materials or technologies. 9. Scalability: The membrane must be scalable for mass manufacture and incorporation into commercial-scale water splitting systems. Scalability allows for the widespread use of water splitting technology in large-scale renewable energy generation. A good membrane can contribute to the efficient and dependable functioning of water splitting systems, allowing for long-term hydrogen generation and other electrochemical processes for renewable energy applications.

4. Types of membranes

4.1. Nafion:

The text underscores the pressing need for cleaner energy sources amidst escalating climate change concerns, with a particular spotlight on hydrogen as a promising substitute for fossil fuels. Traditional methods like steam reforming are critiqued for their energy-intensive processes and associated carbon emissions, prompting a shift towards the potential of photocatalytic water splitting. Originating from Fujishima and Honda's seminal work in 1972, this approach utilizes sunlight and photocatalysts to split water into hydrogen and oxygen. While early photocatalysts faced limitations, the emergence of Z-scheme photocatalysis, inspired by natural photosynthesis, has driven innovation. Various Z-scheme systems, employing diverse catalysts and redox mediators, have been explored to enhance hydrogen and oxygen production under visible light. A groundbreaking advancement in this domain is the twin-reactor system, featuring segregated compartments for hydrogen and oxygen generation, promising heightened efficiency, and safety. Central to this innovation is a modified Nafion membrane facilitating efficient ion and electron transport. The narrative unfolds with detailed experimental endeavors, encompassing catalyst preparation, diffusion studies, and comprehensive characterization techniques. Particularly noteworthy is the in-depth analysis of the Pt/SrTiO₃:Rh and BiVO₄ photocatalysts, unveiling their properties and morphologies through various analytical techniques. The elucidation of diffusion behaviors of Fe₃⁺ and Fe₂⁺ ions across modified Nafion membranes underscores the robustness of the twin-reactor setup. Furthermore, the study sheds light on photocatalytic water splitting experiments, revealing insights into hydrogen and

oxygen production rates and identifying potential challenges such as catalyst deactivation. Overall, the narrative emphasizes the feasibility of photocatalytic water splitting as a scalable and sustainable approach to hydrogen production, while also indicating avenues for further optimization and improvement.

Nafion, a remarkable proton exchange membrane (PEM), stands at the forefront of water splitting reactions, particularly in electrolyzers, owing to its exceptional properties. Acting as a separator between the anode and cathode compartments in water electrolysis, Nafion facilitates the controlled generation of hydrogen and oxygen gases.

The photocatalytic water-splitting reaction occurs in a twin reactor setup using Pt/SrTiO₃:Rh as the H₂-photocatalyst and BiVO₄ as the O₂ photocatalyst. The reaction takes place under irradiation with a 300W Xe lamp, and the pH of the solution is adjusted to 2.4 by H₂SO₄. The modified Nafion membrane (Nafion Fe₃⁺ or Nafion Fe₂⁺) separates the compartments of the twin reactor, allowing the diffusion of mediator ions (Fe₃⁺ or Fe₂⁺).

The water-splitting reaction in the twin reactor with a modified Nafion membrane:

i. Anode Compartment (H₂-Generating Side):

- The Pt/SrTiO₃:Rh photocatalyst is immersed in a solution containing Fe₂⁺ ions.
- Under irradiation, the Pt/SrTiO₃:Rh catalyst facilitates the reduction of water to produce hydrogen gas (H₂).
- The Nafion membrane selectively allows the transport of protons (H⁺) generated during water reduction.

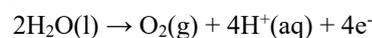
ii. Cathode Compartment (O₂-Generating Side):

- The BiVO₄ photocatalyst is immersed in a solution containing Fe₃⁺ ions.
- Under irradiation, the BiVO₄ catalyst facilitates the oxidation of water to produce oxygen gas (O₂).
- Protons (H⁺) generated at the anode compartment migrate through the Nafion membrane to the cathode compartment to maintain charge neutrality.

iii. Overall Reaction:



At the anode:



At the cathode:





Water is split into hydrogen gas (H₂) at the anode compartment and oxygen gas (O₂) at the cathode compartment.

iv. Nafion Membrane Function:

- The modified Nafion membrane (Nafion Fe₃⁺ or Nafion Fe₂⁺) separates the anode and cathode compartments.
- It allows selective transport of protons (H⁺) generated during the water-splitting reaction, maintaining charge balance between the compartments.
- The Nafion membrane prevents the mixing of gases (H₂ and O₂) produced at the anode and cathode compartments, ensuring the collection of pure hydrogen and oxygen gases.

Nafion orchestrates the transport of protons (H⁺) from the anode to the cathode while impeding gas and electron migration. This selective proton conduction across the membrane ensures the isolation of hydrogen and oxygen evolution reactions, guaranteeing the production of pure gases.

Despite its widespread adoption and manifold advantages such as exceptional chemical resilience and mechanical sturdiness, Nafion does confront limitations. It exhibits diminished performance under dehydrated conditions and at temperatures surpassing 80°C, potentially compromising its proton conductivity. Additionally, Nafion's efficacy wanes below 0°C and beyond 100°C, underscoring the necessity for meticulous operational regulation[13].

In response to these challenges and to amplify Nafion's efficacy in water splitting endeavors, ongoing research concentrates on devising novel composite membranes and exploring alternative materials endowed with enhanced attributes. These endeavors aim to broaden the applicability of PEM-based technologies while addressing concerns pertaining to cost, environmental impact, and operational resilience.

Nafion epitomizes a cornerstone in the realm of electrochemical engineering, propelling advancements in energy conversion and storage by facilitating efficacious water splitting reactions in electrolyzers. Its distinctive properties and versatile applications underscore its significance in driving sustainable energy solutions forward.

In summary, the water-splitting reaction in the twin reactor involves the use of photocatalysts immersed in solutions containing mediator ions (Fe₃⁺ and Fe₂⁺), facilitated by irradiation. The modified Nafion

membrane plays a crucial role in facilitating proton transport while separating the compartments and ensuring the efficiency and purity of the gas products.

4.2. Zirfon:

Zirfon membranes represent a significant advancement in the field of electrochemical technologies, owing to their unique composition of zirconium oxide and polysulphone. This composite material offers a combination of high stability, low ionic resistance, and excellent wettability in alkaline mediums, making it exceptionally well-suited for various applications. Notably, recent research efforts have focused on leveraging Zirfon membranes in the development of an innovative Electrode Diaphragm Electrode (EDE) unit, tailored specifically for fixed alkaline electrolyzers, particularly for space applications. The EDE unit comprises a carefully crafted combination of a cast macroporous Zirfon diaphragm and two distinct electrode types: cast Ni/PSU and non-woven Ni[4]. Through rigorous experimentation and testing, researchers have achieved remarkable performance metrics, such as a low cell voltage of 1.63 V at 200 mA/cm² and high oxygen purity, highlighting the efficacy of Zirfon-based systems in electrochemical processes. Furthermore, detailed analyses of cathode potential and anode performance have revealed impressive figures, indicating the robustness and reliability of these systems. Moreover, insights from the third stack test have provided valuable information on operational parameters and potential avenues for improvement, including modeling water vapor and gas transport and optimizing electrode porosity. Beyond electrolysis, Zirfon membranes find widespread application across diverse sectors, including alkaline water electrolysis, fuel cells, and Ni-H₂ batteries, further underscoring their versatility and potential impact on advancing sustainable energy technologies[3]. Overall, the continued research and development of Zirfon membranes hold promise for driving innovation and enhancing the efficiency and sustainability of electrochemical systems in various applications[1].

1. Zirfon: A new separator material for NiH₂ batteries and alkaline fuel cells, composed of zirconium oxide and polysulphone [1].

2. Properties: Zirfon has high chemical and thermal stability, low ionic resistance, good mechanical strength, and excellent wettability in alkaline medium[2].



3. Applications: Zirfon has been tested in alkaline water electrolysis, alkaline fuel cell, and NiH₂ battery cells, showing promising performance and durability.

4. Development: Zirfon is manufactured by film casting technique, and its structure and properties can be adjusted by varying the manufacturing parameters. A new type of Zirfon is being developed for NiH₂ batteries[3].

4.3. EPDM-Rubber Based Membranes for Water Splitting and CO₂ reduction reactions:

In this study, the primary focus is on addressing the critical need for cost-effective and stable membranes suitable for electrochemical cells involved in solar fuel production. These membranes play a pivotal role in the conversion of solar energy into chemical fuels by effectively separating reactants and products during electrochemical reactions. Utilizing CO₂ and water as raw materials aligns with global initiatives aimed at mitigating climate change and transitioning towards sustainable energy sources. The discussion delves into the promise of artificial photosynthesis, mirroring natural processes to convert CO₂ and water into energy-rich chemical fuels like hydrogen, methanol, and gasoline. This exploration underscores significant challenges, notably in developing efficient catalysts, electrodes, and membranes. Introduction of ethylene propylene diene monomer (EPDM) rubber-based membranes as novel separators in electrochemical cells involved in solar fuel production highlights their potential. Evaluation includes performance in water splitting and CO₂ reduction reactions, crucial steps in artificial photosynthesis. Comparative studies with commercial alternatives such as zirfon® perl membranes and other rubber-based membranes assess stability, selectivity, efficiency, and cost-effectiveness. Synthesis of various solar fuels using EPDM rubber-based membranes demonstrates their practical potential. The results underscore the significance of membrane materials in enabling efficient and sustainable solar fuel generation technologies, showcasing promising characteristics such as low cost, stability, and performance parity with commercial counterparts.

For membrane fabrication, two distinct techniques were employed. The phase-inversion technique, utilized for zirfon membranes, involves forming a polymer solution cast onto a substrate and subjected to a phase-inversion process, resulting in a porous structure. The vulcanization process, adopted for rubber-based

membranes, entails cross-linking rubber polymers to enhance mechanical properties and stability, with the incorporation of reinforcing agents like ZrO₂ or CaCO₃ powders.

Various characterization techniques were employed to assess membrane properties comprehensively. These include BET analysis for specific surface area determination, SEM imaging for visualizing surface morphology and pore structure, EDAX analysis for elemental composition determination, and FT-IR spectroscopy for identifying functional groups. These methods collectively provide insights into the physical and chemical properties crucial for evaluating membrane suitability for electrochemical applications.

For evaluation of membrane performance, a combination of cyclic voltammetry (CV) and constant potential bulk electrolysis (CPBE) experiments were conducted. These methods allowed for assessment of stability, efficiency, and long-term performance under continuous operation conditions. Specific experiments, such as cyclic voltammetry in two-compartment cells for CO₂ reduction and comparison studies with other electrode materials, provided detailed insights into membrane performance and its potential for practical applications in artificial photosynthesis systems.

4.3.1. Membrane Fabrication

Two distinct techniques were employed for membrane fabrication:

1. Phase-Inversion Technique for Zirfon Membranes: This method involves the creation of a polymer solution that is cast onto a substrate and then subjected to a phase-inversion process. During this process, the solvent is removed, leading to the formation of a porous membrane structure with the desired composition and properties. Zirfon membranes are specifically fabricated using this technique, resulting in membranes suitable for various electrochemical applications.

2. Vulcanization Process for Rubber-Based Membranes: Rubber-based membranes were fabricated using a vulcanization process. In this process, rubber polymers are cross-linked to improve their mechanical properties and stability. Additionally, reinforcing agents such as ZrO₂ or CaCO₃ powders are incorporated into the rubber matrix to enhance its performance in electrochemical applications. This process results in robust membranes capable of withstanding the harsh conditions of electrochemical reactions.

4.3.2. Membrane Characterization



Various techniques were employed to characterize the fabricated membranes:

1. **BET Analysis:** This analysis determines the specific surface area of the membranes, which is crucial for efficient performance in electrochemical reactions. A higher surface area allows for more active sites available for electrochemical reactions, thus improving overall performance.

2. **SEM Imaging:** Scanning Electron Microscopy (SEM) was used to visualize the surface morphology and pore structure of the membranes. This technique provides detailed information about the membrane's microstructure, including pore size distribution and uniformity, which directly affect permeability and selectivity in electrochemical applications.

3. **EDAX Analysis:** Energy Dispersive X-ray Analysis (EDAX) was employed to determine the elemental composition of the membranes. This analysis helps confirm the presence of desired components, such as ZrO_2 or $CaCO_3$ powders, and assesses their distribution within the membrane matrix. An even distribution of reinforcing agents contributes to improved mechanical strength and stability of the membranes.

4. **FT-IR Spectroscopy:** Fourier Transform Infrared Spectroscopy (FT-IR) was utilized to identify functional groups present in the membrane materials. This technique provides valuable information about chemical bonding and structural characteristics, aiding in the understanding of membrane composition and properties. Identifying functional groups helps evaluate the compatibility of membrane materials with specific electrolytes and environments encountered during electrochemical reactions.

These characterization techniques collectively provide comprehensive insights into the physical and chemical properties of the membranes, essential for evaluating their suitability for electrochemical applications.

The electrochemical reduction (ECR) over TiN thin film is explored in detail:

1. **ECR over TiN thin film:** The onset reduction potential of CO_2 over TiN thin film in a CO_2 -saturated electrolyte solution is exceptionally low at approximately -1.468 V vs. NHE. This low onset reduction potential is significant, as it indicates efficient conversion of CO_2 to CO, highlighting the potential of TiN thin film as an electrode material for electrochemical CO_2 reduction (ECR) reactions (Fig 2).

2. **Effect of bmim-BF₄ concentration:** The concentration of bmim-BF₄ in the electrolyte solution influences the overpotential associated with the ECR to CO formation over TiN. A higher concentration of bmim-BF₄ correlates with a lower overpotential. Specifically, overpotentials of 114 mV, 185 mV, and 330 mV are noted for bmim-BF₄ concentrations of 500 mM, 100 mM, and 20 mM, respectively. This relationship suggests that bmim-BF₄ acts as a catalyst or promoter, enhancing the efficiency of CO_2 conversion on TiN thin film electrodes.

3. **Comparison with Sn and MoSi₂:** The activities of TiN thin film, Sn, and MoSi₂ for ECR reactions are compared, revealing a trend where MoSi₂ exhibits the highest activity followed by TiN thin film and Sn. TiN thin film electrodes generate a current density of -105 mA/cm² at an onset reduction potential of -1.499 V vs. NHE, with an overpotential of 169 mV. In comparison, MoSi₂ generates a higher current density of -135 mA/cm² at a lower onset reduction potential of -1.389 V vs. NHE, with a lower overpotential of 59 mV. Sn electrodes exhibit the lowest activity, with a current density of -85 mA/cm² at an onset reduction potential of -1.512 V vs. NHE and an overpotential of 182 mV.

4. **Advantages of TiN thin film:** TiN thin film emerges as a highly advantageous cathode material for ECR reactions. It is noted for its low cost, high activity, and robustness, making it suitable for use in MeCN electrolyte solutions containing $n-Bu_4NPF_6$ and bmim-BF₄ helper catalyst. Additionally, TiN thin film is characterized by its high electrical conductivity and durability, making it an attractive option for various electrochemical applications.

These findings highlight the potential of TiN thin film as a promising electrode material for efficient and cost-effective electrochemical CO_2 reduction, offering advantages in terms of performance, affordability, and durability compared to other electrode materials.

4.3.3. EPDM-ZrO₂

The utilization of Ethylene Propylene Diene Monomer (EPDM) rubber-based membranes in electrochemical cells presents a significant advancement in sustainable energy technology, particularly in the domain of water splitting. Addressing the pressing need for efficient electricity storage from renewable sources like sunlight, EPDM membranes offer a novel solution by enabling the separation of compartments within electrochemical cells, facilitating water splitting reactions.



In electrochemical water splitting, EPDM rubber-based membranes serve as barriers between the anode and cathode compartments, allowing the selective transport of ions while preventing mixing of reactants and products. This selective permeability ensures efficient water electrolysis while maintaining the integrity of the electrochemical cell. Moreover, EPDM membranes exhibit promising performance in water splitting reactions, with overpotentials noted within a favorable range.

In this study, an exploration into the utilization of Ethylene Propylene Diene Monomer (EPDM) rubber-based membranes, specifically EPDM-ZrO₂ membranes, in electrochemical cells for water splitting. The motivation stems from the imperative need for an inexpensive and suitable anion transporting membrane to harness sunlight effectively through hydrolysis processes, ultimately aiming to meet society's energy needs solely through solar energy without reliance on fossil fuels.

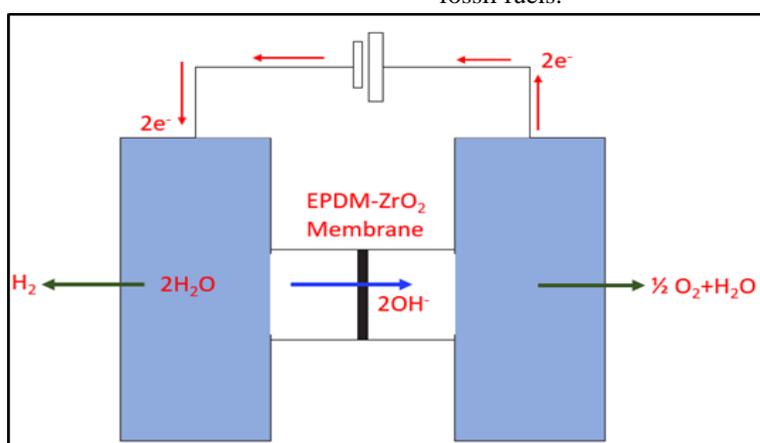


Fig. 1: The electrochemical division of water into H₂ and O₂ gases occurs within a two-compartment electrochemical cell, EPDM-ZrO₂ membrane separating the compartments

The EPDM-ZrO₂ membranes are developed through a systematic investigation to fabricate cost-effective membranes suitable for electrochemical water splitting in alkaline electrolyzers in the absence of protons derived from water. The objective is to replace expensive membranes like zircon® perl membranes. The fabrication process ensures affordability, with the EPDM-ZrO₂ membranes costing less than \$10 USD per square meter. For comparison, natural rubber (NR) membranes and commercial zircon® perl membranes are also evaluated.

The fabrication process involves the development of rubberized nylon cloth-reinforced zircon membranes, where a porous thin solid zircon matrix is created using conventional tape-casting techniques followed by coagulation via a phase-inversion technique. The zircon membrane is then sandwiched between layers of rubberized nylon cloth and subjected to vulcanization. This method ensures the robustness and stability of the membranes under operating conditions.

For experimental evaluation, a zero-gap single-cell alkaline electrolyzer stack is fabricated in-house, featuring SS304 material and nickel foam electrodes.

The PP cloth web-reinforced EPDM rubber-ZrO₂ composite membrane serves as the separator between the anodic and cathodic compartments. The construction also includes insulation layers and electrical connections to ensure efficient operation and prevent electrolyte leakage. Peristaltic pumps are employed to circulate the aqueous KOH electrolyte solution, while a multi-meter records voltages during the hydrolysis process. The evolution of H₂ and O₂ gas bubbles is monitored to assess the efficiency of the electrolysis process.

Additionally, a custom-manufactured SS-304 two-compartment electrochemical cell is utilized to measure bubble-point pressure and membrane stability. This cell features a proprietary rubber lining technology developed by the author's lab to withstand high pressures.

4.3.4. EPDM-CaCO₃

The utilization of Ethylene Propylene Diene Monomer (EPDM) rubber-based membranes in electrochemical cells also holds immense promise for carbon dioxide (CO₂) reduction reactions. These membranes demonstrate remarkable stability in non-aqueous aprotic



electrolyte solutions, notably in acetonitrile (MeCN) supplemented with specific additives.

As the world seeks innovative strategies for carbon capture and utilization, EPDM membranes offer a viable solution by facilitating CO₂ reduction within electrochemical cells. EPDM rubber-based membranes exhibit exceptional stability in non-aqueous aprotic electrolyte solutions, making them ideal candidates for CO₂ reduction reactions in various electrochemical environments.

EPDM membranes serve an important role in CO₂ reduction processes by separating the cathode compartment, where reduction reactions occur, from the anode compartment, limiting unwanted side reactions and providing excellent selectivity for desired carbon products. These membranes exhibit promising performance in CO₂ reduction processes with diverse cathode materials, demonstrating their adaptability and

usefulness in reducing CO₂ into value-added chemicals and fuels.

Furthermore, EPDM membranes are less expensive than traditional membranes, making them ideal for large-scale deployment in CO₂ reduction methods. This study presents in-depth insights into the synthesis, characteristics, and performance of EPDM rubber-based membranes for CO₂ reduction applications, highlighting their benefits and future applications in the field of sustainable carbon usage. Overall, this research makes a substantial contribution to improving the efficiency and sustainability of CO₂ reduction systems provide a possible approach for reducing carbon emissions and reaching carbon neutrality [10].

Overall, the study demonstrates EPDM-Rubber Based membranes' potential as cost-effective options for electrochemical water splitting and CO₂ reduction, paving the door for sustainable energy generation.

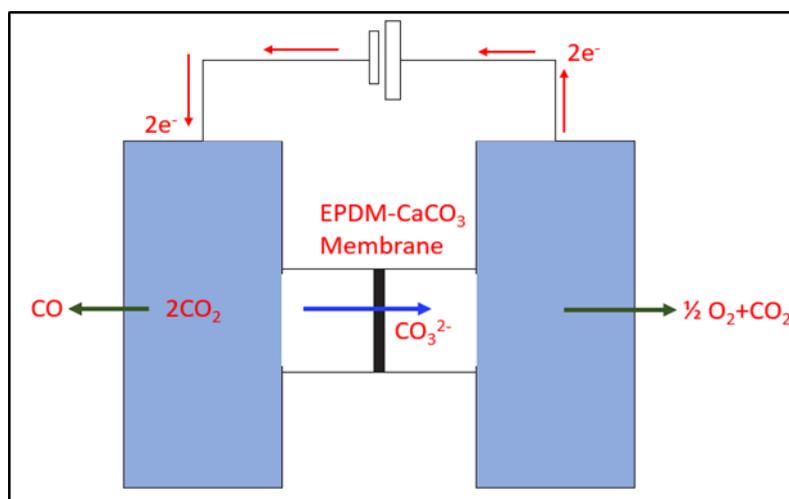


Fig. 2: The electrochemical reduction of carbon dioxide to carbon monoxide takes place within a two-compartment electrochemical cell, EPDM-CaCO₃ membrane dividing the compartments

4.4. Bipolar membrane for water splitting:

The passage delves into the intricate development and fine-tuning of a zero-gap water electrolyzer employing innovative bipolar membranes (BPM) and interfaces, with the goal of amalgamating the advantageous features of proton exchange membrane water electrolysis (PEMWE) and anion exchange membrane water electrolysis (AEMWE). This fusion is achieved by incorporating a bipolar interface within the membrane electrode assembly (MEA), which fosters local pH

gradients within the MEA, thereby optimizing the operational conditions for each electrode.

Two distinct configurations are proposed to facilitate the desired electrolysis mechanisms: the water recombination configuration (wrBPMWE) and the reverse bias setup (wsBPMWE). In the wrBPMWE configuration, a low-pH environment at the anode side and a high-pH environment at the cathode side catalyze the formation of H⁺ and OH⁻ ions, which subsequently recombine at the bipolar interface to produce water. Conversely, in the wsBPMWE setup, cost-effective



anode materials and mature PEM technology are leveraged to ensure efficient water dissociation.

Central to the success of these configurations is the meticulous management of water supply to the bipolar interface and the careful adjustment of the ratio of AEM to PEM thicknesses within the MEA. Adequate water transport through the membrane is paramount to prevent membrane drying and ensure the continuous progression of the electrolysis reaction. Furthermore, it is suggested that thinner AEM layers within the MEA could effectively minimize OH^- transport resistance, thereby enhancing overall performance.

In addition to exploring water as the primary electrolyte, the passage touches upon the possibility of utilizing acid and base solutions to feed the cathode and anode, respectively. However, the feasibility of this approach is challenged by considerations of cost-effectiveness compared to traditional water electrolysis methods.

The fabrication process of the MEAs involves a comprehensive array of steps and parameters, including the assembly of catalyst-coated electrodes with commercially available membranes. Various techniques such as spray-coating of catalyst ink onto electrodes, determination of binder content through thermogravimetric analysis, and conditioning of Nafion membranes are meticulously executed to ensure the integrity and functionality of the MEAs.

Electrochemical testing is conducted under precisely controlled conditions, with careful monitoring of parameters such as temperature, pressure, and flow rate. Structural analysis of catalyst layers is performed using sophisticated techniques like scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), providing invaluable insights into the composition and morphology of the electrodes.

Key findings from the study include the selection of suitable materials, optimization of fabrication approaches, enhancement of performance through parameter adjustments, and assessment of durability over prolonged operation. These findings collectively contribute to advancing the understanding and applicability of KOH-free AEMWE systems within bipolar membrane electrode assemblies, thus paving the way for significant strides in the field of water electrolysis technology.

Bipolar membranes, comprising an anion exchange membrane (AEM) and a cation exchange membrane (CEM) laminated together, represent a breakthrough in

electrochemical processes. These membranes selectively transport H^+ and OH^- ions under an applied electric field, enabling the generation of acids and bases from water splitting. By leveraging electromigration principles, bipolar membranes facilitate sustainable production of chemicals through processes such as water electrolysis and electrosynthesis. They play a pivotal role in various electrochemical applications, offering a pathway towards environmentally friendly chemical production[11].

4.5. Anion exchange membrane:

The study conducted by Pengzuo Chen and Xile Hu from EPFL, Switzerland, and published in *Advanced Energy Materials* in 2020, delves into the realm of anion exchange membrane (AEM) electrolyzers with a focus on utilizing non-noble metal catalysts to enhance efficiency in water electrolysis. Their primary goal is to develop electrocatalysts capable of facilitating both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) based on NiMo oxide. To achieve this, the researchers employed various reduction processes of NiMoO_4 under different gas atmospheres and temperatures, resulting in the synthesis of HER-active NiMo compounds. Remarkably, the NiMo-NH₃/H₂ catalyst exhibited exceptional activity, necessitating a mere 11 mV overpotential for a current density of 10 mA cm^{-2} .

Moreover, the team introduced Fe ions into the NiMo catalysts to augment OER activity. This modification led to the creation of the Fe-NiMo-NH₃/H₂ catalyst, which displayed a significantly reduced overpotential of 244 mV for a current density of 500 mA cm^{-2} . Subsequently, these innovative catalysts were integrated into AEM electrolyzers, where the best-performing membrane electrode assembly (MEA) achieved a notable current density of 1 A cm^{-2} at a cell voltage of 1.57 V, operating at 80°C. Impressively, this setup exhibited an energy conversion efficiency of 75.1%.

Of particular significance is the finding that this efficiency outstrips that of prior AEM electrolyzers, including those utilizing noble-metal catalysts. This outcome underscores the immense potential of earth-abundant electrocatalysts in driving high-efficiency AEM electrolyzers. Furthermore, the study sets a crucial benchmark for future research endeavors in this domain, indicating promising directions for the advancement of sustainable energy technologies[8].

4.6. proton exchange membrane:



The introduction section sets the stage by discussing the significance of proton exchange membranes (PEMs) in fuel cell technology, emphasizing the need for improvements in managing heat, water, and catalyst efficiency. It highlights the promising solution of high-temperature PEMFCs and introduces phosphoric acid-doped polybenzimidazole (PA-PBI) membranes, noting their challenges related to high phosphoric acid (PA) uptake. Additionally, it explores the potential of incorporating ionic liquids (ILs) and polymeric ionic liquids (PILs) to enhance membrane properties, offering a comprehensive overview of the current landscape and motivating the study's objectives.

The experimental section provides detailed insights into the methodology, including the synthesis of materials and membrane preparation procedures. It meticulously outlines the characterization techniques employed, ranging from spectroscopic analyses like NMR and FT-IR to imaging techniques such as SEM, and thermal analyses like TGA. This section serves as a roadmap for replicating the study's procedures and understanding the intricacies of material synthesis and characterization.

In the results and discussion section, the study delves into the synthesis and characterization of materials, evaluating their thermal and oxidative stability and analyzing membrane structure through techniques like WAXD. It provides comprehensive insights into phosphoric acid uptake, mechanical properties, proton conductivity, and PA retention, elucidating the influence of ILs and PILs on membrane performance. Through rigorous analysis and interpretation, this section elucidates the key findings and their implications for advancing PEM technology, providing a deeper understanding of the interplay between material composition and membrane properties.

The conclusion succinctly summarizes the study's findings, emphasizing the potential of PIL-based membranes for high-temperature PEMFCs and proposing future research directions. It underscores the significance of the study's contributions in addressing critical challenges in fuel cell technology, paving the way for further advancements and applications in renewable energy systems.

4.7. Sustainion anion exchange- membrane:

The Sustainion anion exchange-membrane plays a pivotal role in facilitating the electrochemical reduction of carbon dioxide (CO₂) to formate in the filter press

reactor setup described in the study. In this electrocatalytic reduction experiment targeting the conversion of CO₂ to formate, a filter press reactor setup is employed, featuring a working electrode (cathode) and a counter electrode (anode), alongside a reference electrode, all integrated with an anion exchange membrane (Sustainion® X37- 50 Grade RT) for compartmental separation. Additionally, gas diffusion electrodes (GDEs) with a Bi catalyst loading (Bi/C-GDE) and a dimensionally stable anode (DSA/O₂) are utilized. The operational conditions entail the utilization of an aqueous 1 M KOH solution as anolyte, while pure gaseous CO₂ is directed to the cathode side. This setup, maintained at a controlled room temperature of 20°C, facilitates continuous flow with a single pass of reactants. Gas and liquid phases are subsequently analyzed employing micro gas chromatography and ion chromatography techniques, respectively, providing insights into the electrochemical conversion process.

Regarding the reactions involved, at the cathode, CO₂ is reduced to formate (HCOO⁻) with the consumption of protons and electrons. At the anode, water is oxidized to oxygen (O₂) along with the release of protons and electrons. These reactions occur simultaneously within the electrochemical cell, with the cathode facilitating the reduction of CO₂ to formate while the anode promotes the oxidation of water to oxygen. The anion exchange membrane allows for the selective transport of ions between the cathodic and anodic compartments, enabling the separation of the formate product from other reaction products.

4.7.1. function and process:

- i. Membrane Function: The Sustainion membrane acts as a physical barrier between the cathodic and anodic compartments of the electrochemical reactor. It selectively allows the passage of specific ions, particularly hydroxide ions (OH⁻), while blocking the transport of other ions and molecules. This selective permeability is crucial for maintaining the desired reaction pathways and preventing undesired side reactions.
- ii. Ion Transport: In the anodic compartment, water is oxidized to produce oxygen gas and protons (H⁺). These protons migrate through the Sustainion membrane to the cathodic compartment, where they participate in the reduction reaction. At the same time, hydroxide ions generated in the anodic compartment also migrate through the membrane to the cathodic



compartment. This ion transport process is essential for maintaining charge balance and facilitating the electrochemical reactions.

- iii. **CO₂ Reduction:** In the cathodic compartment, CO₂ is introduced and undergoes electrochemical reduction facilitated by a catalyst, such as a Bi/C catalyst, deposited on the cathode electrode. The presence of hydroxide ions and protons, as well as the electric field established across the membrane, promotes the reduction of CO₂ to formate. The Sustainion membrane ensures that only the necessary ions are transported between compartments, maintaining the integrity of the reaction environment.
- iv. **Product Separation:** By separating the cathodic and anodic compartments, the Sustainion membrane prevents the mixing of gases and liquids between the compartments. This separation allows for the collection of the desired product, formate, while facilitating the removal of oxygen gas produced at the anode. The membrane's selective permeability ensures the efficient separation of products and reactants, contributing to the purity of the formate product.
- v. **Continuous Operation:** The use of the Sustainion membrane enables continuous operation of the electrochemical reactor, with a single pass of reactants through the cell. This continuous flow setup allows for consistent reaction conditions and steady production of formate over time. The membrane's stability and durability under alkaline conditions ensure long-term performance and reliability of the electrochemical process.
- vi. Overall, the Sustainion anion exchange-membrane serves as a critical component in the electrochemical conversion of CO₂ to formate, providing selective ion transport, compartmentalization, and continuous operation capabilities essential for efficient and sustainable formate production[6].

4.8. Bipolar membrane for CO₂ Reduction:

The text explores the potential of utilizing electrolyzers with bipolar membranes (BPM) for CO₂ reduction, addressing challenges like high H₂ evolution and low selectivity. It introduces Co phthalocyanine (CoPc) as a promising catalyst for a zero-gap BPM device, achieving 53% Faradaic efficiency to CO at 100 mA cm⁻² with pure water and CO₂ feeds. Strategies to decrease cell voltage using a TiO₂ catalyst and enhance selectivity by switching to KOH anolyte are examined. The comparison of different BPM configurations and

methods to mitigate carbonate formation is discussed. Efforts to enhance stability and decrease cell voltage by introducing Co-based molecular catalysts and water dissociation catalysts are also mentioned. The study proposes practical-scale CO₂-to-chemicals conversion strategies in BPM electrolyzers.

1. **Initial Faradaic Efficiencies:** CO production efficiencies ranged from 34% to 69% at various current densities (25 to 200 mA cm⁻²), attributed to CoPc's resistance to CO product inhibition and deactivation.
2. **Full Cell Voltage and CO Partial Current Densities:** CO partial current density plateaued at higher total current densities, likely due to intrinsic turnover frequency of CoPc rather than mass transport limitations.
3. **Stability and Selectivity:** CoPc demonstrated stable selectivity for CO over time, with minor declines at higher current densities possibly due to cathode gas diffusion layer (GDL) partial flooding.
4. **Characterization and Degradation Analysis:** XPS and SEM/EDX were used to analyze CoPc's stability; while some Co loss occurred, a significant portion remained active.
5. **Effect of BPM Design:** A custom BPM with TiO₂ particles showed lower selectivity attributed to a more acidic cathode environment compared to a commercial BPM (Fumasep FBM).
6. **Electrochemical Impedance Spectroscopy (EIS) Analysis:** EIS highlighted membrane properties, water dissociation, and charge transfer processes' impact on voltage losses.
7. **Effect of Anolyte Composition:** Switching to alkaline anolyte (1M KOH) improved CO selectivity and reduced cell voltage possibly due to cation crossover effects enhancing CO production.
8. **Conclusion:** CoPc-based cathodes in BPM electrolyzers can achieve high Faradaic efficiencies for CO production, with optimization of BPM design and reaction conditions offering further improvements.

The study provides valuable insights into BPM electrolyzer development for efficient CO₂ reduction[5].

5. Parameters Affecting the Membrane-Based Electrolysis

Operating parameters such as temperature, electrolyte concentration, flow rate, pH, applied voltage, pressure, catalyst materials, and membrane thickness all play significant roles in influencing hydrogen production within electrolysis systems. Temperature fluctuations,



for instance, can impact the effectiveness and viability of various electrolysis techniques, generally favoring higher temperatures for increased reaction rates. Electrolyte concentration directly affects ionic conductivity and reaction kinetics, necessitating precise calibration to optimize yield while safeguarding system integrity. The flow rate, meanwhile, is pivotal in regulating electrolysis kinetics, demanding a delicate equilibrium to ensure effective ionization without constraining reactions. pH levels exert influence over reaction selectivity and catalyst activity, with optimal values subject to the specific

materials and operating conditions. Applied voltage governs reaction rates, requiring meticulous adjustment to sidestep energy wastage and material wear. Pressure dynamics influence gas solubility and mass transport, thereby impacting production rates and system efficiency. Catalyst materials and membrane thickness are instrumental in facilitating reactions and ion transport, with meticulous selection pivotal for system effectiveness and robustness. Ultimately, fine-tuning these parameters is paramount for maximizing hydrogen yield and securing the efficiency and longevity of electrolysis systems.

Table 1: Comparative Analysis of Membrane Technologies for Electrochemical Processes

Membrane	Composition	Advantages	Disadvantages	Challenges	Cost	Future Trends
Nafion	Perfluorosulfonic acid polymer(cation exchange membrane)	Excellent chemical and mechanical stability	Limited performance at high temperature and low humidity	Requires strict operational control	moderate	Development of composite membranes and alternative materials for wider applicability
Zirfon	Zirconium oxide and polysulphone composite	High stability, low ionic resistance, good wettability in alkaline media	Limited commercial availability	Continuous optimization for specific applications	moderate	Advancements in fabrication and cost reduction
EPDM-ZrO₂	Ethylene Propylene Diene Monomer rubber with ZrO ₂	Low ionic resistance, pressure resistance, stability	Limited operating temperature range	Exploration of wider applications and optimization for various electrochemical cells	low	Development of more durable and cost-effective versions
EPDM-CaCO₃	Ethylene Propylene Diene Monomer rubber with CaCO ₃	Stable in non-aqueous electrolyte solutions, facilitates CO ₂ reduction, cost-effective	Lower selectivity and efficiency compared to other CO ₂ reduction membranes	Optimization of catalyst compatibility and CO ₂ conversion efficiency	low	Exploration of alternative cost-effective materials for CO ₂ capture and utilization
Bipolar membrane	Anion exchange membrane (AEM) and cation exchange membrane (CEM) laminated	Potential for efficient and cost-effective water splitting without KOH	Complex fabrication process, requires precise water management	Optimization of membrane design, water transport, and cell parameters	moderate	Development of commercially viable and durable systems for real-world applications



Anion exchange membrane	Various polymer materials	Enables use of non-noble metal catalysts for water splitting	Lower efficiency and durability compared to PEMs	Research on advanced catalysts and membrane materials for improved performance	moderate	Development of cost-effective and stable AEM electrolyzers for large-scale deployment
Proton exchange membrane	Typically perfluorinated sulfonic acid polymers	High efficiency and durability in PEM fuel cells	High cost, limited operating temperature range	Exploration of alternative high-temperature membranes with improved conductivity and cost	high	Development of membranes compatible with renewable energy sources like biofuels
Sustainion	Quaternary ammonium hydroxide functionalized poly (arylene ether)	Selective ion transport, compartmentalization for CO ₂ reduction	Limited scalability and cost	Optimization for industrial-scale CO ₂ conversion processes	moderate	Exploration of alternative materials and designs for broader applications
Bipolar membrane for CO₂ Reduction	Combines AEM and CEM with specific catalysts	High Faradaic efficiency for CO production with CoPc catalyst	High H ₂ evolution at higher current densities	Optimization of BPM design, reaction conditions, and catalyst development	moderate	Exploration of practical CO ₂ -to-chemicals conversion strategies using BPM electrolyzers

6. Conclusion:

In conclusion, the review highlights the diverse array of membrane compositions and their respective advantages and challenges in advancing sustainable energy solutions and environmental protection. Nafion membranes, characterized by their excellent chemical and mechanical stability, face limitations in high-temperature and low-humidity conditions, necessitating stringent operational control. To overcome such challenges, the development of composite membranes and alternative materials holds promise for broader applicability across varying environments. Similarly, Zirfon membranes exhibit high stability and low ionic resistance, particularly suitable for alkaline media, yet their limited commercial availability underscores the need for continuous optimization to cater to specific applications. EPDM-ZrO₂ membranes offer low ionic resistance, pressure resistance, and stability, albeit within a restricted operating temperature range. Further exploration of their potential applications and

optimization for various electrochemical cells could lead to the development of more durable and cost-effective versions. EPDM-CaCO₃ membranes, while stable in non-aqueous electrolyte solutions and cost-effective for CO₂ reduction, suffer from lower selectivity and efficiency compared to other membranes. Therefore, ongoing efforts focus on optimizing catalyst compatibility and CO₂ conversion efficiency, as well as exploring alternative cost-effective materials for CO₂ capture and utilization. The potential of bipolar membranes for efficient and cost-effective water splitting without the need for KOH is evident, albeit with challenges such as complex fabrication processes and precise water management. Future endeavors aim at optimizing membrane design, water transport, and cell parameters to develop commercially viable and durable systems for real-world applications. Additionally, advancements in anion exchange membranes enable the use of non-noble metal catalysts for water splitting, albeit with lower efficiency and durability compared to



PEMs. Research efforts concentrate on developing cost-effective and stable AEM electrolyzers for large-scale deployment. Proton exchange membranes exhibit high efficiency and durability in PEM fuel cells; however, their high cost and limited operating temperature range pose challenges. Exploring alternative high-temperature membranes with improved conductivity and cost could pave the way for their compatibility with renewable energy sources like biofuels. Sustainion membranes offer selective ion transport and compartmentalization for CO₂ reduction, yet their limited scalability and cost present obstacles for industrial-scale processes. Future exploration of alternative materials and designs aims to broaden their applications. Finally, bipolar membranes for CO₂ reduction demonstrate high Faradaic efficiency for CO production with specific catalysts, albeit with challenges such as high H₂ evolution at higher current densities. Ongoing optimization efforts in BPM design, reaction conditions, and catalyst development aim to explore practical CO₂-to-chemicals conversion strategies using BPM electrolyzers. In summary, the review underscores the critical role of membrane technologies in advancing sustainable energy solutions, highlighting the importance of continued research and innovation to address existing challenges and capitalize on emerging opportunities for a cleaner and more sustainable future.

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