

Review

Membranes for Electrochemical Carbon Dioxide Conversion to Multi-Carbon Products

Thao-Nguyen Ho, Duc-Minh Phan-Pham, Anh-Dao Ho , Tuan Anh Bui , Guorui Gao and Cao-Thang Dinh 

Department of Chemical Engineering, Queen's University, Kingston, ON K7N 3N6, Canada;
ho.dao@queensu.ca (A.-D.H.); tuananh.bui@queensu.ca (T.A.B.)

* Correspondence: caothang.dinh@queensu.ca

Abstract

Electrochemical carbon dioxide reduction reaction (CO₂RR) offers a promising route to mitigate climate change while simultaneously enabling renewable energy storage and the sustainable production of value-added chemicals. A wide variety of CO₂RR reactor designs have been developed, including both liquid-phase cells and gas-phase configurations. Among these, gas-phase systems, particularly flow-cell and membrane electrode assembly (MEA) designs, have become the primary focus of recent research due to their ability to overcome mass transport limitations and operate at high currents. While catalyst development has received considerable attention in advancing CO₂RR performance, the role of membranes in these gas-phase electrolyzers has been less systematically reviewed. This article addresses that gap by critically examining the functions, advantages, and limitations of the major membrane classes used in CO₂ electrolysis: anion exchange membranes, cation exchange membranes, bipolar membranes, and non-ion-exchange porous membranes within flow-cell and MEA configurations. We highlight how membrane properties influence local pH regulation, water management, crossover behavior, and overall reactor performance, while emphasizing that product identity is primarily catalyst-determined. By analyzing recent progress and remaining challenges, this review provides design insights for membrane selection and development toward efficient, stable, and scalable CO₂ electrolysis systems.

Keywords: CO₂ reduction reaction; membranes; membrane electrode assembly; gas-phase electrolyzers; ion-exchange membrane; non-ionic membrane

1. Introduction

Since the 1950s, fossil fuel consumption and petrochemical production have increased more than fifteenfold, leading to a dramatic rise in carbon dioxide (CO₂) emissions [1,2]. As CO₂ accounts for roughly three-quarters of global greenhouse gas output, it is widely recognized as the main driver of global warming and environmental degradation [3]. Developing technologies that minimize CO₂ accumulation in the atmosphere are therefore urgently needed [4]. One promising approach is the creation of an anthropogenic carbon cycle, in which CO₂ is converted into fuels and chemicals using renewable energy [5]. Such a strategy not only addresses the environmental and energy challenges related to CO₂ emissions but also creates a profitable carbon economy [6]. In such a system, renewable energy is converted to chemical energy stored in CO₂-derived fuels and chemicals.

A variety of pathways have been explored for CO₂ conversion, including biological, thermochemical, photochemical, and electrochemical methods [7–11]. Among these, the



Academic Editor: Enrico Negro

Received: 17 December 2025

Revised: 11 January 2026

Accepted: 20 January 2026

Published: 2 February 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

electrochemical CO₂ reduction reaction (CO₂RR) is particularly attractive as it operates under mild conditions, allows reaction rates and product selectivity to be tuned by the applied potential, and offers scalability through modular electrolyzer designs [12]. When coupled with intermittent renewable energy sources, CO₂RR represents a compelling route for integrating renewable energy into the fuels and chemicals sector.

In CO₂RR, CO₂ is supplied to an electrochemical reactor, often referred to as a “cell” or “electrolyzer”, where it is converted on a catalyst surface under an applied electrical potential. Current electrolyzer configurations for CO₂RR fall into three categories: H-cells, flow cells, and membrane electrode assembly (MEA) cells. An H-cell is a two-compartment design, with separate chambers for anode and cathode reactions, and connected by an ionic exchange membrane in between [13]. In this setup, the membrane acts as a central barrier that allows ionic transport while preventing bulk mixing of the solutions in the two compartments. The reference and the working electrodes are located in a sealed cathodic chamber, whereas the counter electrode is in the anodic chamber, thus establishing a three-electrode electrochemical system. However, because CO₂ must first dissolve in the electrolyte and then diffuse to the catalyst layer, mass transport limitations severely restrict reaction rates and achievable current densities [14,15]. As a result, H-cells are not suitable for CO₂RR at practical applications which require high operating current densities (>200 mA/cm²). In contrast, flow-cell and MEA designs have emerged as preferred configurations for achieving higher efficiencies and current densities [16]. These systems generally eliminate the use of bulk liquid chambers and instead rely on current collectors on both the anode and cathode sides. Together with gas diffusion electrodes (GDEs), such configurations shorten the diffusion path of CO₂ to the reaction interface, thus enhancing mass transport and improving reaction rates [17].

Extensive research has been devoted to the development of catalysts for efficient CO₂ conversion, but the role of membranes in gas-phase electrolyzers has received far less attention [18–23]. Broadly, membranes used in these systems can be divided into two categories: ion-exchange and non-ion-exchange membranes. Ion-exchange membranes include anion exchange, cation exchange, and bipolar membranes, while non-ion-exchange membranes are typically porous separators. Membranes have several critical functions, including preventing CO₂ reduction products from crossing over to the anode where they may be re-oxidized to CO₂, and limiting the transport of O₂ evolved at the anode to the cathode, where it could participate in the oxygen reduction reaction and compete with CO₂RR for electrons [8]. The selection of an appropriate membrane is therefore crucial, as it directly controls ion transport and strongly influences the local reaction environment at the cathode, which in turn affects the product selectivity and overall performance. In addition, CO₂ electrolyzers also face recurring technical challenges arising from the tight coupling between ion transport, reaction environment, and mass transport, such as carbonate formation, pH imbalance, ohmic losses, and product crossover [24,25]. These challenges call for the use of different membrane types, each offering distinct advantages and trade-offs depending on the experimental conditions and performance priorities.

Motivated by the growing diversity of available membranes and their use across a wide range of configurations, this paper provides a comprehensive examination of the membranes commonly used in CO₂ electrolyzers. While prior studies have largely focused on ion-exchange membranes, this work places particular emphasis on porous membranes, which have received comparatively less systematic attention despite their increasing relevance in MEA-based CO₂ electrolyzers. The discussion begins with an overview of flow-cell and MEA systems, followed by an analysis of four membrane types (i.e., anion/cation exchange membranes, bipolar membranes, porous membranes) with emphasis on their functions and impacts in these configurations. Particular attention is

given to their respective advantages and limitations, as well as recent strategies aimed at mitigating these challenges.

2. CO₂ Electrolyzers

To address the mass transport limitations inherent in conventional H-cells, GDEs have been developed to deliver gaseous CO₂ directly to catalysts supported on a gas diffusion layer (GDL) at the cathode side [26]. Both flow-cell and MEA systems adopt GDEs as a core component. The primary distinction between the two configurations lies in the cathode-membrane interface: in flow-cells, a liquid catholyte separates the cathode from the membrane, whereas MEA cells compress the GDE directly against the membrane, forming a zero-gap configuration.

Flow-cells (Figure 1a) typically consist of a cathode, anode, reference electrode, electrolyte compartments, and a membrane, with current collectors that also function as flow channels for gas or electrolyte circulation [16,27,28]. The cathode commonly uses a GDE positioned with its GDL toward the current collector and catalyst layer facing the membrane, while the anode places its catalyst close to the membrane to reduce ohmic loss. This design overcomes low CO₂ solubility and long diffusion path in aqueous media in H-cells, enabling significantly enhanced gas transport and allowing industrial-level current densities above 200 mA·cm^{−2} [29,30]. Compared to MEA architecture, the placement of a reference electrode enables in situ half-cell studies, making flow-cells highly attractive for mechanistic investigation and catalyst screening. Additionally, circulating with liquid catholyte improves ionic conductivity and thermal management throughout the catalyst layer, mitigates GDL/membrane dry-out, and permits electrolyte composition tuning to regulate the local reaction environment. Applying this approach with a 7M KOH electrolyte, Sargent's research group reported a peak ethylene (C₂H₄) Faradaic efficiency (FE) of 75% at a partial current density of 1.3 A·cm^{−2}, corresponding to a cathodic energy efficiency of 45% [31]. In an acidic environment (pH ≤ 1), Ma et al. [32] leveraged the combined effects of confinement and cations to obtain an FE exceeding 80% for C₂₊ products at 560 mA·cm^{−2}. Their findings indicate that the presence of K⁺ ions in the Helmholtz plane enhances product selectivity by kinetically suppressing proton coverage at the electrode surface.

However, flow-cells also face challenges related to long-term materials durability, where prolonged electrolyte exposure can induce corrosion and metal ion leaching, while shear force may cause mechanical degradation or catalyst-layer delamination. The liquid electrolyte also introduces additional ionic resistance, often resulting in higher cell voltages and reduced energy efficiency. Furthermore, catholyte circulation, pumps, and fluid-handling components increase system complexity and cost, creating challenges for large-scale deployment.

MEA cells (Figure 1b), also referred to as “zero-gap” or “catholyte-free” cells [33–35], eliminate the catholyte gap by placing the GDE directly against the membrane [36]. Humidified CO₂ is commonly supplied to the cathode, whereas the anode is fed with a liquid anolyte as the water source [37]. A key advantage over the flow-cell is that this configuration reduces ion-transport distance and achieves lower cell voltages with improved energy efficiency, while its compact structure enhances stack integration and scalability. The absence of catholyte further helps prevent solution-induced GDE degradation, reduces flooding risks, and limits impurity deposition, improving long-term operational stability. Several studies have demonstrated the strong performance advantages of MEA-based CO₂ electrolyzers. For instance, ethylene-dominant C₂₊ production with a total C₂₊ FE of nearly 90% was reported at a current density of over 1 A·cm^{−2}, with C₂H₄ accounting for more than 60% of the product distribution [38]. In addition to high activity and selectivity, Li et al. [39] demonstrated excellent durability in an MEA configuration, achieving stable

operation at $600 \text{ mA}\cdot\text{cm}^{-2}$ for up to 190 h while maintaining an C_2H_4 FE of around 60%. Moreover, a full-cell energy efficiency of 20% was reported, which showcases the potential of MEA cells for sustained, high-rate CO_2RR .

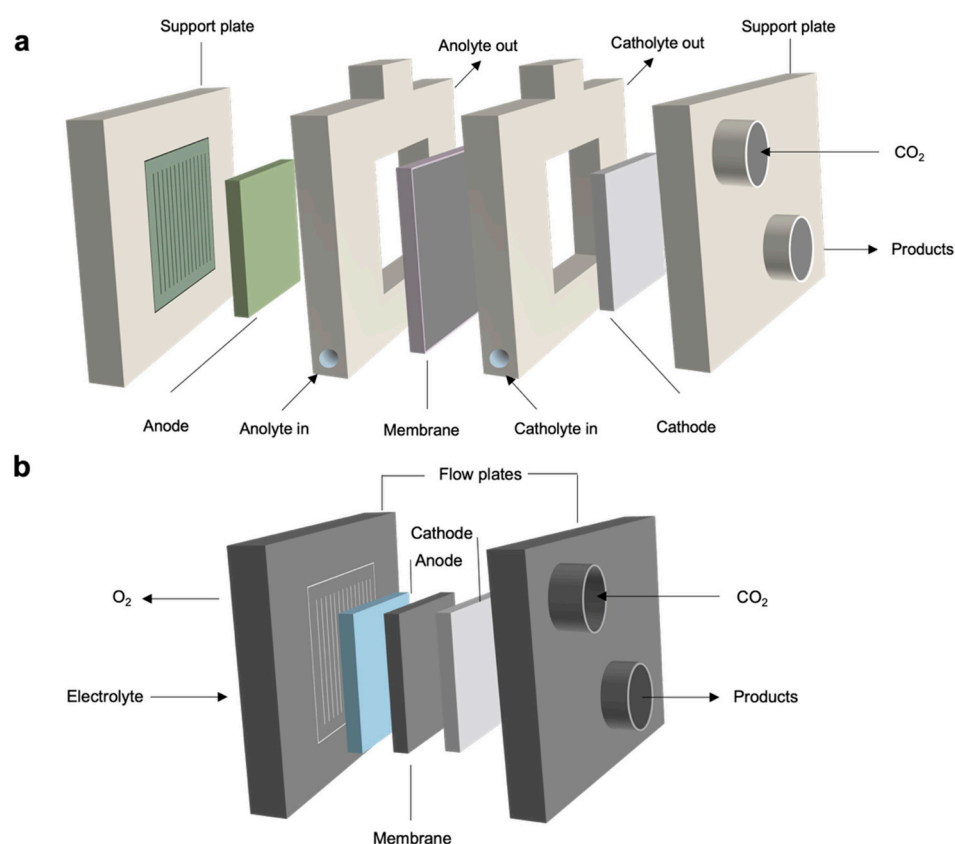


Figure 1. Visual representation of (a) a flow cell, and (b) an MEA setup.

Despite significant progress, both flow-cell and MEA systems suffer from salt precipitation within the GDE, where carbonate and bicarbonate species crystallize as CO_2 reacts with locally generated OH^- . At high current densities, the sharp rise in interfacial alkalinity drives salt formation, progressively blocking GDE pores, increasing mass-transfer resistance, causing flooding, and restricting CO_2 access to active sites, ultimately shifting selectivity toward H_2 .

Considerable efforts have been made to alleviate this issue. Xu et al. [40] proposed a self-cleaning strategy in which the applied cell voltage was periodically alternated between normal operating conditions and a lower regeneration voltage, effectively reducing the current density to nearly $0 \text{ mA}\cdot\text{cm}^{-2}$. Using this approach, system stability was improved by nearly 16-fold, which extended the operating time from 10 h to about 157 h while keeping an 80% FE for C_2 products. However, this strategy was demonstrated at a partial current density of only $138 \text{ mA}\cdot\text{cm}^{-2}$, which remains lower than that achieved in many state-of-the-art systems. In a separate approach, Wang's group introduced acid-humidified CO_2 gas to suppress salt crystallization within the GDE [41]. This strategy enabled stable operation for up to 4500 h in a 100 cm^2 electrolyzer without compromising catalyst activity. Nevertheless, the reported performance was limited to CO production rather than multi-carbon products. Thus, while these strategies effectively address one key drawback of MEA cells, limitations remain, and further development in reactor engineering is therefore required.

Overall, each electrolyzer design offers specific advantages that can be utilized based on the desired performance goals. While the formation of specific CO₂RR products is primarily governed by the choice of catalyst, reactor design has become increasingly important for achieving stable operation, high efficiency, and scalability by shaping the local reaction environment. Membrane type and cell configuration do not uniquely determine product identity, but they regulate ion transport, hydration, and local pH, which in turn influence reaction pathways in conjunction with catalyst properties and operating conditions. Currently, four main categories of membranes are used in CO₂ electrolyzers: anion exchange membranes (AEMs), cation exchange membranes (CEMs), bipolar membranes (BPMs), and non-ion-exchange porous membranes. The following section examines each membrane type in detail, highlighting its functional roles, operational advantages, and associated challenges in CO₂ electrolysis systems.

3. Membranes for CO₂ Electrolyzers

Membranes play a central role in CO₂ electrolyzers by providing ion transport pathways, maintaining separation between anodic and cathodic environments, and suppressing the crossover of reactants and products [42]. Their performance is dictated largely by the functional groups within the polymer matrix, which determine whether the membrane operates under acidic, alkaline, or neutral conditions. These functional groups also control critical properties such as charge-carrier mobility and water uptake [43–45]. Given the wide diversity of membrane chemistries, fabrication methods, and testing conditions reported in the literature, this review does not attempt to comprehensively catalogue all membrane properties. Instead, we focus on representative membrane classes and the key properties most relevant to CO₂ electrolysis performance.

Traditionally, three classes of membranes have been used in CO₂RR systems: AEMs, CEMs, and BPMs, similar to those applied in water splitting electrolyzers [46–49]. In this review, we additionally highlight the emerging class of porous membranes [50]. As illustrated in Figure 2a–d, the type of membrane directly defines the ion transport pathway across the electrolyzer, thus influencing both efficiency and product selectivity. The membrane type determines the dominant charge carriers (e.g., OH[−] in AEMs, H⁺ in CEMs, H⁺/OH[−] generated in BPMs), which controls the local pH, water activity, and ion availability near the catalyst surface. Unlike bulk liquid electrolytes, membrane-catalyst interactions are highly localized and arise from coupled ion transport, hydration, and mass-transfer effects rather than direct coordination chemistry.

In addition to intrinsic transport properties, long-term stability in CO₂ electrolyzers is strongly influenced by membrane swelling, interfacial resistance, and chemical compatibility between the membrane and catalyst layers. Excessive membrane swelling can degrade mechanical integrity, alter interfacial contact, and increase ohmic resistance during extended operation, particularly in MEA configurations [51]. Similarly, increased interfacial resistance arising from poor membrane-electrode contact can lead to performance decay over time [52]. Chemical incompatibility between membranes, ionomers, and catalysts may further accelerate degradation through polymer decomposition, catalyst poisoning, or changes in local hydration and pH [47,53]. These interfacial effects highlight that membrane stability must be evaluated not only by bulk properties but also by long-term interactions within the complete electrolyzer design.

To better understand these effects, it is necessary to examine the fundamental membrane characteristics, including chemical composition, concentration and distribution of functional groups, and overall structural design.

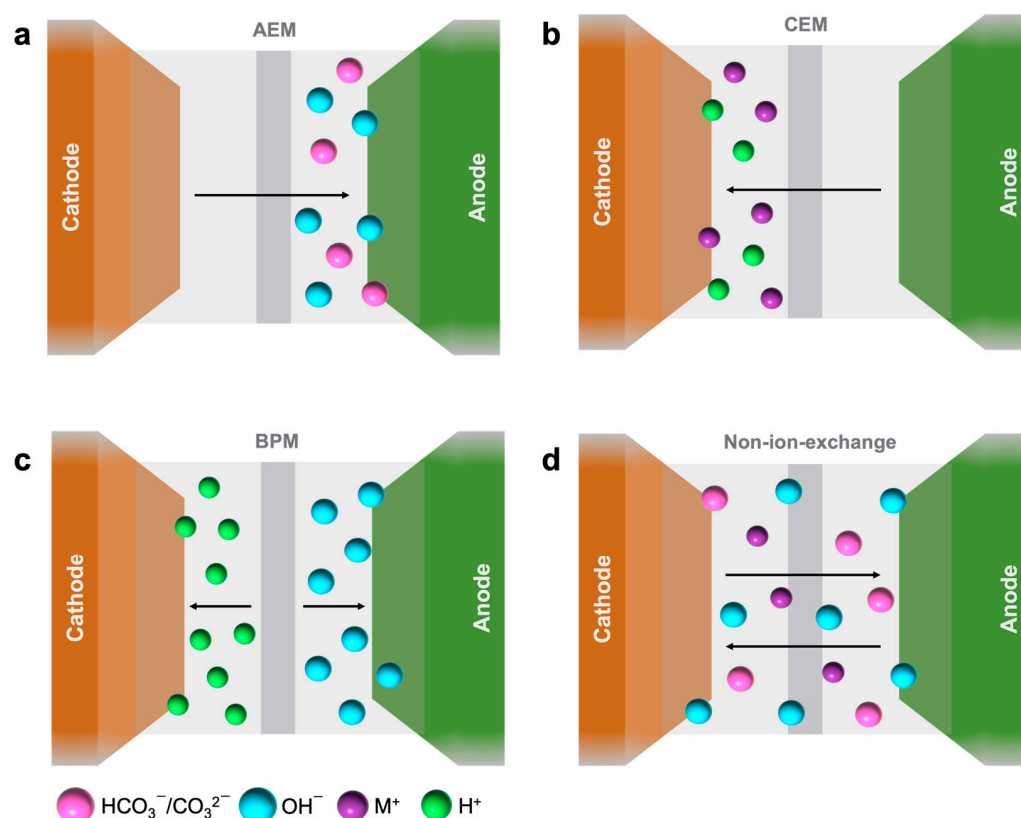


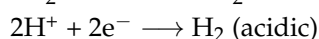
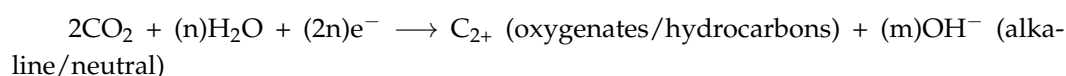
Figure 2. Illustration of ion transport in CO₂RR systems using different membrane types: (a) AEM, (b) CEM, (c) conventional BPM, and (d) non-ion-exchange membrane (e.g., PVDF, Nylon).

3.1. Anion Exchange Membranes (AEMs)

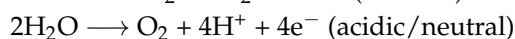
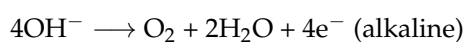
AEMs are polymeric membranes that transport anions such as hydroxide (OH[−]) and carbonate/bicarbonate (CO₃^{2−}/HCO₃[−]) between the cathode and anode in CO₂RR systems (Figure 2a). Their structure consists of positively charged functional groups, typically ammonium, diammonium, imidazolium, and phosphonium, anchored to a polymer backbone [54] (Figure 3a). Adapted from mature technologies (i.e., water electrolysis, fuel cells), AEMs bring several well-established advantages to CO₂RR applications [55–57]. Academic studies have further demonstrated the potential of imidazolium-functionalized AEMs, which exhibit high conductivity and enhanced alkaline stability, thus enabling long-term electrolysis performance [58].

In principle, the positively charged functional groups on the polymer backbone of AEMs facilitate anion transport from the cathode to the anode, allowing the CO₂RR to occur in a basic environment through the generation of OH[−] ions at the surface of the cathode [51]. In an MEA setup, the use of AEMs helps reduce cell voltage and enhance current density by minimizing ionic resistance and improving both mass and charge transport, thus increasing overall energy efficiency (Figure 3b). Their compatibility with gas-fed systems makes AEMs particularly attractive for industrial-scale CO₂ electrolysis. The half-reactions occurring at the cathode and anode in AEM-based systems are summarized as follows.

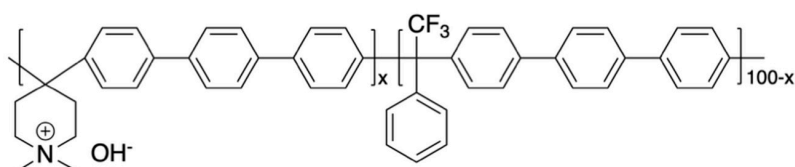
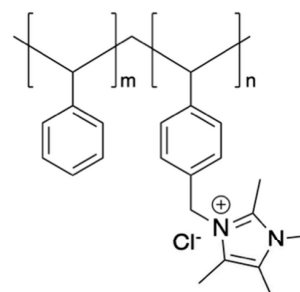
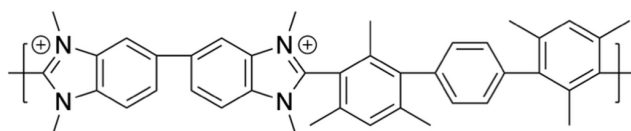
Cathode:



Anode:



a



b

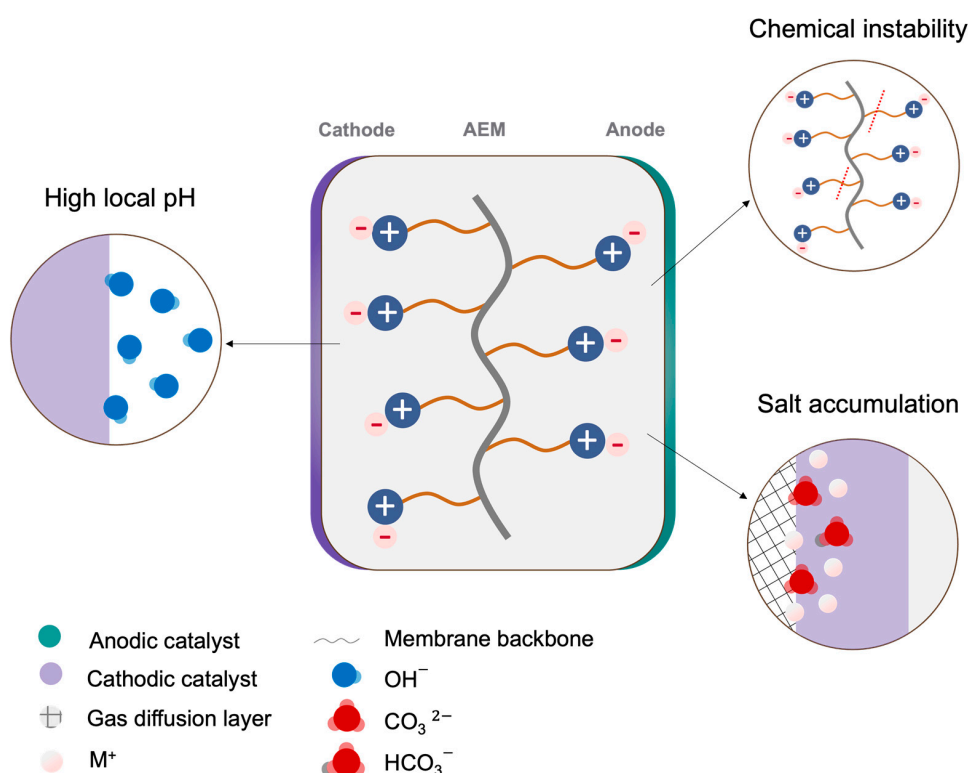


Figure 3. (a) Structures of representative AEMs—methylated polybenzimidazole (commercialized as Aemion[®]), polystyrene tetramethyl imidazolium chloride (Sustainion[®]), poly(aryl piperidinium) (PiperION); and (b) schematic of anion transport through the polymer network. These systems benefit from high local pH, which reduces cell voltage and ionic resistance. However, they suffer from CO₂ crossover, chemical instability, and salt accumulation due to the reaction of HCO₃[−] / CO₃^{2−} species with OH[−]. The purple region denotes the cathode side, and the indicated salt accumulation corresponds to the cathode environment in AEM-based operation rather than within the membrane itself.

AEMs have also shown promise in both zero-gap and flow-cell configurations for gas-phase CO₂ reduction. In an MEA setup employing an AEM as the separator, Gabardo et al. [59] reported an FE of 50% for C₂H₄ and 80% for total C₂₊ products, with stable operation over 100 h at current densities >100 mA·cm⁻². Similarly, Xu et al. [40] achieved an 80% FE for C₂ products at roughly 180 mA·cm⁻², maintaining stable performance over 236 h of total duration. In a flow-cell study, Dinh et al. [60] used a sputtered Cu catalyst on a polymer-based gas diffusion electrode, obtaining a 70% FE for C₂H₄ and 87% for total C₂₊ products at current densities exceeding 250 mA·cm⁻². These results highlight the effectiveness of AEMs in enabling efficient ion transport and promoting selective CO₂ conversion in high-performance systems. From an economic perspective, AEMs can be synthesized from common hydrocarbon polymers and functionalized with inexpensive quaternary ammonium (QA) salts, offering low cost and tunable water transport properties [61,62].

Despite their advantages, AEMs have yet to achieve widespread commercial application due to issues of chemical instability and salt accumulation [63,64] (Figure 3b). Under alkaline condition, CO₂ readily reacts with OH⁻ ions to form CO₃²⁻ and HCO₃⁻ species. Meanwhile, the diffusion of aqueous electrolyte through concentration gradients and electroosmotic drag over solvated cations promotes the migration of metallic cations from the anolyte to the cathode. This process leads to the formation of salt precipitates within the cathode, which can clog the pores of the gas diffusion electrode and obstruct the flow channels in the cathode field. As a result, CO₂ transport to catalyst surface is hindered, increasing cell pressure and reducing system efficiency [65]. In addition, AEMs are prone to degradation in highly concentrated alkaline environments, which shortens their operational lifetime [66]. Under such conditions, both the cationic functional groups and the polymer backbone are vulnerable to nucleophilic attack by OH⁻ ions, leading to chemical breakdown. Meanwhile, mechanical durability is another major concern in CO₂ electroreduction systems, as prolonged exposure to CO₂ streams can make the membrane brittle [52,67]. This brittleness can lead to rupture and severe flooding, eventually lowering CO₂RR selectivity and limiting long-term stability.

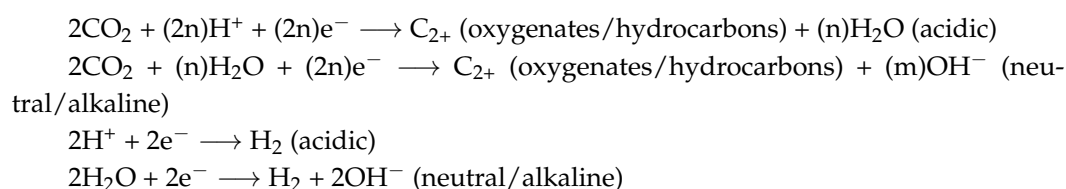
To mitigate the undesired crossover of CO₂RR products through the AEM, careful control of water uptake and ion exchange capacity (IEC) is essential [68,69]. Regulating these parameters reduces the mixing of liquid products with water and minimizes electroosmotic drag toward the anode, while maintaining high anion conductivity. This balance also helps suppress CO₃²⁻/HCO₃⁻ transport by limiting the aqueous CO₂ content within the membrane and reducing its reaction with OH⁻. One effective strategy involves designing AEMs with internal microchannels, which not only lower K⁺ crossover but also enable operando water management for improved stability [70]. In another study, Kim et al. [71] developed a QA-based membrane paired with an ionomer binder, achieving high anion conductivity, low water uptake, and enhanced mechanical and chemical durability compared to commercial AEMs. Further advancements have been reported by Wang's group [72] and Zhang's group [73], who modified polybenzimidazole membranes through crosslinking and grafting to improve dimensional stability and mechanical robustness, highlighting ongoing efforts to balance conductivity, durability, and selective ion transport in next-generation AEMs.

At present, no standardized protocols or performance metrics exist for the commercialization of AEMs in CO₂RR electrolyzers [43]. Thus, the development of AEMs tailored specifically for CO₂RR is critical to advancing commercially viable MEA configurations. Although certain design principles and operational strategies can be adapted from related electrochemical technologies, novel membranes with different materials and morphologies will be required to address the unique challenges of CO₂RR.

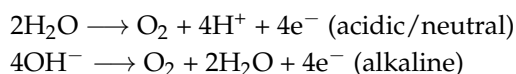
3.2. Cation Exchange Membranes (CEMs)

Cation-exchange membranes (CEMs) are composed of polymer backbones containing fixed anionic functional groups such as sulfonic ($-\text{SO}_3^-$) or carboxylate ($-\text{COO}^-$). Common examples include perfluorosulfonic acid (PFSA)-based polymers like Nafion, as well as sulfonated hydrocarbon frameworks such as SPEEK, and Selemion (Figure 4a). These fixed negative sites facilitate selective transport of cations (e.g., H^+ , K^+ , Cs^+) while effectively blocking anionic species such as HCO_3^- and CO_3^{2-} (Figure 2b). CEM-based systems often operate with acidic electrolytes, in which the electrolyte itself supplies a high concentration of H^+ , thus establishing and maintaining an acidic environment at the cathode. This condition suppresses the formation of CO_3^{2-} and HCO_3^- species, which otherwise consume CO_2 and hinder reaction efficiency [74]. However, it is in principle possible to use neutral or alkaline electrolytes depending on the specific objectives and design choices of a given study. Under such conditions, the dominant ion transport pathways differ from those in acidic operation and must be reconsidered accordingly. The half-reactions occurring at the cathode and anode in CEM-based systems are summarized as follows.

Cathode:



Anode:



CEMs facilitate the transport of H^+ ions from the anode to the cathode, which in turn create and maintain an acidic interface. This localized acidity can help prevent salt precipitation and prevent CO_2 crossover to the anode (Figure 4b).

Several studies have explored CEMs for CO_2 electroreduction across both flow-cell and MEA configurations. In a flow-cell setup, Zhang et al. [75] employed a CEM, reporting an FE of ~75% and an energy efficiency of 40% for C_{2+} products, with stable operation for nearly 30 h and minimal catalyst degradation. Similarly, Huang et al. [76] incorporated a CEM to functionalize the surface of Cu catalyst, which enabled efficient ion transport and stable reaction environment at high current densities. Their system reached a CO_2 single-pass utilization of 77% and an FE exceeding 40% for C_{2+} products at $1.2 \text{ A}\cdot\text{cm}^{-2}$. Collectively, these studies highlight the promise of CEM-based electrolyzers for high-rate CO_2 electroreduction with enhanced carbon efficiency and operational durability.

Despite their advantages, CEM-based systems also face several drawbacks that limit their long-term performance (Figure 4b). One key issue is proton accumulation near the cathode, which can lower the local pH, suppress C-C coupling and favor the competing hydrogen evolution reaction (HER) [77]. However, both theoretical analyses and experimental observations suggest that such strongly acidic conditions primarily occur at low current densities or during the initial stages of operation. Beyond this, the major challenges in CEM-based configurations stem from catalyst deactivation and poor long-term durability [78]. Moreover, unintended ion crossover remains a critical concern. Acidic liquid products such as acetic acid or formic acid do not readily deprotonate into anionic species under operating conditions and can therefore diffuse across the membrane as neutral molecules [79]. This neutral species crossover not only lowers product selectivity and carbon utilization efficiency but also complicates downstream separation and recycling processes. Addressing these limitations requires careful optimization of membrane

composition, ion exchange capacity, and interfacial architecture to stabilize the reaction environment and extend operational lifetime.

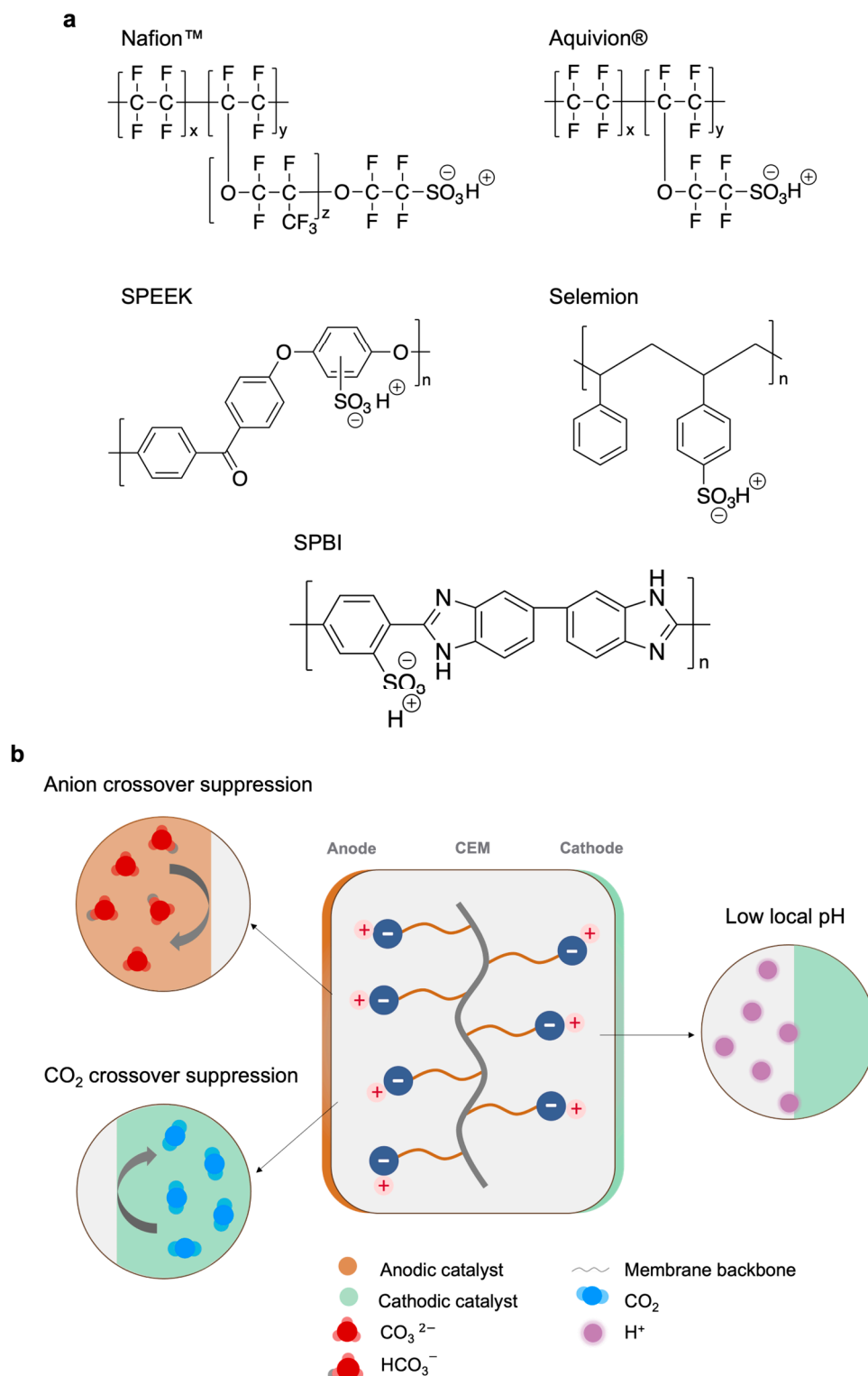


Figure 4. (a) Structures of representative CEMs—perfluorosulfonic acid (commercialized as Nafion™ and Aquivion®), sulfonated poly(ether ketone) (SPEEK), sulfonated polybenzimidazole (SPBI); and (b) schematic illustration of cation transport through the polymer network. CEMs effectively block the migration of anions from the anode to the cathode and prevent CO₂ crossover to the anode side. Thus, CEM-based systems do not experience salt precipitation or pore blockage. However, the formation of acidic microenvironment near the catalyst layer remains a key limitation.

As established in mature electrochemical technologies, mitigation strategies for CEMs typically focus on optimizing their physical and chemical properties. These include tuning the ion exchange capacity and membrane thickness to restrict carbonate transport, designing ionomers that stabilize interfacial alkalinity, and incorporating crosslinked polymer matrices to enhance mechanical durability and suppress swelling [80–82]. Building on these principles, recent studies have explored tailored designs for CEM-based CO₂RR systems. Park et al. [83] introduced an approach by coating an anion exchange ionomer (AEI) onto a CEM, thus creating a locally alkaline microenvironment at the cathode while preserving the advantages of a single-membrane system. They demonstrated that optimizing AEI content, alkali cation concentration, and catalyst layer thickness enhanced the pH gradient across the membrane, effectively expanding the alkaline reaction zone and improving CO₂RR selectivity. Similarly, O'Brien et al. [77] developed a permeable CO₂ regeneration layer that maintained an alkaline interface and facilitated local CO₂ regeneration within a CEM configuration. This design reduced CO₂ crossover to 15% and obtained a single-pass CO₂ conversion of 85% at 100 mA·cm^{−2}, with a hydrocarbon FE close to 60%. Moreover, hybrid approaches that integrate both AEM and CEM functionalities have also emerged as promising alternatives, as discussed in the following subsection.

3.3. Bipolar Membranes (BPMs) or CEM/AEM Hybrid

BPMs are composed of two layers: a cation exchange layer (CEL) containing fixed sulfonic acid groups and an anion exchange layer (AEL) with fixed QA groups. These layers form a junction, which may be a direct CEL-AEL interface or may incorporate a thin catalytic interlayer [84]. Importantly, the fundamental working mode of BPMs (reverse bias, forward bias) is controlled by the membrane polarity and electric field direction and is not altered by whether the interface is laminated or catalyst assisted. Under reverse bias (i.e., CEL at the cathode), water at this junction dissociates into H⁺ and OH[−] ions. The generated H⁺ migrates through the CEL toward the cathode, while OH[−] migrates through the AEL toward the anode (Figure 5a). Although H⁺ and OH[−] generated at the bipolar junction are the dominant charge carriers under this working mode, alkali cations (M⁺) may still reach or accumulate near the cathode side due to electro-osmotic drag, and the local concentration polarization under high current density operation.

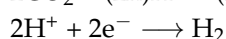
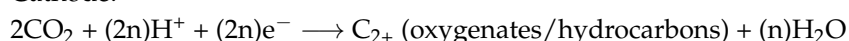
In contrast, under forward bias (i.e., CEL at the anode), H⁺ and OH[−] ions are transported from the respective layers into the BPM, where they recombine to form water at the interface (Figure 5b). The distribution of ionic species under both bias directions is illustrated in Figure 2c.

The cathodic and anodic half-reactions, together with the BPM interfacial reaction (water dissociation or acid-based recombination) under the corresponding operating modes, are summarized below.

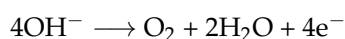
BPM interface:



Cathode:



Anode:



In conventional alkaline gas-fed cells, CO₂ reacts with cathodic OH[−] to form CO₃^{2−}, which then migrates across the membrane, reducing overall efficiency [85]. In contrast, a BPM in a gas-fed MEA helps stabilize the cathode pH and suppress the prod-

uct crossover [86,87]. The junction continuously generates H^+ that neutralize cathodic OH^- , which minimizes CO_3^{2-} formation and maintains a basic environment at the anode side [84]. This dynamic sustains charge balance: electrons flow from the anode to the cathode, while H^+ and OH^- produced at the junction move in opposite directions to keep electro-neutrality. As a result, CO_2 reaching the cathode is efficiently converted, and any CO_3^{2-} or HCO_3^- formed is immediately reconverted by the BPM-derived H^+ , preventing loss through crossover. In essence, the BPM acts as a selective ionic conduit that directs H^+ and OH^- where they are needed while blocking unwanted ion transport. Considering this principle, Wang et al. [88] coupled a BPM with a tandem catalyst architecture, achieving a total FE of approximately 77% toward C_{2+} products, of which 43% was attributed to C_2H_4 , at a high current density of $726\text{ mA}\cdot\text{cm}^{-2}$. Similarly, Khan et al. [89] employed BPM in a flow-cell configuration for the co-electrolysis of CO_2 to C_2H_4 at the cathode and glycolic acid at the anode. Remarkably, FEs of 50% for C_2H_4 at current densities of $175\text{--}225\text{ mA}\cdot\text{cm}^{-2}$ and around 50% for glycolic acid on the anode side were achieved. This dual-product operation highlights the economic potential of BPM-based systems, as two value-added products can be generated simultaneously within a single electrolyzer.

Despite recent advances in applying BPMs to CO_2 RR electrolyzers, these systems still face several drawbacks. The main limitation is the additional voltage required to drive water dissociation (WD) at the junction, which results in higher cell voltages compared to single-membrane systems operating at the same current density [90]. Mechanical stresses at the CEL/AEL interface, arising from swelling, water flux, or gas bubble formation, can further cause delamination or blistering during extended high-current operation [77,91]. In addition, the alkaline degradation of AEM chemistries remains a concern for long-term durability [92].

To overcome these challenges, researchers have focused on engineering specialized interfacial catalysts, polymer designs, and structural modifications. Enhancing the compatibility between the AEL and CEL has been shown to improve interfacial adhesion, ionic conductivity, and water management, which are all crucial for maintaining stable operation under high current densities [93,94]. Another effective strategy involves introducing a buffering catholyte layer between the CEL and the cathode to counteract cathode acidification, which helps stabilize local pH and sustain optimal reaction conditions [95,96].

Chen et al. [97] demonstrated that using optimally thin TiO_2 nanoparticle films enabled a BPM-based cell to operate at $500\text{ mA}\cdot\text{cm}^{-2}$ with a cell voltage below 2.0 V. They further showed that adding electronic conductors (e.g., carbon black) into the catalyst layer enhanced the local electric field at the junction, improving WD rates. In another study, Xie et al. [98] incorporated a stationary catholyte layer between the catalyst and the BPM, yielding a CO_2 electrolysis system capable of producing multicarbon products with carbon efficiencies $>70\%$. Their BPM-based cell attained around 78% single-pass CO_2 utilization for C_{2+} products and exhibited C_2H_4 selectivity comparable to the best neutral MEAs. Remarkably, the system delivered $\sim 42\%$ FE for C_2H_4 at $200\text{ mA}\cdot\text{cm}^{-2}$ and a full-cell voltage of roughly 3.8 V. This performance improvement was attributed to the controlled local pH and the optimized CO_2 transport pathways provided by the buffered interface.

In addition to modified BPMs, many studies have highlighted the efficiency of integrating both AEM and CEM in CO_2 RR systems. For example, Alkayyali et al. [99] introduced a direct membrane deposition approach to fabricate a monolithic AEM|CEM composite structure within an MEA. This design offered flexibility in tuning the composite's properties and optimizing the AEM:CEM ratio to achieve both low ionic resistance and reduced H_2 evolution. Compared to a conventional BPM, their system decreased mass transport resistance by over 50% and increased selectivity toward multicarbon products from 29% to 65% at $300\text{ mA}\cdot\text{cm}^{-2}$. Building on this, She et al. [100] demonstrated a pure-water membrane

assembly with an AEM on the cathode side and a CEM on the anode side (referred to as an APMA configuration) that effectively eliminated CO_3^{2-} formation. Their six-cell stack operated for over 1000 h at a total current of 10 A without any CO_2 or electrolyte loss, achieving approximately 50% FE toward C_2H_4 . In this configuration, OH^- ions produced at the cathode and H^+ ions at the anode migrated through their respective membranes and recombined at the interface to form water, effectively shuttling water between compartments (Figure 5c). In the APMA system, the AEM interfaces with the cathode to establish an alkaline cathode environment that is favorable for CO_2RR , while the CEM positioned at the anode effectively blocks anion crossover. Together, this configuration enables the use of pure water as the electrolyte. This research highlights that employing CEM/AEM hybrid can sustain high hydrocarbon yields with Cu catalysts while operating with dry gas feed.

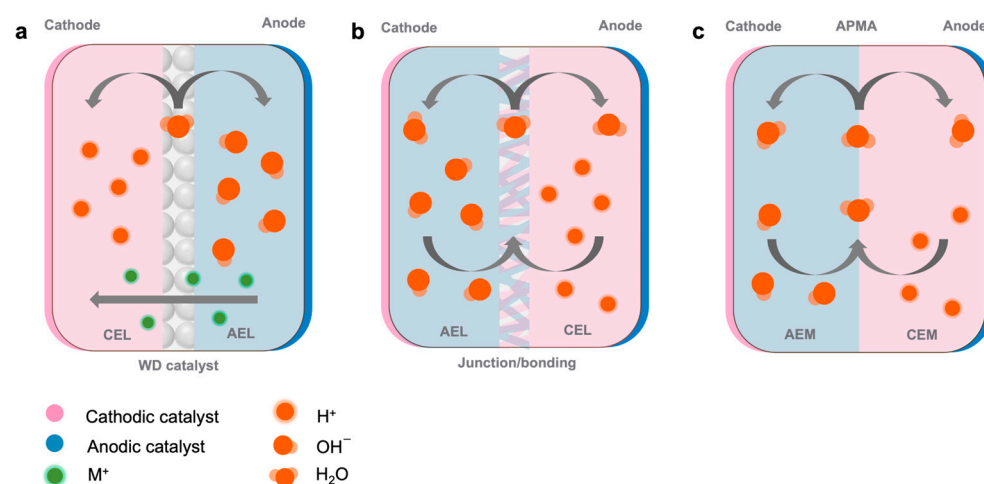


Figure 5. Schematic illustration of ion transport in BPMs: (a) Conventional BPM under reverse bias, where water dissociation occurs at the junction, aided by a catalyst that promotes the splitting of H_2O into H^+ and OH^- ions, which migrate toward the cathode and anode, respectively; (b) Conventional BPM under forward bias, in which the AEL and CEL are bonded together, allowing spontaneous recombination of OH^- and H^+ at the junction to form H_2O ; (c) Modified BPM, integrating an AEM and a CEM under forward bias, while supplying H_2O as the electrolyte to maintain a basic environment near the catalyst and prevent salt precipitation [100]. Note that the junction shown in (a) and (b) may be interchanged, and the AEL/CEL junction can adopt different interfacial morphologies, without changing the fundamental operating modes of the BPM.

In summary, by tailoring both the structure and chemistry of BPMs or employing the AEM/CEM combination, recent designs have significantly improved alkaline stability and mechanical integrity. Therefore, despite the added complexity, BPM-based electrolyzers continue to offer a key advantage in delivering intrinsically high carbon efficiency [101], while hybrid AEM/CEM configurations mitigate the limitations associated with each membrane type when used individually.

3.4. Non-Ion-Exchange Membranes

Porous membranes (PMs) or non-ion-exchange membranes have been widely studied for alkaline water electrolysis, but their use in CO_2RR systems remains relatively under-explored. Acting as porous diaphragms or separators with open pores, PMs enable ionic transport without fixed charges [102] (Figure 2d). PMs are typically fabricated from low-cost inorganic or composite polymers such as polysulfone blends and zirconia-reinforced asbestos. Unlike polymer-based AEMs, these materials remain chemically stable in alkaline environments [103,104]. The key advantages of PMs lie in their tunable pore size, wetta-

bility, and thickness. These properties can be adjusted to optimize ionic transport and gas access, which allows PMs to meet the specific demands of different CO₂RR systems.

Representative examples of PMs include Zirfon PERL™, a polysulfone-zirconia composite widely used for its chemical stability and mechanical strength, as well as polymer membranes such as polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE) [50,105,106] (Figure 6a). PVDF is relatively hydrophilic, allowing strong electrolyte uptake and high ionic conductivity, while PTFE is intrinsically hydrophobic, less effective at retaining electrolyte but useful in mitigating flooding and influencing selectivity. Other tested materials include cellulose filters, nylon, and polyethersulfone (PES), which are all attractive for their robustness and ease of handling without chemical modification. In general, thinner hydrophilic membranes reduce ohmic loss, whereas thicker membranes with small pores increase resistance. For now, PMs are mainly used in MEA configurations. In this setup, they are placed between the anode and cathode electrodes, where their structural and transport properties significantly influence performance.

Deng et al. [106] demonstrated that the porous separators with well-defined structures can also be filled with KOH electrolyte, functioning in a similar way to AEMs by enabling K⁺ and OH[−] transport between electrodes. This creates a strongly alkaline environment at the cathode, which suppresses the HER and enhances CO₂ reduction selectivity. The robustness of PMs under these conditions was further confirmed through long-term operation. Using a 5 μm PVDF membrane paired with a sputtered Cu catalyst, Pham et al. [107] achieved an FE of 75% toward C₂ products at 110 mA·cm^{−2}, maintaining stable performance for more than 950 h. Building on these insights into ionic transport and durability, Lee et al. [105] investigated the effect of membrane wettability by comparing PVDF (i.e., hydrophilic) with PTFE (i.e., hydrophobic) under identical conditions. Moreover, intermediate PVDF pore sizes were optimal, leading to an achievable FE(C₂H₄) of ~41% at 300 mA·cm^{−2}.

Although the applications of PMs in CO₂RR remains limited, recent studies on CO electrolysis suggest their strong potential for future integration. For instance, Deng et al. [106] demonstrated efficient CO conversion to hydrocarbon products at current densities ranging from 50 to 400 mA·cm^{−2} using Zirfon 500+, PES, and Nylon membranes. All tested membranes delivered C₂₊ FEs exceeding 80%, with product distributions comparable to those achieved using AEMs. These results underscore the potential of PMs as low-cost and scalable alternatives to conventional ion-exchange membranes for practical CO electrolysis. Moreover, the Zirfon-based cell maintained an acetate FE of 45% over 250 h, outperforming the ~150 h stability typically observed in AEM-based systems. Similar stable performance was also reported by Miao et al. [108] in a CO₂-to-CO cascade followed by CO electroreduction, achieving an energy efficiency of 51% toward C₂₊ products and a CO single-pass conversion of up to 97%. The authors further compared different PMs, including polypropylene (PP), PES, PVDF, and PTFE, with varying pore sizes to identify the optimal configuration for their setup. They found that using a thin, highly porous separator with an interelectrode gap of ~60 μm resulted in the best performance, lowering the full-cell voltage by about 150 mV compared to an AEM-based system.

While ion-exchange membranes do not electrostatically block neutral products, their polymer chemistry and water uptake can influence the diffusion of neutral species by regulating membrane swelling, free volume, and hydrated transport pathways. In contrast, PMs suppress product crossover through a fundamentally different mechanism. In PM-based systems, the pores are typically fully wetted by the electrolyte, such that gas phase carbon-containing products must overcome capillary and osmotic pressure barriers to diffuse through liquid-filled pores, suppressing spontaneous gas crossover unless driven by significant pressure gradients. Moreover, the high FEs for C₂₊ products reported for PM-based systems also arise from system-level effects (e.g., reduced carbonate formation,

efficient gas removal at the cathode, minimized product re-oxidation at the anode, improved carbon utilization) rather than superior intrinsic product-blocking capability.

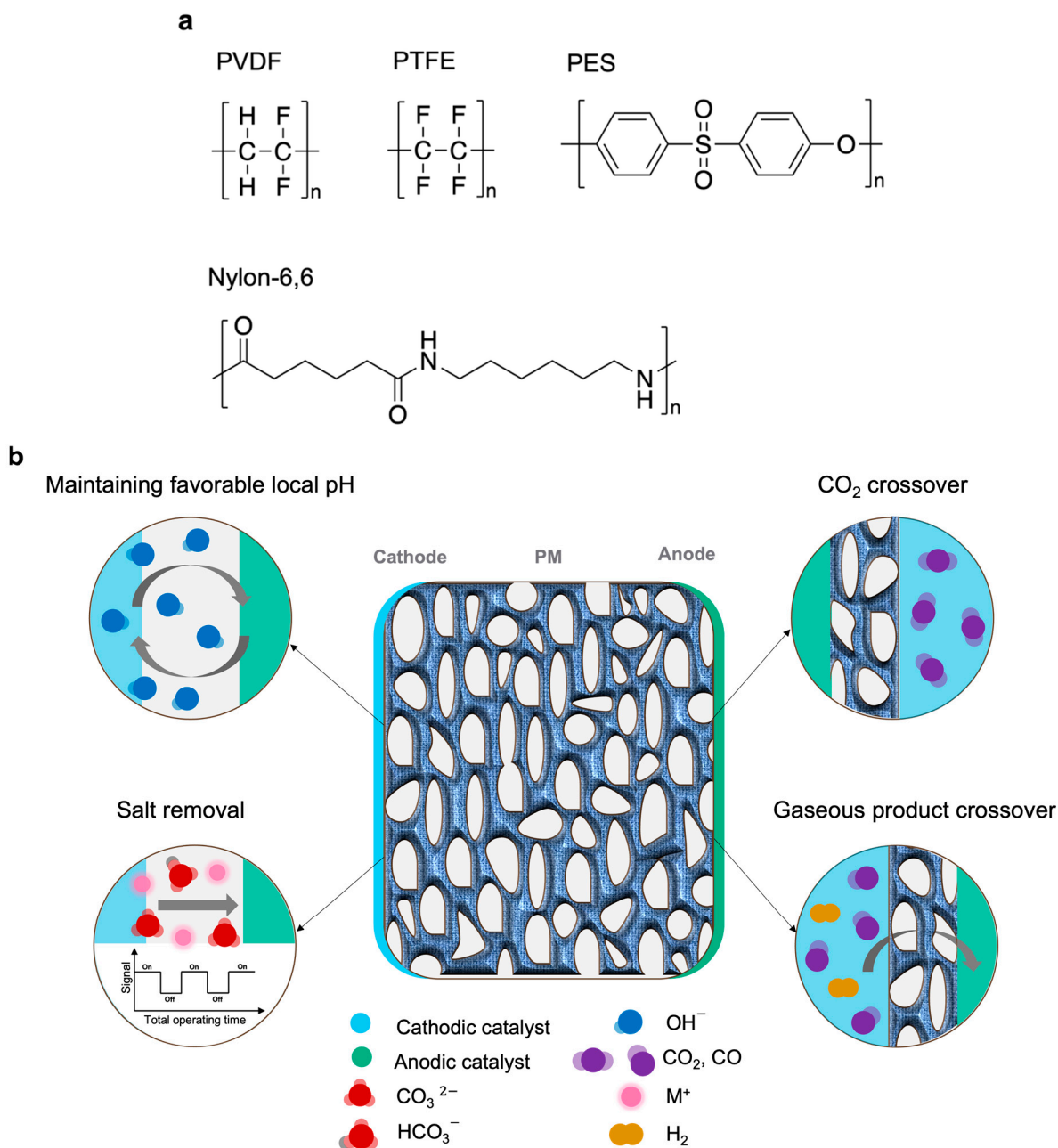


Figure 6. (a) Structures of representative PMs—polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethersulfone (PES), nylon-6,6; and (b) schematic illustration summarizing their advantages and limitations. PMs allow both cations and anions to move freely, maintaining a favorable local pH near the catalyst layer. In addition, salt deposits can be removed through operating with on-off strategy. However, CO₂ and gaseous products crossover remain significant challenges for PM-based systems.

Despite their advantages, studies have also highlighted notable drawbacks of PMs [105,106] (Figure 6b). A major issue is CO₂ crossover, particularly in hydrophobic membranes, where unreacted CO₂ and other gaseous products can diffuse through the porous structure. This direct penetration from cathode to anode arises from insufficient interaction between the membrane and the electrolyte. To address this, mitigation strategies such as reducing pore size or applying hydrophilic surface coatings have been proposed.

In one study, switching to a 200 nm PTFE membrane modified with a hydrophilic layer effectively reduced crossover [105].

Overall, from an economic perspective, PMs remain more favorable than AEMs, though the savings are partially offset by the additional costs of CO₂ capture. Finally, while PMs are mechanically robust and chemically stable, their long-term durability in CO₂RR systems as well as product crossover have not yet been fully established, and achieving extended stable operation remains a key challenge for both membranes and catalysts.

4. Conclusions and Outlook

The electrochemical CO₂RR has emerged as a promising strategy for closing the anthropogenic cycle by converting CO₂ into fuels and chemicals using renewable electricity. Among the critical components in these electrolyzers, membranes play an essential role in facilitating ion transport, maintaining pH balance, and preventing reactant and product crossover. Through these functions, membrane properties strongly influence energy efficiency, operational stability, and achievable reaction environments. This makes membrane selection and design critical to overall electrolyzer performance. This review highlights four primary membrane types: AEMs, CEMs, BPMs, and PMs, with each offering distinct advantages and facing unique challenges that shape their applicability in CO₂RR systems.

AEMs have shown strong potential for CO₂RR in alkaline environments by enabling efficient anion transport and lowering cell voltage. Their compatibility with hydrocarbon polymers makes them cost-effective, but chemical instability and excessive swelling under basic conditions remain key challenges. Recent advances in crosslinked structures and more stable cationic groups have improved durability, yet large-scale commercialization still requires standardized testing and long-term validation.

CEMs provide selective cation transport and effective anion blocking, which can suppress carbonate crossover and enable operation under acidic or near-acidic conditions. While C₂₊ products can be achieved in CEM-based systems under appropriate catalyst and interface design, challenges related to proton availability, hydrogen evolution, and local acidification remain.

BPMs offer unique advantages by generating H⁺ and OH[−] in situ, enabling decoupled pH control and high carbon efficiency while mitigating CO₂ crossover. However, their broader adoption is constrained by additional voltage losses associated with water dissociation and ongoing concerns regarding mechanical and chemical durability, despite recent advances in catalytic interlayers and interfacial engineering.

PMs offer a simple, low-cost alternative with good mechanical strength and tunable transport properties. While they can facilitate efficient ion movement, CO₂ crossover through their open structure remains a significant drawback. Surface modification and optimized pore structures show promise, but further improvements in stability and selectivity are needed for practical CO₂RR applications.

Looking ahead, the development of next-generation membranes for CO₂ electrolysis will require integrating material innovation with system-level engineering. Future research should focus on creating chemically stable and scalable polymers, improving ion selectivity to minimize crossover, and establishing standardized testing protocols for cross-comparability. Additionally, coupling membrane advances with optimized electrode and reactor designs will be crucial to achieving high energy efficiency and extended operational lifetimes. Ultimately, no single membrane type is likely to meet all performance criteria, but instead a hybrid or composite designs (e.g., CEM-AEM combinations or coated porous structures) may offer the best balance of cost, stability, and selectivity. As these technologies evolve, membranes will remain central to the advancement of efficient, durable, and commercially viable CO₂ electrolyzers capable of enabling a sustainable carbon economy.

Author Contributions: Conceptualization, T.-N.H. and C.-T.D.; Investigation, T.-N.H., D.-M.P.-P., A.-D.H., T.A.B., G.G. and C.-T.D.; Resources, C.-T.D.; Writing—Original Draft Preparation, T.-N.H. (Sections 1, 2, 3.3 and 4), D.-M.P.-P. (Section 3.2), A.-D.H. (Section 3.1) and T.A.B. (Section 3.4); Writing—Review and Editing, T.-N.H. and C.-T.D.; Visualization, T.-N.H.; Supervision, C.-T.D.; Project Administration, C.-T.D.; Funding Acquisition, C.-T.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Research Chairs Program and Queen’s University.

Data Availability Statement: Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Woodruff, T.J. Health Effects of Fossil Fuel–Derived Endocrine Disruptors. *N. Engl. J. Med.* **2024**, *390*, 922–933. [\[CrossRef\]](#)
- Rahman, A.; Murad, S.M.W.; Mohsin, A.K.M.; Wang, X. Does Renewable Energy Proactively Contribute to Mitigating Carbon Emissions in Major Fossil Fuels Consuming Countries? *J. Clean. Prod.* **2024**, *452*, 142113. [\[CrossRef\]](#)
- Coskuner, C.; Paskeh, M.K.; Olasehinde-Williams, G.; Akadiri, S.S. Economic and Social Determinants of Carbon Emissions: Evidence from Organization of Petroleum Exporting Countries. *J. Public Aff.* **2020**, *20*, e2092. [\[CrossRef\]](#)
- Vasileff, A.; Zheng, Y.; Qiao, S.Z. Carbon Solving Carbon’s Problems: Recent Progress of Nanostructured Carbon-Based Catalysts for the Electrochemical Reduction of CO₂. *Adv. Energy Mater.* **2017**, *7*, 1700759. [\[CrossRef\]](#)
- Zhang, X.; Guo, S.-X.; Gandionco, K.A.; Bond, A.M.; Zhang, J. Electrocatalytic Carbon Dioxide Reduction: From Fundamental Principles to Catalyst Design. *Mater. Today Adv.* **2020**, *7*, 100074. [\[CrossRef\]](#)
- Alli, Y.A.; Ejeromedoghene, O.; Dembaremba, T.O.; Adawi, A.; Alimi, O.A.; Njei, T.; Bamisaye, A.; Kofi, A.; Anene, U.Q.; Adewale, A.M.; et al. Perspectives on the Status and Future of Sustainable CO₂ Conversion Processes and Their Implementation. *Carbon Capture Sci. Technol.* **2025**, *16*, 100496. [\[CrossRef\]](#)
- Sultana, S.; Chandra Sahoo, P.; Martha, S.; Parida, K. A Review of Harvesting Clean Fuels from Enzymatic CO₂ Reduction. *RSC Adv.* **2016**, *6*, 44170–44194. [\[CrossRef\]](#)
- Kibria, M.G.; Edwards, J.P.; Gabardo, C.M.; Dinh, C.; Seifitokaldani, A.; Sinton, D.; Sargent, E.H. Electrochemical CO₂ Reduction into Chemical Feedstocks: From Mechanistic Electrocatalysis Models to System Design. *Adv. Mater.* **2019**, *31*, 1807166. [\[CrossRef\]](#)
- Habisreutinger, S.N.; Schmidt-Mende, L.; Stolarczyk, J.K. Photocatalytic Reduction of CO₂ on TiO₂ and Other Semiconductors. *Angew. Chem. Int. Ed.* **2013**, *52*, 7372–7408. [\[CrossRef\]](#)
- Grodzowski, J.; Neta, P. Copper-Catalyzed Radiolytic Reduction of CO₂ to CO in Aqueous Solutions. *J. Phys. Chem. B* **2001**, *105*, 4967–4972. [\[CrossRef\]](#)
- Wang, W.; Wang, S.; Ma, X.; Gong, J. Recent Advances in Catalytic Hydrogenation of Carbon Dioxide. *Chem. Soc. Rev.* **2011**, *40*, 3703. [\[CrossRef\]](#)
- Yu, F.; Deng, K.; Du, M.; Wang, W.; Liu, F.; Liang, D. Electrochemical CO₂ Reduction: From Catalysts to Reactive Thermodynamics and Kinetics. *Carbon Capture Sci. Technol.* **2023**, *6*, 100081. [\[CrossRef\]](#)
- Zhao, J.Y.; Liu, Y.; Li, W.; Wen, C.F.; Fu, H.Q.; Yuan, H.Y.; Liu, P.F.; Yang, H.G. A Focus on the Electrolyte: Realizing CO₂ Electroreduction from Aqueous Solution to Pure Water. *Chem. Catal.* **2023**, *3*, 100471. [\[CrossRef\]](#)
- Nesbitt, N.T.; Burdyny, T.; Simonson, H.; Salvatore, D.; Bohra, D.; Kas, R.; Smith, W.A. Liquid–Solid Boundaries Dominate Activity of CO₂ Reduction on Gas-Diffusion Electrodes. *ACS Catal.* **2020**, *10*, 14093–14106. [\[CrossRef\]](#)
- Weekes, D.M.; Salvatore, D.A.; Reyes, A.; Huang, A.; Berlinguette, C.P. Electrolytic CO₂ Reduction in a Flow Cell. *Acc. Chem. Res.* **2018**, *51*, 910–918. [\[CrossRef\]](#)
- Nguyen, T.N.; Dinh, C.-T. Gas Diffusion Electrode Design for Electrochemical Carbon Dioxide Reduction. *Chem. Soc. Rev.* **2020**, *49*, 7488–7504. [\[CrossRef\]](#)
- Zheng, H.; Shi, K.; Dong, H.; Yang, Y.; Yin, P.; Shen, B.; Wang, J. Electrochemical Reduction of CO₂ to Multicarbon Products: A Review on Catalysts and System Optimization toward Industrialization. *Energy Fuels* **2025**, *39*, 9316–9344. [\[CrossRef\]](#)
- Yang, X.; Xiang, X.; Zhou, L.; Fan, J.; Chen, J.; Liu, Y.; Zhou, C.; Fan, W.; Han, M.; Pu, Z.; et al. Catalyst Design Strategies for Highly Efficient CO₂ Electroreduction. *Coord. Chem. Rev.* **2025**, *536*, 216650. [\[CrossRef\]](#)
- Tan, X.; Zhu, H.; He, C.; Zhuang, Z.; Sun, K.; Zhang, C.; Chen, C. Customizing Catalyst Surface/Interface Structures for Electrochemical CO₂ Reduction. *Chem. Sci.* **2024**, *15*, 4292–4312. [\[CrossRef\]](#)
- Ma, J.; Liu, C.; Bai, M.; Fu, Z.; Zhao, P.; Gao, Y.; Zhao, M.; He, Y.; Xiao, H.; Jia, J. Recent Advances in Application of Tandem Catalyst for Electrocatalytic CO₂ Reduction. *Mol. Catal.* **2023**, *551*, 113632. [\[CrossRef\]](#)

21. Lu, R.; Liu, Y.; Wang, Z. Advances in the Understanding of Selective CO₂ Reduction Catalysis. *EcoEnergy* **2024**, *2*, 695–713. [\[CrossRef\]](#)
22. Woldu, A.R.; Yohannes, A.G.; Huang, Z.; Kennepohl, P.; Astruc, D.; Hu, L.; Huang, X. Experimental and Theoretical Insights into Single Atoms, Dual Atoms, and Sub-Nanocluster Catalysts for Electrochemical CO₂ Reduction (CO₂ RR) to High-Value Products. *Adv. Mater.* **2024**, *36*, 2414169. [\[CrossRef\]](#)
23. Ho, T.-N.; Pham, T.H.; Li, Y.; Esmaeili, H.; Dinh, C.-T. From Lab to Industry: Challenges in Scaling Cu-Based Electrodes for CO₂ Electroreduction to Multi-Carbon Products. *Curr. Opin. Electrochem.* **2025**, *54*, 101769. [\[CrossRef\]](#)
24. Lai, W.; Qiao, Y.; Wang, Y.; Huang, H. Stability Issues in Electrochemical CO₂ Reduction: Recent Advances in Fundamental Understanding and Design Strategies. *Adv. Mater.* **2023**, *35*, 2306288. [\[CrossRef\]](#)
25. Overa, S.; Ko, B.H.; Zhao, Y.; Jiao, F. Electrochemical Approaches for CO₂ Conversion to Chemicals: A Journey toward Practical Applications. *Acc. Chem. Res.* **2022**, *55*, 638–648. [\[CrossRef\]](#)
26. Lin, J.; Zhang, Y.; Xu, P.; Chen, L. CO₂ Electrolysis: Advances and Challenges in Electrocatalyst Engineering and Reactor Design. *Mater. Rep. Energy* **2023**, *3*, 100194. [\[CrossRef\]](#)
27. Li, G.; Liu, Y.; Zhang, Q.; Hu, Q.; Guo, W.; Cao, X.; Dou, Y.; Cheng, L.; Song, Y.; Su, J.; et al. Development of Catalysts and Electrolyzers toward Industrial-Scale CO₂ Electroreduction. *J. Mater. Chem. A Mater.* **2022**, *10*, 19254–19277. [\[CrossRef\]](#)
28. Fang, W.; Wang, M.; Cai, L.; Xia, B.Y. Fundamental Insights for Practical Electrocatalytic CO₂ Reduction. *Acc. Chem. Res.* **2025**, *58*, 2365–2378. [\[CrossRef\]](#)
29. Xu, D.; Li, K.; Jia, B.; Sun, W.; Zhang, W.; Liu, X.; Ma, T. Electrocatalytic CO₂ Reduction towards Industrial Applications. *Carbon Energy* **2023**, *5*, e230. [\[CrossRef\]](#)
30. Rabiee, H.; Li, M.; Yan, P.; Wu, Y.; Zhang, X.; Dorosti, F.; Zhang, X.; Ma, B.; Hu, S.; Wang, H.; et al. Rational Designing Microenvironment of Gas-Diffusion Electrodes via Microgel-Augmented CO₂ Availability for High-Rate and Selective CO₂ Electroreduction to Ethylene. *Adv. Sci.* **2024**, *11*, 2402964. [\[CrossRef\]](#)
31. García de Arquer, F.P.; Dinh, C.-T.; Ozden, A.; Wicks, J.; McCallum, C.; Kirmani, A.R.; Nam, D.-H.; Gabardo, C.; Seifitokaldani, A.; Wang, X.; et al. CO₂ Electrolysis to Multicarbon Products at Activities Greater than 1 A cm⁻². *Science* **2020**, *367*, 661–666. [\[CrossRef\]](#)
32. Ma, Z.; Yang, Z.; Lai, W.; Wang, Q.; Qiao, Y.; Tao, H.; Lian, C.; Liu, M.; Ma, C.; Pan, A.; et al. CO₂ Electroreduction to Multicarbon Products in Strongly Acidic Electrolyte via Synergistically Modulating the Local Microenvironment. *Nat. Commun.* **2022**, *13*, 7596. [\[CrossRef\]](#)
33. Lee, W.; Kim, Y.E.; Youn, M.H.; Jeong, S.K.; Park, K.T. Catholyte-Free Electrocatalytic CO₂ Reduction to Formate. *Angew. Chem. Int. Ed.* **2018**, *57*, 6883–6887. [\[CrossRef\]](#)
34. Ju, H.; Kaur, G.; Kulkarni, A.P.; Giddey, S. Challenges and Trends in Developing Technology for Electrochemically Reducing CO₂ in Solid Polymer Electrolyte Membrane Reactors. *J. CO₂ Util.* **2019**, *32*, 178–186. [\[CrossRef\]](#)
35. Yin, Z.; Peng, H.; Wei, X.; Zhou, H.; Gong, J.; Huai, M.; Xiao, L.; Wang, G.; Lu, J.; Zhuang, L. An Alkaline Polymer Electrolyte CO₂ Electrolyzer Operated with Pure Water. *Energy Environ. Sci.* **2019**, *12*, 2455–2462. [\[CrossRef\]](#)
36. Yang, Y.; Li, F. Reactor Design for Electrochemical CO₂ Conversion toward Large-Scale Applications. *Curr. Opin. Green Sustain. Chem.* **2021**, *27*, 100419. [\[CrossRef\]](#)
37. Wheeler, D.G.; Mowbray, B.A.W.; Reyes, A.; Habibzadeh, F.; He, J.; Berlinguette, C.P. Quantification of Water Transport in a CO₂ Electrolyzer. *Energy Environ. Sci.* **2020**, *13*, 5126–5134. [\[CrossRef\]](#)
38. Zhang, T.; Bui, J.C.; Li, Z.; Bell, A.T.; Weber, A.Z.; Wu, J. Highly Selective and Productive Reduction of Carbon Dioxide to Multicarbon Products via in Situ CO Management Using Segmented Tandem Electrodes. *Nat. Catal.* **2022**, *5*, 202–211. [\[CrossRef\]](#)
39. Li, F.; Thevenon, A.; Rosas-Hernández, A.; Wang, Z.; Li, Y.; Gabardo, C.M.; Ozden, A.; Dinh, C.T.; Li, J.; Wang, Y.; et al. Molecular Tuning of CO₂-to-Ethylene Conversion. *Nature* **2020**, *577*, 509–513. [\[CrossRef\]](#)
40. Xu, Y.; Edwards, J.P.; Liu, S.; Miao, R.K.; Huang, J.E.; Gabardo, C.M.; O'Brien, C.P.; Li, J.; Sargent, E.H.; Sinton, D. Self-Cleaning CO₂ Reduction Systems: Unsteady Electrochemical Forcing Enables Stability. *ACS Energy Lett.* **2021**, *6*, 809–815. [\[CrossRef\]](#)
41. Hao, S.; Elgazzar, A.; Zhang, S.-K.; Wi, T.-U.; Chen, F.-Y.; Feng, Y.; Zhu, P.; Wang, H. Acid-Humidified CO₂ Gas Input for Stable Electrochemical CO₂ Reduction Reaction. *Science* **2025**, *388*, eadr3834. [\[CrossRef\]](#)
42. O'Brien, C.P.; Miao, R.K.; Shayesteh Zeraati, A.; Lee, G.; Sargent, E.H.; Sinton, D. CO₂ Electrolyzers. *Chem. Rev.* **2024**, *124*, 3648–3693. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Salvatore, D.A.; Gabardo, C.M.; Reyes, A.; O'Brien, C.P.; Holdcroft, S.; Pintauro, P.; Bahar, B.; Hickner, M.; Bae, C.; Sinton, D.; et al. Designing Anion Exchange Membranes for CO₂ Electrolysers. *Nat. Energy* **2021**, *6*, 339–348. [\[CrossRef\]](#)
44. Mustain, W.E.; Kohl, P.A. Improving Alkaline Ionomers. *Nat. Energy* **2020**, *5*, 359–360. [\[CrossRef\]](#)
45. Mauritz, K.A.; Moore, R.B. State of Understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4535–4586. [\[CrossRef\]](#)
46. Li, Y.; Chen, G.; Fei, L.; Zhou, W.; Shao, Z. Designing Better Electrocatalysts via Ion Exchange for Water Splitting. *Adv. Funct. Mater.* **2025**, *35*, 2417880. [\[CrossRef\]](#)

47. Du, N.; Roy, C.; Peach, R.; Turnbull, M.; Thiele, S.; Bock, C. Anion-Exchange Membrane Water Electrolyzers. *Chem. Rev.* **2022**, *122*, 11830–11895. [[CrossRef](#)] [[PubMed](#)]
48. Adisasmito, S.; Khoiruddin, K.; Sutrisna, P.D.; Wenten, I.G.; Siagian, U.W.R. Bipolar Membrane Seawater Splitting for Hydrogen Production: A Review. *ACS Omega* **2024**, *9*, 14704–14727. [[CrossRef](#)]
49. Lee, J.W.; Kim, B.; Seo, J.Y.; Kim, Y.S.; Yoo, P.J.; Chung, C.-H. Water Electrolysis and Desalination Using an AEM/CEM Hybrid Electrochemical System. *Appl. Surf. Sci.* **2023**, *610*, 155524. [[CrossRef](#)]
50. Ha, M.G.; Lim, C.; Oh, C.; Kim, H.; Choi, J.-Y.; Lee, W.H.; Oh, H.-S. Efficient and Durable Porous Membrane-Based CO₂ Electrolysis for Commercial Zero-Gap Electrolyzer Stack Systems. *Chem. Eng. J.* **2024**, *496*, 154060. [[CrossRef](#)]
51. Habibzadeh, F.; Mardle, P.; Zhao, N.; Riley, H.D.; Salvatore, D.A.; Berlinguette, C.P.; Holdcroft, S.; Shi, Z. Ion Exchange Membranes in Electrochemical CO₂ Reduction Processes. *Electrochem. Energy Rev.* **2023**, *6*, 26. [[CrossRef](#)]
52. Larrazábal, G.O.; Strøm-Hansen, P.; Heli, J.P.; Zeiter, K.; Therkildsen, K.T.; Chorkendorff, I.; Seger, B. Analysis of Mass Flows and Membrane Cross-over in CO₂ Reduction at High Current Densities in an MEA-Type Electrolyzer. *ACS Appl. Mater. Interfaces* **2019**, *11*, 41281–41288. [[CrossRef](#)]
53. Yan, J.; Yu, W.; Wang, Z.; Wu, L.; Wang, Y.; Xu, T. Review on High-performance Polymeric Bipolar Membrane Design and Novel Electrochemical Applications. *Aggregate* **2024**, *5*, e527. [[CrossRef](#)]
54. Varcoe, J.R.; Atanassov, P.; Dekel, D.R.; Herring, A.M.; Hickner, M.A.; Kohl, P.A.; Kucernak, A.R.; Mustain, W.E.; Nijmeijer, K.; Scott, K.; et al. Anion-Exchange Membranes in Electrochemical Energy Systems. *Energy Environ. Sci.* **2014**, *7*, 3135–3191. [[CrossRef](#)]
55. Barnes, A.M.; Liu, B.; Buratto, S.K. Humidity-Dependent Surface Structure and Hydroxide Conductance of a Model Quaternary Ammonium Anion Exchange Membrane. *Langmuir* **2019**, *35*, 14188–14193. [[CrossRef](#)]
56. Pavel, C.C.; Cecconi, F.; Emiliani, C.; Santiccioli, S.; Scaffidi, A.; Catanorchi, S.; Comotti, M. Highly Efficient Platinum Group Metal Free Based Membrane-Electrode Assembly for Anion Exchange Membrane Water Electrolysis. *Angew. Chem. Int. Ed.* **2014**, *53*, 1378–1381. [[CrossRef](#)] [[PubMed](#)]
57. Henkensmeier, D.; Najibah, M.; Harms, C.; Žitka, J.; Hnát, J.; Bouzek, K. Overview: State-of-the Art Commercial Membranes for Anion Exchange Membrane Water Electrolysis. *J. Electrochem. Energy Convers. Storage* **2021**, *18*, 024001. [[CrossRef](#)]
58. Kutz, R.B.; Chen, Q.; Yang, H.; Sajjad, S.D.; Liu, Z.; Masel, I.R. Sustainion Imidazolium-Functionalized Polymers for Carbon Dioxide Electrolysis. *Energy Technol.* **2017**, *5*, 929–936. [[CrossRef](#)]
59. Gabardo, C.M.; O'Brien, C.P.; Edwards, J.P.; McCallum, C.; Xu, Y.; Dinh, C.-T.; Li, J.; Sargent, E.H.; Sinton, D. Continuous Carbon Dioxide Electroreduction to Concentrated Multi-Carbon Products Using a Membrane Electrode Assembly. *Joule* **2019**, *3*, 2777–2791. [[CrossRef](#)]
60. Dinh, C.-T.; Burdyny, T.; Kibria, M.G.; Seifitokaldani, A.; Gabardo, C.M.; García de Arquer, F.P.; Kiani, A.; Edwards, J.P.; De Luna, P.; Bushuyev, O.S.; et al. CO₂ Electroreduction to Ethylene via Hydroxide-Mediated Copper Catalysis at an Abrupt Interface. *Science* **2018**, *360*, 783–787. [[CrossRef](#)]
61. Lee, J.; Lim, J.; Roh, C.-W.; Whang, H.S.; Lee, H. Electrochemical CO₂ Reduction Using Alkaline Membrane Electrode Assembly on Various Metal Electrodes. *J. CO₂ Util.* **2019**, *31*, 244–250. [[CrossRef](#)]
62. Mardle, P.; Chen, B.; Holdcroft, S. Opportunities of Ionomer Development for Anion-Exchange Membrane Water Electrolysis. *ACS Energy Lett.* **2023**, *8*, 3330–3342. [[CrossRef](#)]
63. Willdorf-Cohen, S.; Zhegur-Khais, A.; Ponce-González, J.; Bsoul-Haj, S.; Varcoe, J.R.; Diesendruck, C.E.; Dekel, D.R. Alkaline Stability of Anion-Exchange Membranes. *ACS Appl. Energy Mater.* **2023**, *6*, 1085–1092. [[CrossRef](#)]
64. Hagesteijn, K.F.L.; Jiang, S.; Ladewig, B.P. A Review of the Synthesis and Characterization of Anion Exchange Membranes. *J. Mater. Sci.* **2018**, *53*, 11131–11150. [[CrossRef](#)]
65. Zhang, Z.; Huang, X.; Chen, Z.; Zhu, J.; Endrődi, B.; Janáky, C.; Deng, D. Membrane Electrode Assembly for Electrocatalytic CO₂ Reduction: Principle and Application. *Angew. Chem.* **2023**, *135*, e202302789. [[CrossRef](#)]
66. Zhao, Y.; Hua, H.; Wei, S.; Luo, J. Screening Anion Exchange Membranes for CO₂ Electrolysis. *ACS Appl. Mater. Interfaces* **2025**, *17*, 56164–56174. [[CrossRef](#)]
67. Weng, L.-C.; Bell, A.T.; Weber, A.Z. Towards Membrane-Electrode Assembly Systems for CO₂ Reduction: A Modeling Study. *Energy Environ. Sci.* **2019**, *12*, 1950–1968. [[CrossRef](#)]
68. Wang, Z.; Sun, G.; Lewis, N.H.C.; Mandal, M.; Sharma, A.; Kim, M.; Montes de Oca, J.M.; Wang, K.; Taggart, A.; Martinson, A.B.; et al. Water-Mediated Ion Transport in an Anion Exchange Membrane. *Nat. Commun.* **2025**, *16*, 1099. [[CrossRef](#)] [[PubMed](#)]
69. Krödel, M.; Carter, B.M.; Rall, D.; Lohaus, J.; Wessling, M.; Miller, D.J. Rational Design of Ion Exchange Membrane Material Properties Limits the Crossover of CO₂ Reduction Products in Artificial Photosynthesis Devices. *ACS Appl. Mater. Interfaces* **2020**, *12*, 12030–12042. [[CrossRef](#)]
70. Petrov, K.V.; Bui, J.C.; Baumgartner, L.; Weng, L.-C.; Dischinger, S.M.; Larson, D.M.; Miller, D.J.; Weber, A.Z.; Vermaas, D.A. Anion-Exchange Membranes with Internal Microchannels for Water Control in CO₂ Electrolysis. *Sustain. Energy Fuels* **2022**, *6*, 5077–5088. [[CrossRef](#)]

71. Kim, Y.E.; Kim, J.H.; Kwon, H.; Lee, H.; Min, H.J.; Bae, B.; Ko, Y.N.; Chun, D.H.; Youn, M.H.; Rhim, G.B.; et al. Efficient and Stable CO₂ Reduction Using Quaternary Ammonium-Based High-Durability Polymer Membrane and Ionomer in Zero-Gap Electrolyzers. *J. Membr. Sci.* **2026**, *738*, 124724. [\[CrossRef\]](#)
72. Li, X.; Qiu, Z.; Yun, Y.; He, M.; Wang, L. Highly Performance Polybenzimidazole/Zirconia Composite Membrane with Loosened Chain Packing for Anion Exchange Membrane Water Electrolysis and Electrochemical CO₂ Reduction. *Sep. Purif. Technol.* **2025**, *362*, 131675. [\[CrossRef\]](#)
73. Li, J.; Li, J.; Cao, Z.; Zhang, B.; Zhang, X.; Liu, X.; Liu, T.; Zhang, Y. Enhanced OH[−] Conductivity and Stability of Polybenzimidazole Membranes for Electrocatalytic CO₂ Reduction via Grafting and Crosslinking Strategies. *J. Membr. Sci.* **2023**, *685*, 121985. [\[CrossRef\]](#)
74. Pan, B.; Fan, J.; Zhang, J.; Luo, Y.; Shen, C.; Wang, C.; Wang, Y.; Li, Y. Close to 90% Single-Pass Conversion Efficiency for CO₂ Electroreduction in an Acid-Fed Membrane Electrode Assembly. *ACS Energy Lett.* **2022**, *7*, 4224–4231. [\[CrossRef\]](#)
75. Zhang, X.; Li, J.; Li, Y.-Y.; Jung, Y.; Kuang, Y.; Zhu, G.; Liang, Y.; Dai, H. Selective and High Current CO₂ Electro-Reduction to Multicarbon Products in Near-Neutral KCl Electrolytes. *J. Am. Chem. Soc.* **2021**, *143*, 3245–3255. [\[CrossRef\]](#)
76. Huang, J.E.; Li, F.; Ozden, A.; Sedighian Rasouli, A.; García de Arquer, F.P.; Liu, S.; Zhang, S.; Luo, M.; Wang, X.; Lum, Y.; et al. CO₂ Electrolysis to Multicarbon Products in Strong Acid. *Science* **2021**, *372*, 1074–1078. [\[CrossRef\]](#)
77. O'Brien, C.P.; Miao, R.K.; Liu, S.; Xu, Y.; Lee, G.; Robb, A.; Huang, J.E.; Xie, K.; Bertens, K.; Gabardo, C.M.; et al. Single Pass CO₂ Conversion Exceeding 85% in the Electrosynthesis of Multicarbon Products via Local CO₂ Regeneration. *ACS Energy Lett.* **2021**, *6*, 2952–2959. [\[CrossRef\]](#)
78. Disch, J.; Bohn, L.; Metzler, L.; Vierrath, S. Strategies for the Mitigation of Salt Precipitation in Zero-Gap CO₂ Electrolyzers Producing CO. *J. Mater. Chem. A Mater.* **2023**, *11*, 7344–7357. [\[CrossRef\]](#)
79. Lees, E.W.; Mowbray, B.A.W.; Parlane, F.G.L.; Berlinguette, C.P. Gas Diffusion Electrodes and Membranes for CO₂ Reduction Electrolysers. *Nat. Rev. Mater.* **2021**, *7*, 55–64. [\[CrossRef\]](#)
80. Nara, M.; Fujii, K.; Matsui, D.; Ogura, A.; Murakami, T.; Ogawa, T.; Ito, S.; Cheng, C.D.; Scholes, C.A.; Wada, S. Evaluating Cation-Exchange Membrane Properties Affecting Polymer Electrolyte Membrane Water Electrolysis. *ACS Omega* **2025**, *10*, 10425–10431. [\[CrossRef\]](#)
81. Lee, Y.-S.; Park, D.-H.; Park, S.-H.; Gu, Y.-H.; Lim, D.-M.; Han, S.-B.; Park, K.-W. Lithium-Ion Exchange Membrane Water Electrolysis Using a Cationic Polymer-Modified Polyethersulfone Membrane. *ACS Sustain. Chem. Eng.* **2023**, *11*, 10183–10190. [\[CrossRef\]](#)
82. Barnett, A.; Karnes, J.J.; Clemens, A.L.; Oakdale, J.S.; Molinero, V. Post-Hydration Crosslinking of Ion Exchange Membranes to Control Water Content. *J. Phys. Chem. C* **2023**, *127*, 5613–5621. [\[CrossRef\]](#)
83. Park, J.; Ko, Y.; Lim, C.; Kim, H.; Min, B.K.; Lee, K.-Y.; Koh, J.H.; Oh, H.-S.; Lee, W.H. Strategies for CO₂ Electroreduction in Cation Exchange Membrane Electrode Assembly. *Chem. Eng. J.* **2023**, *453*, 139826. [\[CrossRef\]](#)
84. Pärnamäe, R.; Mareev, S.; Nikonenko, V.; Melnikov, S.; Sheldeshov, N.; Zabolotskii, V.; Hamelers, H.V.M.; Tedesco, M. Bipolar Membranes: A Review on Principles, Latest Developments, and Applications. *J. Membr. Sci.* **2021**, *617*, 118538. [\[CrossRef\]](#)
85. Rabinowitz, J.A.; Kanan, M.W. The Future of Low-Temperature Carbon Dioxide Electrolysis Depends on Solving One Basic Problem. *Nat. Commun.* **2020**, *11*, 5231. [\[CrossRef\]](#) [\[PubMed\]](#)
86. Li, Y.C.; Zhou, D.; Yan, Z.; Gonçalves, R.H.; Salvatore, D.A.; Berlinguette, C.P.; Mallouk, T.E. Electrolysis of CO₂ to Syngas in Bipolar Membrane-Based Electrochemical Cells. *ACS Energy Lett.* **2016**, *1*, 1149–1153. [\[CrossRef\]](#)
87. Yan, Z.; Hitt, J.L.; Zeng, Z.; Hickner, M.A.; Mallouk, T.E. Improving the Efficiency of CO₂ Electrolysis by Using a Bipolar Membrane with a Weak-Acid Cation Exchange Layer. *Nat. Chem.* **2021**, *13*, 33–40. [\[CrossRef\]](#)
88. Wang, C.; Sun, Y.; Chen, Y.; Zhang, Y.; Yue, L.; Han, L.; Zhao, L.; Zhu, X.; Zhan, D. In Situ Electropolymerizing Toward EP-CoP/Cu Tandem Catalyst for Enhanced Electrochemical CO₂-to-Ethylene Conversion. *Adv. Sci.* **2024**, *11*, 2404053. [\[CrossRef\]](#)
89. Khan, M.A.; Nabil, S.K.; Al-Attas, T.; Yasri, N.G.; Roy, S.; Rahman, M.M.; Larter, S.; Ajayan, P.M.; Hu, J.; Kibria, M.G. Zero-Crossover Electrochemical CO₂ Reduction to Ethylene with Co-Production of Valuable Chemicals. *Chem. Catal.* **2022**, *2*, 2077–2095. [\[CrossRef\]](#)
90. Blommaert, M.A.; Sharifian, R.; Shah, N.U.; Nesbitt, N.T.; Smith, W.A.; Vermaas, D.A. Orientation of a Bipolar Membrane Determines the Dominant Ion and Carbonic Species Transport in Membrane Electrode Assemblies for CO₂ Reduction. *J. Mater. Chem. A Mater.* **2021**, *9*, 11179–11186. [\[CrossRef\]](#)
91. Shafaque, H.W.; Lee, C.; Fahy, K.F.; Lee, J.K.; LaManna, J.M.; Baltic, E.; Hussey, D.S.; Jacobson, D.L.; Bazylak, A. Boosting Membrane Hydration for High Current Densities in Membrane Electrode Assembly CO₂ Electrolysis. *ACS Appl. Mater. Interfaces* **2020**, *12*, 54585–54595. [\[CrossRef\]](#)
92. Fischer, R.; Dessieux, M.A.; Marone, F.; Büchi, F.N. Gas-Induced Structural Damages in Forward-Bias Bipolar Membrane CO₂ Electrolysis Studied by Fast X-Ray Tomography. *ACS Appl. Energy Mater.* **2024**, *7*, 3590–3601. [\[CrossRef\]](#)
93. Yu, W.; Zhang, Z.; Luo, F.; Li, X.; Duan, F.; Xu, Y.; Liu, Z.; Liang, X.; Wang, Y.; Wu, L.; et al. Tailoring High-Performance Bipolar Membrane for Durable Pure Water Electrolysis. *Nat. Commun.* **2024**, *15*, 10220. [\[CrossRef\]](#) [\[PubMed\]](#)

94. Shen, C.; Wycisk, R.; Pintauro, P.N. High Performance Electrospun Bipolar Membrane with a 3D Junction. *Energy Environ. Sci.* **2017**, *10*, 1435–1442. [[CrossRef](#)]
95. Ma, M.; Clark, E.L.; Therkildsen, K.T.; Dalsgaard, S.; Chorkendorff, I.; Seger, B. Insights into the Carbon Balance for CO₂ Electroreduction on Cu Using Gas Diffusion Electrode Reactor Designs. *Energy Environ. Sci.* **2020**, *13*, 977–985. [[CrossRef](#)]
96. Salvatore, D.A.; Weekes, D.M.; He, J.; Dettelbach, K.E.; Li, Y.C.; Mallouk, T.E.; Berlinguette, C.P. Electrolysis of Gaseous CO₂ to CO in a Flow Cell with a Bipolar Membrane. *ACS Energy Lett.* **2018**, *3*, 149–154. [[CrossRef](#)]
97. Chen, L.; Xu, Q.; Oener, S.Z.; Fabrizio, K.; Boettcher, S.W. Design Principles for Water Dissociation Catalysts in High-Performance Bipolar Membranes. *Nat. Commun.* **2022**, *13*, 3846. [[CrossRef](#)]
98. Xie, K.; Miao, R.K.; Ozden, A.; Liu, S.; Chen, Z.; Dinh, C.-T.; Huang, J.E.; Xu, Q.; Gabardo, C.M.; Lee, G.; et al. Bipolar Membrane Electrolyzers Enable High Single-Pass CO₂ Electroreduction to Multicarbon Products. *Nat. Commun.* **2022**, *13*, 3609. [[CrossRef](#)]
99. Alkayyali, T.; Zeraati, A.S.; Mar, H.; Arabyarmohammadi, F.; Saber, S.; Miao, R.K.; O'Brien, C.P.; Liu, H.; Xie, Z.; Wang, G.; et al. Direct Membrane Deposition for CO₂ Electrolysis. *ACS Energy Lett.* **2023**, *8*, 4674–4683. [[CrossRef](#)]
100. She, X.; Zhai, L.; Wang, Y.; Xiong, P.; Li, M.M.-J.; Wu, T.-S.; Wong, M.C.; Guo, X.; Xu, Z.; Li, H.; et al. Pure-Water-Fed, Electrocatalytic CO₂ Reduction to Ethylene beyond 1000 h Stability at 10 A. *Nat. Energy* **2024**, *9*, 81–91. [[CrossRef](#)]
101. Wu, H.; Karamoko, B.A.; Wang, W.; Liu, J.; Petit, E.; Li, S.; Salameh, C.; Voiry, D. Engineering the Catalyst Interface Enables High Carbon Efficiency in Both Cation-Exchange and Bipolar Membrane Electrolyzers. *Appl. Catal. B Environ. Energy* **2025**, *361*, 124691. [[CrossRef](#)]
102. Henkensmeier, D.; Cho, W.-C.; Jannasch, P.; Stojadinovic, J.; Li, Q.; Aili, D.; Jensen, J.O. Separators and Membranes for Advanced Alkaline Water Electrolysis. *Chem. Rev.* **2024**, *124*, 6393–6443. [[CrossRef](#)] [[PubMed](#)]
103. Xu, Z.; Liu, Y.; Cheng, X.; Shang, Y.; Wang, Y.; Wang, J.; Li, W.; He, G. A Catalyst-Coated Diaphragm Assembly to Improve the Performance and Energy Efficiency of Alkaline Water Electrolysers. *Commun. Eng.* **2025**, *4*, 9. [[CrossRef](#)] [[PubMed](#)]
104. Lira Garcia Barros, R.; Kraakman, J.T.; Sebrechts, C.; van der Schaaf, J.; de Groot, M.T. Impact of an Electrode-Diaphragm Gap on Diffusive Hydrogen Crossover in Alkaline Water Electrolysis. *Int. J. Hydrogen Energy* **2024**, *49*, 886–896. [[CrossRef](#)]
105. Lee, W.H.; Kim, K.; Lim, C.; Ko, Y.-J.; Hwang, Y.J.; Min, B.K.; Lee, U.; Oh, H.-S. New Strategies for Economically Feasible CO₂ Electroreduction Using a Porous Membrane in Zero-Gap Configuration. *J. Mater. Chem. A Mater.* **2021**, *9*, 16169–16177. [[CrossRef](#)]
106. Deng, W.; Xing, S.; Maia, G.W.P.; Wang, Z.; Crandall, B.S.; Jiao, F. Diaphragm-Based Carbon Monoxide Electrolyzers for Multicarbon Production under Alkaline Conditions. *Nat. Commun.* **2025**, *16*, 8444. [[CrossRef](#)]
107. Pham, T.H.; Lai, H.D.T.; Dang, N.K.; Nguyen, T.N.; Golovanova, V.; Dias, E.H.; Ho, A.; Xia, L.; Crane, J.; de Arquer, F.P.G.; et al. Ambipolar Ion Transport Membranes Enable Stable Noble-Metal-Free CO₂ Electrolysis in Neutral Media. *Adv. Energy Mater.* **2025**, *15*, e04286. [[CrossRef](#)]
108. Miao, R.K.; Fan, M.; Wang, N.; Zhao, Y.; Li, F.; Liu, M.; Arabyarmohammadi, F.; Liang, Y.; Ni, W.; Xie, K.; et al. CO Electrolysers with 51% Energy Efficiency towards C₂₊ Using Porous Separators. *Nat. Energy* **2025**, *10*, 1197–1204. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.