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Recent Advances in Anion-Exchange and Bipolar Membranes for CO_2-to-Ethanol Electroreduction: Mechanistic and System-Level Insights

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Abstract

Electrochemical CO_2 reduction to ethanol is a promising route for circular-carbon fuel and chemical production, but practical implementation remains limited by coupled membrane, catalyst, transport and system-integration constraints. This Communication reassesses anion-exchange membranes (AEMs) and bipolar membranes (BPMs) using recent 2024–2026 literature. The central argument is that membrane selection is not a passive separation choice; it controls local pH, charge carriers, CO_2 availability, carbonate formation, water activity, proton/cation delivery, product crossover and downstream techno-economic assessment (TEA) and life cycle assessment (LCA) burdens. AEM operation can create alkaline cathodic microenvironments that favor C–C coupling, but bicarbonate/carbonate formation imposes carbon-loss, salt-management and recovery penalties. BPM operation can improve pH separation and carbon management through water dissociation and bicarbonate acidification, but its viability depends on water-dissociation efficiency, co-ion exclusion, junction stability and voltage control. Recent ethanol-selective catalyst studies further show that copper oxidation state, grain boundaries, subsurface dopants, ionomers, interfacial wettability and dynamic operation interact strongly with membrane-imposed microenvironments. The Communication proposes a membrane-centered decision framework linking AEM/BPM selection with ethanol selectivity, single-pass carbon utilization, energy efficiency, durability, TEA/LCA boundaries and future reactor design.

Keywords: CO_2 electroreduction; ethanol; anion-exchange membrane; bipolar membrane; membrane electrode assembly; carbon utilization; carbonate crossover; C–C coupling; catalyst–membrane coupling; techno-economic assessment; life cycle assessment; zero-gap electrolyzer

1. Introduction

Electrochemical CO_2 reduction has reached a stage at which the central question is no longer whether CO_2 can be converted into fuels and chemicals, but whether the conversion can be made selective, durable, energy-efficient and environmentally meaningful at industrially relevant current densities. Recent reviews and system analyses published from 2024 to 2026 emphasize that electrochemical CO_2 conversion should be assessed across linked catalyst, electrolyte, membrane, reactor and process boundaries rather than through isolated half-cell metrics [1–8]. Ethanol is a particularly attractive C_2 product because it is liquid, readily stored, compatible with existing distribution infrastructure and useful as both a fuel additive and chemical intermediate. However, ethanol formation requires multiple proton–electron transfers, stabilization of CO-derived intermediates and C–C coupling, making its selectivity highly sensitive to the catalyst-layer microenvironment.

The membrane is a decisive component of this microenvironment. In AEM-based devices, hydroxide, bicarbonate and carbonate transport can sustain alkaline conditions that suppress hydrogen evolution and enhance C_2+ formation; however, the same chemistry converts incoming CO_2 into carbonate species that migrate away from the cathode [9,15–18]. In BPM-based devices, water dissociation at the membrane junction can generate separated acid/base environments and reduce net carbon crossover, although additional voltage losses and ion leakage may weaken the apparent carbon-utilization benefit [10–14,21–24]. Therefore, an AEM-versus-BPM comparison should not be based only on Faradaic efficiency or current density. It should also include carbon accounting, energy demand, membrane durability, product crossover, electrolyte management and downstream separation.

Accordingly, this Communication presents a concise decision framework developed from recent 2024–2026 evidence and membrane-centered CO_2-to-ethanol process-design considerations. It is not intended as a broad historical review or an invited Perspective; instead, it communicates a focused interpretative finding: membrane selection should be treated as an active system-design parameter that determines carbon utilization, energy demand, product selectivity, durability and downstream process burden. The manuscript therefore evaluates when AEM, BPM, acidic zero-gap, hybrid membrane or membrane–electrode-interface strategies are most suitable for ethanol-oriented CO_2 electroreduction.

2. Literature Selection, Scope and Communication Framework

The literature basis was restricted to recent sources published or made available from 2024 to 2026. The selected studies cover five connected domains: membrane electrode assemblies and CO_2 crossover [9], BPM stability and water dissociation [10–14], AEM screening and acidic zero-gap strategies [15–20], BPM/forward-bias operation [21–25], and ethanol-selective catalyst or interface design [26–64]. This recency boundary highlights the rapidly developing state of the field and avoids overreliance on older foundational CO_2RR literature.

The literature selection was conducted as a focused narrative search rather than a systematic review. Inclusion was limited to peer-reviewed articles, reputable technical reports and article-in-press records from 2024 to 2026 that directly addressed CO_2 electroreduction membranes, membrane electrode assemblies, BPM operation, AEM screening, acidic or zero-gap operation, ethanol-selective catalysts, or TEA/LCA and carbon-accounting implications. This boundary makes the Communication transparent: the cited sources can be checked against the five thematic domains used to organize the manuscript.

The contribution of this Communication is threefold. First, it formulates AEM and BPM operation as a carbon-efficiency versus energy-efficiency problem rather than a simple membrane-classification problem. Second, it links recent ethanol-selective catalyst findings with membrane-controlled variables such as water activity, cation availability, local pH, anion identity and interfacial wettability [26–44]. Third, it translates these mechanisms into TEA/LCA-relevant indicators, including single-pass CO_2 utilization, carbonate crossover, stack voltage, separation energy, membrane lifetime, catalyst lifetime and electricity carbon intensity [7,8,54–64]. The framework is intended to help readers compare membrane options at the level of the full ethanol-production system rather than at the level of isolated electrochemical performance.

3. AEM Operation: Alkaline C–C Coupling Promotion and Carbonate Burden

AEM-based CO_2 electrolyzers are attractive because they can support high current densities, alkaline cathodic conditions and relatively low membrane-related voltage penalties compared with BPM systems. The alkaline environment can favor CO_2 activation and C–C coupling by suppressing hydrogen evolution and increasing the residence time of CO-derived intermediates near copper-based active sites [15–17,26–34]. In ethanol-oriented systems, this is beneficial because ethanol formation competes with ethylene, acetate, methane, formate and hydrogen. The pathway after CO dimerization is sensitive to the balance among *CO, *CHO, *CHCO, *CHCHO and hydrogenated oxygenate intermediates, and this balance is strongly affected by local water and proton availability [26,31–38].

The major limitation is that the same alkaline conditions promote homogeneous carbonate chemistry. CO_2 reacts with OH^- to form HCO_3^-, and HCO_3^- can further react to form CO_3^{2-}. These anions migrate through an AEM to preserve charge neutrality, carrying carbon away from the cathode without generating ethanol [9,15,18]. Once carbon is transported to the anode, it may be released as CO_2, mix with oxygen, or contribute to salt and electrolyte-management issues. Therefore, AEM systems can appear efficient when only cathodic Faradaic efficiency is reported, but less attractive when true feed-carbon utilization and recovery duties are included [7–9].

Recent AEM screening and acidic zero-gap studies show that performance cannot be improved simply by replacing one membrane class with another. AEM material chemistry, ion-exchange capacity, water uptake, fixed-charge density, carbonate affinity, thickness, mechanical stability and catalyst-layer ionomer compatibility all influence performance [14–18]. Acidic and porous-membrane strategies aim to reduce carbonate formation while maintaining high-rate CO_2 transport, but they introduce new constraints, including proton management, flooding, membrane conductivity and selectivity losses [17–20]. For ethanol production, the design target is therefore not maximum alkalinity, but a controlled microenvironment that provides sufficient alkalinity for C–C coupling without sacrificing excessive inlet CO_2 as carbonate.

4. BPM Operation: Carbon Management, pH Decoupling and Water-Dissociation Penalty

BPMs combine a cation-exchange layer and an anion-exchange layer. Under reverse-bias operation, water dissociation at the internal interface generates H^+ and OH^- fluxes. This architecture can decouple cathodic and anodic pH, regenerate CO_2 from bicarbonate/carbonate near the cathode side and sustain alkaline anolyte operation when oxygen evolution is paired with non-precious-metal catalysts [10–13]. BPMs are therefore increasingly discussed as routes toward carbon-efficient CO_2 electrolysis, rather than merely as separators.

However, BPM advantages are conditional. Water dissociation adds a voltage penalty; insufficient water-dissociation efficiency can acidify or destabilize the wrong compartment; and co-ion leakage can gradually erode pH separation during long-term operation [12–14,21–24]. Forward-bias BPM designs and pure-water-fed BPM cells address some salt and pumping concerns, but can introduce gas-generation and delamination risks near the membrane junction [22–24]. BPMs can therefore improve carbon management only when the junction, catalyst layer, ionomer distribution and hydration state are optimized simultaneously.

For ethanol, BPM operation is especially nuanced. A proton flux can help convert bicarbonate to CO_2 and support oxygenate hydrogenation steps, but excessive proton availability may favor hydrogen evolution or alter the ethylene/ethanol branching pathway. Recent BPM electrode-assembly studies show that local ionic transport and catalyst-layer architecture can determine whether CO_2 utilization and product selectivity remain stable [10–13,23]. BPM selection should therefore be coupled to catalyst design rather than chosen after the catalyst has been optimized in a separate H-cell or flow-cell configuration.

5. Catalyst–Membrane Coupling for Ethanol Selectivity

Recent ethanol-selective catalyst studies show that ethanol production depends on both surface chemistry and the surrounding ionic microenvironment. Zhan et al. identified key intermediates and copper active-site features that distinguish ethylene and ethanol pathways [26]. Liu et al. reported stable high-rate ethanol electrosynthesis over CuAg@NTA, while Gu et al. showed that subsurface engineering can direct CO_2 electroreduction toward ethanol in both flow-cell and MEA configurations [27,28]. These examples indicate that catalysts capable of high ethanol selectivity should be evaluated under membrane-relevant operating conditions, not only in dilute bicarbonate H-cells.

Copper oxidation state and interfacial structure are especially important. Stabilized Cu^+ species, mixed Cu(I)/Cu(0) grain-boundary sites, Cu_2Mg intermetallic sites, Cu dual-atom sites, inverse oxide/Cu interfaces and low-nuclearity metal–organic-framework-supported clusters have all been reported as routes toward ethanol or C_2+ oxygenates [29–40]. The recurring mechanistic theme is that ethanol selectivity improves when the surface stabilizes oxygenated C_2 intermediates while avoiding excessive hydrogenation toward methane or dehydration toward ethylene. Membrane choice affects this balance because it controls local pH, water activity, cation delivery, carbonate species and proton availability.

Several recent studies directly connect local environment and selectivity. Cation-induced hydrophobic microenvironments can promote C–C coupling [34]; anion modulation can improve energy-efficient ethanol formation [38]; amine-modified copper nanoparticles can enable acidic production of multicarbon alcohols [49]; and polymer or ionomer microenvironments can switch pathways between ethylene and ethanol [41,54]. These findings suggest that future AEM and BPM cells should be designed around catalyst–membrane–ionomer co-optimization rather than catalyst screening alone.

6. Membrane Electrode Assembly and Interface Design

MEA cells reduce ohmic losses and enable industrially relevant current densities, but they also intensify coupled transport problems. In zero-gap designs, gaseous CO_2, liquid water, ions, electrons and products must move through thin catalyst layers with steep gradients in pH, potential and composition. Recent MEA studies highlight that CO_2 reduction and crossover are inseparable phenomena, because the same ions that maintain conductivity also influence carbonate transport and product distribution [9,18–20].

AEM-type MEAs require attention to carbonate precipitation, water management, membrane swelling and anolyte contamination. BPM-type MEAs require attention to water-dissociation catalysts, junction stability, co-ion rejection and delamination resistance [10–14,21–24]. Pure-water, porous-membrane and permeable-interface strategies attempt to reduce electrolyte complexity while preserving high CO_2 flux and ionic conductivity [18–20,22]. These architectures are promising, but they should be tested with complete carbon balances rather than only product Faradaic efficiencies.

Interface engineering is becoming as important as membrane selection. Catalyst–ionomer contact, ionomer hydrophilicity, cation pathways, water activity, gas–liquid–solid triple-phase boundaries and catalyst-layer thickness can alter both energy efficiency and ethanol selectivity [19,20,23,41,54,64]. For a CO_2-to-ethanol MEA, the ideal interface should sustain high local CO_2 concentration, sufficient *CO coverage, controlled proton delivery and rapid product removal while preventing flooding, salt precipitation and ethanol crossover.

7. System-Level Assessment: TEA, LCA and Carbon Accounting

TEA and LCA should not be appended after electrochemical optimization; they should be integrated with membrane choice from the beginning. Recent process and TEA studies emphasize that ethanol production economics depend on cell voltage, Faradaic efficiency, product concentration, current density, single-pass conversion, downstream separation and recycle requirements [7,8,54–64]. A low-voltage AEM cell can become unattractive if carbonate crossover requires expensive CO_2 recovery and compression. Conversely, a higher-voltage BPM cell can become attractive if improved carbon utilization reduces upstream capture demand and downstream recycle.

The functional unit should be defined as purified ethanol, for example 1 kg of ethanol at a specified purity leaving the separation section. The system boundary should include CO_2 source/capture, compression, humidification, electrolysis, product recovery, electrolyte management, membrane replacement, catalyst replacement, separation heat and electricity supply. The inventory should distinguish inlet CO_2, reacted CO_2, carbonate-crossed CO_2, vented CO_2, recycled CO_2 and CO_2 embedded in products. Without these flows, sustainability claims remain incomplete [7–9].

Electricity carbon intensity is also decisive. Even high-selectivity ethanol production can have poor climate performance if powered by carbon-intensive electricity. Conversely, a membrane configuration with modestly higher voltage may perform better under renewable electricity if it reduces carbon loss, separation energy and material replacement. The best membrane is therefore not necessarily the one with the highest local current density, but the one with the lowest combined cost and environmental burden per unit of purified ethanol.

8. Decision Framework for AEM, BPM and Hybrid Designs

The AEM/BPM decision can be summarized as follows. AEM systems are preferred when the objective is high-rate operation, lower voltage, simpler cell architecture and strongly alkaline C–C coupling. Their disadvantages are carbonate crossover, carbon loss, salt precipitation and downstream recovery burdens [9,15–18]. BPM systems are preferred when carbon efficiency, pH separation and anode compatibility are the main goals. Their disadvantages are water-dissociation voltage, junction stability and co-ion leakage [10–14,21–24]. Hybrid or porous designs are preferred when the objective is to combine high CO_2 availability with controlled ion transport and reduced carbonate accumulation [18–20].

For ethanol, catalyst and membrane should be selected together. Ethanol-favoring catalysts with stable Cu^+ or mixed Cu(I)/Cu(0) sites may benefit from microenvironments that supply sufficient water-derived hydrogen for oxygenate formation without triggering excessive hydrogen evolution [29–40]. Catalysts that rely on acidic operation or amine/anion-modulated interfaces may be better paired with porous membranes or acid-compatible MEA designs [17–20,38,49]. Catalysts that require sustained alkalinity and high *CO coverage may be better paired with AEMs or hybrid BPM/AEM architectures, provided carbonate management is addressed [15–18,34].

The most realistic scale-up path is unlikely to involve a universal membrane choice; instead, it will be application-specific. A demonstration aimed at maximum ethanol Faradaic efficiency may prioritize catalyst and local microenvironment. A process aimed at minimum cost per tonne of ethanol should prioritize stack voltage, product concentration, lifetime and separation cost. A process aimed at the lowest climate impact should prioritize electricity mix, carbon utilization, durable materials and avoided downstream recovery. For this reason, a membrane-centered decision map is more useful than a binary AEM-versus-BPM ranking.

9. Future Research Directions

Four research directions emerge from the 2024–2026 literature. First, future experiments should report complete carbon balances, including carbonate crossover and CO_2 release at the anode, rather than only cathodic Faradaic efficiency [9,12,18]. Second, BPM studies should report water-dissociation efficiency, co-ion leakage, pH drift and long-duration stability under realistic current densities [10–14,21–24]. Third, ethanol-oriented catalyst studies should be repeated in MEA environments using the intended membrane and ionomer, because H-cell selectivity may not translate to zero-gap operation [26–44]. Fourth, TEA/LCA should use measured values for product concentration, single-pass conversion, membrane lifetime and separation demand rather than idealized assumptions [7,8,54–64].

A practical next-generation CO_2-to-ethanol cell may combine an ethanol-selective copper-based catalyst, a tailored ionomer, a membrane or porous separator with controlled cation/proton transport, and dynamic operating protocols. Pulsed electrolysis, hydration cycling and pressure control may help maintain active copper structures, reduce salt precipitation and tune the ethylene/ethanol branch [31,47,48]. However, each improvement should be evaluated against total energy demand, product recovery and lifetime. A configuration that improves ethanol Faradaic efficiency but reduces durability or increases separation energy may not improve the system-level result.

10. Conclusions

This Communication shows that AEM and BPM selection for CO_2-to-ethanol electroreduction should be treated as a system-level design decision. AEMs can support alkaline C–C coupling and lower cell voltage, but they are affected by carbonate formation, carbon crossover and downstream recovery burdens. BPMs can improve pH separation and carbon utilization, but their advantages depend on low water-dissociation overpotential, high co-ion rejection, stable junctions and careful proton/cation management.

The central conclusion is that membrane, catalyst, ionomer and reactor should not be optimized independently. Recent 2024–2026 literature shows that ethanol selectivity is governed by copper active-site structure, oxygenated C_2 intermediates, water activity, local pH, cation/anion effects, interfacial wettability and MEA transport. Therefore, the preferred membrane configuration will be the one that minimizes total cost and climate impact per kilogram of purified ethanol while maintaining stable operation, not simply the one that maximizes current density or Faradaic efficiency in the electrolyzer.

Table 1. Membrane-centered comparison of AEM and BPM CO_2-to-ethanol systems.

Criterion	AEM-dominated behavior	BPM-dominated behavior	System-level implication
Main ion transport	OH^-, HCO_3^- and CO_3^{2-} transport through the membrane.	H^+ and OH^- are generated at the BPM junction; co-ion leakage must be minimized.	Controls local pH, conductivity, carbonate migration and pH stability.
CO_2 utilization	High risk of bicarbonate/carbonate formation and carbon crossover.	Potential bicarbonate acidification and CO_2 regeneration near the cathode side.	Determines single-pass carbon utilization and recycle duty.
Energy demand	Usually lower membrane-related voltage penalty.	Additional water-dissociation and interfacial voltage losses.	Determines electricity consumption per kilogram of ethanol.
Ethanol selectivity	Alkalinity can favor C–C coupling, but CO_2 depletion can limit sustained ethanol formation.	pH separation can improve carbon availability, but excessive proton flux can promote hydrogen evolution.	Requires catalyst–membrane–ionomer co-design.
Durability	Carbonate precipitation, swelling and alkaline-degradation risks.	Junction stability, gas-induced damage and co-ion leakage risks.	Determines membrane replacement needs and long-term economics.

Table 2. Decision map for membrane selection in CO_2-to-ethanol electrolysis.

Development objective	More suitable configuration	Rationale
Highest current density with simpler operation	AEM or optimized alkaline MEA	Lower membrane voltage and a favorable alkaline microenvironment can support high-rate C_2+ formation.
Highest single-pass carbon utilization	BPM or hybrid BPM architecture	Bicarbonate/carbonate acidification or CO_2 regeneration can reduce net carbon loss.

Low direct electricity consumption	Usually AEM	Avoids the BPM water-dissociation penalty, but carbon recovery must still be counted.
Low carbon-recovery burden	Usually BPM or acidic porous-membrane strategy	Improves carbon accounting if voltage and leakage remain controlled.
Ethanol-selective catalyst testing	Membrane matched to catalyst microenvironment	Cu active sites, ionomer chemistry and local pH must be co-optimized.
Best TEA/LCA result	Case-specific	Depends on voltage, product concentration, single-pass conversion, separation duty, electricity mix and lifetime.

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