

Efficient Bicarbonate Electrolyzer with a Forward-Bias Bipolar Membrane

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ABSTRACT: Direct electrolysis of carbon dioxide (CO_2)-captured bicarbonate solutions offers a promising route for CO_2 valorization, as it avoids the energy-intensive regeneration and compression steps required to supply purified gaseous CO_2 . However, most bicarbonate electrolyzers rely on proton-driven *in situ* CO_2 release at the cathode, which promotes hydrogen evolution, increases the cell voltage, and limits energy efficiency. Here, we demonstrate a bicarbonate electrolyzer based on a forward-bias bipolar membrane (fBPM) that decouples local CO_2 release from direct proton flux. The fBPM cell delivers a carbon monoxide (CO) partial current density of $167.1 (\pm 2.6) \text{ mA cm}^{-2}$ at $4.44 (\pm 0.03) \text{ V}$, with CO Faradaic efficiencies of up to 71% at 100 mA cm^{-2} , surpassing the reverse-bias BPM and cation-exchange membrane configurations and comparing favorably with state-of-the-art bicarbonate systems. *Operando* Raman spectroscopy revealed that the fBPM maintains a more alkaline cathode-membrane microenvironment, increasing the availability of locally released CO_2 . A system-level energy analysis indicates an energy cost of 36.7 GJ per tonne of CO, highlighting fBPM-enabled bicarbonate electrolysis as a viable approach for integrated CO_2 capture and electrochemical conversion.

KEYWORDS: bicarbonate electrolysis, membrane electrode assembly, forward-bias bipolar membrane, CO production, energy efficiency

1. INTRODUCTION

The electrochemical reduction of carbon dioxide (CO_2) to value-added chemicals using renewable electricity has emerged as a promising decarbonization strategy, offering a route toward closing the carbon loop in alignment with global net-zero emission goals.^{1,2} However, most CO_2 reduction reaction (CO_2RR) platforms still rely on high-purity and often pressurized CO_2 gas. Producing that feed from captured CO_2 adds energy- and capital-intensive steps, including sorbent regeneration, dehydration, and compression,^{3–5} which can dominate the process cost and erode the life-cycle and techno-economic advantages of electrochemical CO_2 utilization.^{6,7} This mismatch between the promise of the CO_2RR and the practical burden of conditioning CO_2 feedstocks motivates approaches that couple capture and conversion more tightly.

A direct alternative is to electrolyze CO_2 -captured liquids rather than purified gaseous CO_2 . Capture media, such as amine,⁸ carbonate,^{9,10} and bicarbonate solutions,^{10–12} can in principle serve as both the capture reservoir and the carbon source for electrolysis, enabling *in situ* CO_2 release followed immediately by reduction at the cathode interface. Among these candidates, amine systems face fundamental and practical barriers: the strong C–N bonding in carbamates makes CO_2 liberation kinetically and energetically difficult, and amine

environments can accelerate corrosion and material degradation.⁴ Carbonate feeds have also been explored, but typically deliver lower selectivity than bicarbonate feeds under comparable conditions.¹³ Bicarbonate solutions, by contrast, tend to enable higher CO_2RR efficiency and are more amenable to efficient electrolysis.

State-of-the-art bicarbonate electrolysis is often performed in a zero-gap membrane electrode assembly (MEA) configuration, in which a suitable ion-exchange membrane (IEM) facilitates *in situ* CO_2 delivery to the cathode.^{4,14} In early designs, reverse-bias bipolar membranes (rBPMs) were used to supply protons for CO_2 release. During rBPM operation, the cation-exchange layer (CEL) faces the cathode, and the anion-exchange layer (AEL) faces the anode.^{15,16} Water dissociation at the bipolar junction produces H^+ and OH^- , and the proton flux through the CEL neutralizes bicarbonate near the cathode to generate CO_2 for the subsequent CO_2RR (Figure 1a).^{6,14,17}

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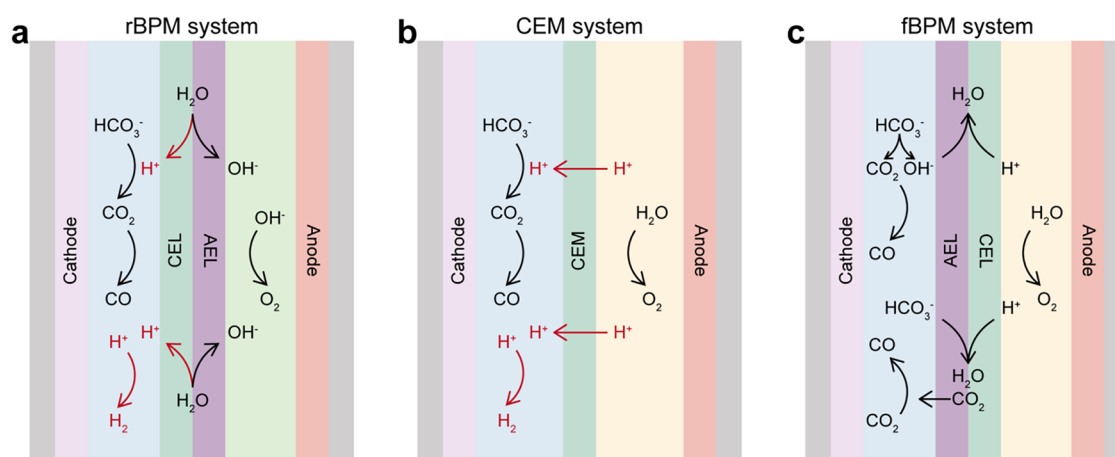


Figure 1. Schematic illustration of three bicarbonate electrolyzers with different ion-exchange membranes and the corresponding reaction mechanisms. (a) rBPM system. *In-situ* CO₂ release is achieved through the reaction of HCO₃[−] with proton flux, which comes from water dissociation in the BPM. (b) CEM system. *In-situ* CO₂ release is achieved through the reaction of HCO₃[−] with proton flux, which comes from the acid anolyte and water oxidation. (c) fBPM system. Local CO₂ is generated through disequilibrium of HCO₃[−] induced by electro-migration of OH[−] and diffusion of CO₂, which is released by HCO₃[−] neutralization in the BPM.

While this architecture avoids reliance on gas-phase CO₂ transport, it introduces interlinked penalties. The proton-rich cathode environment promotes the competing hydrogen evolution reaction (HER), which directly suppresses carbon product selectivity.^{15,17,18} Moreover, sustaining water dissociation in the BPM requires a substantial additional overpotential that becomes more severe at high current density.^{7,15,19} These issues both diminish the energy efficiency of rBPM-based bicarbonate electrolyzers.

Alternatively, modified bicarbonate electrolyzers were developed using a cation-exchange membrane (CEM) in place of the BPM. In CEM-based systems, CO₂ is still generated locally via protonation of HCO₃[−], but the protons are supplied by an acidic anolyte (and the anodic water oxidation reaction) and migrate across the CEM to the cathode compartment (Figure 1b).^{11,20} Eliminating BPM water dissociation lowers the ionic resistance and enables substantially reduced cell voltages.^{7,9,21,22} However, the same proton-flux mechanism inevitably acidifies the cathode interface, sustaining competitive HER and parasitic H₂ formation.^{18,23} Buffer layers or porous interlayers have been introduced to locally regulate pH and limit direct proton access,^{9,24,25} but these added structures increase complexity and typically lack durability, often degrading within ~20 h under operating conditions.^{9,19} Consequently, a new electrolyzer architecture is needed that releases CO₂ from bicarbonate without exposing the cathode to unhindered proton flux.

The forward-bias operation of bipolar membranes offers a compelling way to decouple CO₂ release chemistry from cathode proton exposure.^{26–28} In a forward-bias BPM (fBPM), the membrane orientation is inverted relative to the rBPM: the AEL faces the cathode, and the CEL faces the anode.^{16,29} This arrangement fundamentally alters the cathode environment. Under forward bias, the cathode is bathed under alkaline conditions, which strongly suppresses the HER side reaction and instead favors the CO₂RR pathway.^{15,30} Anions and cations migrate toward the bipolar junction and recombine at the internal interface. Importantly, internal neutralization can generate a potential contribution that offsets part of the applied cell voltage, effectively recovering energy that would otherwise be dissipated.^{15,16,31} These features suggest that an fBPM could

simultaneously address the selectivity problem (by keeping the cathode alkaline) and the efficiency problem (by reducing voltage losses) that limit existing bicarbonate electrolyzers.

Here, we implemented this concept by designing a zero-gap bicarbonate electrolyzer equipped with an fBPM and target carbon monoxide (CO) as a technologically mature and economically relevant product.^{32,33} In our fBPM system (Figure 1c), two mechanisms jointly ensure a continuous supply of CO₂ to the cathode: (1) continuous electro-migration of OH[−], coupled to the HCO₃[−]/CO₂ equilibrium, drives local CO₂ liberation (eq 1).^{18,34}



(2) The protons generated in the acidic anolyte by anodic water oxidation react with HCO₃[−] at the BPM junction to form CO₂ within the membrane, and a fraction of this CO₂ can diffuse back to the cathode.^{26,35} Importantly, both pathways generate CO₂ without imposing direct proton flux at the cathode catalyst layer, thereby suppressing the competitive HER. Consequently, the electrolyzer delivers CO Faradaic efficiency (FE_{CO}) of 71.2 (±1.6)% and 55.7 (±0.9)% at 100 and 300 mA cm^{−2}, respectively, and achieves a maximum CO partial current density (*j*_{CO}) of 167.1 (±2.6) mA cm^{−2} at a low cell voltage (*E*_{cell}) of 4.44 (±0.03) V. The resulting energy efficiency exceeds that of rBPM- and CEM-based bicarbonate electrolyzers and compares favorably with that of most reported bicarbonate electrolysis systems. Finally, an energy-cost assessment and techno-economic analysis further support the promise of the fBPM strategy for practical CO₂ upcycling.

2. RESULTS AND DISCUSSION

We first benchmarked bicarbonate electrolysis in three zero-gap MEA architectures that differ only in membrane type and operating polarity: reverse-bias bipolar membrane, cation-exchange membrane, and forward-bias bipolar membrane (Figure S1). All measurements were conducted in a two-electrode MEA electrolyzer under otherwise identical hardware and operating conditions. A hydrophilic carbon-paper gas-diffusion electrode coated with commercial Ag (Ag/C) served as the cathode for bicarbonate-to-CO conversion (Figures S2–S4). Ti mesh coated with IrO_x (IrO_x/Ti mesh) was used as the

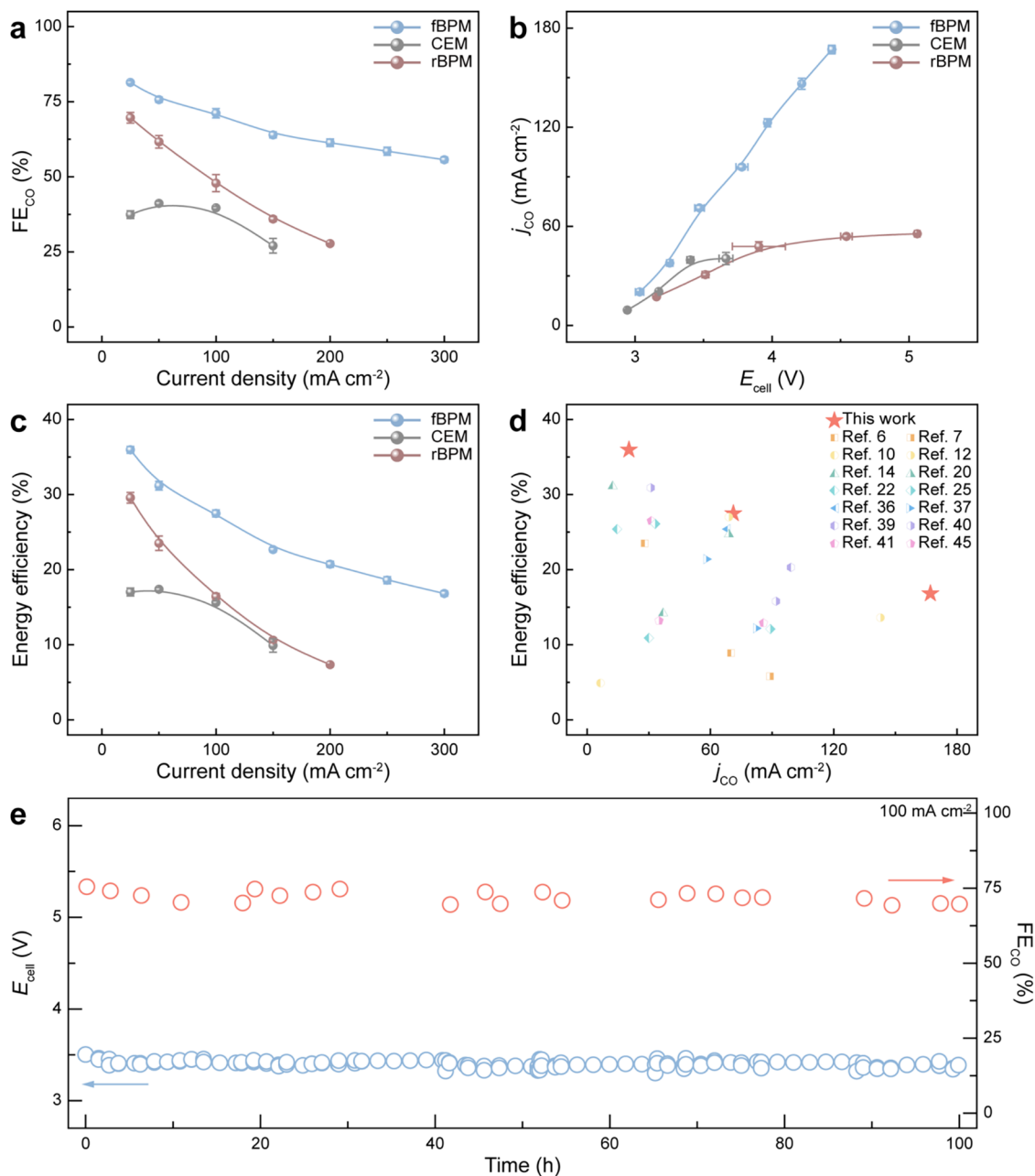


Figure 2. Bicarbonate electrolysis performance of the rBPM, CEM, and fBPM electrolyzers. (a) FE_{CO} at various current densities. (b) j_{CO} and the corresponding E_{cell} . (c) Energy efficiency at different current densities. The error bars in (a–c) correspond to the standard deviation of three independent measurements with Ar bubbling into the catholyte reservoir. (d) Comparison of the energy efficiency of the fBPM system at various j_{CO} with that of other state-of-the-art bicarbonate electrolysis systems measured at ambient temperature reported in the literature. (e) Stability test of the fBPM electrolyzer at a current density of 100 mA cm⁻² over 100 h with CO₂ bubbling into the catholyte reservoir.

anode, and the corresponding ion-exchange membrane was sandwiched between the electrodes (Figure S5). An aqueous KHCO₃ solution was continuously fed to the cathode. To establish the appropriate ion-transport environment in each configuration, the rBPM cell was operated with an alkaline KOH anolyte, whereas the CEM and fBPM cells employed an acidic H₂SO₄ anolyte to support proton migration. During electrolysis, argon (Ar) gas was purged through the catholyte reservoir to deliver gaseous products to online gas chromatography (GC) for Faradaic efficiency (FE) analysis (Figure S6).

Across all configurations, CO was the dominant product on Ag, with H₂ being the only detectable gaseous byproduct from the HER. The summed FE of CO and H₂ remained at ~100%

(Figure S7), indicating near-complete charge closure to gas-phase products. Consistently, proton nuclear magnetic resonance (¹H NMR) analysis of the postelectrolysis catholyte revealed no detectable liquid products (Figure S8). These results allow a direct comparison of membrane architectures in terms of CO selectivity, HER suppression, and cell-voltage requirements. The fBPM configuration outperformed both rBPM and CEM in terms of selectivity and rate. At 100 mA cm⁻², the fBPM cell delivered an FE_{CO} of 71.2 (±1.6)% with HER suppressed below 34%, whereas the rBPM and CEM cells achieved only 47.9 (±2.9)% and 39.7 (±0.5)% FE_{CO}, respectively (Figures 2a and S7). The advantage persisted at higher current densities. At 300 mA cm⁻², the fBPM cell

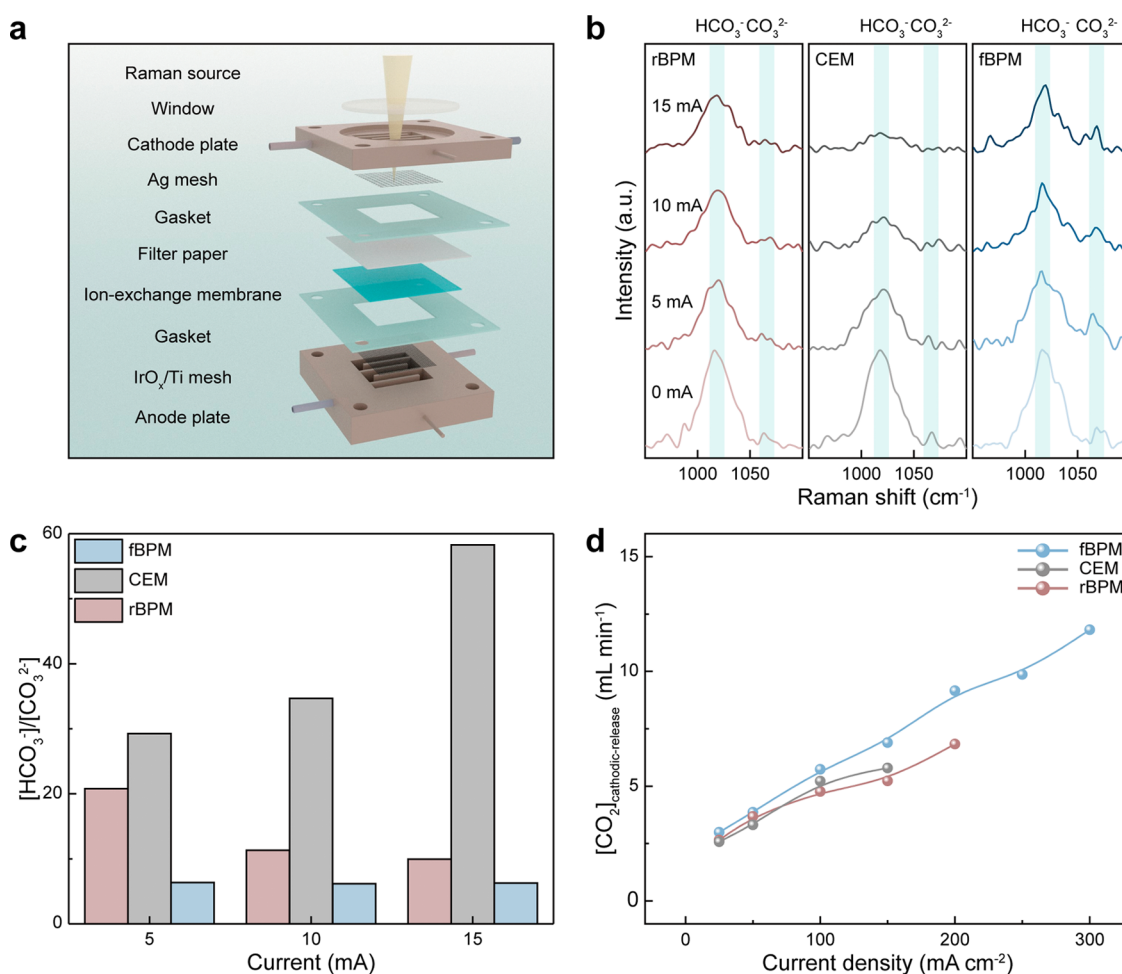


Figure 3. Mechanistic study of bicarbonate electrolysis on the rBPM, CEM, and fBPM systems. (a–c) *Operando* Raman characterization to explore the interfacial microenvironment. (a) Schematic illustration of the setup for the homemade MEA used in this *operando* Raman characterization. (b) *Operando* Raman spectra collected at different currents. Two stark Raman peaks correspond to HCO_3^- (approximately 1018 cm^{-1}) and CO_3^{2-} (approximately 1065 cm^{-1}) species. (c) Peak area ratios of HCO_3^- and CO_3^{2-} at various currents. (d) The amount of cathodic CO_2 release as a function of current density.

maintained an FE_{CO} of $55.7 (\pm 0.9)\%$. In parallel, the fBPM device showed favorable voltage-rate behavior, reaching a maximum j_{CO} of $167.1 (\pm 2.6)\text{ mA cm}^{-2}$ at an E_{cell} of $4.44 (\pm 0.03)\text{ V}$ (Figure 2b). When the current density of the fBPM cell was further increased to higher levels of 350 and 400 mA cm^{-2} , the FEs for CO declined to $47.2 (\pm 2.5)\%$ and $40.9 (\pm 2.5)\%$, respectively (Figure S7c). In contrast, the corresponding j_{CO} remained high at $165.3 (\pm 8.9)\text{ mA cm}^{-2}$ and $163.7 (\pm 9.9)\text{ mA cm}^{-2}$ (Figure S9), exhibiting a characteristic limiting current plateau. This behavior could be attributed to insufficient mass transport under such severe current densities. Future efforts focused on the systematic optimization of reactor design and operating conditions hold promise for mitigating these challenges and further enhancing cell performance.

Because the rBPM operation uses an alkaline anolyte, we examined whether the anode catalyst could influence the comparison. Replacing IrO_x/Ti mesh with Ni foam, an inexpensive and commonly used alkaline water-oxidation electrode in rBPM-based bicarbonate electrolyzers,^{36–42} produced negligible changes in the FE_{CO} and E_{cell} , and the rBPM cell remained consistently inferior to the fBPM benchmark (Figure S10). This control supports that the performance differences are governed primarily by the

membrane operating mode and the resulting cathode environment rather than by anode selection. These gains translate into higher energy efficiency. Owing to simultaneous HER suppression and a reduced E_{cell} , the fBPM cell exhibited higher energy efficiency than the rBPM and CEM systems did (Figure 2c), and compared favorably with representative state-of-the-art bicarbonate electrolyzers (Figure 2d). A multidimensional comparison is also provided in Table S1, which further highlights the comprehensive advantage of the fBPM configuration over other reported bicarbonate electrolyzers.

We next assessed the stability of the fBPM cell. Under galvanostatic operation at 100 mA cm^{-2} , the FE_{CO} decreased from 71.5% to 59.4% over 210 min, accompanied by a slight increase in the E_{cell} from 3.45 to 3.56 V (Figure S11). Both metrics recovered immediately upon refreshing the circulating catholyte (FE_{CO} to 72.1% and E_{cell} to 3.47 V), indicating that the apparent decay arises mainly from catholyte depletion (bicarbonate consumption reducing local CO_2 release)^{23,43} rather than irreversible catalyst or membrane degradation. This identifies bicarbonate availability as an operational variable that must be controlled during extended electrolysis. To minimize depletion effects and mimic continuous capture conditions,^{44,45} we replaced Ar with CO_2 bubbling at the same flow rate. Considering that gaseous CO_2 may be introduced

into the cathode via the catholyte flow under CO₂ bubbling, we performed a control experiment to assess its contribution to electrolysis. In this setup, the KHCO₃ catholyte was replaced with a KCl solution to create a HCO₃[−]-free environment, ensuring that no CO₂ was locally generated and that any CO₂RR could only arise from the externally supplied CO₂. Under this scenario, only HER selectivity was observed, with no detectable CO₂RR signal (Figure S12), suggesting the CO₂ bubbling served to maintain a stable concentration of KHCO₃ in the reactor, without introducing CO₂ into the electrolysis chamber for direct reduction. Under CO₂-saturated conditions, the fBPM performance was essentially unchanged (Figure S13) compared to that with Ar bubbling, indicating that CO formation is driven predominantly by CO₂ released locally from bicarbonate rather than by bulk dissolved CO₂. Using CO₂ bubbling, the fBPM cell operated stably for 100 h at 100 mA cm^{−2}, maintaining an FE_{CO} near 70% with an average *E*_{cell} of ~3.4 V and no measurable drift (Figure 2e). Post-test characterization of the Ag/C cathode and BPM revealed no discernible changes in morphology or structure relative to the pristine components (Figures S14–S17), corroborating the long-term robustness of the fBPM-based bicarbonate electrolyzer under continuous operation at 100 mA cm^{−2}. Furthermore, to evaluate the stability of the fBPM cell under more demanding conditions, we increased the sustained current density to 350 mA cm^{−2}. Over 20 h of electrolysis, the FE_{CO} remained relatively stable at approximately 45%, while the cell voltage exhibited several significant fluctuations (Figure S18). Postelectrolysis inspection revealed the formation of blisters on the BPM surface after 20 h at 350 mA cm^{−2} (Figure S19), suggesting possible mechanical degradation under the elevated current density.

To rationalize these contrasting behaviors in voltage stability between 100 and 350 mA cm^{−2}, we consider the underlying mechanisms governing CO₂ transport and bubble dynamics at the AEL/CEL interface. The minimal voltage oscillations (Figure 2e) at 100 mA cm^{−2} indicate that the CO₂ generated at the AEL/CEL interface largely redissolved and transported through hydrated membrane domains by diffusion and convective flow, whereas the tightly compressed AEL/CEL contact suppresses bubble growth and prevents junction delamination (Figure S17).²⁷ At the larger current density of 350 mA cm^{−2}, however, excessive CO₂ accumulates as macroscopic bubbles in the middle of BPM due to the relatively lower diffusion efficiency of CO₂ compared to its production efficiency, consequently exacerbating the ohmic polarization and even damaging the membrane skeleton.^{15,30} Future effort on improving bubble management within the fBPM could mitigate such voltage fluctuations under high current densities, enabling even greater practicality of the fBPM cell.

To link the observed electrolysis metrics to the membrane configuration, we combined *operando* interfacial pH probing with the quantification of *in situ* CO₂ release. We first examined the cathode-membrane microenvironment to test whether the fBPM configuration suppresses direct proton flux to the cathode. In bicarbonate electrolytes, the speciation between bicarbonate and carbonate is governed by the acid–base equilibrium (eq 2).



Therefore, the HCO₃[−]/CO₃^{2−} molar ratio decreases as the pH increases. We therefore used *operando* Raman spectroscopy

to track the relative abundance of HCO₃[−] and CO₃^{2−} near the cathode-membrane interface as an indirect pH reporter.^{43,46,47} Because the zero-gap MEA places the cathode in intimate contact with the membrane, and the carbon-paper substrate can block optical access from the back side,⁴³ we built a modified Raman-accessible MEA (Figure 3a). The Ag/C cathode was replaced by a Ag mesh to allow the laser to reach the interface through open apertures. In addition, the smooth membrane surface produced a strong specular reflection that interfered with signal collection. To mitigate this, we inserted thin, rough, porous filter paper between the cathode and the membrane. This spacer both suppresses reflection and allows the interfacial electrolyte to wick to the probed region from the membrane side.

The *operando* spectra collected while stepping the current from the open circuit show two prominent bands (Figure 3b). The band at ~1018 cm^{−1} was assigned to the symmetric C–O stretch of HCO₃[−] (1010–1020 cm^{−1}), and the band at ~1065 cm^{−1} was assigned to the symmetric C–O stretch of CO₃^{2−} (1060–1070 cm^{−1}).⁴⁷ Following a reported analysis protocol,⁴³ we integrated these two bands and calculated the area ratio ([HCO₃[−]]/[CO₃^{2−}]) as a comparative descriptor of local pH. As shown in Figure 3c, the fBPM cell exhibited a markedly lower [HCO₃[−]]/[CO₃^{2−}] under electrolysis than did the rBPM and CEM cells. This trend suggests a more alkaline interfacial microenvironment in the fBPM configuration, which can be attributed to two main factors: (1) the fixed positive charges within the AEL of the fBPM attract and transport the alkaline species (e.g., OH[−] and HCO₃[−]) from the cathode to the AEL surface and onward to the AEL/CEL junction, thereby establishing an alkaline microenvironment at the cathode/AEL interface; (2) the fBPM mitigates the proton flux from the acidic anode by Donan exclusion, and thus preventing cathode acidification typical of rBPM and CEM systems.^{15,29,48} These *operando* Raman results align with the electrochemical performance, indicating that an alkaline cathodic microenvironment established in the fBPM effectively suppresses the severe HER and enables selective bicarbonate electrolysis.

Local CO₂ availability is also a key factor affecting CO selectivity in bicarbonate electrolysis. More locally released CO₂ leads to an enhanced mass transfer of the CO₂ supply and thus a higher selectivity.^{18,36,37,49,50} We therefore quantified the amount of CO₂ released on the cathode side ([CO₂]_{cathodic-release}) following eq 3, by accounting for two contributions measured by GC: the fraction converted to CO ([CO₂]_{CO}) and the unreacted CO₂ exiting the cathode outlet ([CO₂]_{cathodic-outlet}).^{18,36,37}

$$[\text{CO}_2]_{\text{cathodic-release}} = [\text{CO}_2]_{\text{CO}} + [\text{CO}_2]_{\text{cathodic-outlet}} \quad (3)$$

For all three configurations, [CO₂]_{cathodic-release} increases with current density (Figures 3d and S20). Notably, the fBPM system consistently delivers the highest [CO₂]_{cathodic-release}. This observation is mechanistically consistent with the distinct roles of charge carriers in the three cells. Under ideal electromigration, each transferred electron is coupled to the transport of one charge-equivalent ion and can, in principle, drive stoichiometric CO₂ liberation from bicarbonate. In the rBPM and CEM cells, however, a fraction of the migrated protons is consumed directly by the HER rather than by bicarbonate neutralization. That parasitic pathway reduces both CO₂ release and CO selectivity. In contrast, the fBPM architecture limits direct proton delivery to the cathode surface, which simultaneously suppresses the HER and preserves the charge-

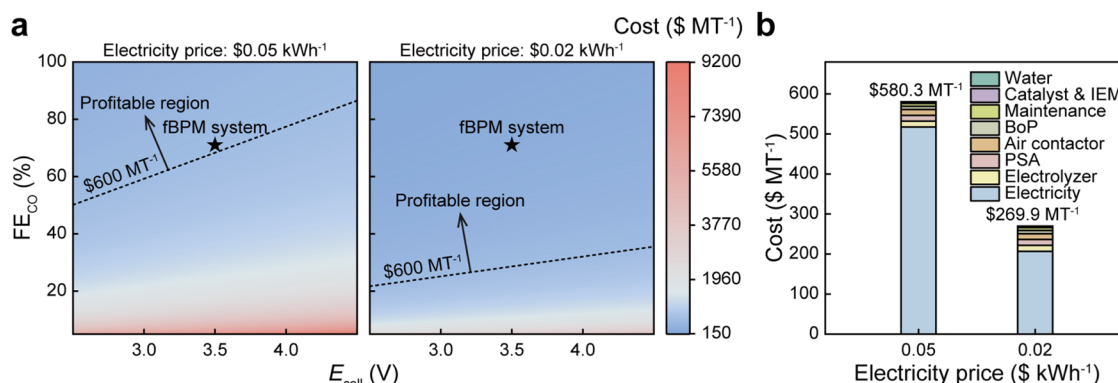


Figure 4. Techno-economic analysis of CO₂ to CO upgrading from dilute sources with the fBPM system at a current density of 100 mA cm⁻². (a) Contour plots of the calculated total cost for 1 tonne of CO production under different FE_{CO} and E_{cell}. The left plot shows the cost with an electricity price of \$0.05 kWh⁻¹, which is the cheapest currently available for industrial electricity. The right one is the result with a renewable electricity price of \$0.02 kWh⁻¹. Above the dashed lines are the regions where the total costs are lower than the current CO market price of \$600 MT⁻¹. The stars represent the situations of the fBPM system with an FE_{CO} of 71% and an E_{cell} of 3.5 V. (b) The detailed subdivided production costs with the fBPM system.

equivalent flux for CO₂ generation. The higher measured [CO₂]_{cathodic-release} therefore provides a quantitative basis for the higher FE_{CO} observed in the fBPM cell.

Because part of the CO₂ in the fBPM cell can be generated at the AEL/CEL junction and potentially cross toward the anode ([CO₂]_{anodic-outlet}),²⁶ we also analyzed anode exhaust by GC. A measurable CO₂ signal appears above 50 mA cm⁻² and increases with current density. We define the CO₂ crossover ratio following eq 4

$$\text{CO}_2 \text{ crossover ratio} = \frac{[\text{CO}_2]_{\text{anodic-outlet}}}{[\text{CO}_2]_{\text{cathodic-release}} + [\text{CO}_2]_{\text{anodic-outlet}}} \quad (4)$$

which remained at ~10% under the conditions examined (Figure S21), indicating only modest crossover within the fBPM cell.

To evaluate the practical implications, we performed a system-level energy-cost assessment comparing the fBPM bicarbonate electrolyzer with representative CO₂-upgrading platforms, including three gas-fed CO₂ electrolyzers (alkaline flow cell,^{51,52} alkaline MEA,^{32,53} and acidic MEA⁵⁴) and two bicarbonate electrolyzers (the rBPM and CEM). The details could be found in the Supporting Information. The accounting spans the CO₂-use chain from upstream feed preparation (including capture, and where applicable, regeneration and compression) through electrolysis and downstream separations (Tables S2–S5). As shown in Table S5, bicarbonate-fed systems incur substantially lower feedstock-preparation energy than do gas-fed CO₂ systems because they avoid the regeneration and compression steps needed to produce purified CO₂ gas. However, the total energy demand of rBPM and CEM bicarbonate electrolyzers can exceed that of leading gas-fed MEA systems because lower selectivity and higher voltage increase electrolysis energy and elevate separation penalties associated with H₂ coproduction. These comparisons highlight two decisive levers for bicarbonate electrolysis: improving the energy efficiency (lower E_{cell} at high j_{CO}) and suppressing the HER (higher FE_{CO}) to reduce both electrolysis and separation burdens. Within this framework, the fBPM design achieves the lowest total energy cost in our comparison, reaching 36.7 GJ per tonne of CO, which supports its potential as an energy-advantaged route for CO₂ upcycling.

We further evaluated economic viability via techno-economic analysis (TEA) for converting CO₂ to CO from dilute sources (details are provided in the Supporting Information). The TEA includes capital expenditures, operating costs, and materials, and maps the CO production cost as a function of the FE_{CO} and E_{cell} at two electricity prices of \$0.05 kWh⁻¹ and \$0.02 kWh⁻¹ (Figure 4a).⁵⁵ The “profitable” region is defined relative to a benchmark CO market price of \$600 MT⁻¹.⁷ The fBPM operating point at a current density of 100 mA cm⁻² corresponds to a unit cost of \$580.3 MT⁻¹ at \$0.05 kWh⁻¹ and \$269.9 MT⁻¹ at \$0.02 kWh⁻¹, placing it within the profitable region under both pricing scenarios. The cost breakdowns (Figure 4b) show that electricity dominates the total cost and remains the largest contributor, even at \$0.02 kWh⁻¹ (76.7%). This sensitivity underscores that continued reductions in low-carbon electricity prices will further improve the economic headroom for bicarbonate-to-CO electrolyzers, and particularly reward architectures that minimize voltage losses while maintaining high selectivity. Considering the diverse capacity requirements in practical applications, we further evaluated the TEA across a spectrum of current densities. As shown in Figure S22, under the current density of 50 mA cm⁻², the fBPM system also demonstrates highly competitive CO production costs. However, as the operating current density increases, electricity cost emerges as a significant economic constraint, particularly under the current electricity price scenario (\$0.05 kWh⁻¹). With the ongoing advancement of sustainable energy technologies, the projected reduction in electricity prices could substantially improve the economics of such CO electrosynthesis, positioning the fBPM reactor as a compelling solution within a clean energy framework.

3. CONCLUSIONS

In summary, we developed a forward-bias bipolar membrane (fBPM)-enabled bicarbonate electrolyzer that improves CO production by mitigating cathodic proton flux and thereby suppressing the competitive HER. The resulting MEA delivers high CO selectivity with sustained stability and energy efficiency that surpasses those of most reported bicarbonate electrolysis systems. *Operando* Raman analysis supported the formation of a more alkaline interfacial microenvironment in

the fBPM configuration, whereas CO₂-release quantification indicated increased cathodic CO₂ availability. Beyond device metrics, a system-level energy-cost assessment and techno-economic analysis further support the practical promise and economic competitiveness of this capture-to-conversion strategy. Overall, this study highlights fBPM operation as a useful membrane-configuration strategy for bicarbonate electrolysis, and future work will focus on catalyst development and mass-transport optimization to further improve performance and operational robustness.

4. EXPERIMENTAL SECTION

4.1. Materials

KHCO₃ (99.7%, Sigma-Aldrich), Nafion 117 solution (5.0–5.4%, Sigma-Aldrich), IrCl₃·xH₂O (99.9%, Sigma-Aldrich), KOH (95%, Macklin), Ag nanoparticles (99.5%, 60–120 nm, Macklin, abbreviated as Ag NPs), isopropanol (99.5%, Macklin), H₂SO₄ (98%, Xilong Scientific), Ni foam (1 mm thickness, Kunshan Jiayisheng Electronics), Ag mesh (20 mesh, Kunshan Shengzhaoquan New Materials), and dimethyl sulfoxide (Sigma-Aldrich, abbreviated as DMSO) were used as received. The TYPE 7 BPM was obtained from TingRun Membrane Tech and soaked in deionized water for storage. The Nafion N117 CEM was purchased from SCI Materials Hub, and the activation method was the same as that used in previous studies.^{56,57} The hydrophilic carbon paper (Freudenberg H23) was also purchased from SCI Materials Hub. Ti mesh (100 mesh, 0.26 mm thick) was purchased from a commercial supplier and etched in a 6 M HCl solution at 90 °C for 45 min before use. Deionized water without any further treatment was used in all the experiments.

4.2. Cathode Preparation

The Ag/C cathode was prepared through a universal air-spray method. First, a catalyst ink was prepared through mixing 80 mg of Ag NPs, 120 μL of Nafion 117 solution, and 40 mL of isopropanol, and then sonicating to disperse the catalyst. The resulting ink was then sprayed onto a gas-diffusion electrode using an airbrush at 80 °C. The gas-diffusion layer used was a hydrophilic carbon paper selected based on comparative testing with its hydrophobic counterpart (Figure S23), as the hydrophobic variant may hinder bicarbonate mass transfer and bubble detachment,^{37,58} resulting in inferior electrochemical performance. The catalyst loading was controlled to 2.8 (±0.2) mg cm⁻² by weighing. Finally, the resulting Ag/C cathode was used for subsequent electrolysis (Figures S2–S4).

4.3. IrO_x/Ti Mesh Anode Preparation

The IrO_x/Ti mesh anode was prepared using a soaking and calcination method.⁵⁹ The soaking solution was prepared by dissolving 360 mg of IrCl₃·xH₂O into 120 mL of isopropanol solution containing 10% HCl in volume. The etched Ti mesh was soaked in the soaking solution and then dried in a 100 °C oven for 10 min, followed by 10 min of calcination at 500 °C in a muffle furnace. The soaking and calcination processes were repeated several times. The loading was controlled to 1.0 (±0.2) mg cm⁻² by weighing. Finally, the resulting IrO_x/Ti mesh anode was used for subsequent electrolysis.

4.4. Characterizations

X-ray diffraction (XRD) patterns were collected using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation, for which the standard λ value was 0.154178 nm. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Supra photoelectron spectrometer with an exciting source of Al Kα radiation (1486.6 eV). The binding energies were corrected by selecting the C 1s peak (284.8 eV) as a reference. The morphologies of Ag/C and BPM were characterized by a Thermo Scientific Apreo 2 field emission scanning electron microscope (SEM) under a 15 kV accelerating voltage with an energy dispersive spectrometer (EDS). The ¹H NMR spectrum of the postelectrolysis catholyte was obtained using a Nanalysis 100e

benchtop NMR spectrometer. DMSO was chosen as an internal standard.

4.5. Electrochemical Measurements

All the electrochemical measurements were performed using a CHI1140c electrochemical workstation in a two-electrode MEA electrolyzer. The cathode and anode plates were commercial stainless steel and titanium serpentine-channel plates, respectively, each with an effective area of 2 × 2 cm². Further geometric details are provided in Figure S24. The as-prepared Ag/C and IrO_x/Ti mesh or Ni foam were used as the cathode and anode, respectively. The corresponding ion-exchange membrane was placed between the cathode and the anode and separated from them by gaskets (Figure S5). The catholyte of 3 M KHCO₃ and the anolyte of 3 M KOH or 3 M H₂SO₄ were pumped into the electrolyzer using peristaltic pumps. The electrolyte flow rate was optimized to an optimum of 25 mL min⁻¹, as the higher rate may accelerate CO₂ escape, while the lower value may limit HCO₃⁻ mass transfer—both of which are unfavorable to electrolysis (Figure S25).^{42,60} The sweep gas of Ar or CO₂ was bubbled into the catholyte reservoir (not directly into the reactor) at a flow rate of 35 sccm to carry the cathodic gas (i.e., gaseous products of CO and H₂, and unreacted CO₂) into the GC (Figure S6). In the test of the [CO₂]_{anodic-outlet} for the fBPM system, 35 sccm Ar gas was also purged into the anolyte reservoir. Electrolysis tests were conducted for 8 min using chronopotentiometry, and the corresponding *E*_{cell} was recorded. Before each test, the catholyte would be refreshed to maintain the concentration of bicarbonate. The stability test was conducted using the same method at a current density of 100 mA cm⁻².

4.6. Gas Analyses

The gaseous products of CO and H₂ were analyzed through an online GC (Shimadzu GC-2014C) equipped with a thermal conductivity detector (TCD) for analyzing H₂ and a flame ionization detector (FID) for analyzing CO. A calibration curve was established using standard gases at various concentrations. The FE for gas *i* was calculated following eq 5 below

$$FE_i = \frac{x_{i,c} \times v_c \times z_i \times F \times P_0}{R \times T \times j \times S} \quad (5)$$

where *x*_{*i,c*} is the volume fraction of gas *i* in the cathodic outlet, *v*_{*c*} is the gas flow rate in the cathodic outlet measured by a flow meter, *z*_{*i*} is the number of electrons required to produce one mole of gas *i* (i.e., 2 for CO or H₂), *F* is the Faraday constant (96485 C mol⁻¹), *P*₀ is the atmosphere pressure, *R* is the ideal gas constant, *T* is the temperature, which we assume to be 25 °C, *j* is the current density, and *S* is the effective area of 4 cm². With the FE_{CO}, the energy efficiency can be calculated following eq 6 below

$$\text{Energy efficiency} = \frac{(E_a^0 - E_{CO}^0) \times FE_{CO}}{E_{cell}} \quad (6)$$

where *E*_{*a*}⁰ is the thermodynamic potential of the anodic reaction, which is 1.23 V vs reversible hydrogen electrode (RHE) for the water oxidation reaction or 0 V vs RHE for the hydrogen oxidation reaction (HOR), and *E*_{CO}⁰ is the thermodynamic potential for the CO₂RR to CO (−0.11 V vs RHE).⁶¹

The [CO₂]_{CO} is equal to the CO flux in the cathodic outlet and can be calculated following eq 7.

$$[CO_2]_{CO} = x_{CO} \times v_c \quad (7)$$

The measurements of CO₂ flux in the cathodic and anodic outlets (i.e., [CO₂]_{cathodic-outlet} and [CO₂]_{anodic-outlet}) were conducted through the TCD of a PerkinElmer Clarus 690 online GC. A calibration curve was also established using standard gases with various concentrations of CO₂. The calculation formulas are given in eqs 8–9 below

$$[CO_2]_{cathodic-outlet} = x_{CO_2,c} \times v_c \quad (8)$$

$$[CO_2]_{anodic-outlet} = x_{CO_2,a} \times v_a \quad (9)$$

where $x_{\text{CO}_2,a}$ is the volume fraction of CO_2 in the anodic outlet, and v_a is the gas flow rate in the anodic outlet, which was also measured by a flow meter.

4.7. Operando Raman Analysis

The operando Raman analysis was conducted on a Renishaw inVia Raman analyzer. The excitation source was a 532 nm laser, and the acquisition time was 30 s. The electrolyzer used for operando Raman was a homemade MEA, which contained a quartz window on the cathode flow plate. Unlike the electrolyzer configuration used in electrochemical measurements, the cathode here is Ag mesh rather than Ag/C. Additionally, a piece of filter paper (Beimu 101, 20–25 μm pore size, cut to $3 \times 3 \text{ cm}^2$) is placed between the ion-exchange membrane and the cathode (Figure 3a). Chronopotentiometry was used to apply electrical signals to the electrolyzer. The peak areas of the resulting Raman spectra were integrated via OriginLab 2021.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.6c00072>.

Energy cost assessment, TEA, results of structural and morphological characterizations, illustrations of the electrochemical test system and MEA structure, product distribution, constitution of $[\text{CO}_2]_{\text{cathodic-release}}$, CO_2 crossover ratio, and additional experimental data (PDF)

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Notes

The authors declare the following competing financial interest(s): A published Chinese provisional patent application (CN120776326A) based on the technology described in this work was filed in July 2025 by M.W., C.L., T.Z., and C.X. and published in October 2025.

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