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Broader Context Statement

Efforts to mitigate the adverse effects of carbon dioxide emissions while meeting global energy demands have driven extensive research in carbon capture and utilization technologies. Electrochemical CO₂ reduction reactions (CO₂RR) have emerged as a promising pathway to convert CO₂ into valuable products such as carbon monoxide, formate, and hydrocarbons using renewable electricity. Among these, CO is particularly attractive due to its versatility in producing chemicals and fuels with positive technoeconomic potential. Advancements in CO₂RR, particularly under industrially relevant conditions, hold the potential to revolutionize sustainable energy and environmental catalysis by reducing reliance on fossil fuels and lowering greenhouse gas emissions. The successful integration of optimized reaction parameters, such as high pressure and temperature, addresses mass transport and kinetic limitations, advancing scalable solutions for industrial CO₂ conversion. As renewable-powered CO₂ electrolyzers develop, they could seamlessly integrate with CO₂ capture systems, offering a circular carbon economy that aligns with decarbonization goals.



Elevated Temperature and Pressure Drive Ampere-Level CO₂ electroreduction to CO in a Membrane Electrode Assembly Electrolyzer

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Abstract

Achieving high selectivity for carbon monoxide (CO) in the electrochemical reduction of carbon dioxide (CO₂) at industrially relevant current densities, particularly with dilute CO₂ feedstocks, remains a significant challenge. Herein, we demonstrate that combining elevated temperature and CO₂ pressure substantially enhances CO production in a membrane electrode assembly (MEA) electrolyzer using commercially available silver nanoparticles. Elevated CO₂ pressures increase CO₂ concentration and reduce diffusion layer, counteracting the reduced CO₂ solubility caused by high temperature. The synergy of high pressure and temperature still ensure high CO₂ flux to the catalyst surface while leveraging elevated temperatures to accelerate reaction kinetics. Therefore, the pressurized and heated CO₂ electrolyzer achieves an FE_{CO} of 92% at a high current density of 2 A cm⁻² and a low cell voltage of 3.8 V under 10 bar and 80 °C when using 0.1 M KHCO₃ as the anolyte. Even when using pure water as the anolyte, the system maintains a FE_{CO} of 90% at 300 mA cm⁻² and a cell voltage of 3.6 V. Furthermore, the system demonstrates exceptional performance with dilute 10 vol% CO₂ feedstocks, achieving a FE_{CO} of 96% at 100 mA cm⁻² and 2.4 V. These findings underscore the potential of combined temperature and pressure optimization to overcome mass transport limitations and enhance reaction kinetics, offering a viable pathway for scaling CO₂ electrolyzers to industrial applications.

KEYWORDS: CO₂-to-CO conversion, pressurization, temperature, MEA, pure-water fed, dilute CO₂ reduction



1. Introduction

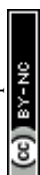
In response to the escalating carbon dioxide (CO₂) emissions driven by increased fossil fuel consumption, CO₂ capture and utilization has become a global priority with accelerated research efforts.¹ The electrochemical CO₂ reduction reaction (CO₂RR) presents a dual function to mitigate greenhouse gas emissions and generate sustainable feedstocks by integrating with renewable electricity.² By tailoring the catalyst, reaction environment, and operating potential, CO₂RR enables the production of a wide array of valuable products.³⁻⁶ Among these, carbon monoxide (CO) stands out as a versatile feedstock for downstream upgrading to various hydrocarbon chemicals and fuels with promising market potential. Technoeconomic assessments indicate that CO is among the few CO₂RR products capable of achieving positive gross margins.⁷ Extensive research has identified silver (Ag) as an optimal catalyst for selective CO production, yet achieving high CO selectivity at a high current density (>1 A cm⁻²) remains a significant challenge due to the high energy barrier of CO₂ activation and sluggish kinetics of multi-electrons/protons transfer steps.⁸

A significant advancement in CO₂RR systems was achieved with the introduction of gas diffusion electrodes (GDEs), which effectively reduce the diffusion layer of gas phase CO₂, thereby enabling operation at industrially relevant current densities.⁹⁻¹¹ Among various cell configurations, the membrane electrode assembly (MEA) cell stands out as a promising approach, integrating GDEs to offer low ohmic resistance and scalability potential for multicell stacks.¹²⁻¹³ It is widely considered that, under operating conditions, the catalyst layer pores become saturated with liquid electrolyte, limiting the reaction primarily to the aqueous phase via dissolved CO₂.¹⁵⁻¹⁷ However, high current densities often induce electrode flooding that thickens the diffusion layer of CO₂, posing mass transfer limitation in MEA cell. Efforts to overcome these current density limitations have primarily focused on modifying catalyst layer with materials such as incorporating polytetrafluoroethylene (PTFE) to enhance hydrophobicity, silicon dioxide (SiO₂) to consume the hydroxide ions and thereby reducing the local pH, and cesium (Cs⁺) with induced electric field to lower the barrier of CO₂ activation at high current densities.¹⁸⁻²⁰ Despite these advances, there has been comparatively little exploration of process intensification. To date, most CO₂RR-MEA cell studies have been



conducted under ambient conditions, with only limited reports investigating pressurized MEA cells.^{21,22} In these studies, pressure was typically applied only to the cathode side, leading to gas crossover through the membrane due to pressure imbalances when the differential exceeded 6 bar, ultimately resulting in decreased performance.²³

On the other hand, raising the reaction temperature enhances CO₂RR kinetics, as the rate generally increases exponentially with temperature.^{24,25} Industrial CO₂ electrolyzers are expected to operate under elevated temperatures due to heat generated by overpotentials, resistive losses, as well as the high temperatures of flue gas streams, often exceeding 100 °C.^{26,27} However, as temperature rises, CO₂ solubility in aqueous electrolytes decreases, where the hydrogen evolution reaction (HER) tends to accelerate, complicating the optimization of CO₂RR selectivity.²⁸ Several studies have examined the effects of temperature on GDE-based CO₂RR systems with varying results depending on catalysts and cell configurations. For instance, in MEA cells using Ag catalysts, rising temperatures have been associated with reduced j_{CO} and FE_{CO} at reported cell voltages of 2.2-3.4 V, largely attributed to diminished CO₂ adsorption, lower solubility, and increased water presence.^{21,23} Conversely, under constant current conditions (100-500 mA cm⁻²), elevated temperatures have been shown to enhance FE_{CO} .¹⁹ In flow cell systems, peak FE_{CO} occurred at moderate temperatures under certain current, with performance declining at higher temperatures due to CO₂ solubility constraints.²⁹ For Au catalysts, FE_{CO} generally decreased with increasing temperature under both constant potential (-0.7 V_{RHE} in the flow cell) and constant current conditions (100 mA cm⁻² in the MEA cell), consistent with CO₂ solubility limitations.^{30,31} Similarly, Sn-based catalysts exhibited a decline in formate selectivity at higher temperatures in both flow cell and MEA cell systems under the same cell voltage of 2.2 V, although partial current densities of formate plateau at elevated temperatures in MEA systems.²⁵ Notably, these previous studies often focused on a single cell voltage or a narrow temperature range at ambient pressure, leaving a gap in understanding how combined temperature and pressure impacts catalytic performance across varying cell voltages. Given that practical CO₂ electrolyzers are expected to operate at elevated temperatures and pressures for seamless integration with upstream and downstream processes,^{32,33} a systematic investigation into the interplay of these parameters on CO₂RR performance is essential to advance catalyst and electrode design as well as



intensifying process operation.

In this work, by systematically varying reaction temperature and pressure using a commercial Ag catalyst in a MEA cell, we demonstrate the synergy of high temperature and pressure operation to drive the CO₂-to-CO conversion at simultaneously high current density and selectivity. Our results reveal that (i) High-pressure operation effectively enhances CO₂ availability and promotes selective CO₂ adsorption, thus facilitating CO₂RR at high current density while suppressing parasitic HER; (ii) The effect of temperature on j_{CO} is strongly influenced by the cell voltage and CO₂ partial pressure. At lower cell voltages and higher CO₂ pressures, elevated temperatures positively improve the CO formation rate. The combined effects of high temperature and pressure achieve an impressive FE_{CO} exceeding 92% at a current density of 2 A cm⁻² at a cell voltage of 3.8 V when using 0.1 M KHCO₃ as the anolyte, a stark improvement over that of ambient condition, where FE_{CO} drops from 95% at 100 mA cm⁻² to 73% at 200 mA cm⁻². Additionally, pressurized and high-temperature operation presents a compelling strategy to substantially enhance CO₂RR performance when using pure water as the anodic feedstock or processing dilute CO₂ concentrations.

2. Experimental Section

2.1. Chemicals

Potassium bicarbonate (KHCO₃, 99.7%) and potassium hydroxide (KOH, 99.99%) were purchased from Sigma-Aldrich and used as received without further purification. Silver nanoparticles (Ag, 20-40 nm) were purchased from Thermo Scientific. All solutions were prepared with Milli-Q water (17.8 MΩ cm).

2.2. Preparation of the Ag electrode

The Ag electrodes were fabricated using a standard air-brush technique. Initially, the Ag catalyst ink was prepared by dispersing Ag nanoparticles (40 mg) in iso-propanol (4 mL), followed by sonication for 30 minutes. The resulting ink was uniformly air-brushed onto carbon paper (Sigracet GDL 34BC, Fuel Cell Store) to achieve a catalyst loading of approximately 0.8 mg cm⁻². The geometric area of the GDE cathode was 1.0 cm × 1.0 cm.



2.3. Electrochemical measurements

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The CO₂RR performance under varying temperatures and pressures was evaluated in a MEA cell with 0.1 M KHCO₃ as the anolyte. The GDE cathode and an IrO₂/Ti felt anode were separated by a PiperION anion exchange membrane (AEM, 20 μm, Fuel Cell Store). For pure CO₂RR, dry CO₂ gas was supplied to the cathode at a flow rate of 250 sccm via a mass flow controller (Alicat Scientific) without external humidification. For diluted CO₂RR, a CO₂/N₂ gas mixture was used, with the total mass flow controlled at 250 sccm. For instance, for 10 vol% CO₂RR, 25 sccm of CO₂ was mixed with 225 sccm of N₂, whereas for 50 vol% CO₂RR, 125 sccm of CO₂ was mixed with 125 sccm of N₂. A potentiostat (Gamry Interface 5000E) was used to apply a constant current to the MEA cell and record the corresponding cell voltage without iR correction. The cell temperature was controlled by electrical heating rods directly connected to both the cathode and anode flow fields, with a thermocouple inserted into the cell to maintain the desired temperature (Figure S1), which was regulated by a PID temperature controller (Cole-Parmer TC5000).

A schematic and photograph of the pressure setup is shown in Figure S2-3. In all pressurized MEA setups, the pressures on the cathode and anode sides were balanced to ensure consistent conditions. The anode side pressure was controlled using a back-pressure regulator (BPR, Equilibar model LF2 with PEEK non-reinforced diaphragm) downstream of the cell, equipped with a high-pressure electronic pilot controller (Equilibar). The anolyte was fed to the anode using a high-pressure syringe pump (Fusion 6000X, Chemyx) at a flow rate of 0.5 mL min⁻¹. For cathode side, gas pressure was maintained using stacked back-pressure regulators (Swagelok, KBP1J0A4A5A20000). A cold trap was positioned downstream of the cathode effluent to separate gaseous and liquid products. Due to liquid product crossover, the FEs of the liquid products were calculated based on the total amount collected from both the anode and cathode sides during the same time period. Gas samples were collected downstream of the BPR, ensuring that the gas was at atmospheric pressure.

2.4. Product detection

During the electrochemical reaction, an in-line gas chromatograph (GC, Agilent 8860) was employed to monitor gaseous products. To calibrate the outlet gas flow rate of CO₂, a mass



flow meter (MFM, Alicat Scientific) was used to measure the outlet gas stream from the cathode prior to sampling to the GC loop.³⁴ The FE for gaseous products was calculated using the following equation:

$$FE(\%) = \frac{zFxV}{j_{total}} \times 100\%$$

where z is the number of electrons transferred for producing a target product; F is the Faraday constant; x is the molar fraction of a target product determined by GC; V is the molar flow rate of gas; and j_{total} is the total current density.

The liquid products after electrolysis were collected and quantified via ^1H nuclear magnetic resonance (NMR) spectroscopy using a Bruker NEO 400 MHz spectrometer. The electrolyte (500 μL) was mixed with an internal standard (100 μL of 5 mM 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt in D_2O). The partial current densities of CO and H_2 (j_{CO} and j_{H_2}) at different cell voltages were determined by multiplying the overall current density by the corresponding FE. The single-pass CO_2 conversion efficiency (SPCE) is calculated as follows:

$$SPCE = \frac{\frac{j_{\text{CO}}}{zF} * \frac{RT}{P}}{\text{CO}_2 \text{ flow rate}}$$

where R is the gas constant, T is the reaction temperature, P is the reaction pressure.

3. Results and discussion

3.1. Pressurized Electrolysis of CO_2 to CO

We systematically examined the effects of CO_2 partial pressure on the performance of an Ag GDE for CO_2RR over a pressure range of 1 to 10 bar. Figure 1 illustrates the influence of pressure on FE_{CO} and cell voltage under galvanostatic conditions at various temperatures of 20 $^\circ\text{C}$, 40 $^\circ\text{C}$, 60 $^\circ\text{C}$, and 80 $^\circ\text{C}$. We note that only CO and H_2 were detected across all experiments, with no liquid products observed or under the detection limit. Under ambient pressure and temperature (Figure 1a), FE_{CO} reached 95% at 100 mA cm^{-2} , demonstrating the superior capability of Ag catalyst in converting CO_2 to CO. However, FE_{CO} sharply declined to below 40% as the current density increased to 600 mA cm^{-2} . This trend highlights a key challenge in MEA cell with AEM: high current densities drive substantial electroosmotic water



flow accompanied with cation migration from the anode, resulting in electrode flooding and thickened CO₂ diffusion layer. The reduced flux of CO₂ near the catalyst surface leads to HER dominance.

Meanwhile, the elevated CO₂ consumption rate at higher current densities exacerbates mass transport limitations, hindering conversion efficiency. To substantiate this claim, we evaluated the CO₂ single pass conversion efficiency (SPCE) under varying current densities at 1 bar and 10 bar CO₂ pressures. As shown in Figure S4, under 1 bar CO₂, SPCE initially increases with current density but plateaus at ~400 mA cm⁻², indicating mass transport constraints. In contrast, at 10 bar CO₂, SPCE continues to rise, reaching a maximum at ~800 mA cm⁻². These observations confirm that rapid CO₂ consumption at high current densities intensifies mass transport limitations, particularly under low CO₂ partial pressures.

By increasing the CO₂ pressure up to 10 bar, we effectively mitigate these limitations, resulting in higher FE_{CO} at elevated current densities. Specifically, under 10 bar and 20 °C, FE_{CO} remained above 95% even at 600 mA cm⁻². This trend was also observed at higher temperature conditions (Figure 1b–d). FE_{CO} consistently increased with pressure under the current density, signaling the effectiveness of pressurized conditions for CO₂RR to CO production.

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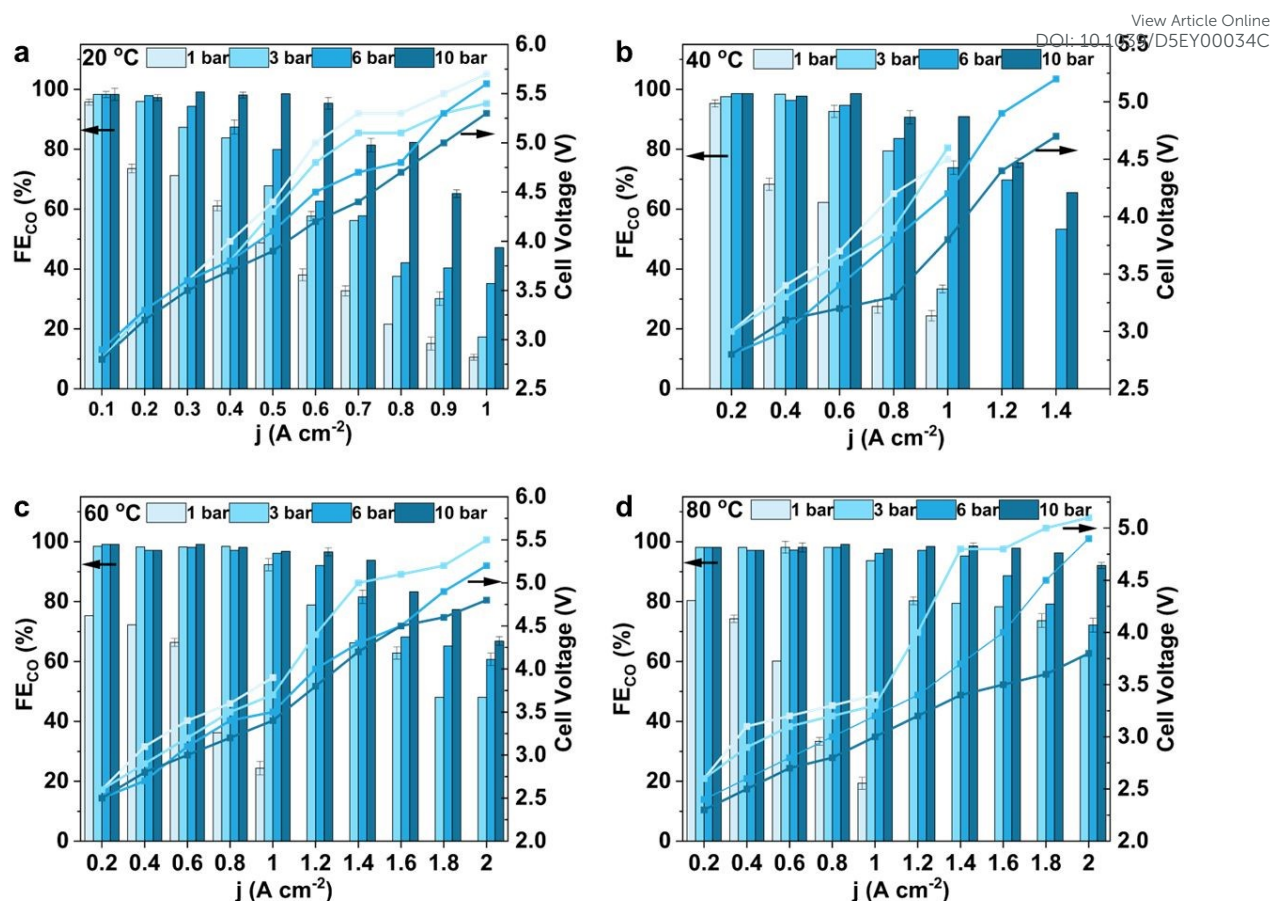


Figure 1. FE_{CO} and cell voltage as a function of current density for CO₂RR at various pressures (1 bar, 3 bar, 6 bar, and 10 bar) and temperatures: (a) 20 °C, (b) 40 °C, (c) 60 °C, and (d) 80 °C. A consistent input flow of 250 sccm CO₂ was employed in all experiments. The cathode was Ag GDE and the anode was Ir/Ti felt. 0.1M KHCO₃ was used as an anolyte. The error bars represent standard deviations of three independent measurements.

The enhancement of FE_{CO} at high j with increasing pressure is associated with multiple factors: (i) Henry's law predicts that elevated CO₂ pressure increases the dissolved CO₂ concentration,³⁵ boosting CO₂ availability in the wetted catalyst layer as well as reducing proton adsorption, thereby effectively suppressing HER; (ii) Elevated pressure reduces the density difference between gas and liquid phases, thereby mitigating water flooding under high current densities.³⁶

Encouragingly, elevated pressures across all temperatures consistently led to reductions in cell voltage, as shown in Figure 1. At relatively lower current density, the drop is insignificant, as shown in Figure 1(a), from 100 mA cm⁻² to 300 mA cm⁻², the cell voltage



variation is within 0.1 V from 1 bar to 10 bar. However, at higher current densities, the decrease of cell voltage with increasing of pressure becomes particularly evident. For instance, at 80 °C under a current density of 1.8 A cm⁻², increasing the pressure from 3 bar to 10 bar lowers the cell voltage from 5 V to 3.6 V. Calculations of thermodynamic potential across the studied range of pressure and temperature indicate minimal variation (~0.1 V; see Figures S5 and S6) for both CO₂RR and OER. Considering that under high current density, the fast CO₂ consumption rate leads to severe mass transfer limitation, we assume that the cell voltage reductions with increasing pressure are primarily due to decreased mass transfer resistance.

3.2. Effect of Elevated Temperature on CO₂-to-CO Conversion

Increasing the temperature also effectively reduces the overall cell voltage across all CO₂ pressures under a current density range of 0.1 to 2 A cm⁻² (Figure S7), consistent with previous high temperature MEA studies. The AEM shows negligible increase of ionic conductivity by 10 mS cm⁻¹ from 20 to 80 °C at 1 bar,^{30,37,38} corresponding to Ohmic potential drop of around 0.20 V at 1 A cm⁻², much lower than the cell voltage drop by 2.3 V. Considering the minimal thermodynamic potential variations for the pressure and temperature range under investigation (Figures S5 and S6), we posited that the reduction in cell voltage mainly arises from diminished kinetic overpotentials.

Figure 2(a–c) illustrates the trend of FE_{CO} and j_{CO} as temperature increases under different CO₂ pressures (0.1 bar to 10 bar) and different applied cell voltages of 3 V, 3.4 V, and 3.8 V. At ambient CO₂ pressure (1 bar), FE_{CO} and j_{CO} exhibit a distinct temperature-dependent response related to cell voltage. Specifically, at a lower cell voltage of 3 V, FE_{CO} initially increased slightly as temperature rose from 20 to 40 °C before decreasing beyond 60 °C. Conversely, at higher cell voltages (3.4 V and 3.8 V), a progressive decline in FE_{CO} was observed with an increasing of temperature from 20 to 80 °C, with the rate of decrease becoming more pronounced at higher cell voltage. Regarding j_{CO}, at 3 V, a positive correlation with temperature was observed from 20 °C to 80 °C. However, at elevated cell voltages, j_{CO} followed a volcano-shaped trend, peaking at 60 °C for 3.4 V and at 40 °C for 3.8 V, indicating excessive heating suppresses CO production at higher cell voltages.

Temperature influences not only the intrinsic reaction kinetics of CO₂RR but also other



critical parameters, such as CO₂ solubility and diffusion coefficients.³⁹ With increasing temperature, the diffusion coefficient of CO₂ in water rises (Figure S8),⁴⁰ potentially enhancing mass transport. However, CO₂ solubility within the wet catalyst layer decreases (Figure S9), which could limit CO₂ availability at the catalyst surface. The interplay of these factors can be described by the diffusion-limited current density equation:

$$j = nF \frac{D \cdot C}{\delta}$$

Where j is the limiting current density, n is Number of electrons transferred per mole of reactant ($n = 2$ for CO₂ reduction to CO), D is diffusion coefficient of CO₂ in the electrolyte, C is concentration (or solubility) of CO₂, and δ is diffusion layer.

As demonstrated in Figures S8 and S9, increasing the temperature from 20 °C to 80 °C results in a 3-fold decrease in CO₂ solubility while a concurrent ~3-fold increase in its diffusivity. Intuitively, this would suggest a neutral net effect on j_{CO} if only D and C were considered. The decrease of j_{CO} with increasing of temperature is linked to the improved surface wettability. Elevated temperatures also reduce the contact angle of water on the cathode surface, from 137 ° at 20 °C to 122 ° at 80 °C (Figure S10). Enhanced wettability increases the effective diffusion layer (δ), imposes an additional mass transport barrier for CO₂.

At lower cell voltages (e.g., 3.0 V), CO₂ consumption rates are modest, and the available CO₂ concentration remains in excess across the studied temperature range. Under these conditions, mass transport limitations are minimal, and j_{CO} benefits from enhanced intrinsic reaction kinetics as temperature rises under 1 bar CO₂ (Figure 2a). In contrast, at higher cell voltages (e.g., 3.4 V and 3.8 V), CO₂ consumption rates rise substantially, and mass transport limitations become a dominant factor. As temperature increases, the combined effects of reduced CO₂ solubility and increased diffusion layer limit CO₂ flux to catalyst surface. This results in a decline in j_{CO} with increasing temperature under ambient pressure (Figures 2b and 2c).

While δ , D , and CO₂ solubility are all sensitive to temperature, CO₂ solubility is also tunable by pressure. Elevating CO₂ pressure above 1 bar significantly increases solubility, thereby improving CO₂ flux and enabling a linear increase in j_{CO} as temperature rises (Figures 2b-c). This synergy between high pressure and high temperature effectively overcomes the



limitations imposed by mass transport and enhances overall CO₂RR performance. Conversely, reducing the operating pressure below 1 bar shifts the temperature for peak j_{CO} to lower values (Figure 2d), as the system becomes increasingly constrained by limited CO₂ solubility.

The temperature-dependent performance of CO₂ reduction at varying cell voltages is closely linked to the shift in the reaction order of CO₂. As shown in Figure 3a, at 3 V, the reaction order approaches zero from a pressure range of 0.75 bar to 10 bar, indicating sufficient CO₂ availability to drive the reduction process. In contrast, at 3.4 V and 3.8 V, the reaction order increases to 0.15 and 0.3, respectively. At higher cell voltages, increased adsorption free energy of CO₂, as well as the rising surface coverage of adsorbed hydrogen ($\theta_{H_{ad}}$), which introduces repulsive effects on the adsorbed carboxyl intermediate ($\theta_{COOH_{ad}}$), improve the reliance on CO₂ availability.^{41,42}

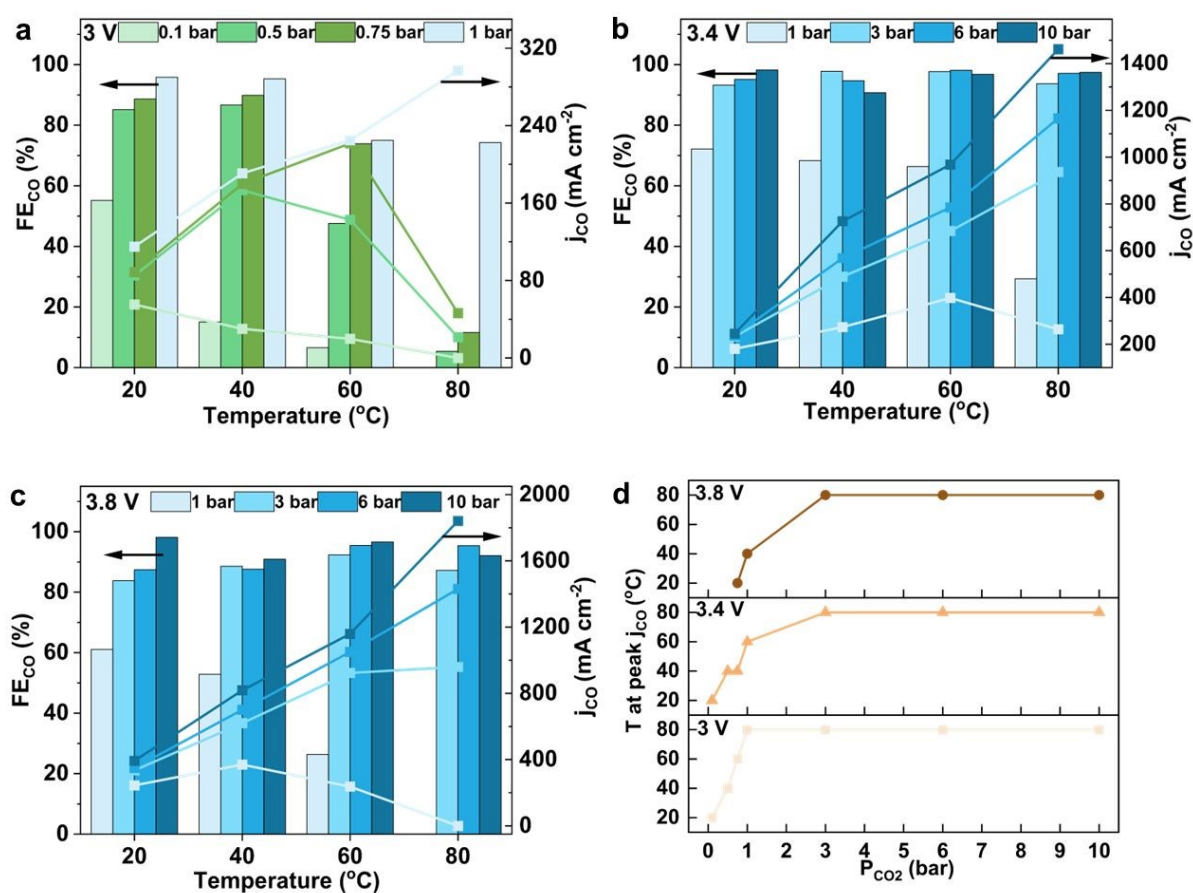


Figure 2. Effect of reaction temperature on the CO₂RR performance. (a-c) FE_{CO} and j_{CO} as a function of temperature at various CO₂ pressures for applied cell voltages of (a) 3 V, (b) 3.4 V, and (c) 3.8 V, (d) Temperature for peak j_{CO} as a function of CO₂ pressure under different cell voltages. For diluted CO₂RR (0.1 bar to 0.75 bar) in (a), a CO₂/N₂ gas mixture was fed with a



total mass flow rate of 250 sccm. For CO₂RR under 1 bar and above in (b-c), dry pure CO₂ gas was supplied to the cathode at a flow rate of 250 sccm.

To elucidate the temperature dependence of product selectivity in CO₂RR, the j_{CO} and j_{H_2} were analyzed as a function of reciprocal temperature. Here we define the electrochemical driving energy (E_d) using the following relationship:⁴³

$$\ln(j) = -\frac{E_d}{R} \left(\frac{1}{T} \right) + \ln(A) \quad (1)$$

$$E_d = E_a - \alpha F \eta \quad (2)$$

where E_a is the activation energy, A is the pre-exponential factor, α is charge transfer coefficient, η is the overpotential. As illustrated in Figure 3(b,c), Ag exhibits a notably lower E_d for CO formation (17.97 kJ mol⁻¹) compared to that for H₂ (49.38 kJ mol⁻¹) at 3 V under 1 bar, underscoring the inherent capability of Ag to suppress the HER in favor of CO production under CO₂RR conditions. In addition, this difference of E_d suggests that HER is significantly more sensitive to temperature variations than CO formation, benefiting more from elevated temperatures. As a result, at a CO₂ pressure of 1 bar, while the temperature dependence of j_{CO} varies with applied cell voltages, j_{H_2} consistently increases with temperature across all cell voltages (Figure S11). As expected, both E_d values for CO₂-to-CO conversion and HER exhibit a decreasing trend with increasing cell voltage. Meanwhile, as the pressure further increased to 10 bar, we found a rising trend of E_d of CO₂RR while decreasing trend of E_d of HER (Figure S12), which might be related to the change of α under different pressures.

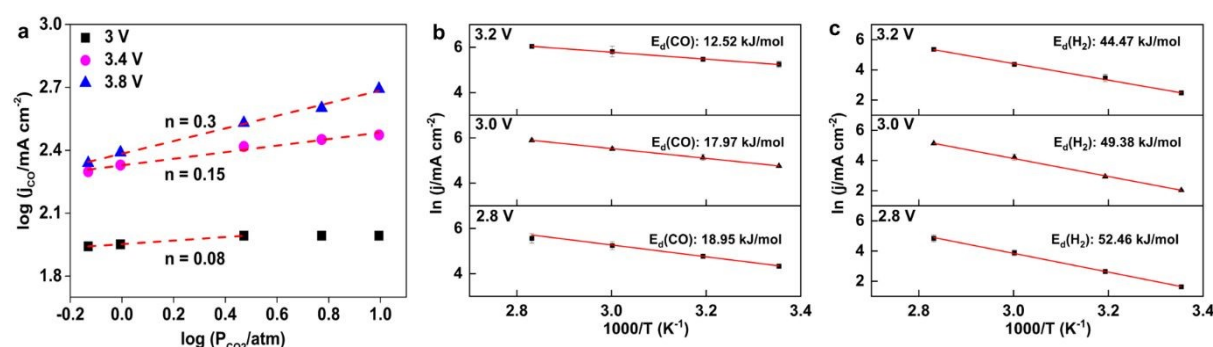


Figure 3. (a) Reaction order for CO₂ derived from the logarithmic dependence of j_{CO} on CO₂ pressure at various applied cell voltages (3 V, 3.4 V, and 3.8 V) from a pressure range of 0.75 bar to 10 bar. (b) E_d for CO₂RR to CO at 2.8 V, 3 V, 3.2 V at 1 bar. (c) E_d for HER at 2.8 V, 3



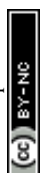
V, 3.2 V at 1 bar. The error bars represent the standard deviations of three independent measurements.

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3.3. Synergy of pressure and temperature effects

Temperature and pressure were found to have synergistic effects on CO₂RR performance. The CO₂ availability plays a crucial role in modulating the temperature effect on CO₂RR performance, including the FE_{CO} and j_{CO}. Under a constant current density for CO₂RR, at a pressure of 1 bar, increasing the temperature from 20 to 40 °C slightly enhances the FE_{CO} ranging from 100 to 1000 mA cm⁻² (Figure S13). Specifically, at 500 mA cm⁻², increasing the temperature from 20 to 40 °C leads to the FE_{CO} increase from 48% to 64%. However, further increasing the temperature did not result in substantial improvements in FE_{CO}, with only a 10% variation (60 °C > 80 °C > 40 °C) in FE_{CO} observed. In contrast, at pressures exceeding 3 bar, the FE_{CO} shows a gradual increase with rising temperatures from 20 to 80 °C, signaling that the impact of temperature on FE_{CO} under constant current density is more evident at higher pressures, particularly under high current densities. This trend underscores the critical interplay between pressure and temperature in enhancing FE_{CO} under constant current density. At higher pressures, the increased CO₂ concentration around the catalyst layer counteracts the solubility limitation imposed by elevated temperatures, overcoming mass transfer limitations of reactants to sustain high reaction rates of CO₂RR. Remarkably, as illustrated in Figure 1d, at 80 °C, the FE_{CO} increases from 19% at 1 bar to nearly 100% at 10 bar under a current density of 1 A cm⁻², further maintaining a high FE_{CO} close to 95% from 1 A cm⁻² to 2 A cm⁻².

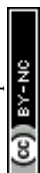
Under constant cell voltage conditions for CO₂RR, the intrinsic temperature-dependent increase in reaction rates drives simultaneous rises in j_{CO} and j_{H₂} at lower cell voltages where CO₂ availability remains sufficient to sustain CO₂RR despite diminished solubility at elevated temperatures (e.g., 80 °C) even under ambient pressure, demonstrating the positive kinetic effects of temperature. However, at higher cell voltages, where CO₂ reliance and mass transfer limitations increases, the reduced CO₂ solubility at elevated temperatures results in a decline in j_{CO}. Increasing CO₂ availability through elevated CO₂ pressure mitigates these limitations and allows for the full utilization of the temperature-dependent enhancement of j_{CO}. As shown in Figure 2(c), at an applied cell voltage of 3.8 V and a pressure of 3 bar, j_{CO} increases steadily



with temperature up to 60 °C, although the rate of improvement diminishes at 80 °C. However, as long as the CO₂ pressure is sufficiently high (above 6 bar), the positive temperature effects on j_{CO} still consistently outweigh the adverse impact of reduced CO₂ solubility, enabling sustained increases in j_{CO} with temperature. Additionally, we observed that elevated pressure effectively constrains the increase in j_{H_2} with temperature (Figure S11), further underscoring the efficacy of high-pressure operations at high temperatures to constrain HER.

To further validate the critical role of CO₂ availability in shaping the temperature dependence of CO₂RR performance, we explored CO₂RR performance under diluted CO₂ conditions at varying temperatures. CO₂ was mixed with N₂ to get controlled concentrations of 10 vol%, 50 vol%, and 75 vol% (with a total flow rate of 250 sccm). As shown in Figure 2a, at 3 V, both FE_{CO} and j_{CO} declined sharply with increasing temperatures under extremely low CO₂ partial pressure (0.1 bar), where the positive kinetic effect of temperature on CO₂RR is entirely offset by reduced CO₂ solubility. In contrast, when CO₂ pressure exceeded 0.5 bar, FE_{CO} shows a slight increase from 20 to 40 °C before declining significantly above 60 °C. Interestingly, with increasing CO₂ pressure, the peak temperature for j_{CO} gradually shifted to a higher position: 20 °C, 40 °C, 60 °C, and 80 °C for 0.1 bar, 0.5 bar, 0.75 bar, and 1 bar, respectively (Figure 2d). It highlights that the temperature effect on j_{CO} is highly reliable on CO₂ pressure: as CO₂ partial pressure increases, CO₂RR could benefit more from temperature elevation. In addition, we investigated the effect of CO₂ supply rate on CO₂RR performance by varying flow rates (10-250 sccm) under pure CO₂ conditions. The nearly constant FE_{CO} across all flow rates at 20-80 °C suggests that reduced performance at low CO₂ partial pressure is due to decreased CO₂ concentration rather than the absolute CO₂ supply (Figure S14).

Although previous studies have explored the individual effects of elevated pressure and temperature on Ag-based catalysts for CO₂ reduction to CO, comprehensive investigations that systematically examine the combined influence of temperature, pressure, and cell voltage within MEA systems remain limited. In contrast, our study presents a holistic optimization strategy, integrating temperature, pressure, and cell voltage control within an MEA system. Notably, we demonstrate a remarkable j_{CO} of 1,840 mA cm⁻² with a FE_{CO} of 92% at 10 bar and 80 °C. To the best of our knowledge, this represents one of the highest performances reported for CO₂RR to CO under industrially relevant conditions in an MEA configuration. This



performance significantly surpasses previous reports that explored either elevated temperature or pressure independently (Figure S16).

Furthermore, while earlier studies have investigated pressurization in MEA cells, they typically applied pressure solely to the cathode compartment. Such asymmetric pressurization can result in significant pressure differentials across the membrane, leading to gas crossover, increased membrane degradation, and ultimately compromised system stability and performance. Our study, by contrast, adopts a balanced pressure strategy, applying equalized pressures to both the anode and cathode compartments. This approach mitigates pressure-driven membrane stress, eliminates crossover issues, and enables stable operation at high pressures, thereby advancing MEA durability and practical scalability.

To evaluate long-term operational stability, the pressurized CO₂ electrolyzer employing an Ag-based cathode was tested at 40 °C and 10 bar for over 100 hours at a constant current density of 300 mA cm⁻². During earlier experiments, we found that the 20 μm AEM was prone to mechanical failure under combined high-temperature (> 60 °C) and high-pressure (> 6 bar) conditions. To address this, a thicker 40 μm AEM was employed for the stability test. While this modification improved mechanical robustness, it also led to higher cell voltages due to increased ohmic resistance.

As shown in Figure 4, the FE_{CO} remained above 95% for the first 83 hours, indicating highly stable performance. Beyond this point, a gradual decline in FE_{CO} was observed. Notably, this drop in selectivity was not accompanied by a significant increase in HER, and the total FE remained around 85% after 95 hours. We hypothesize that the decline in FE_{CO} arises from increased gas permeability of the membrane. This is supported by the observed 10% reduction in the measured flow rate at the cathode outlet and the presence of gas bubbles on the anode side when the electrochemical reaction was paused. These signs suggest that prolonged exposure to elevated pressure and temperature may compromise membrane integrity. In additional tests conducted at 60 °C and 10 bar, membrane degradation occurred more rapidly, with total FE decreasing from nearly 100 % to 60 % within 30 hours, further highlighting the challenge of maintaining membrane stability under desired temperature and pressure conditions.



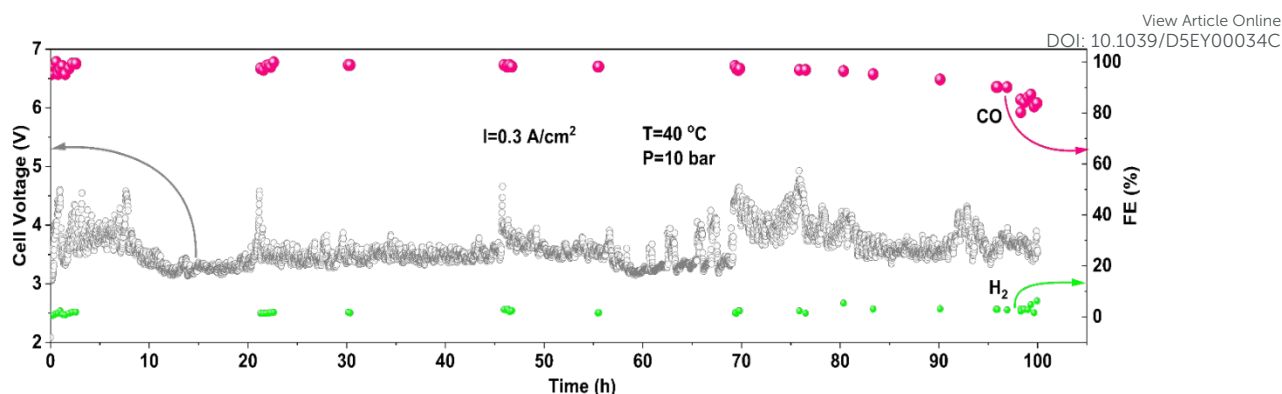
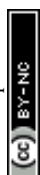


Figure 4. Long-term stability test of the pressurized CO₂ electrolyzer using Ag cathode at 40 °C and 10 bar with a constant current density of 300 mA cm⁻². The cell voltage (left axis, grey) and FE_{CO} (pink) and H₂ (green) (right axis) are shown over 100 hours of continuous operation. A 40 μm AEM was employed.

3.4. Pure-Water-fed electrolysis under high pressure and temperature

To reduce the cell voltage, we explored the use of 1 M KOH as the anolyte. Alkaline electrolytes like 1 M KOH offer reduced ohmic losses compared to 0.1 M KHCO₃ due to their higher conductivity. As shown in Figure 5a, substituting 1 M KOH for 0.1 M KHCO₃ did not affect the FE_{CO}, which still reached 90% at 2 A cm⁻² under 10 bar and 80 °C. Importantly, the cell voltage was further reduced to 3.2 V for 2 A cm⁻² (Figure S17).

During experimentation, however, we observed that using 1 M KOH under 10 bar and 20 °C led to blockage of cathode flow field due to salt precipitation within five minutes, causing the CO₂ inlet pressure rising over 1.4 bar. This effect is likely due to the increased CO₂ concentration, which enhances the reaction between CO₂ and cathodically generated OH⁻, resulting in intense salt formation. The resulting salt precipitation obstructs the flow field and GDE, limiting CO₂ mass transfer. Interestingly, when operating at an elevated temperature of 80 °C under the same 10 bar pressure, salt precipitation is significantly mitigated. Blockage only occurred after two hours of continuous operation, as indicated by a similar rise in CO₂ inlet pressure beyond 1.4 bar. While some studies suggest that K₂CO₃ is the dominant salt precipitating at the cathode and that CO₂ crossover occurs primarily via carbonate ions rather than bicarbonate,^{23,44,45} others observed the exclusive formation of KHCO₃ at the cathode which have lower solubility than K₂CO₃.⁴⁶ Regardless of the specific salt species, elevated



temperatures effectively increase the solubility of both KHCO_3 and K_2CO_3 (Figure S18 and S19), thereby reducing the extent of salt buildup and mitigating flow field obstruction.

Although elevated temperatures can mitigate salt accumulation, eventual blockage remains inevitable due to the crossover of K^+ ions, resulting in system instability over time.⁴⁷ Several strategies have been explored to address this issue. Acidic electrolytes, for example, allow bulk protons to react with carbonate, regenerating CO_2 locally. However, acidic media require high concentrations of alkali metal cations to suppress HER in the proton-rich environment.⁴⁸⁻⁵¹ Their continuous accumulation in the Helmholtz layer can eventually cause alkali metal salt crystallization on the catalyst and GDL.⁵² Bipolar membrane (BPM) systems present an alternative strategy by creating an acidic cathode environment that eliminates carbonate formation. These systems regenerate CO_2 through the reaction of carbonate or bicarbonate with protons, effectively addressing salt precipitation.^{53,54} However, the acidic cathode environment promotes HER, thus reducing CO_2RR selectivity, while BPM systems suffer from intrinsic drawbacks, including high resistance and long-term instability.

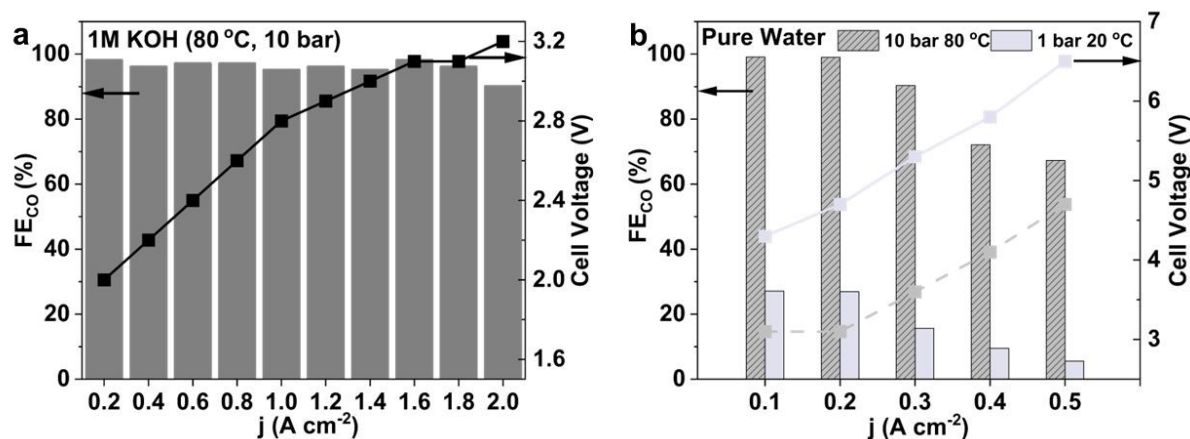


Figure 5. (a) FE_{CO} and cell voltage as a function of current density for CO_2RR in 1 M KOH anolyte at 80 °C and 10 bar. (b) Comparison of FE_{CO} and cell voltage at varying current densities for pure-water-fed CO_2RR at 10 bar and 80 °C versus ambient conditions (1 bar, 20 °C).

We employed a pure water feed (deionized water, 17.8 MΩ cm) at the anode of the AEM-based MEA cell. No anion exchange ionomer was incorporated into the cathodic catalyst layer. However, the PiperION AEM used in this study is functionalized with highly stable



piperidinium cations, which are embedded within a rigid, hydrophobic, ether-bond-free aryl backbone⁵⁵. Recent studies suggest that organic cations, such as tetraalkylammonium species, could efficiently catalyze CO₂RR by modulating the interfacial electric field, facilitating the activation of CO₂ and stabilizes the transition state, improving both the rate and selectivity of CO₂RR⁵⁶. Similarly, the piperidinium cations in the PiperION AEM are proposed to enhance CO₂RR performance via a comparable mechanism, despite the absence of alkali metal cations in the cathode compartment.

Under ambient conditions, HER was the dominant reaction. FE_{CO} was below 30% at 100 mA cm⁻², further dropping to less than 10% at 500 mA cm⁻² (Figure 5b). In stark contrast, under 10 bar and 80 °C, FE_{CO} reached nearly 100% at 100 mA cm⁻² and 200 mA cm⁻², with a slight reduction to 90% at 300 mA cm⁻². In addition, the cell voltage decreased dramatically under high-pressure and high-temperature conditions. For example, at 300 mA cm⁻², the cell voltage dropped from 5.3 V at ambient conditions to 3.6 V under 10 bar and 80 °C.

Compared to previous MEA studies employing pure water feeds to anode, our system exhibits comparatively lower performance^{21,30}. Notably, Zhuang et al³⁰. reported an impressive FE_{CO} exceeding 85% at 60 °C and 1 bar, achieving current densities as high as 500 mA cm⁻². Our system achieved 65% FE_{CO} at 500 mA cm⁻² at 10 bar and 80 °C. This performance difference likely arises from variations in membrane composition and the use of ionomers with smaller organic cations, known to strengthen interfacial electric fields and enhance CO₂ activation kinetics⁵⁷. Nevertheless, our findings uniquely highlight that increasing CO₂ pressure markedly improves CO₂RR efficiency beyond ambient limitations, thus presenting a promising strategy for optimizing electrochemical CO₂ conversion under H₂O feedstock.

3.5. CO₂RR using dilute CO₂ feedstock

Currently, CO₂ capture and reduction are typically conducted as separate processes, with the purification of CO₂ from flue gas contributing substantially to the overall cost of CO₂ electrolysis system.⁵⁸ Industrial CO₂ capture technologies, such as those using monoethanolamine (MEOA), are estimated to cost at least \$44 per ton of CO₂ captured.⁵⁹ Direct utilization of low-concentration CO₂ (10 vol% balanced by N₂), similar to real flue gas compositions,⁶⁰ as a feedstock for CO₂RR could drastically lower costs and enhance the overall



efficiency of the process.^{61,62} However, the low volume fraction of CO₂ in such streams limits the electroreduction process and exacerbates the HER, particularly at high current densities where CO₂ consumption increases rapidly.^{63,64}

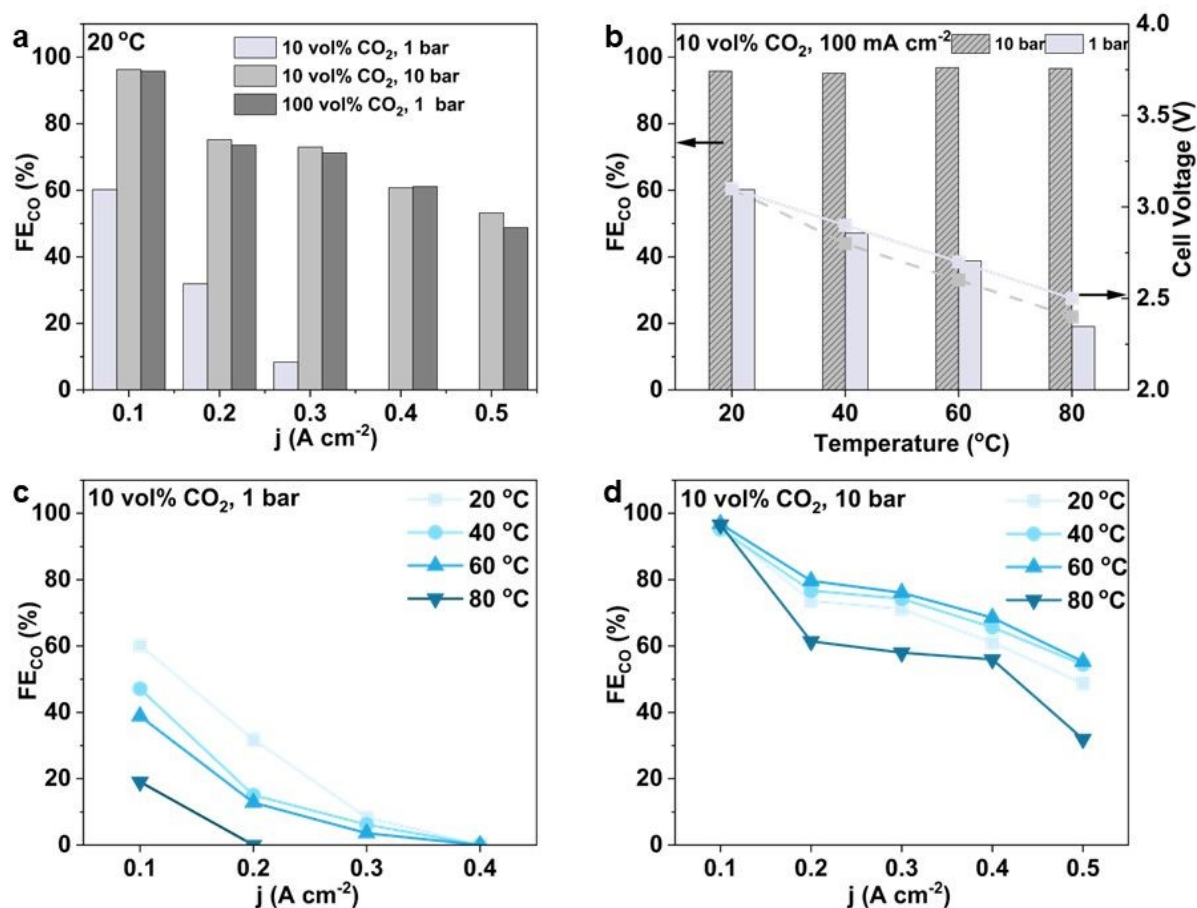


Figure 6. (a) FE_{CO} as a function of current density under different CO₂ concentrations (10 vol% and 100 vol%) and reaction pressures (1 bar and 10 bar) at 20 °C. (b) FE_{CO} and cell voltage as functions of temperature for CO₂RR at 100 mA cm⁻² for 10 vol% CO₂ and reaction pressure of 1 bar and 10 bar. (c-d) FE_{CO} at different temperatures (20 °C, 40 °C, 60 °C, and 80 °C) for 10 vol% CO₂ and reaction pressure of (c) 1 bar and (d) 10 bar.

We establish that our pressurized MEA configuration could significantly enhance the conversion of dilute CO₂ feedstocks. Electrolysis experiments were conducted using gas feeds where CO₂ was diluted with N₂, with pressurization employed to elevate the partial pressure of CO₂. Using a dilute CO₂ feed (10 vol%) at 1 bar resulted in consistently low FE_{CO} across 100-500 mA cm⁻², with nearly zero FE_{CO} beyond 400 mA⁻² (Figure 6a). However, when 10 vol% CO₂ feed was pressurized to 10 bar, there was a notable enhancement in FE_{CO}, similar to that



of pure CO₂ feeds, demonstrating that elevated pressure effectively increases CO₂ availability at the catalyst surface and overcomes the mass transfer limitations under diluted CO₂RR. Notably, pressurized (10 bar) CO₂RR with 10 vol% CO₂ demonstrated performance comparable to, or slightly exceeding, that of 1 bar CO₂RR with 100% CO₂ (Figure 6a).

Additionally, we observed that for the 10 vol% CO₂RR at 1 bar, elevated temperatures adversely affected FE_{CO} (Figure 6b-c). However, for the 10 vol% CO₂RR at 10 bar, increasing temperature had minimal effect on FE_{CO} at a current density of 100 mA cm⁻², while dramatically reducing the cell voltage by 0.7 V from 20 to 80 °C (Figure 6b and Figure S20). At higher current densities (200-500 mA cm⁻²), an operational temperature of 60 °C yielded the maximum FE_{CO}. Further increasing the temperature to 80 °C resulted in the decline of performance, as the decreased CO₂ solubility at this elevated temperature offsets the kinetic benefits gained from temperature increase.

Techno-economic analysis (see Supplementary Notes) reveals that operating under elevated pressure introduces only a modest increase in dedicated capital and operating costs. In contrast, the enhanced reaction rate at higher current densities substantially reduces the required electrolyzer area, resulting in a net reduction in system-scale cost. For pure CO₂ feedstock, this corresponds to a ~90% reduction in electrolyzer capital cost compared to operation under ambient conditions. Furthermore, for low-purity feedstocks (e.g., 10% CO₂ in simulated flue gas), the cost of direct pressurization to 10 bar is estimated at US\$23 per ton CO₂ equivalent, which is nearly 80% lower than the cost of conventional CO₂ capture technologies (~US\$100 per ton CO₂)⁶⁵.

4. Conclusion

In summary, this study demonstrates that the combined effects of elevated temperature and pressure significantly enhance CO₂ electrolysis to CO at industrially relevant current densities in a MEA electrolyzer employing commercial Ag nanoparticles. Pressurized CO₂ not only increases the CO₂ concentration at the catalyst surface, thereby suppressing the competing HER at ambient temperatures, but also sustaining high CO₂ reduction rates at elevated



temperatures by counteracting the reduced CO₂ solubility caused by rising temperatures. This unique synergy of high temperature and pressure boosts CO current density to 2 A cm⁻² with exceptional FE_{CO} (> 90%) under 80 °C and 10 bar. This is because increased thermal energy accelerates reaction kinetics while sufficient CO₂ availability by high pressure mitigates mass transport limitations. Meanwhile, elevated temperature and pressure effectively lowers the cell voltage by reducing the mass transfer and kinetic overpotentials. Additionally, the pressurized MEA cell exhibits stable CO production, achieving FE_{CO} > 90% at 300 mA cm⁻² and a cell voltage of 3.6 V under 80 °C and 10 bar, even using pure water as the anolyte. Moreover, under dilute CO₂ feed conditions (10 vol% CO₂), the system achieves an FE_{CO} of 96% at 100 mA cm⁻², under 10 bar and ambient temperature. Increasing the temperature to 80 °C maintains the FE_{CO} while dramatically reducing the cell voltage by 0.7 V. Given that the operational conditions of commercial CO₂ electroreduction systems are expected to function at elevated temperatures and pressures, these findings present a scalable pathway for CO₂ electrolyzers to meet the demands of industrial applications.

ASSOCIATED CONTENT

Supporting Information

Additional information of schematic of setup; calculated thermodynamic potential; temperature effect on diffusivity of CO₂ in water, solubility of CO₂, K₂CO₃ and KHCO₃, and electrochemical results.

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Author Contributions

J.W. conceptualized and led the project, supervised the research activities, and provided critical revisions to the manuscript. Y.L. performed the experiments, analyzed the data, and drafted the manuscript. H.L. and R.J. contributed to the construction of the experimental setup. P.M. helped characterization.

Notes

The authors declare no competing financial interest.

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References:

- (1) Rode, A.; Carleton, T.; Delgado, M.; Greenstone, M.; Houser, T.; Hsiang, S.; Hultgren, A.; Jina, A.; Kopp, R. E.; McCusker, K. E.; Nath, I.; Rising, J.; Yuan, J. Estimating a Social Cost of Carbon for Global Energy Consumption. *Nature* **2021**, *598* (7880), 308–314.
- (2) Tang, B.; Xiao, F. An Overview of Solar-Driven Photoelectrochemical CO₂ Conversion to Chemical Fuels. *ACS Catal.* **2022**, *12* (15), 9023–9057.
- (3) Cheng, Q.; Huang, M.; Xiao, L.; Mou, S.; Zhao, X.; Xie, Y.; Jiang, G.; Jiang, X.; Dong, F. Unraveling the Influence of Oxygen Vacancy Concentration on Electrocatalytic CO₂ Reduction to Formate over Indium Oxide Catalysts. *ACS Catal.* **2023**, *13* (6), 4021–4029.
- (4) Li, P.; Liu, J.; Wang, Y.; Zhang, X.; Hou, Y.; Zhang, Y.; Sun, X.; Kang, X.; Zhu, Q.; Han, B. Manipulation of Oxygen Species on an Antimony-Modified Copper Surface to Tune the Product Selectivity in CO₂ Electroreduction. *J. Am. Chem. Soc.* **2024**, *146* (38), 26525–26533.
- (5) Jin, J.; Wicks, J.; Min, Q.; Li, J.; Hu, Y.; Ma, J.; Wang, Y.; Jiang, Z.; Xu, Y.; Lu, R.; Si, G.; Papangelakis, P.; Shakouri, M.; Xiao, Q.; Ou, P.; Wang, X.; Chen, Z.; Zhang, W.; Yu, K.; Song, J.; Jiang, J.; Qiu, P.; Lou, Y.; Wu, D.; Mao, Y.; Ozden, A.; Wang, C.; Xia, B. Y.; Hu, X.; Dravid, V. P.; Yiu, Y. M.; Sham, T. K.; Wang, Z.; Sinton, D.; Mai, L.; Sargent, E. H.; Pang, Y. Constrained C₂ Adsorbate Orientation Enables CO-to-Acetate Electroreduction. *Nature* **2023**, *617* (7962), 724–729.
- (6) Deng, H.; Liu, T.; Zhao, W.; Wang, J.; Zhang, Y.; Zhang, S.; Yang, Y.; Yang, C.; Teng, W.; Chen, Z.; Zheng, G.; Li, F.; Su, Y.; Hui, J.; Wang, Y. Substituent Tuning of Cu Coordination Polymers Enables Carbon-Efficient CO₂ Electroreduction to Multi-Carbon Products. *Nat. Commun.* **2024**, *15* (1), 1–12.
- (7) Verma, S.; Kim, B.; Jhong, H.-R.; Ma, S.; Kenis, P. J. A. A Gross-Margin Model for Defining Technoeconomic Benchmarks in the Electroreduction of CO₂. *ChemSusChem* **2016**, *9* (15), 1972–1979.



- (8) Reyes, A.; Jansonius, R. P.; Mowbray, B. A. W.; Cao, Y.; Wheeler, D. G.; Chau, J.; Dvorak, D. J.; Berlinguette, C. P. Managing Hydration at the Cathode Enables Efficient CO₂ Electrolysis at Commercially Relevant Current Densities. *ACS Energy Lett.* **2020**, *5* (5), 1612–1618. View Article Online
DOI: 10.1039/C5EE00034C
- (9) Kopljär, D.; Inan, A.; Vindayer, P.; Wagner, N.; Klemm, E. Electrochemical Reduction of CO₂ to Formate at High Current Density Using Gas Diffusion Electrodes. *J. Appl. Electrochem.* **2014**, *44* (10), 1107–1116.
- (10) Ma, S.; Sadakiyo, M.; Luo, R.; Heima, M.; Yamauchi, M.; Kenis, P. J. One-Step Electrosynthesis of Ethylene and Ethanol from CO₂ in an Alkaline Electrolyzer. *J. Power Sources* **2015**, *301*, 219–228.
- (11) Rabiee, H.; Ge, L.; Zhang, X.; Hu, S.; Li, M.; Yuan, Z. Gas Diffusion Electrodes (GDEs) for Electrochemical Reduction of Carbon Dioxide, Carbon Monoxide, and Dinitrogen to Value-Added Products: A Review. *Energy Environ. Sci.* **2021**, *14* (4), 1959–2008.
- (12) Lees, E. W.; Mowbray, B. A. W.; Parlange, F. G. L.; Berlinguette, C. P. Gas Diffusion Electrodes and Membranes for CO₂ Reduction Electrolysers. *Nat. Rev. Mater.* **2021**, *7* (1), 55–64.
- (13) Wakerley, D.; Lamaison, S.; Wicks, J.; Clemens, A.; Feaster, J.; Corral, D.; Jaffer, S. A.; Sarkar, A.; Fontecave, M.; Duoss, E. B.; Baker, S.; Sargent, E. H.; Jaramillo, T. F.; Hahn, C. Gas Diffusion Electrodes, Reactor Designs, and Key Metrics of Low-Temperature CO₂ Electrolysers. *Nat. Energy* **2022**, *7* (2), 130–143.
- (14) Salvatore, D. A.; Gabardo, C. M.; Reyes, A.; O'Brien, C. P.; Holdcroft, S.; Pintauro, P.; Bahar, B.; Hickner, M.; Bae, C.; Sinton, D.; Sargent, E. H.; Berlinguette, C. P. Designing Anion Exchange Membranes for CO₂ Electrolysers. *Nat. Energy* **2021**, *6* (4), 339–348.
- (15) Xing, Z.; Hu, L.; Ripatti, D. S.; Feng, X. Enhancing Carbon Dioxide Gas-Diffusion Electrolysis by Creating a Hydrophobic Catalyst Microenvironment. *Nat. Commun.* **2021**, *12* (1), 136.
- (16) Weng, L.; Bell, A. T.; Weber, A. Z. Modeling Gas-Diffusion Electrodes for CO₂ Reduction. *Phys. Chem. Chem. Phys.* **2018**, *20* (25), 16973–16984.
- (17) Burdyny, T.; Smith, W. A. CO₂ Reduction on Gas-Diffusion Electrodes and Why Catalytic Performance Must Be Assessed at Commercially Relevant Conditions. *Energy Environ. Sci.* **2019**, *12* (5), 1442–1453.
- (18) Xing, Z.; Hu, X.; Feng, X. Tuning the Microenvironment in Gas-Diffusion Electrodes Enables High-Rate CO₂ Electrolysis to Formate. *ACS Energy Lett.* **2021**, *6* (5), 1694–1702.
- (19) Sun, Y.; Chen, J.; Du, X.; Cui, J.; Chen, X.; Wu, C.; Yang, X.; Liu, L.; Ye, J. Anchoring Cs⁺ Ions on Carbon Vacancies for Selective CO₂ Electroreduction to CO at High Current Densities in Membrane Electrode Assembly Electrolyzers. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202410802.
- (20) Lim, C.; Kim, S.; Song, J. H.; Han, M. H.; Ko, Y.; Lee, K.; Choi, J.; Lee, W. H.; Oh, H. Breaking the Current Limitation of Electrochemical CO₂ Reduction via a Silica-Hydroxide Cycle. *Energy Environ. Sci.* **2024**, *17* (17), 6215–6224.
- (21) Heßelmann, M.; Lee, J. K.; Chae, S.; Tricker, A.; Keller, R. G.; Wessling, M.; Su, J.; Kushner, D.; Weber, A. Z.; Peng, X. Pure-Water-Fed Forward-Bias Bipolar Membrane CO₂ Electrolyzer. *ACS Appl. Mater. Interfaces* **2024**, *16* (19), 24649–24659.
- (22) Park, J.; Kim, E.; Kim, S.; Lim, C.; Kim, H.; Ko, Y.; Choi, J.; Oh, H.; Lee, W. H. Deriving



- an Efficient and Stable Microenvironment for a CO₂ MEA Electrolyzer by Reverse Osmosis. *ACS Energy Lett.* **2024**, *9* (7), 3342–3350.
- (23) Endrödi, B.; Kecsenvity, E.; Samu, A.; Darvas, F.; Jones, R. V.; Török, V.; Danyi, A.; Janáky, C. Multilayer Electrolyzer Stack Converts Carbon Dioxide to Gas Products at High Pressure with High Efficiency. *ACS Energy Lett.* **2019**, *4* (7), 1770–1777.
- (24) Yang, B.; Liu, K.; Li, H. J. W.; Liu, C.; Fu, J.; Li, H.; Huang, E. J.; Ou, P.; Alkayyali, T.; Cai, C.; Duan, Y.; Liu, H.; An, P.; Zhang, N.; Li, W.; Qiu, X.; Jia, C.; Hu, J.; Chai, L.; Lin, Z.; Gao, Y.; Miyauchi, M.; Cortés, E.; Maier, S. A.; Liu, M. Accelerating CO₂ Electroreduction to Multicarbon Products via Synergistic Electric-Thermal Field on Copper Nanoneedles. *J. Am. Chem. Soc.* **2024**, *144* (7), 3039–3049.
- (25) 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* (23), 6883–6887.
- (26) Küngas, R. Review—Electrochemical CO₂ Reduction for CO Production: Comparison of Low- and High-Temperature Electrolysis Technologies. *J. Electrochem. Soc.* **2020**, *167* (4), 044508.
- (27) Aaron, D.; Tsouris, C. Separation of CO₂ from Flue Gas: A Review. *Sep. Sci. Technol.* **2005**, *40* (1–3), 321–348.
- (28) Piontek, S.; Andronescu, C.; Zaichenko, A.; Konkana, B.; Puring, K. J.; Marler, B.; Antoni, H.; Sinev, I.; Muhler, M.; Mollenhauer, D.; Cuenya, B. R.; Schuhmann, W.; Apfel, U. Influence of the Fe:Ni Ratio and Reaction Temperature on the Efficiency of (Fe_xNi_{1-x})₉S₈ Electrocatalysts Applied in the Hydrogen Evolution Reaction. *ACS Catal.* **2017**, *8* (2), 987–996.
- (29) Dufek, E. J.; Lister, T. E.; McIlwain, M. E. Bench-Scale Electrochemical System for Generation of CO and Syn-Gas. *J. Appl. Electrochem.* **2011**, *41* (6), 623–631.
- (30) 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* (8), 2455–2462.
- (31) Li, K.; Zou, S.; Zhang, J.; Huang, Y.; He, L.; Feng, X. Superhydrophobicity-Enabled Efficient Electrocatalytic CO₂ Reduction at High Temperature. *ACS Catal.* **2023**, *13* (14), 9346–9351.
- (32) Boot-Handford, M. E.; Abanades, J. C.; Anthony, E. J.; Blunt, M. J.; Brandani, S.; Mac Dowell, N.; Fernández, J. R.; Ferrari, M.; Gross, R.; Hallett, J. P.; Haszeldine, R. S.; Heptonstall, P.; Lyngfelt, A.; Makuch, Z.; Mangano, E.; Porter, R. T. J.; Pourkashanian, M.; Rochelle, G. T.; Shah, N.; Fennell, P. S. Carbon Capture and Storage Update. *Energy Environ. Sci.* **2013**, *7* (1), 130–189.
- (33) Corral, D.; Feaster, J. T.; Sobhani, S.; DeOtte, J. R.; Lee, D. U.; Wong, A. A.; Hamilton, J.; Beck, V. A.; Sarkar, A.; Hahn, C.; Jaramillo, T. F.; Baker, S. E.; Duoss, E. B. Advanced Manufacturing for Electrosynthesis of Fuels and Chemicals from CO₂. *Energy Environ. Sci.* **2021**, *14* (5), 3064–3074.
- (34) Simonson, H.; Klein, W. E.; Henckel, D.; Verma, S.; Neyerlin, K. C.; Smith, W. A. Direct Measurement of Electrochemical Selectivity Gradients over a 25 cm² Copper Gas Diffusion Electrode. *ACS Energy Lett.* **2023**, *8* (9), 3811–3819.
- (35) Li, J.; Wang, Z.; McCallum, C.; Xu, Y.; Li, F.; Wang, Y.; Gabardo, C. M.; Dinh, C. T.;



- Zhuang, T.-T.; Wang, L.; Howe, J. Y.; Ren, Y.; Sargent, E. H.; Sinton, D. Constraining CO Coverage on Copper Promotes High-Efficiency Ethylene Electroproduction. *Nat. Catal.* **2019**, 2 (11), 1124–1131. View Article Online
DOI: 10.1039/C9CY00034C
- (36) Wu, H.; Tian, B.; Xu, W.; Abdalla, K. K.; Kuang, Y.; Li, J.; Sun, X. Pressure-Dependent CO₂ Electroreduction to Methane over Asymmetric Cu–N₂ Single-Atom Sites. *J. Am. Chem. Soc.* **2024**, 146 (32), 22266–22275.
- (37) Rodriguez, C. A. G.; Kani, N. C.; Moss, A. B.; Joensen, B. O.; Garg, S.; Deng, W.; Wilson, T.; Varcoe, J. R.; Chorkendorff, I.; Seger, B. Insights into Zero-Gap CO₂ Electrolysis at Elevated Temperatures. *EES Catal.* **2024**, 2 (3), 850–861.
- (38) She, X.; Zhai, L.; Wang, Y.; Xiong, P.; Li, M. M.; Wu, T.; Wong, M. C.; Guo, X.; Xu, Z.; Li, H.; Xu, H.; Zhu, Y.; Tsang, S. C. E.; Lau, S. P. Pure-Water-Fed Electrocatalytic CO₂ Reduction to Ethylene Beyond 1,000 h Stability at 10 A. *Nat. Energy* **2024**, 9 (1), 81–91.
- (39) Vos, R. E.; Smaak, J. P.; Koper, M. T. M. The Temperature Dependence of Electrochemical CO₂ Reduction on Ag and CuAg Alloys. *J. Catal.* **2024**, 436 (1), 115613.
- (40) Löwe, A.; Rieg, C.; Hierlemann, T.; Salas, N.; Kopljar, D.; Wagner, N.; Klemm, E. Influence of Temperature on the Performance of Gas Diffusion Electrodes in the CO₂ Reduction Reaction. *ChemElectroChem* **2019**, 6 (17), 4497–4506.
- (41) Singh, M. R.; Goodpaster, J. D.; Weber, A. Z.; Head-Gordon, M.; Bell, A. T. Mechanistic Insights into Electrochemical Reduction of CO₂ over Ag Using Density Functional Theory and Transport Models. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, 114 (42), E8812–E8821.
- (42) Zhu, X.; Huang, J.; Eikerling, M. Electrochemical CO₂ Reduction at Silver from a Local Perspective. *ACS Catal.* **2021**, 11 (23), 14521–14532.
- (43) Koshy, D. M.; Nathan, S. S.; Asundi, A. S.; Abdellah, A. M.; Dull, S. M.; Cullen, D. A.; Higgins, D.; Bao, Z.; Bent, S. F.; Jaramillo, T. F. Bridging Thermal Catalysis and Electrocatalysis: Catalyzing CO₂ Conversion with Carbon-Based Materials. *Angew. Chem., Int. Ed.* **2021**, 60 (32), 17472–17480.
- (44) Mardle, P.; Cassegrain, S.; Habibzadeh, F.; Shi, Z.; Holdcroft, S. Carbonate Ion Crossover in Zero-Gap, KOH Anolyte CO₂ Electrolysis. *J. Phys. Chem. C* **2021**, 125 (46), 25446–25454.
- (45) Kim, J. Y.; Zhu, P.; Chen, F.; Wu, Z.; Cullen, D. A.; Wang, H. Recovering Carbon Losses in CO₂ Electrolysis Using a Solid Electrolyte Reactor. *Nat. Catal.* **2021**, 5 (4), 288–299.
- (46) Moss, A. B.; Garg, S.; Mirolo, M.; Rodriguez, C. A. G.; Ilvonen, R.; Chorkendorff, I.; Drnec, J.; Seger, B. In Operando Investigations of Oscillatory Water and Carbonate Effects in MEA-Based CO₂ Electrolysis Devices. *Joule* **2023**, 7 (2), 350–365.
- (47) Weng, L.; Bell, A. T.; Weber, A. Z. Towards Membrane-Electrode Assembly Systems for CO₂ Reduction: A Modeling Study. *Energy Environ. Sci.* **2019**, 12 (6), 1950–1968.
- (48) Monteiro, M. C. O.; Dattila, F.; López, N.; Koper, M. T. M. The Role of Cation Acidity on the Competition between Hydrogen Evolution and CO₂ Reduction on Gold Electrodes. *J. Am. Chem. Soc.* **2021**, 144 (4), 1589–1602.
- (49) Huang, J. E.; Li, F.; Ozden, A.; Rasouli, A. S.; De Arquer, F. P. G.; Liu, S.; Zhang, S.; Luo, M.; Wang, X.; Lum, Y.; Xu, Y.; Bertens, K.; Miao, R. K.; Dinh, C.; Sinton, D.; Sargent, E. H. CO₂ Electrolysis to Multicarbon Products in Strong Acid. *Science* **2021**, 372 (6546), 1074–1078.
- (50) Gu, J.; Liu, S.; Ni, W.; Ren, W.; Haussener, S.; Hu, X. Modulating Electric Field



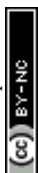
Distribution by Alkali Cations for CO₂ Electroreduction in Strongly Acidic Medium. *Nat. Catal.* **2022**, 5 (4), 268–276. View Article Online
DOI: 10.1039/D1CY00034C

- (51) Hou, J.; Xu, B.; Lu, Q. Influence of Electric Double Layer Rigidity on CO Adsorption and Electroreduction Rate. *Nat. Commun.* **2024**, 15, 1926.
- (52) 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 (2), 809–815.
- (53) Siritanaratkul, B.; Forster, M.; Greenwell, F.; Sharma, P. K.; Yu, E. H.; Cowan, A. J. Zero-GAP Bipolar Membrane Electrolyzer for Carbon Dioxide Reduction Using Acid-Tolerant Molecular Electrocatalysts. *J. Am. Chem. Soc.* **2022**, 144 (17), 7551–7556.
- (54) Yang, K.; Li, M.; Subramanian, S.; Blommaert, M. A.; Smith, W. A.; Burdyny, T. Cation-Driven Increases of CO₂ Utilization in a Bipolar Membrane Electrode Assembly for CO₂ Electrolysis. *ACS Energy Lett.* **2021**, 6 (12), 4291–4298.
- (55) Wang, J.; Zhao, Y.; Setzler, B. P.; Rojas-Carbonell, S.; Yehuda, C. B.; Amel, A.; Page, M.; Wang, L.; Hu, K.; Shi, L.; Gottesfeld, S.; Xu, B.; Yan, Y. Poly(aryl piperidinium) membranes and ionomers for hydroxide exchange membrane fuel cells. *Nat. Energy* **2019**, 4 (5), 392–398.
- (56) Weng, S.; Toh, W. L.; Surendranath, Y. Weakly coordinating organic cations are intrinsically capable of supporting CO₂ reduction catalysis. *J. Am. Chem. Soc.* **2023**, 145 (30), 16787–16795.
- (57) McGregor, J.; Bender, J. T.; Petersen, A. S.; Cañada, L.; Rossmeisl, J.; Brennecke, J. F.; Resasco, J. Organic electrolyte cations promote non-aqueous CO₂ reduction by mediating interfacial electric fields. *Nat. Catal.* **2025**, 8 (1), 79–91.
- (58) Chen, S.; Liu, J.; Zhang, Q.; Teng, F.; McLellan, B. C. A Critical Review on Deployment Planning and Risk Analysis of Carbon Capture, Utilization, and Storage (CCUS) Toward Carbon Neutrality. *Renewable Sustainable Energy Rev.* **2022**, 167, 112537.
- (59) Raksajati, A.; Ho, M. T.; Wiley, D. E. Reducing the Cost of CO₂ Capture from Flue Gases Using Aqueous Chemical Absorption. *Ind. Eng. Chem. Res.* **2013**, 52 (47), 16887–16901.
- (60) Last, G. V.; Schmick, M. T. A Review of Major Non-Power-Related Carbon Dioxide Stream Compositions. *Environ. Earth Sci.* **2015**, 74 (2), 1189–1198.
- (61) Liu, Y.; Huang, J.; Zhu, H.; Liao, P.; Chen, X. Simultaneous Capture of CO₂ Boosting Its Electroreduction in the Micropores of a Metal–Organic Framework. *Angew. Chem., Int. Ed.* **2023**, 62, No. e202311265.
- (62) Wang, Z.; Zhou, Y.; Liu, D.; Qi, R.; Xia, C.; Li, M.; You, B.; Xia, B. Y. Carbon-Confined Indium Oxides for Efficient Carbon Dioxide Reduction in a Solid-State Electrolyte Flow Cell. *Angew. Chem., Int. Ed.* **2022**, 61, No. e202200552.
- (63) Zhao, Z.; Huang, J.; Huang, D.; Zhu, H.; Liao, P.; Chen, X. Efficient Capture and Electroreduction of Dilute CO₂ into Highly Pure and Concentrated Formic Acid Aqueous Solution. *J. Am. Chem. Soc.* **2024**, 146 (20), 14349–14356.
- (64) Kim, D.; Choi, W.; Lee, H. W.; Lee, S. Y.; Choi, Y.; Lee, D. K.; Kim, W.; Na, J.; Lee, U.; Hwang, Y. J.; Won, D. H. Electrocatalytic Reduction of Low Concentrations of CO₂ Gas in a Membrane Electrode Assembly Electrolyzer. *ACS Energy Lett.* **2021**, 6 (10), 3488–3495.
- (65) Service, R. F. Cost of carbon capture drops, but does anyone want it? *Science* **2016**, 354



(6318), 1362–1363.

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DOI: 10.1039/D5EY00034C



Data Availability Statement

All data supporting the findings of this study are included within the article and its supplementary materials. Any additional information related to the data is available upon request from the corresponding author.

