

Electrolysis of Gaseous CO₂ to CO in a Flow Cell with a Bipolar Membrane

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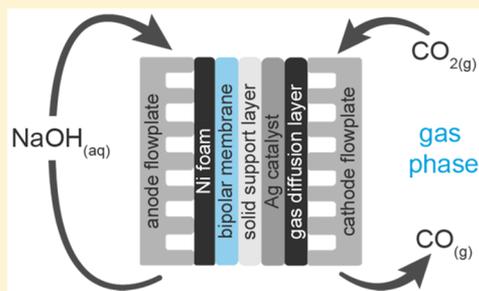
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Supporting Information

ABSTRACT: The conversion of CO₂ to CO is demonstrated in an electrolyzer flow cell containing a bipolar membrane at current densities of 200 mA/cm² with a Faradaic efficiency of 50%. Electrolysis was carried out by delivering gaseous CO₂ at the cathode with a silver catalyst integrated in a carbon-based gas diffusion layer. Nonprecious nickel foam in a strongly alkaline electrolyte (1 M NaOH) was used to mediate the anode reaction. While a configuration where the anode and cathode were separated by only a bipolar membrane was found to be unfavorable for robust CO₂ reduction, a modified configuration with a solid-supported aqueous layer inserted between the silver-based catalyst layer and the bipolar membrane enhanced the cathode selectivity for CO₂ reduction to CO. We report higher current densities (200 mA/cm²) than previously reported for gas-phase CO₂ to CO electrolysis and demonstrate the dependence of long-term stability on adequate hydration of the CO₂ inlet stream.



There exists the potential to use atmospheric CO₂ as a feedstock for the scalable production of carbon monoxide, formate, methanol, ethylene, and longer-chain alkanes.^{1,2} This possibility has drawn a significant effort toward the discovery of electrocatalysts capable of mediating these transformations with high efficiency and selectivity.^{3–7} The economic viability of using renewable electricity to electrolytically convert CO₂ into certain carbon products remains an open question, but there is a potential case for generating CO from CO₂.⁸ The annual global CO production of 210 000 Mt is already significant, and CO serves as an important chemical precursor for a number of industrial processes, including Fischer–Tropsch chemistry that could effectively enable the conversion of sunlight into liquid fuels.^{9,10}

Electrocatalysts capable of converting CO₂ to CO with high selectivity are now known.^{4,10–14} For example, oxide-derived Au electrodes reported by Kanan reach a Faradaic efficiency (FE) of 99% for CO formation at a current density (*J*) of 10 mA/cm².¹⁵ Highly porous silver and copper electrodes reported by Jiao¹⁶ and Mul¹⁷ are also capable of producing CO at these current densities with comparable selectivities. Studies of mixed metal catalysts, such as copper–indium alloys that can produce a CO₂-to-CO FE of ~90% at *J* = 3 mA/cm²,^{7,18} highlight the

possibility of tuning the activity of catalysts by incorporating a secondary metal to yield higher activities. Mediating these reactions in ionic liquids also enables the selective formation of CO at high current densities.^{6,19}

The majority of CO₂ electrolysis studies test catalytic performance at low *J* values (<20 mA/cm²) or use expensive materials (e.g., ionic liquids), yet commercial electrolyzers employ aqueous electrolytes and operate at much higher current densities (>200 mA/cm²).²⁰ The utility of these catalysts therefore needs to be proven out in flow cells (and multiple-cell stacks) in order to be implemented in electrolyzer architectures capable of effective CO₂ reduction at a commercial scale. This line of inquiry has been followed by Masel and co-workers, who reported a flow system based on the ionic-liquid-mediated conversion of CO₂ to CO with a 96% FE for CO at a *J* of ~5 mA/cm².¹⁹ Our previous work utilized a bipolar membrane (BPM) to accommodate the oxygen evolution reaction (OER) in basic media, in order to utilize efficient and earth-abundant transition metal catalysts at the

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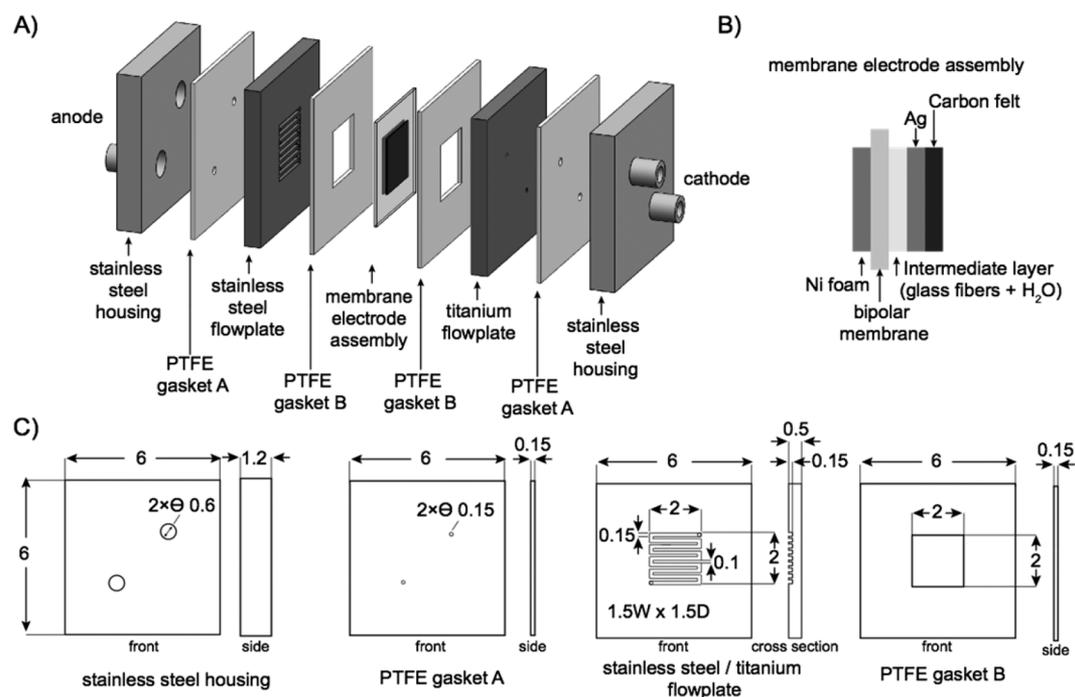


Figure 1. (A) Expanded view of the BPM-based CO₂ electrolyzer cell configuration. (B) Membrane electrode assembly. (C) Dimensions of each component in the electrolyzer cell.

anode while feeding CO₂-saturated NaHCO₃ solution to the cathode. The FE for CO production was stable at ~50% at 30 mA/cm² using this architecture, but the cells showed a diminution in CO evolution efficiencies at progressively higher current densities.²¹ This observation is consistent with other liquid-fed electrolyzers, where the maximum electrocatalytic partial current of CO evolution that has been reached is approximately 30 mA/cm².^{19,22,23}

In order to overcome the inherent diffusion limitations that exist in a low-temperature liquid-fed CO₂ electrolyzer, several groups have modified cells in order to enhance CO₂ availability to reaction sites. Kenis and co-workers introduced a micro-fluidic electrochemical flow reactor, where the liquid electrolyte flows between the cathodic gas diffusion electrode and an anode while a gaseous CO₂ feed flows on the opposing side of the cathode electrode, to reach current densities of 300 mA/cm² for CO production (and 120 mA/cm² for HCOO⁻ production).^{23–25} This chemistry was extended to a three-compartment electrochemical cell configuration capable of producing HCOO⁻ at 140 mA/cm² by Masel and co-workers.²⁶ McIlwain and co-workers used a pressurized electrochemical system to increase the quantity of CO generated by 5-fold (92% FE at 350 mA/cm²) over what was measured at ambient pressures.²⁷

The diffusion limitation in liquid-phase CO₂ electrolyzers originates from the solubility of CO₂ in aqueous electrolyte solutions (~30 mM in H₂O at atmospheric pressure and temperature) as well as a low diffusion coefficient of CO₂ in water (0.0016 mm²/s).²⁸ Gas-phase electrolysis therefore has the potential to increase mass transport and achieve current densities several orders of magnitude greater than liquid-phase electrolysis at atmospheric pressures, yet this strategy has been very rarely used.²¹ There are currently merely two gas-phase CO₂ electrolysis reports to date, one using a proton exchange membrane (PEM) and a second with an anion exchange membrane (AEM). Newman et al. introduced a dual solid

electrolyte configuration consisting of an 800 μm thick glass fiber impregnated with 0.5 M KHCO₃ in between the cathode gas diffusion layer (GDL) and PEM layers.²⁹ The cathode was fed with a humidified stream of CO₂, and the anode was exposed to aqueous solution for the OER chemistry. There was a significant decrease in the FE for CO from 80% at 20 mA/cm² to 20% at 100 mA/cm² with this dual solid electrolyte design. Recently, Masel and co-workers reported a gas-phase system utilizing their specifically designed AEM membranes, achieving high current densities (130 mA/cm²) and 98% FE for CO.³⁰ These membranes incorporate an imidazolium group, similar to the ionic liquid that they reported for high conversion of CO₂ to CO.^{19,30}

We report here a BPM-based gas-phase electrolyzer that converts CO₂ to CO at high current densities of 200 mA/cm². Our CO₂ electrolyzer flow cell was designed around the use of a BPM that dissociates water into H⁺ and OH⁻ under reverse bias (Figure 1). BPMs are more commonly used in electro-dialysis³¹ and solar water splitting^{32,33} but have shown recent use in CO₂ conversion devices.^{21,34,35} We have previously shown that a Nafion-based cell may suffer from stability issues because the anolyte and catholyte can become progressively more acidic and basic, respectively, during electrolysis.²¹ In contrast, the dissociation of water in a BPM drives H⁺ and OH⁻ ions toward the cathode and anode, respectively, enabling the pH of the anode and cathode to remain constant. Using a BPM enables the use of earth-abundant metal anodes that are only stable in basic conditions (e.g., Ni, FeNiO_x)^{36–43} and highly active acid-stable cathodes for CO₂ reduction (e.g., Ag).^{5,44,45} Gas diffusion electrodes also help to overcome the diffusion limitation and to enable more CO₂ to reach the catalyst surface, thereby allowing the cell to operate at higher current densities. A silver catalyst was selected to mediate the cathodic reaction on the basis that it is known to exhibit high selectivity for converting CO₂ to CO.^{5,11,44,45} Nickel anodes were used because of the high stability and activity toward the OER in

basic media.^{36,46} We were able to enhance the FEs and reach current densities for gas-phase CO₂ electrolysis on the order of 200 mA/cm² with a FE for CO production of 50% by incorporating a solid-supported aqueous layer (1.0 M NaHCO₃). We demonstrate an apparent correlation between long-term stability and hydration of the CO₂ inlet stream. We were able to maintain stability for over 24 h at 100 mA/cm² when the solid-state support was adequately hydrated. This result is important for understanding the role of water management in CO₂ electrocatalysis and provides an important guideline for the development of associated electrolyzer technologies.

Cyclic voltammograms over the -1.0 to -3.0 V range were collected for both liquid- and gas-phase flow cell reduction of CO₂ (Figure 2). The cell architectures were the same for both

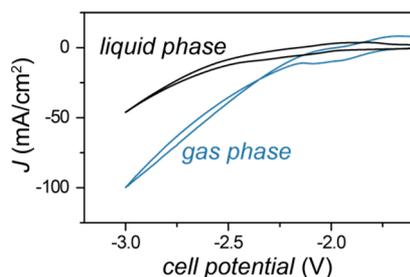


Figure 2. Cyclic voltammograms for gas- and liquid-phase CO₂ electrolyzer cells show higher rates of product formation for gas-fed cathodes. (Scan rate = 100 mV s⁻¹; anode: nickel foam; cathode: silver on carbon GDL; anolyte: 10 mL/min 1 M NaOH; liquid catholyte: 10 mL/min 1 M NaHCO₃; gas catholyte: 100 SCCM humidified CO₂.)

cells (BPM-separated nickel GDL anode and silver-coated carbon GDL cathode), and the anode feed was 1.0 M NaOH. For liquid-phase electrolysis, the cathode feed was CO₂-saturated 0.5 M NaHCO₃; for gas-phase electrolysis, the cathode feed was a humidified gaseous stream of CO₂. Both configurations yielded an increase in *J* with increasing potential (V); however, the gas-fed stream achieves a *J* approximately double that of the liquid-fed system at -3.0 V (100 c.f. 48 mA/cm²). These differences in current densities, while holding all other experimental parameters at parity, provide a clear demonstration of the potential to overcome mass-transport limitations in liquid-fed CO₂ electrolyzer systems by instead using a gas-phase feed.

The physical characteristics of silver-based cathodes before and after gas-phase electrolysis were examined by scanning electron microscopy (SEM), X-ray fluorescence (XRF), and powder X-ray diffraction (XRD) techniques. The cathodes were subjected to 3000 s chronopotentiometric experiments from 20 up to 200 mA/cm² in 20 mA increments, amounting to ~10 h of cumulative electrolysis. The SEM images presented in Figure S1a indicate that the ~100 nm nanoparticles remain unchanged during electrolysis on the basis that there is no apparent loss in surface coverage or change in morphology. XRF analysis of the cathode shows nominal differences in metal loading before and after electrolysis experiments (Figure S1b), and the powder XRD diffractograms show superimposable reflections corresponding to the silver signals indicating no change in the crystalline structure of the catalysts (Figure S1c). These collective results show that the catalytic components of the cell are robust during gas-phase CO₂ electrolysis on the time scale of our experiments.

Gas chromatography (GC) measurements of the expelled gases were used to evaluate the FE values for CO and H₂ production in the gas-phase flow cell system described above. FEs were calculated (as described in the Supporting Information) for *J* values between 20 and 100 mA/cm² after 700 s of electrolysis (Figure 3B). The results show a FE of 25% for CO at low current densities (*J* = 20 mA/cm²) and diminish to below 10% with increasing *J* up to 100 mA/cm². In the only other previous example of gas-phase CO₂ reduction to CO in a flow cell (Newman et al.),²⁹ the authors were able to increase the selectivity for CO by introducing a solid-supported aqueous NaHCO₃ (1.0 M) layer between the BPM and the cathodic electrocatalyst. We were able to reproduce this result by incorporating this layer into our configuration (Figure 3B): A dramatic improvement in CO selectivity was observed for all *J* values (Figure 3B), with moderate FE for CO (67%) retained at *J* = 100 mA/cm². Indeed, we were able to reach higher *J* values (200 mA/cm²) and only witness a minor decrease in FE for CO (50% at 200 mA/cm²) with this configuration. These results demonstrate the ability to perform CO₂ to CO reduction in a flow cell at the high current densities relevant to industrial electrolysis.²⁰

While the inclusion of the solid-supported aqueous electrolyte layer is evidently necessary to achieve high CO selectivity in our flow cell configuration, the exact role of this layer is unclear. We therefore sought to clarify this role by replacing the solid-supported aqueous NaHCO₃ layer with a solid-supported

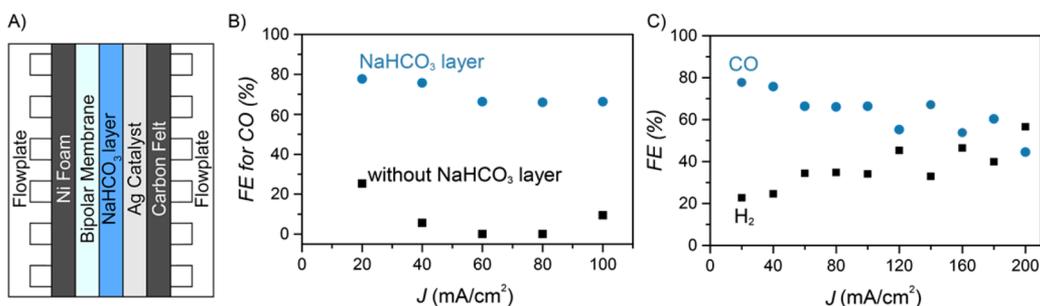


Figure 3. (A) Cross-sectional configuration of the gas-fed CO₂ flow cell showing the location of the solid-supported aqueous NaHCO₃ layer between the BPM and cathode silver catalyst. (B) FE (%) for CO production at current densities between 20 and 100 mA cm⁻² both with (blue) and without (black) the aforementioned NaHCO₃ layer. (C) Faradaic efficiencies for CO₂ to CO and H₂ products measured by GC after 700 s of gas-phase CO₂ electrolysis in a flow cell configuration containing a solid-supported aqueous NaHCO₃ solution. (Anode: nickel foam; cathode: silver on carbon GDL; anolyte: 10 mL/min 1 M NaOH; gas catholyte: 100 SCCM humidified CO₂.)

water layer (i.e., NaHCO_3 was omitted). The FE for CO production in the bicarbonate-free system was comparable (within 15% discrepancy) at all J values up to 200 mA/cm^2 to the system containing NaHCO_3 (Figure 4). This result suggests

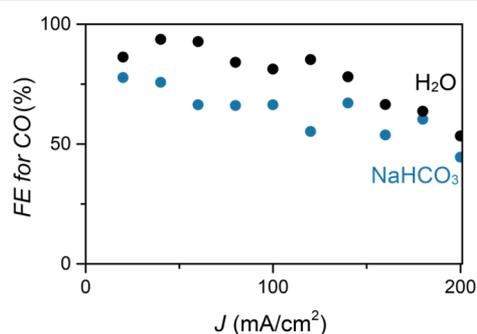


Figure 4. FEs for CO and H_2 production measured by GC after 700 s of gas-phase CO_2 electrolysis in a flow cell configuration containing a solid-supported aqueous NaHCO_3 layer (blue) and a solid-supported water layer (black). (Anode: nickel foam; cathode: silver on C-GDL; anolyte: 10 mL/min 1 M NaOH; gas catholyte: 100 SCCM humidified CO_2 .)

that the water component of the solid support layer is responsible for mediating electrolytic performance, and not NaHCO_3 . The addition of the solid-supported aqueous layer (with or without NaHCO_3) made no significant differences to the voltages required to drive CO_2 reduction chemistry at higher current densities. This point is supported by the data shown in Figure S2 that reveals nominal changes in the measured cell potential for three cases where the support layer is modified (i.e., no support layer, H_2O layer, and NaHCO_3 layer) and held at a constant current of 100 mA/cm^2 . We conclude from these results that there is no apparent voltage or resistance losses arising from the solid support layer.

We then set out to validate the importance of maintaining hydration to the solid support layer by running our cell continuously at 100 mA/cm^2 with a low-humidity CO_2 inlet stream. A 15% relative humidity (RH) for the CO_2 inlet stream can be achieved by bypassing the CO_2 inlet water bath (passing CO_2 through the water bath reaches a RH of 90%). The result of using a low-humidity CO_2 inlet was a rapid decay in cell performance within 2 h, as indicated by the sharp rise in required bias above 4 V (Figure 5A). This decline in performance occurred concomitantly with dehydration of the

aqueous support layer. This result suggests that the physical change of the cathode support layer induced by dehydration precludes facile delivery of the protons to the catalytic sites. Replenishing the support layer with water resulted in full recovery of J and FE for CO production (relative to the initial values) (Figure S3), supporting our hypothesis that adequate hydration of the support layer needs to be preserved in order to maintain prolonged electrolytic stability. Adequate hydration during sustained electrolysis can be achieved by supplying the flow cell with humidified CO_2 on the basis that we measured stable CO_2 to CO electrolysis at 65% FE and 100 mA/cm^2 for >24 h (Figure 5B).

We report here an electrolysis flow cell for the gas-phase reduction of CO_2 to CO at high current densities ($J = 200 \text{ mA/cm}^2$) that provides stable performance for 24 h. Robust performance is contingent on delivering a hydrated gas-phase CO_2 stream to the cathode. This inlet stream produces nearly double the current density than a CO_2 -saturated aqueous solution can produce when all other experimental parameters are held at parity. These differences, which are primarily because of mass transport limitations associated with aqueous CO_2 chemistry that are overcome by working in the gas phase, sets the agenda for our future flow cell designs for CO_2 electrolysis.

We also lay out the critical role that hydration has on the performance of the cathode. It is necessary to include a water support layer (or aqueous NaHCO_3 layer)²⁹ in order to achieve reasonable FEs for CO formation at higher current densities (e.g., 200 mA/cm^2). By maintaining a hydrated CO_2 stream (>90% RH), we are able to maintain hydration of the support layer, and our cell stability was over 24 h at 100 mA/cm^2 . These values represent the highest reported current densities for gas-phase CO_2 -to-CO flow cell electrolysis in a BPM-based cell.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenerylett.7b01017.

Detailed experimental methods; design criteria for an electrolyzer based on a bipolar membrane for the conversion of CO_2 to CO; scanning electron microscopy, X-ray fluorescence and X-ray diffraction images of the Ag cathode; and chronopotentiometric measurements (PDF)

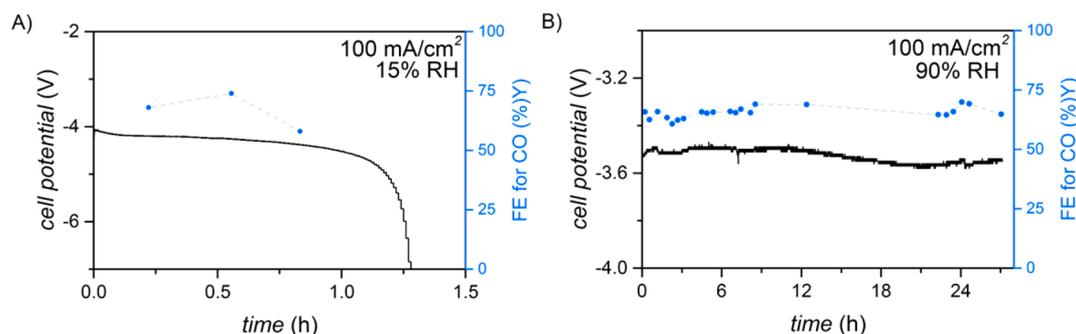


Figure 5. FEs and chronopotentiometry data showing required bias (V) for CO_2 to CO measured by GC of gas-phase CO_2 electrolysis in a flow cell configuration containing a solid-supported aqueous H_2O solution. (A) Inlet CO_2 without hydration; RH = 15%. (B) Inlet CO_2 hydrated at RT; RH = 90%. (Anode: nickel foam; cathode: silver on carbon GDL; anolyte: 10 mL/min 1 M NaOH; gas catholyte: 100 SCCM CO_2 .)

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Notes

The authors declare no competing financial interest.

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