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Investigation of CO₂ single-pass conversion in a flow electrolyzer†

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Flow electrolyzers are attracting significant attention because of their unique capability of facilitating carbon dioxide (CO₂) electroreduction at high reaction rates. Among all figures of merit, CO₂ single-pass conversion is an important factor that can strongly affect the product separation cost of the whole process but often neglected in the literature. In this study, CO₂ single-pass conversion was investigated using a flow electrolyzer under various operating conditions to identify the operating constraints on achieving a maximum single-pass CO₂ conversion. The maximum amount of CO₂ being converted to CO is limited to approximately 43% regardless of CO₂ feeding rate, operating current density, and reaction temperature. Further investigation shows that the remaining CO₂ feed was mainly consumed by the side reaction of carbonate formation between the CO₂ feed and the hydroxide anions generated during the electrolysis. As a result, the gas effluent stream from the cathode chamber contains mainly CO (~80%), together with 15% H₂ and 5% unreacted CO₂.

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1. Introduction

There has been growing concern about the rapid increase of the atmospheric carbon dioxide (CO₂) concentration causing global warming and climate change.¹ As a result, renewable energy resources, such as solar and wind, are being utilized more extensively to reduce the energy dependence on fossil sources,² which also leads to a significant cost reduction of renewable electricity production.^{3,4} The low electricity price opens up potential opportunities for electricity driven chemical and fuel production using CO₂ as the carbon feedstock. For instance, CO₂ can be electrochemically converted into several products, including carbon monoxide (CO), formate, ethylene, and oxygenates, depending on the catalyst.^{5–7} In the past few years, significant progress has been made in the development of CO₂ flow electrolyzers,^{8–12} which enable high-rate CO₂ electroreduction reaction (eCO₂RR) by allowing a direct feed of gaseous CO₂ reactant to the electrode–electrolyte interface through a gas-diffusion layer (GDL). The employment of a GDL largely addresses the CO₂ mass transport limitations that are often seen in batch

reactors where the current density is greatly limited by the low solubility of CO₂ in the aqueous electrolyte (~30 mM).^{13–15}

To date, the primary focus of flow cell studies in the literature has been the improvement of the performance of catalysts and gas-diffusion electrodes with higher current densities, better Faradaic efficiencies (FEs), and lower overpotentials of the eCO₂RR. For example, Jiao *et al.* showed that a nanoporous copper (Cu) coated GDL was able to deliver a current density of 653 mA cm⁻² with a multi-carbon selectivity of 62% at -0.67 V vs. reversible hydrogen electrode (RHE).¹⁶ In a more recent study, Sargent *et al.* demonstrated eCO₂RR at a current density up to 1.2 A/cm² together with a total eCO₂RR FE of ~90% at a cell potential of 4.0 V in a flow electrolyzer, representing the state-of-the-art performance for CO₂ electrolysis in a flow cell.¹⁷ While CO₂ flow electrolyzers show promising performances, much less attention has been devoted to engineering challenges related to CO₂ single-pass conversion in the flow cells, which is also an important aspect of the overall eCO₂RR process because the CO₂ single-pass conversion is closely associated with the product separation cost. Taking eCO₂RR to CO as an example, the separation cost of a gas product stream (*i.e.*, a mixture of CO₂ and CO) by pressure swing adsorption is approximately 23% of the total operational costs at a 10% CO₂ single-pass conversion.¹⁸ Theoretically, improving the CO₂ single-pass conversion to 50% will reduce the separation cost by 78% (*i.e.*, 6% of the total cost).¹⁸ However, the flow cell studies in the literature often use a largely excessive amount of CO₂ in order to

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achieve high FEs and current densities, where the CO₂ single-pass conversion is typically lower than 10% (ESI† Table S1) and usually not reported.^{9,10,19–23}

In a flow electrolyzer, the CO₂ single-pass conversion could be influenced by many factors, such as the choice of CO₂ electrocatalyst, the configuration of the flow cell, the type of polymer membrane electrolyte, and the operating conditions (*e.g.*, CO₂ feeding rate, applied potentials and reactor temperatures). Because of its complex nature, a systematic study would be appreciated to elucidate the interplay between CO₂ single-pass conversion and other parameters. In this paper, we chose a silver (Ag) based CO₂ flow electrolyzer as a model system to investigate the CO₂ single-pass conversion to CO. A series of experiments were conducted by varying the operating conditions, such as the CO₂ feeding rate, the applied current density, and the reactor temperature. The experimental results show that the CO₂ single-pass conversion through eCO₂RR does not exceed 43% under all testing conditions, although a total consumption of CO₂ can be as high as 95%. The high consumption but low single-pass electrochemical conversion of CO₂ is mainly caused by the carbonate formation at the catalyst–electrolyte interface, a side reaction that consumes up to 55% of the total CO₂ feed even when a neutral potassium bicarbonate electrolyte is used.

2. Experimental methods

2.1 Materials preparation

For both electrodes (cathode and anode), catalyst slurries were prepared by mixing 300 mg of catalyst powder, 1 mL of deionized water, 2 mL of isopropanol, and 100 μm of Sustainion™ ionomer (Dioxide Materials). The cathode was prepared by spraying a slurry containing 100 nm Ag nanoparticles (Sigma-Aldrich) onto a 5 × 5 cm GDL (Sigracet 29BC) using a spray gun, and the catalyst loading was measured by using a balance, until 1 mg cm⁻² loading of Ag catalyst was achieved. For the anode, iridium oxide (IrO₂) nanoparticles (Alfa-Aesar, Cat No. 43396) were used as the catalyst material and the rest of the procedure is identical to the one for the cathode. Anion exchange membranes (Sustainion™ membranes from Dioxide Materials) were used in the flow electrolyzers for all studies. The membranes were activated in 1 M potassium hydroxide (KOH) solution following a reported procedure.²⁴

2.2 Electrolyzer set-up

In all experiments, a membrane electrode assembly (MEA) set-up was used, in which a Sustainion™ membrane was placed between the cathode and the anode. The MEA with an active electrode area of 25 cm² was then put inside a flow electrolyzer made of two gold-plated stainless-steel plates (9.5 × 9.5 × 1 cm). The cathode plate has a multiple-channel serpentine flow field, whereas a single-channel serpentine flow field is used for the anode plate. The gold-plating on the stainless-steel plates prevent any potential issues with

corrosion and side reactions (ESI† Fig. S1). Silicone gaskets with a thickness of 0.05 inches (McMaster Carr) were used for good sealing. The plates were tightened by using a torque wrench at 20 lb-in torque, to ensure consistent contact distribution between the electrodes and the membrane for each test.

2.3 Electrolyzer testing

The CO₂ gas feeding rate at the cathode chamber was set using a mass flow controller (MKS). On the anode side, a 0.05 M potassium bicarbonate (KHCO₃) electrolyte was continuously circulated at a flow rate of approximately 70 mL min⁻¹ using a peristaltic pump (Cole Parmer). The flow electrolyzer was then connected to an external power source (National Instruments), which controls the applied cell potentials or currents. The gas effluent of the flow electrolyzer was analyzed by inline gas chromatography (GC) (SRI) to quantify the gas products. The gas flow rate of the effluent was measured using a gas flow meter (Agilent), which is used for product quantifications. All the half-cell potentials reported in this study are adjusted to the RHE scale.

To calculate the CO₂ single-pass conversion to CO, the following equation was used:

$$\gamma_{\text{CO}} = \frac{x_{\text{CO}} Q_{\text{outlet}}}{Q_{\text{inlet}}}$$

where γ_{CO} is the fraction of CO₂ feed being converted electrocatalytically to CO, x_{CO} is the volume fraction of CO in the gas effluent quantified by the GC, Q_{outlet} is the flow rate of the gas effluent measured by the flow meter, and Q_{inlet} is the CO₂ feeding rate into the flow electrolyzer. The fraction of unreacted CO₂ was calculated similarly, except the volume fraction of CO₂ (x_{CO_2}) instead of the mole fraction of CO was used. The following equation was used to calculate the fraction of CO₂ feed being converted to carbonates ($\gamma_{\text{carbonates}}$) through side-reactions with hydroxide:

$$\gamma_{\text{carbonates}} = \frac{Q_{\text{inlet}} - (x_{\text{CO}} + x_{\text{CO}_2}) Q_{\text{outlet}}}{Q_{\text{inlet}}}$$

For temperature effect studies, a 0.05 M KHCO₃ aqueous solution was used as the anolyte, which was preheated to the desired temperature (either 45 °C or 60 °C) using a heating mantle with a temperature controller (OptiChem). At the beginning of each test, both the CO₂ gas feed and the anolyte solution were continuously circulated until the temperature of the whole reactor reached the designated temperature. The rest of the experimental procedure is identical to the one for room temperature tests.

3. Results and discussion

There are multiple ways to configure the CO₂ flow electrolyzer. In this study, we conducted all experiments

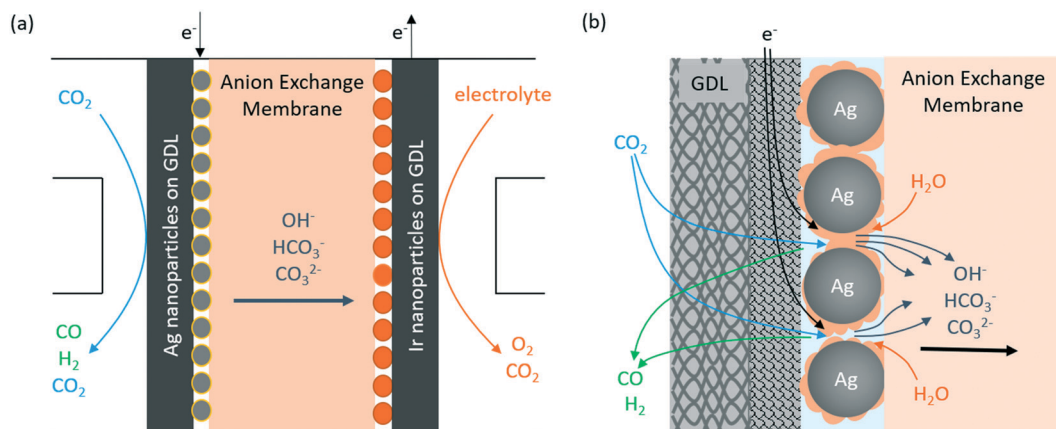


Fig. 1 Schematic diagrams of (a) the CO₂ flow electrolyzer configuration and (b) the cathode-membrane interface with multiple competing reactions.

using a MEA type flow reactor as a model system, which is the most commonly used flow electrolyzer design for eCO₂-RR. A schematic representation of the flow electrolyzer

configuration is shown in Fig. 1a, where an anion exchange membrane is sandwiched between two electrodes. The cathode consists of a 25 cm² GDL coated with 100 nm Ag

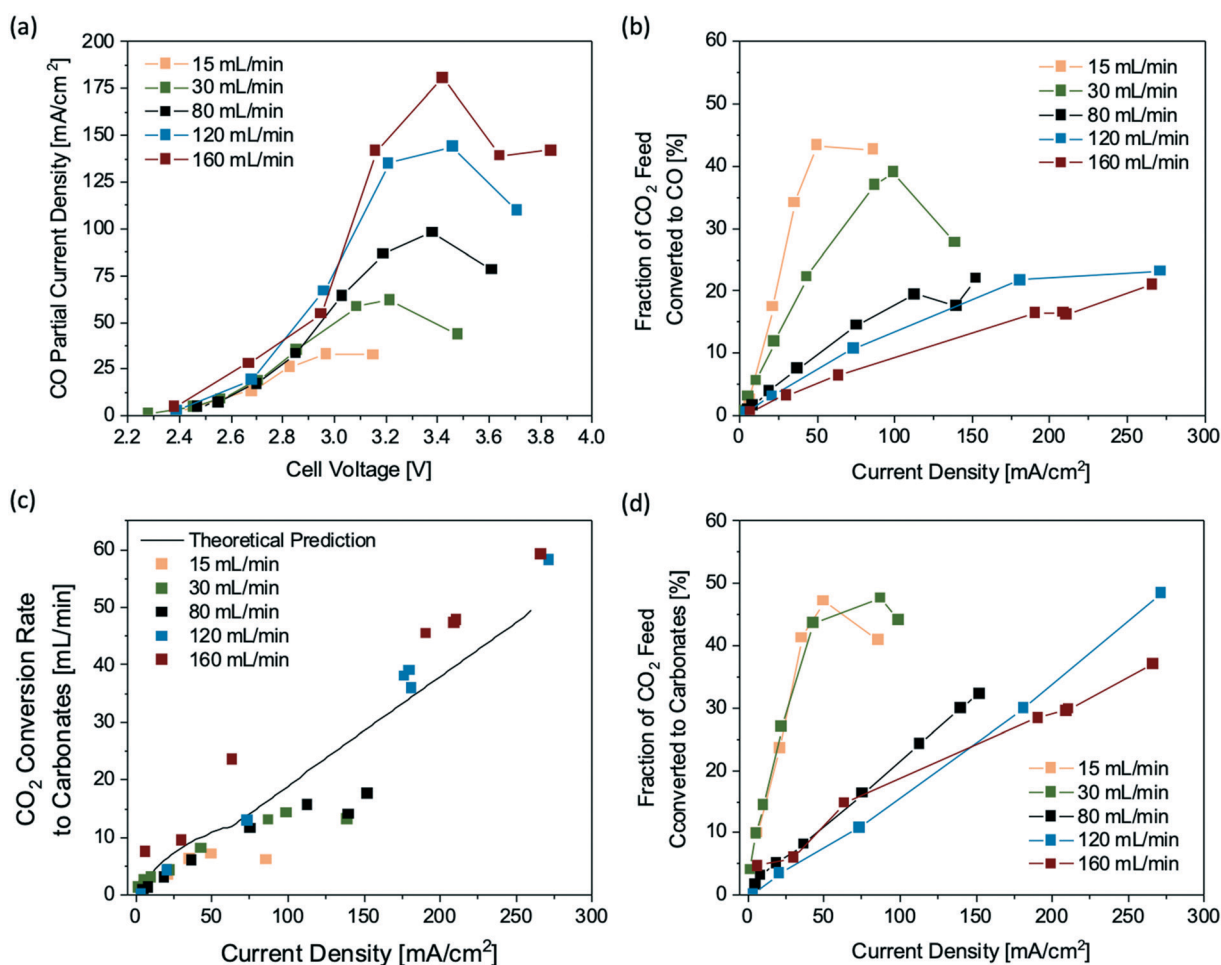


Fig. 2 Performance of a 25 cm² flow electrolyzer operated at different CO₂ feeding rates: (a) CO partial current density profiles at various cell voltages, (b) fraction of CO₂ feed being converted to CO via eCO₂RR, (c) rates of CO₂ being consumed due to carbonate formation, and (d) fraction of unreacted CO₂ feed at various current densities. The solid curve in (c) is the theoretical rate of CO₂ conversion to carbonates estimated by the Nernst-Planck equation (ESI† the Method section).

nanoparticles to facilitate the electroreduction of CO₂ to CO, whereas an IrO₂-nanoparticle coated GDL is used as the anode for stable performance in the neutral electrolyte (*i.e.*, 0.05 M KHCO₃). A Sustanion membrane was chosen as the membrane material because it has a relatively high ionic conductivity in bicarbonate electrolytes compared to other anion exchange membranes.^{11,24} Fig. 1b shows a zoom-in view of the gas-diffusion electrode (GDE) on the cathode side, where Ag nanoparticles are deposited on a hydrophobic GDL (ESI† Fig. S2) to facilitate the gas diffusion of reactants (*i.e.*, CO₂) and products (*i.e.*, CO and H₂) across the interface. On the surface of the Ag catalyst, the CO₂ molecules are electrochemically reduced to CO and the water (H₂O) molecules donate protons to form hydroxide anions. At the electrode–membrane interface, two side reactions, *i.e.*, the hydrogen evolution reaction through water reduction and carbonate formation between CO₂ and hydroxide anions, also occur simultaneously. Both reactions compete with eCO₂RR and have significant impacts on the CO₂ single-pass conversion, which will be discussed in detail in the following paragraphs.

We first examined how the single-pass conversion of CO₂ is affected by applied cell potentials and CO₂ feeding rates. The cell potential was varied from 2.2 V to 3.9 V and the CO₂ feeding rate was set at 15–160 mL min⁻¹. As seen in Fig. 2a, at low cell potentials (<2.8 V), the CO partial current densities are similar regardless of the CO₂ feeding rates, because the eCO₂RR rate is controlled by kinetic activation and ohmic resistances.²⁵ When the cell voltage increases beyond 2.8 V, the CO partial current densities show a clear dependence on the CO₂ feeding rate, in which a greater CO partial current density was observed at a higher CO₂ feeding rate, suggesting that the system becomes CO₂ mass transport limited. Increasing the applied potential further resulted in a decrease in the CO partial current density, possibly due to more severe competing reactions, such as the hydrogen evolution reaction, at high cell potentials.

Based on the CO partial current densities, the fractions of the CO₂ feed being converted electrocatalytically to CO are calculated (Fig. 2b). At a CO₂ feeding rate of 15–30 mL min⁻¹, the maximum of CO₂ conversion to CO is 43% at a current density of 80 mA cm⁻², corresponding to a current of 2 A. Further tuning the total applied current density and the CO₂ feeding rate did not result in a higher CO₂ single-pass conversion, which is likely due to the carbonate formation at the electrode–membrane interface. During the eCO₂RR, hydroxide ions are generated at the interface as a by-product from the electroreduction process, which increases the local pH and consequently leads to the formation of carbonates, consuming a significant amount of CO₂ feed. At steady state, the reaction rate of carbonate formation with CO₂ and hydroxide should be equal to the rate of carbonate transport across the membrane. Since most of the ion transport across the membrane is dependent on electromigration²⁶ or the electric potential driving the ion transport, a modified version of the Nernst–Planck equation²⁷ can be used to

estimate the flux of carbonates and bicarbonates expected to travel across the membrane based on the total current (ESI† the Method section). This method enables us to calculate the CO₂ consumption due to the carbonate formation at the interface at any given current, which is shown as the theoretical prediction (a solid line) in Fig. 2c. As the total current increases, the consumption rate of CO₂ to carbonates increases nearly linearly.

The amount of CO₂ that is consumed by the carbonate formation can also be estimated using the experimental data. Based on the product selectivity and the gas flow rates at the gas inlet and outlet of the CO₂ flow electrolyzer, we calculated the CO₂ consumption rates due to the carbonate formation at all flow rates and currents, which match the general trend of the theoretical prediction using the Nernst–Planck equation (Fig. 2c). Assuming that the by-product of the side reaction between CO₂ and hydroxide ions is exclusively carbonate (CO₃²⁻), the overall reaction at the cathode can be expressed as 2CO₂ + 2e⁻ → CO + CO₃²⁻, suggesting that for every CO₂ molecule being converted to CO *via* eCO₂RR there is another CO₂ molecule that is consumed by the side reaction of carbonate formation. As a result, the theoretical CO₂ conversion to CO is limited to approximately 50% regardless of the operating conditions of the flow electrolyzer, such as current densities and CO₂ feeding rates. The 50% conversion limit prediction is well supported by the experimental data shown in Fig. 2b and d, indicating that CO₃²⁻ is likely the dominant product of the side reaction between CO₂ and hydroxide.

We further examined the temperature effect on the CO₂ conversion to verify if the 50% limit of CO₂ conversion to CO is valid at elevated reaction temperatures. The reaction temperature of the flow electrolyzer was raised from room temperature to 45 °C and 60 °C, whereas the CO₂ feeding rate was maintained at 80 mL min⁻¹ across all temperature effect studies. Fig. 3a shows that a larger CO partial current density was obtained at lower overpotentials when the reaction temperature was increased, as expected based on the Butler–Volmer equation.²⁵ Additionally, the limiting CO partial current densities are 135 mA cm⁻² and 160 mA cm⁻² at 45 °C and 60 °C, respectively, a substantial improvement over 88 mA cm⁻² obtained at 25 °C. The higher limiting CO partial current densities at elevated temperatures are likely due to the improved gas diffusivity of CO₂ to the catalyst surface.²⁸ At 60 °C, about 40% of the CO₂ feed was converted to CO electrochemically (Fig. 3b), which is twice as high as the CO₂ conversion obtained at 25 °C, showing that the reaction temperature plays an important role in boosting the CO₂ single-pass conversion. On the other hand, the increase in reaction temperature also promoted the carbonate formation, resulting in a higher fraction of the CO₂ feed being converted to carbonates, as shown in Fig. 3c. For a reaction temperature of 60 °C, ~55% of the CO₂ feed formed carbonates, and consequently, less than 5% CO₂ remained unreacted in the flow cell (Fig. 3d). The results clearly show that increasing the reaction temperature promotes not only the

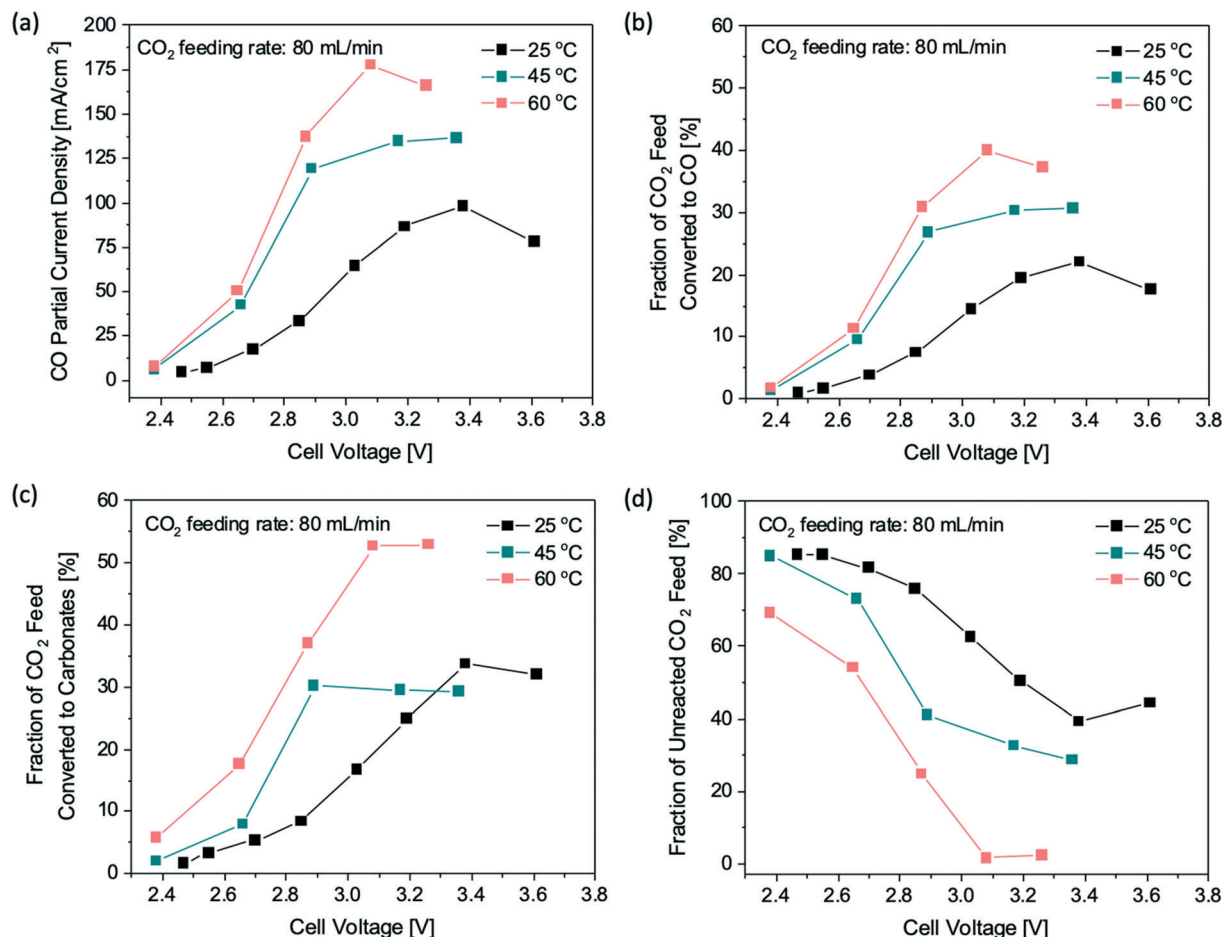


Fig. 3 Effects of reaction temperature on the CO₂ single-pass conversion at a fixed CO₂ feeding rate of 80 mL min⁻¹: (a) CO partial current densities, (b) fraction of CO₂ feed being converted to CO via eCO₂RR, (c) fraction of CO₂ feed consumed by the carbonate formation, and (d) fraction of unreacted CO₂ feed in the gas effluent at various cell voltages.

electrochemical reduction of CO₂ to CO, but also the side reaction of carbonate formation. Since the two reactions compete for the CO₂ feed and the reaction temperature affects both reaction rates in a similar way, it is not possible to improve the overall CO₂ single-pass conversion to CO beyond 50% by simply changing the reaction temperature.

Although the CO₂ single-pass conversion to CO via eCO₂RR is limited to less than 50%, the total consumption of the CO₂ feed can be as high as 95% (Fig. 3d). As a result, the composition of the gas effluent from the cathode chamber is dominated by the gas product CO under certain operating conditions. Such a phenomenon could be used as a potential strategy to generate a relatively pure gas product stream containing a limited amount of unreacted CO₂ without any gas separation processes. As shown in Fig. 4, the gas effluent compositions are tunable by adjusting the operating current and CO₂ feeding rate to achieve a wide range of CO-to-H₂ ratios from 1 to 5. The presence of unreacted CO₂ in the gas product stream can be largely suppressed at relatively low CO₂ feeding rates. Under optimal conditions, the highest concentration of CO in the gas

product stream is ~80% together with ~15% H₂ and 5% unreacted CO₂. For a fair comparison of the results at different current densities, the CO₂ feeding rates were normalized by the theoretical rate of eCO₂RR estimated from the total current by assuming 2 electrons per product molecule (Fig. 4d). After normalizing the CO₂ feeding rate, the CO fractions in the gas effluent streams at different current densities all show a maximum value of ~1.75, suggesting that the maximum CO concentration in the gas product stream is mainly controlled by the ratio between the amount of the CO₂ feed and the operating current.

All the results presented in this work suggest that the 50% limit of CO₂ single-pass conversion is a fundamental challenge in anion-exchange-membrane-based CO₂ flow electrolyzers. The locally generated hydroxide anions from eCO₂RR inevitably react with CO₂ to form carbonates even when a neutral pH supporting electrolyte is used. Switching the anion exchange membrane to a proton exchange membrane could prevent the carbonate formation at the interface; however, the strong acidic environment likely promotes the hydrogen evolution

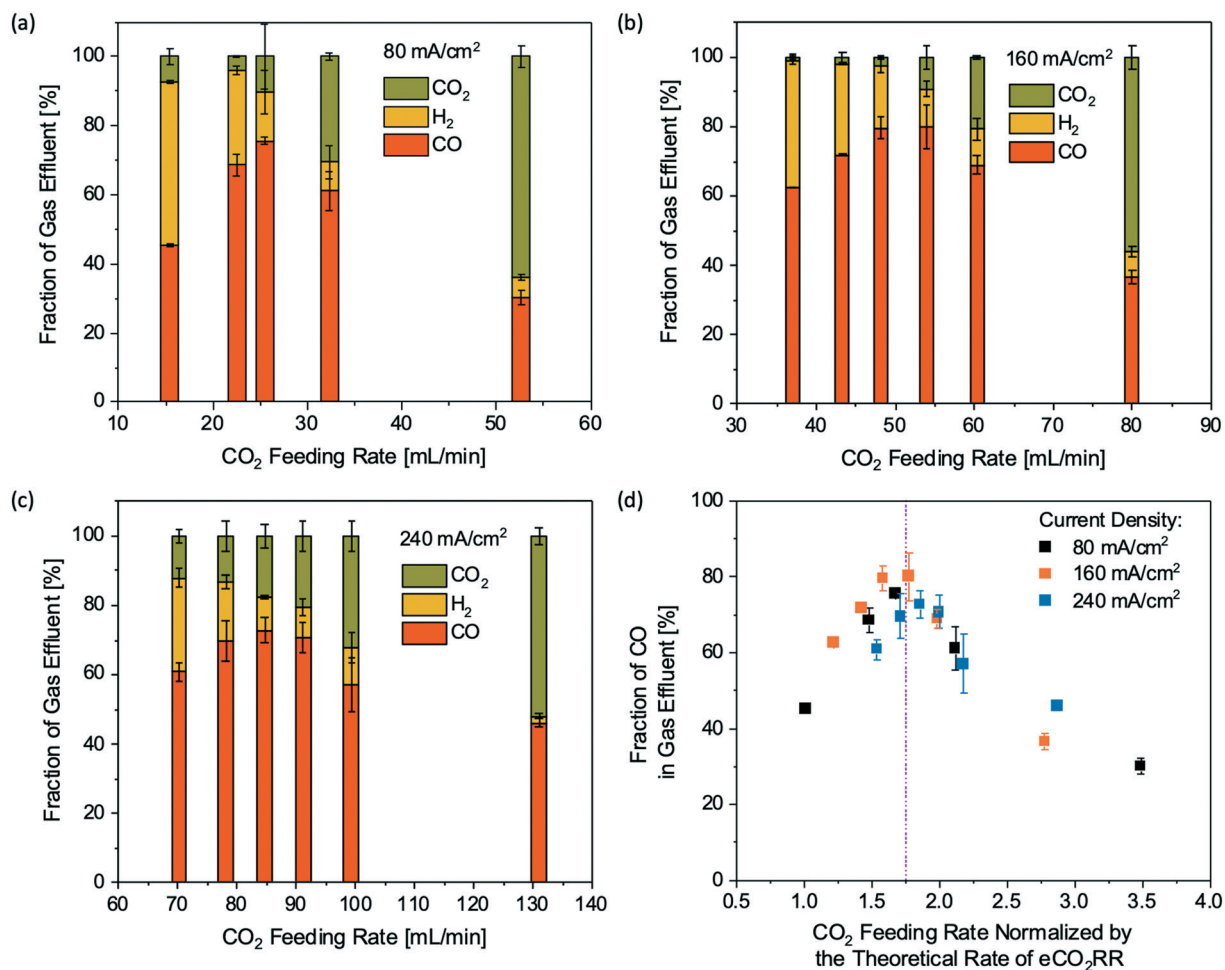


Fig. 4 Compositions of the gas effluent from the cathode chamber of a CO₂ flow electrolyzer (25 cm² active electrode area) at different operating current densities: (a) 80 mA cm⁻², (b) 160 mA cm⁻², and (c) 240 mA cm⁻². (d) shows a comparison among the fractions of CO in the gas product streams under different operating conditions. The x-axis of (d) is the CO₂ feeding rate [mL min⁻¹] divided by the theoretical rate of eCO₂RR [mL min⁻¹], estimated from the total current.

reaction, an undesired reaction competing with eCO₂RR at the cathode.²⁹ Employment of a bipolar membrane combined with a bicarbonate²³ or carbonate³⁰ supporting electrolyte could be a potential solution. To date, the CO FEs for most bipolar-membrane-based flow electrolyzers are still relatively low at industrially relevant current densities (>100 mA cm⁻²). Another alternative could be a non-aqueous electrolyte system. In that case, a beneficial organic oxidation reaction could be considered as an alternative to the water oxidation reaction for the anode to provide protons for CO₂ reduction on the cathode. Several technical challenges associated with organic electrolytes include the suppression of hydrogen evolution in an acidic environment, relatively low ionic conductivity of organic electrolytes to support cell operation under high current densities, and decomposition of organic electrolytes on the anode. More research efforts are needed to develop new strategies for a high CO₂ single-pass conversion together with a high CO selectivity at large current densities in CO₂ flow electrolyzers.

4. Conclusion

In summary, we studied the potential impacts of current densities, CO₂ feeding rates, and reaction temperatures on the single-pass conversion of CO₂ in a typical CO₂ flow electrolyzer. The CO₂ single-pass conversion to CO is limited to ~43% regardless of operating conditions, which is due to the carbonate formation reaction between the CO₂ feed and the locally generated hydroxide ions. The side reaction consumes a substantial fraction of the CO₂ feed and leaves a very small amount of unreacted CO₂ in the system. Under certain conditions, nearly 95% of the CO₂ feed are consumed through either eCO₂RR or the carbonate formation reaction. Because of the high CO₂ consumption, the gas product stream from the cathode chamber contains predominantly CO (80%), a small amount of H₂ (15%) and unreacted CO₂ (5%), which could be considered as a potential strategy to produce a relatively concentrated product stream without any gas separation processes.

Conflicts of interest

There are no conflicts to declare.

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