Influence of Dilute Feed and pH on Electrochemical Reduction of CO₂ to CO on Ag in a Continuous Flow Electrolyzer

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Abstract

Electrochemical conversion of CO₂ to useful chemical intermediates may be a promising strategy to help reduce CO₂ emissions, while utilizing otherwise wasted excess renewable energy. Here we explore the effect of diluted CO₂ streams (10 to 100% by volume using N₂ as diluting inert gas) on the product selectivity and on the CO/CO₂ conversion ratio for the electrochemical reduction of CO₂ into CO, specifically using a gas diffusion electrode loaded with Ag catalyst in a continuous flow electrolyzer. When using diluted CO₂ feeds for the electrolyzer, we still observed high Faradaic efficiencies for CO (>80%), high conversion ratios (up to 32% per pass), and partial current densities for CO of 29 mA/cm² when operating the cell at 3.0 V. Most notably, we observed that the decrease in partial current density for CO was less than 45% when switching from a 100% CO₂ feed to a 10% CO₂ feed. Also, we studied the effect of pH and the interplay between pH and the diluted CO₂ feed. We observed higher levels of CO formation as well as a higher Faradaic efficiency for CO when using an alkaline electrolyte, compared to when using a neutral or acidic electrolyte. However, the effect of CO₂ concentration in the feed is more significant than the effect of pH on electrochemical reduction of CO₂ to CO.

Keywords: carbon dioxide; electrochemical reduction; dilute feed; carbon monoxide; electrolyte pH

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1. Introduction

Excessive carbon dioxide (CO₂) emissions have been identified as a significant contributor to global climate change [1]. Two of the major sources of CO₂ emissions are transportation (cars and trucks) and power-plants, whose flue gas contains about 15% CO₂ [2]. To reduce CO₂ emissions, multiple strategies are being considered, including the improvement of fuel efficiency of cars, building energy efficiency, the increased utilization of renewable energy resources, and carbon capture and sequestration (CCS) [3]. For example, carbon capture and sequestration (CCS) technology could contribute a 19% reduction in CO₂ emissions, but at tremendous cost [4]. Recently, the conversion of CO₂ into useful chemicals such as carbon monoxide (CO) [5-10], formic acid [10-12], methanol [13-15], and ethylene [11,15] has been proposed. This strategy utilizes CO₂ as feedstock, so it not only reduces CO₂ emissions and reduces dependency on fossil fuels, but also has the potential to provide economic value [16]. Along these lines photochemical [13,17,18], biochemical [19,20], and electrochemical [13,18,21] approaches are being explored for the conversion of CO₂ into useful chemicals.

The most attractive option to eliminate CO₂ emissions in electrical power generation is to switch to renewable, carbon neutral energy sources such as solar and wind. However, increased use of these sources is hampered by their inherent intermittent nature and the lack of large-scale energy storage capabilities [3,4]. Varying the power output of most traditional fossil fuel power plants, especially coal power plants, in response to a sudden increase or decrease in the availability of power from renewable

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5 sources is challenging. As a result, at times a significant fraction of renewable power when abundantly
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8 available is not being utilized. The electrochemical reduction of CO₂ into value added chemicals, the
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11 topic of this paper, may provide a route to not only help reduce greenhouse gas emissions, it also could
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14 utilize this otherwise wasted excess electrical energy generated from renewable sources to synthesize
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17 chemicals that normally would have been derived from fossil fuels.
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21 A previously reported cost analysis of processes that involves electrochemical conversion of CO₂
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24 for the production of products such as formic acid, methanol, and mixture of short hydrocarbons reveals
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27 that significant improvements in energy efficiency are needed before such processes become cost
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30 effective compared to the various current ways to produce these products [22]. In the last decade,
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33 research to pursue better methods for CO₂ conversion in general [23], and to identify better catalysts for
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36 electroreduction of CO₂, has drastically increased in intensity. On the other hand, process optimization
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39 to maximize overall energy efficiency has received much less attention. One interesting option that has
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42 been studied is the use of effluent gas of power plants directly as the feed for CO₂ conversion processes
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45 because it sidesteps the energy intense steps of CO₂ capture and concentration. For example, Kyriacou
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48 *et al.* reported on the influence of CO₂ partial pressure on the electrochemical reduction of CO₂ to C₂H₄
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51 and CH₄ when using a copper electrode in a three electrode cell [24]. Others reported that the removal
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54 of SO₂ was needed, but the presence of NO in the dilute CO₂ feed had no influence on the
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57 electrochemical reduction of CO₂ to C₂H₄ and HCOOH when using a copper-solid polymer
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electrolyte-based electrode [25].

Here we study the electrochemical reduction of CO₂ into potentially interesting chemicals or intermediates such as formic acid, methanol, and short hydrocarbons. To date many studies have focused on the development of better catalysts [7,11], electrodes [26,27], and electrolytes [5,6,8]. Different catalysts are known to predominantly lead to the formation of specific products; Ag and Au are known to produce carbon monoxide (CO) with Faradaic efficiency often approaching 100% [26-28], while Sn and Pd lead to the production of formic acid and Cu leads to mixtures of short hydrocarbons [11]. Almost all of these research efforts have been conducted using highly pure CO₂ feeds (>98%). Furthermore, very few studies have investigated the effect of electrolyte pH (or the change of pH over the course of cell operation) on the electrochemical reduction of CO₂ [12].

In this paper we report on the electrochemical reduction of CO₂ to CO, a potentially interesting intermediate in the production of a range of chemicals via the Fischer-Tropsch process [29], while using a dilute CO₂ stream (such as the ~15% CO₂ in flue gas) as the feed in an electrolyzer equipped with a Ag-based gas diffusion electrode. To mimic the flue gas we use diluted CO₂ streams (10 to 100% by volume, using N₂ for dilution), and examine its impact on product selectivity (Faradaic efficiency for CO), CO₂ utilization, and overall productivity (partial current density for CO). Furthermore, we study the effect of electrolyte pH (4, 7, and 10) in the presence of different CO₂ feeds (10% and 100%) on product selectivity and overall productivity.

2. Experimental Section

2.1. Electrode preparation

Sigracet 35BC gas diffusion layers (GDLs, Ion Power) comprised of 5 wt% poly-tetrafluoroethylene (PTFE)-treated carbon paper and a teflonized microporous layer, were used for preparing gas diffusion electrode (GDE). Both cathode and anode GDEs were prepared by applying catalyst ink via hand-painting following previously reported methods [7]. In short, the catalyst ink for the cathodes consisted of 4.40 mg Ag catalyst (unsupported Ag nanoparticles, <100 nm particle size, 99.5% trace metals basis, Sigma-Aldrich), 5.20 μ L Nafion solution (5 wt%, Solution Technology, 30:1 catalyst-to-Nafion ratio), as well as 200 μ L of isopropyl alcohol (Sigma-Aldrich) and 200 μ L Millipore water (18.2 M Ω) as the carrier solvents. The catalyst ink for the anodes was comprised of 2.50 mg Pt black (Alfa Aesar), 6.50 μ L Nafion solution, as well as 200 μ L of isopropyl alcohol and 200 μ L Millipore water as the carrier solvents. To achieve uniform mixing, all the catalyst inks were sonicated for 15 minutes prior to use. Then, to cover GDEs with catalysts (total geometric area of 2 cm²), all the inks were applied via hand-painting with a paintbrush onto the teflonized carbon side of the GDL. These GDEs were cut in half to create two electrodes. The weight of the GDEs was measured before/after deposition of catalyst to determine the actual catalyst loading: 0.9 mg Ag/cm² and 1.0 mg Pt/cm², respectively for the cathodes and anodes.

2.2. Cell assembly and testing

A schematic of the electrochemical flow reactor used in this study is shown in **Fig. 1**, as reported

previously [26,30]. Two aluminum current collectors and a graphite collector with a window provide structural support for the electrochemical flow reactor. These windows are used to clamp the two catalyst-coated GDEs, an anode and a cathode. A 0.15-cm thick polyether ether ketone (PEEK) window was placed between the two GDEs, each with a geometric surface area of 1 cm², to provide a flow field for the flowing liquid electrolyte. The electrochemical flow reactor was operated using a potentiostat (Autolab PG30) under ambient pressure and temperature. An aluminum gas flow chamber supplied the feed gas, comprised of CO₂ (S.J. Smith, 100%) and N₂ (S.J. Smith, 100%), on the cathode side while the anode was left open to the atmosphere. The CO₂ concentrations were varied from 10 to 100% by volume using N₂ as the diluting component while the total flow rate was fixed at 7 sccm. A syringe pump (Harvard Apparatus PHD 2000) supplied the electrolyte, either 1 M potassium chloride (KCl, Sigma-Aldrich, ≥99.9995% pure) in water, at 0.4 mL/min, or solutions of mono and dibasic potassium phosphate (KH₂PO₄, K₂HPO₄, Sigma-Aldrich, ≥99.0% pure) for pH dependent experiments (see below). The effluent gas streams were characterized with a gas chromatograph (Trace GC, ThermoFisher Scientific) equipped with a Carboxen 1000 column (Supelco) and a thermal conductivity detector. We did not analyze the liquid stream for the presence of additional products. The sum of the Faradaic efficiencies (lower than 100%) indicates that other products form for some of the operational conditions tested. The identity of these other products is not essential for studying the effect of CO₂ concentration in the feed on CO production. Cell polarization curves were recorded by steady-state

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5 chrono-amperometric measurements. The cell was allowed to reach steady state for 200s, at which
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8 point the current had stabilized. Then, a sample of the effluent stream was injected into gas
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10 chromatography (GC) for product analysis, before stepping to the next potential and waiting for steady
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12 state again. Individual anode and cathode polarization curves were measured using a Ag/AgCl
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14 reference electrode (RE-5B, BASi) that was placed in the outlet reservoir of the electrolyte. A new
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16 anode and cathode were used for every experiment. No deactivation of electrode activity was observed
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18 during these short experiments. Faradaic efficiencies, energetic efficiencies, and current densities are
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20 calculated by using equations reported previously [21].
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30 Experiments with electrolytes of different pH were performed using aqueous phosphate buffer
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32 solutions comprised of mono and dibasic potassium phosphate (KH_2PO_4 , K_2HPO_4 , Sigma-Aldrich,
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34 $\geq 99.0\%$ pure). Phosphate buffer was adjusted to pH 4, 7, or 10 by using 10M H_3PO_4 or 10M KOH.
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36 For these studies we used a dual-electrolyte reactor [5], in which a Nafion-117 membrane separates the
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38 catholyte (phosphate buffer solution) and the anolyte (1M KCl solution).
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49 **3. Results and Discussion**

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51 To study the electrochemical reduction of CO_2 to CO using dilute CO_2 feeds, we used an
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53 electrochemical flow reactor as described in the experimental, equipped with respectively a silver
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55 catalyst and a platinum catalyst based gas diffusion electrode as the cathode and anode (Fig. 1). First
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we will report product selectivity and overall performance (Section 3.1) and then CO₂ utilization (Section 3.2) when using the 1M KCl electrolyte. Next we report cell performance as a function of the pH of the electrolyte (Section 3.3).

3.1. Faradaic efficiency and current density

Fig. 2a shows the product selectivities (Faradaic efficiencies) for CO and H₂ as a function of different CO₂ concentrations, ranging from 10 to 100% by volume, while **Fig. 2b and 2c** show the corresponding partial current density curves for CO and H₂. The equilibrium cell potential for this process is -1.33 V ($E^{\circ}_{\text{CO}_2/\text{CO}}(25^{\circ}\text{C}) = -1.33 \text{ V}$ for $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$), with CO₂ reduction to CO on the cathode ($E^{\circ} = -0.10 \text{ V}$ vs. RHE) and water oxidation to O₂ on the anode ($E^{\circ} = 1.23 \text{ V}$ vs. RHE). Activation losses on each electrode (the anode and cathode overpotentials) will increase the actual cell potential that needs to be applied. Here and in prior work [31,32], an overpotential of at least 140 mV needs to be applied on the cathode, with an anode overpotential on the order of 300 mV.

As expected, we observed almost no CO or H₂ production (less than 5 mA/cm²) at cell potentials of 2.25 V in our flow cell experiments. Also, the Faradaic efficiency for CO at a cell potential of 2.5 V ranges from ~23 to ~60%, decreasing with lower CO₂ concentration of the feed (**Fig. 2a**). At cell potentials of 2.75 V and 3.0 V, partial current densities for CO₂ of, respectively, 23.1 and 51.3 mA/cm² are observed when using a 100% CO₂ feed (**Fig. 2b**). Upon diluting the CO₂ feed, lower partial current densities for CO₂ are observed, but even at a 10% CO₂ feed they still are 11.7 and 29.0 mA/cm²,

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5 respectively, for these two cell potentials. Furthermore, at these cell potentials the Ag cathode still
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8 achieves a Faradaic efficiency exceeding 80% CO, irrespective of the level of CO₂ dilution, ranging
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11 from 10% to pure CO₂ (100%) (**Fig. 2a**). The fact that the drop in CO production is only 40-50% when
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14 changing the feed from pure to 10-20% CO₂ suggests that the electrochemical reduction of CO₂ can be
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17 performed using flue gas from a power plant (~15% CO₂), after the flue gas has been scrubbed of certain
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20 impurities that can act as a poison to the catalysts.
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27 CO₂ concentration in the feed are similar to what has been observed previously for CO₂ reduction in
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30 3-electrode cell and in solid oxide fuel cells [24,33,34]. Specifically, this prior work showed that the
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33 current density observed for both cells are proportional to the partial pressure of reactant with various
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36 diluents. In other words, high performance could be maintained with a certain percentage of reactant.
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39 This is similar to what we observe here (**Fig. 2b**): a higher CO₂ concentration leads to a higher rate of
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49 a cell potential of 3.0 V, the Faradaic efficiencies for H₂ were below 8% at all other conditions,
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52 suggesting that the use of diluted CO₂ as the reactor feed does not significantly affect H₂ evolution (**Fig.**
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55 **2c**). The observed increase in H₂ evolution at 10% CO₂ may be due to the low CO₂ concentration,
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58 which seemingly is not sufficient anymore to suppress H₂ evolution. For all experimental conditions
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(except when using a 10% CO₂ feed in combination with a cell potential of 3.0 V), the partial current density for H₂ stayed below 2 mA/cm², independent of the CO₂ concentration in the feed.

Next, we analyzed the performance of the anode and cathode as a function of CO₂ concentration in the reactant feed (**Fig. 3**). As expected, the polarization curves of the anode all overlap, irrespective of the actual cell potentials used, between 2.25 and 3.0 V. So any changes in performance as a function of CO₂ concentration in the feed must be due to changes in the cathode polarization, as is evident in **Fig. 3**. Irrespective of cell potential applied, minimal or no change in cathode polarization curves is observed when lowering the CO₂ concentration in the feed from 100% to 70%, as is also evident from the data shown in **Fig. 2b**. However, when feeds with lower CO₂ concentrations are used the cathode polarization gradually increases, so at identical cathode potential a lower current density is observed. In summary, lower CO₂ concentrations lead to higher cathode polarization.

3.2. CO₂ utilization per pass

We also studied the utilization of CO₂ per pass, expressed in the ratio of the amount of produced CO over the amount of CO₂ injected, as a function of CO₂ concentration. This ratio represents a measure of the CO₂ utilization toward the desired product CO. Diluted CO₂ feeds lead to higher CO over CO₂ ratios than when using pure CO₂ feeds (**Fig. 4**): Specifically, when using a 10% CO₂ feed, maximum CO over CO₂ ratios of 0.02, 0.13, and 0.32 were achieved at cell potentials of 2.5, 2.75, and 3.0 V cell potentials, whereas minimum CO over CO₂ ratios of 0.01, 0.02, and 0.05, were obtained at these same

cell potentials when using a 100% CO₂ feed. In other words, the utilization of CO₂ per pass increased up to 6 fold by using diluted CO₂ streams. Also, the utilization of CO₂ is enhanced with increasing cell potentials, implying that electrochemical conversion of diluted CO₂ may be more effective at higher cell potentials. Also note that CO formation only increases by a factor of 2 (or less) upon increasing the feed concentration by a factor of 10 (from 10 to 100%; **Fig. 2**). This indicates that catalytic performance is limited by the catalyst used (Ag nanoparticles). Better catalyst will be needed to improve CO₂ utilization at high concentration CO₂ feeds.

3.3. Performance as a function of electrolyte pH

The electrochemical reduction of CO₂ to different products on different catalysts may very well depend on the pH of the electrolyte [12,35]. Furthermore, depending on the specific reactions taking place at the cathode, the pH of the electrolyte may change upon operating the cell. When using 1M KCl as the electrolyte (pH ~6.5), we determined that the pH at the outlet rose to as high as pH 9.5 upon increasing the cell potential, presumably due to the increased production of hydroxyl ions at the cathode. Also, we noted that the change in pH was bigger by 0.5 to 1.0 pH units when using a 10% CO₂ feed instead of a 100% CO₂ feed. This difference can probably be explained by the difference in the amount of CO₂ that dissolves into the electrolyte (reacts with water) and then equilibrates to form protons and HCO₃⁻. When using a 10% feed a smaller amount of protons forms to counteract the hydroxyls being produced at the cathode, leading to a higher (more alkaline) pH.

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5 In order to systematically study how the pH affects CO formation in the electrochemical reduction
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8 of CO₂ we switched to using phosphate buffer (0.5M K₂HPO₄ and 0.5M KH₂PO₄) as the electrolyte,
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11 because the pH of a non-buffered KCl solution cannot be controlled precisely given the amount of
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14 hydroxyl being formed at the cathode (see above). The phosphate buffer was adjusted to pH 4, 7, and
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17 10 using either 10M KOH or 10M H₃PO₄. **Figure 5** shows the Faradaic efficiency for CO and the
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20 partial current density for CO for experiments performed with different CO₂ feeds (10% and 100%) and
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23 electrolytes of different pH (4, 7, and 10). In agreement with the results with 1M KCl electrolyte
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26 reported above (**Figure 2b**), for all cases a 3-16 times higher current density is observed when using a
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29 100% CO₂ feed instead of a 10% CO₂ feed. The highest partial current density for CO is obtained
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32 when using the alkaline electrolyte, particularly at the highest cell potentials, with successively lower
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35 partial current densities being observed when using the neutral and acidic electrolyte (**Figure 5b**). The
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38 increase (or decrease) in current density when changing the pH from neutral to alkaline (or acidic) at the
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44 (about 1.5 times lower in acidic media) than the current density observed in a neutral electrolyte.
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53 electrolyte (up to 80-95%), with successively poorer selectivity for neutral and acidic electrolytes. This
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56 is in agreement with the observations reported above when using 1M KCl electrolyte (**Figure 2**). As
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59 expected, H₂ evolution was predominant when using the acidic electrolyte, and at lower cell potentials.
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5 For most sets of conditions, the difference in Faradaic efficiency when using a 10% feed or 100% feed is
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8 more pronounced when using the neutral or acidic electrolyte.
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11 Interestingly, a higher Faradaic efficiency for CO and a higher partial current density for CO were
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13 observed when using the alkaline electrolyte. In this paper we do not attempt to unravel the specific
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15 mechanism for CO₂ reduction in alkaline electrolyte. One can speculate, however, that the higher
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17 partial current density for CO observed when using an alkaline electrolyte is due to a higher number of
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19 available of active sites, but further research would be needed to confirm this. In general, CO₂
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21 reduction proceeds in competition with H₂ evolution in aqueous electrolytes. For example, Wu *et al.*
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23 emphasized controlling the H⁺ concentration near the cathode surface, because excessive amounts of H⁺
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25 could lead to high H₂ [36]. In acidic and/or neutral electrolyte, the higher H⁺ concentration leads to H⁺
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27 successfully competing with CO₂ for the active sites on the cathode surface, resulting in a significantly
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29 lower Faradaic efficiency for CO [27,36]. Upon increasing the pH (lowering the H⁺ concentration),
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31 more active sites become available, so the CO formation reaction is facilitated while H₂ evolution is
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33 suppressed. In summary, the extent of CO formation can be understood by mediation of the H⁺
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35 concentration near the cathode surface.
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52 In sum, an alkaline pH helps to achieve high Faradaic efficiency for CO, but the effect of CO₂
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54 concentration on the partial current density for CO is more significant than the effect of pH.
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4. Conclusions

We investigated the interplay between cathode performance and CO₂ concentration in the feed as well as electrolyte pH in the electrochemical reduction of CO₂ into CO with respect to selectivity (Faradaic efficiency for CO) and absolute production (partial current density for CO). High Faradaic efficiency for CO (>80%) and high utilization of CO₂ (>30%) could be achieved even at CO₂ concentration down to 10%, provided high cell potentials are used. In terms of absolute CO production, when operating at 10% CO₂ concentration, the partial current density for CO is still 55% (29 vs. 51 mA/cm² at a cell potential of 3.0 V) of the partial current density measured when operating with a 100% CO₂ feed. Higher levels of CO formation and a higher Faradic efficiency for CO are also observed in alkaline electrolyte, compared to neutral or acidic electrolyte. However, the partial current density for CO is affected significantly more by changes in CO₂ concentration than by a pH change. These results suggest that the electrochemical conversion of CO₂ to CO can be performed efficiently while using a diluted CO₂ stream, such as flue gas (~15% CO₂), thus avoiding an energy intensive CO₂ concentration step; The use of a pure or highly concentrated CO₂ feed is not vital for overall efficiency. This implies that the direct use of flue gas as a feed for electrochemical reduction to CO has promise, although further advances in CO separation from gas mixtures resulting as the product stream (CO, as well as unreacted CO₂ and N₂) are needed. Efforts to further improve catalysts and electrodes for electrochemical CO₂ reduction will also help the prospects of using dilute CO₂ streams as the feed.

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Figures

Figure 1. Schematic representation of the electrochemical CO₂ flow reactor used in this study.

Figure 2. (a) Faradaic efficiency for CO and H₂, and partial current density of (b) CO, and (c) H₂ as a function of CO₂ concentration, ranging from 10 to 100 % (v/v) using N₂ for dilution at four different cell potentials. N=4 for each data point.

Figure 3. Individual electrode polarization curves and magnified view of cathode polarization curves for cells operated with different CO₂ concentrations from (10 to 100% (v/v)).

Figure 4. Ratio of CO over CO₂ as a function of CO₂ concentration, ranging from 10 to 100% (v/v) using N₂ for dilution at four different cell potentials. N=4 for each data point.

Figure 5. (a) Faradaic efficiency for CO and (b) Partial current density of CO as a function of cell potential for 3 different pH levels and two different CO₂ concentration (10 and 100%).