# Influence of dilute feed and pH on electrochemical reduction of $CO_2$ to CO on Ag in a continuous flow electrolyzer

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## ABSTRACT

Electrochemical conversion of $CO_2$ to useful chemical intermediates may be a promising strategy to help reduce $CO_2$ emissions, while utilizing otherwise wasted excess renewable energy. Here we explore the effect of diluted $CO_2$ streams (10–100% by volume using $N_2$ as diluting inert gas) on the product selectivity and on the $CO/CO_2$ conversion ratio for the electrochemical reduction of $CO_2$ into CO, specifically using a gas diffusion electrode loaded with Ag catalyst in a continuous flow electrolyzer. When using diluted $CO_2$ 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/cm$^2$ 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% $CO_2$ feed to a 10% $CO_2$ feed. Also, we studied the effect of pH and the interplay between pH and the diluted $CO_2$ 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 $CO_2$ concentration in the feed is more significant than the effect of pH on electrochemical reduction of $CO_2$ to CO.

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## 1. Introduction

Excessive carbon dioxide ($CO_2$) emissions have been identified as a significant contributor to global climate change [1]. Two of the major sources of $CO_2$ emissions are transportation (cars and trucks) and power-plants, whose flue gas contains about 15% $CO_2$ [2]. To reduce $CO_2$ 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 $CO_2$ emissions, but at tremendous cost [4]. Recently, the conversion of $CO_2$ 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 $CO_2$ as feedstock, so it not only reduces $CO_2$ 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 $CO_2$ into useful chemicals.

The most attractive option to eliminate $CO_2$ 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 sources is challenging. As a result, at times a significant fraction of renewable power when abundantly available is not being utilized. The electrochemical reduction of $CO_2$ into value added chemicals, the topic of this paper, may provide a route to not only help reduce greenhouse gas emissions, it also could utilize this otherwise wasted excess electrical energy generated from renewable sources to synthesize chemicals that normally would have been derived from fossil fuels.

A previously reported cost analysis of processes that involves electrochemical conversion of $CO_2$ for the production of products such as formic acid, methanol, and mixture of short hydrocarbons reveals that significant improvements in energy efficiency are needed before such processes become cost effective compared to

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the various current ways to produce these products [22]. In the last decade, research to pursue better methods for $CO_2$ conversion in general [23], and to identify better catalysts for electro-reduction of $CO_2$, has drastically increased in intensity. On the other hand, process optimization to maximize overall energy efficiency has received much less attention. One interesting option that has been studied is the use of effluent gas of power plants directly as the feed for $CO_2$ conversion processes because it sidesteps the energy intense steps of $CO_2$ capture and concentration. For example, Kyriacou et al. reported on the influence of $CO_2$ partial pressure on the electrochemical reduction of $CO_2$ to $C_2H_4$ and $CH_4$ when using a copper electrode in a three electrode cell [24]. Others reported that the removal of $SO_2$ was needed, but the presence of NO in the dilute $CO_2$ feed had no influence on the electrochemical reduction of $CO_2$ to $C_2H_4$ and HCOOH when using a copper-solid polymer electrolyte-based electrode [25].

Here we study the electrochemical reduction of $CO_2$ 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 $CO_2$ 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 $CO_2$ [12].

In this paper we report on the electrochemical reduction of $CO_2$ to CO, a potentially interesting intermediate in the production of a range of chemicals via the Fischer–Tropsch process [29], while using a dilute $CO_2$ stream (such as the ∼15% $CO_2$ 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 $CO_2$ streams (10–100% by volume, using $N_2$ for dilution), and examine its impact on product selectivity (Faradaic efficiency for CO), $CO_2$ 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 $CO_2$ feeds (10% and 100%) on product selectivity and overall productivity.

## 2. Experimental

### 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 nano-particles, <100 nm particle size, 99.5% trace metals basis, Sigma–Aldrich), 5.20 μL Nafion solution (5 wt%, Solution Technology, 30:1 catalyst-to-Nafion ratio), as well as 200 μL of isopropyl alcohol (Sigma–Aldrich) and 200 μL Millipore water (18.2 MΩ) as the carrier solvents. The catalyst ink for the anodes was comprised of 2.50 mg Pt black (Alfa Aesar), 6.50 μL Nafion solution, as well as 200 μL of isopropyl alcohol and 200 μL Millipore water as the carrier solvents. To achieve uniform mixing, all the catalyst inks were sonicated for 15 min prior to use. Then, to cover GDEs with catalysts (total geometric area of 2 $cm^2$), 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/$cm^2$ and 1.0 mg Pt/$cm^2$, 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 $cm^2$, 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 $CO_2$ (S.J. Smith, 100%) and $N_2$ (S.J. Smith, 100%), on the cathode side while the anode was left open to the atmosphere. The $CO_2$ concentrations were varied from 10 to 100% by volume using $N_2$ 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 1M potassium chloride (KCl, Sigma–Aldrich, ≥99.9995% pure) in water, at 0.4 mL/min, or solutions of mono and dibasic potassium phosphate ($KH_2PO_4$, $K_2HPO_4$, Sigma–Aldrich, ≥99.0% pure) for pH dependent experiments (see below). The effluent gas streams were characterized with a gas chromatograph (Trace GC, Thermo-Fisher 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 $CO_2$ concentration in the feed on CO production. Cell polarization curves were recorded by steady-state chrono-amperometric measurements. The cell was allowed to reach steady state for 200s, at which point the current had stabilized. Then, a sample of the effluent stream was injected into gas chromatography (GC) for product analysis, before stepping to the next potential and waiting for steady state again. Individual anode and cathode polarization curves were measured using a Ag/AgCl reference electrode (RE-5B, BASi) that was placed in the outlet reservoir of the electrolyte. A new anode and cathode were used for every experiment. No deactivation of electrode activity was observed during these short experiments. Faradaic efficiencies, energetic efficiencies, and current densities are calculated by using equations reported previously [21].

Experiments with electrolytes of different pH were performed using aqueous phosphate buffer solutions comprised of mono and
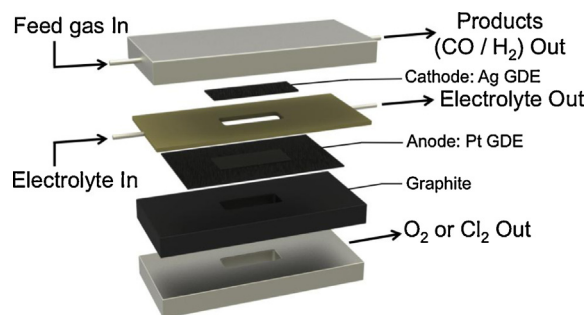


**Fig. 1.** Schematic representation of the electrochemical $CO_2$ flow reactor used in this study.

dibasic potassium phosphate ($KH_2PO_4$, $K_2HPO_4$, Sigma–Aldrich, $\geq$99.0% pure). Phosphate buffer was adjusted to pH 4, 7, or 10 by using 10M $H_3PO_4$ or 10M KOH. For these studies we used a dual-electrolyte reactor [5], in which a Nafion-117 membrane separates the catholyte (phosphate buffer solution) and the anolyte (1M KCl solution).

## 3. Results and discussion

To study the electrochemical reduction of $CO_2$ to CO using dilute $CO_2$ feeds, we used an electrochemical flow reactor as described in the experimental, equipped with respectively a silver catalyst and a platinum catalyst based gas diffusion electrode as the cathode and anode (Fig. 1). First we will report product selectivity and overall performance (Section 3.1) and then $CO_2$ utilization (Section 3.2) when using the 1 M 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 $H_2$ as a function of different $CO_2$ concentrations, ranging from 10 to 100% by volume, while Fig. 2b and c show the corresponding partial current density curves for CO and $H_2$. The equilibrium cell potential for this process is −1.33 V ($E°_{CO2/CO}$ (25 °C) = −1.33 V for $CO_2 \rightarrow CO + {}^{1}/_{2} O_2$), with $CO_2$ reduction to CO on the cathode ($E°$ = −0.10 V vs. RHE) and water oxidation to $O_2$ on the anode ($E°$ = 1.23 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 $H_2$ production (less than 5 mA/cm$^2$) 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 $CO_2$ concentration of the feed (Fig. 2a). At cell potentials of 2.75 V and 3.0 V, partial current densities for $CO_2$ of, respectively, 23.1 and 51.3 mA/cm$^2$ are observed when using a 100% $CO_2$ feed (Fig. 2b). Upon diluting the $CO_2$ feed, lower partial current densities for $CO_2$ are observed, but even at a 10% $CO_2$ feed they still are 11.7 and 29.0 mA/cm$^2$, respectively, for these two cell potentials. Furthermore, at these cell potentials the Ag cathode still achieves a Faradaic efficiency exceeding 80% CO, irrespective of the level of $CO_2$ dilution, ranging from 10% to pure $CO_2$ (100%) (Fig. 2a). The fact that the drop in CO production is only 40–50% when changing the feed from pure to 10–20% $CO_2$ suggests that the electrochemical reduction of $CO_2$ can be performed using flue gas from a power plant (~15% $CO_2$), after the flue gas has been scrubbed of certain impurities that can act as a poison to the catalysts.

The observed trends in the dependence of the partial current density for CO as a function of the $CO_2$ concentration in the feed are similar to what has been observed previously for $CO_2$ reduction in 3-electrode cell and in solid oxide fuel cells [24,33,34]. Specifically, this prior work showed that the current density observed for both cells are proportional to the partial pressure of reactant with various diluents. In other words, high performance could be maintained with a certain percentage of reactant. This is similar to what we observe here (Fig. 2b): a higher $CO_2$ concentration leads to a higher rate of reaction (*i.e.*, higher current density).

In terms of $H_2$ evolution, except for the high $H_2$ evolution observed when using a 10% $CO_2$ feed at a cell potential of 3.0 V, the Faradaic efficiencies for $H_2$ were below 8% at all other conditions, suggesting that the use of diluted $CO_2$ as the reactor feed does not significantly affect $H_2$ evolution (Fig. 2c). The observed increase in $H_2$ evolution at 10% $CO_2$ may be due to the low $CO_2$ concentration,



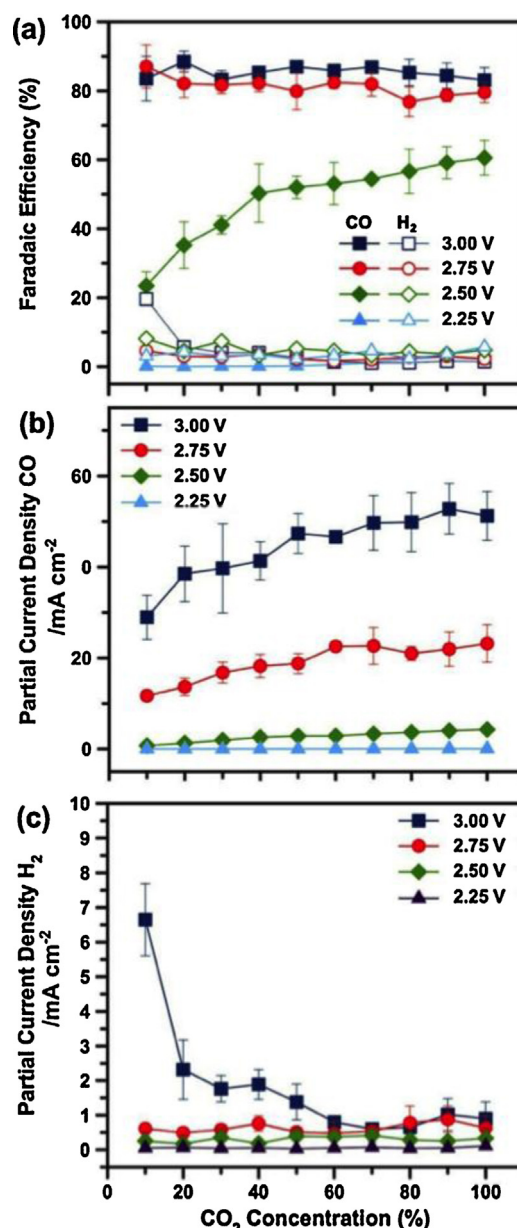**Fig. 2.** (a) Faradaic efficiency for CO and $H_2$, and partial current density of (b) CO, and (c) $H_2$ as a function of $CO_2$ concentration, ranging from 10 to 100% (v/v) using $N_2$ for dilution at four different cell potentials. $N$ = 4 for each data point.

which seemingly is not sufficient anymore to suppress $H_2$ evolution. For all experimental conditions (except when using a 10% $CO_2$ feed in combination with a cell potential of 3.0 V), the partial current density for $H_2$ stayed below 2 mA/cm$^2$, independent of the $CO_2$ concentration in the feed.

Next, we analyzed the performance of the anode and cathode as a function of $CO_2$ 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 $CO_2$ 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 $CO_2$ concentration in the feed from 100% to 70%, as is also evident from the data shown in Fig. 2b. However, when feeds with lower $CO_2$ concentrations are used the cathode polarization gradually increases, so at identical cathode

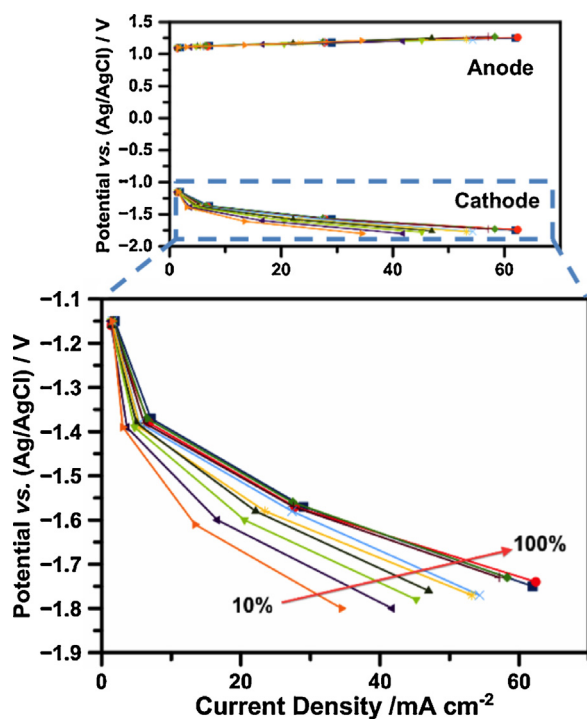**Fig. 3.** Individual electrode polarization curves and magnified view of cathode polarization curves for cells operated with different $CO_2$ concentrations from (10 to 100% (v/v).

potential a lower current density is observed. In summary, lower $CO_2$ concentrations lead to higher cathode polarization.

### 3.2. $CO_2$ utilization per pass

We also studied the utilization of $CO_2$ per pass, expressed in the ratio of the amount of produced CO over the amount of $CO_2$ injected, as a function of $CO_2$ concentration. This ratio represents a measure of the $CO_2$ utilization toward the desired product CO. Diluted $CO_2$ feeds lead to higher CO over $CO_2$ ratios than when using pure $CO_2$ feeds (Fig. 4): Specifically, when using a 10% $CO_2$ feed, maximum CO over $CO_2$ 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 $CO_2$ ratios of 0.01, 0.02, and 0.05, were
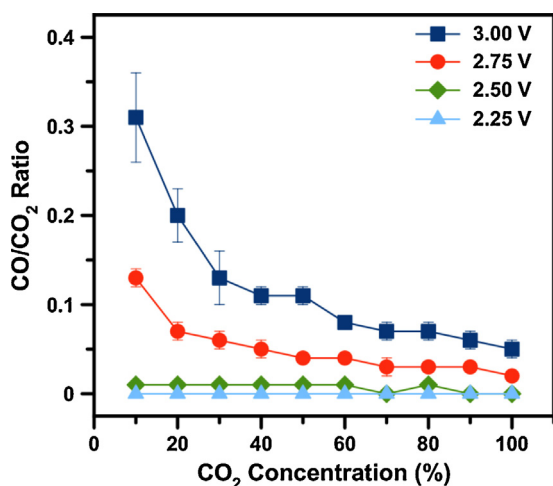


**Fig. 4.** Ratio of CO over $CO_2$ as a function of $CO_2$ concentration, ranging from 10 to 100% (v/v) using $N_2$ for dilution at four different cell potentials. $N = 4$ for each data point.

obtained at these same cell potentials when using a 100% $CO_2$ feed. In other words, the utilization of $CO_2$ per pass increased up to 6 fold by using diluted $CO_2$ streams. Also, the utilization of $CO_2$ is enhanced with increasing cell potentials, implying that electro-chemical conversion of diluted $CO_2$ 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 $CO_2$ utilization at high concentration $CO_2$ feeds.

### 3.3. Performance as a function of electrolyte pH

The electrochemical reduction of $CO_2$ 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 1 M 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% $CO_2$ feed instead of a 100% $CO_2$ feed. This difference can probably be explained by the difference in the amount of $CO_2$ that dissolves into the electrolyte (reacts with water) and then equilibrates to form protons and $HCO_3^-$. 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.

In order to systematically study how the pH affects CO formation in the electrochemical reduction of $CO_2$ we switched to using phosphate buffer (0.5 M $K_2HPO_4$ and 0.5 M $KH_2PO_4$) as the electrolyte, because the pH of a non-buffered KCl solution cannot be controlled precisely given the amount of hydroxyl being formed at the cathode (see above). The phosphate buffer was adjusted to pH 4, 7, and 10 using either 10 M KOH or 10 M $H_3PO_4$. Fig. 5 shows the Faradaic efficiency for CO and the partial current density for CO for experiments performed with different $CO_2$ feeds (10% and 100%) and electrolytes of different pH (4, 7, and 10). In agreement with the results with 1 M KCl electrolyte reported above (Fig. 2b), for all cases a 3–16 times higher current density is observed when using a 100% $CO_2$ feed instead of a 10% $CO_2$ feed. The highest partial current density for CO is obtained when using the alkaline electrolyte, particularly at the highest cell potentials, with successively lower partial current densities being observed when using the neutral and acidic electrolyte (Fig. 5b). The increase (or decrease) in current density when changing the pH from neutral to alkaline (or acidic) at the highest cell potentials is only about 12 mA/cm² which is a factor of about 1.5 higher in alkaline media (about 1.5 times lower in acidic media) than the current density observed in a neutral electrolyte.

The highest Faradaic efficiency for CO is observed at high cell potentials when using the alkaline electrolyte (up to 80-95%), with successively poorer selectivity for neutral and acidic electrolytes. This is in agreement with the observations reported above when using 1 M KCl electrolyte (Fig. 2). As expected, $H_2$ evolution was predominant when using the acidic electrolyte, and at lower cell potentials. For most sets of conditions, the difference in Faradaic efficiency when using a 10% feed or 100% feed is more pronounced when using the neutral or acidic electrolyte.

Interestingly, a higher Faradaic efficiency for CO and a higher partial current density for CO were observed when using the alkaline electrolyte. In this paper we do not attempt to unravel the specific mechanism for $CO_2$ reduction in alkaline electrolyte. One can speculate, however, that the higher partial current density for
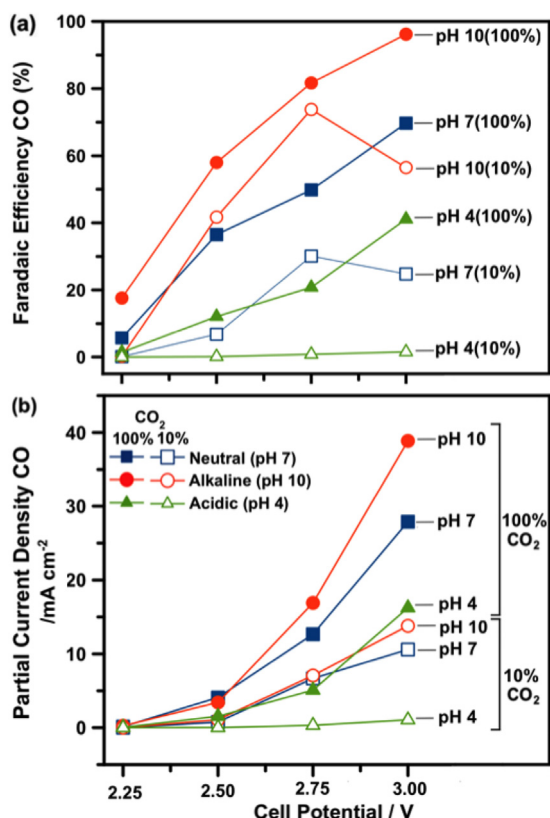
**Fig. 5.** (a) Faradaic efficiency for CO and (b) partial current density of CO as a function of cell potential for 3 different pH levels and two different $CO_2$ concentration (10 and 100%).

CO observed when using an alkaline electrolyte is due to a higher number of available of active sites, but further research would be needed to confirm this. In general, $CO_2$ reduction proceeds in competition with $H_2$ evolution in aqueous electrolytes. For example, Wu et al. emphasized controlling the $H^+$ concentration near the cathode surface, because excessive amounts of $H^+$ could lead to high $H_2$ [36]. In acidic and/or neutral electrolyte, the higher $H^+$ concentration leads to $H^+$ successfully competing with $CO_2$ for the active sites on the cathode surface, resulting in a significantly lower Faradaic efficiency for CO [27,36]. Upon increasing the pH (lowering the $H^+$ concentration), more active sites become available, so the CO formation reaction is facilitated while $H_2$ evolution is suppressed. In summary, the extent of CO formation can be understood by mediation of the $H^+$ concentration near the cathode surface.

In sum, an alkaline pH helps to achieve high Faradaic efficiency for CO, but the effect of $CO_2$ concentration on the partial current density for CO is more significant than the effect of pH.

## 4. Conclusions

We investigated the interplay between cathode performance and $CO_2$ concentration in the feed as well as electrolyte pH in the electrochemical reduction of $CO_2$ 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 $CO_2$ (>30%) could be achieved even at $CO_2$ concentration down to 10%, provided high cell potentials are used. In terms of absolute CO production, when operating at 10% $CO_2$ concentration, the partial current density for CO is still 55% (29 vs. 51 mA/cm$^2$ at a cell potential of 3.0 V) of the partial current density measured when operating with a

100% $CO_2$ feed. Higherlevels 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 $CO_2$ concentration than by a pH change. These results suggest that the electrochemical conversion of $CO_2$ to CO can be performed efficiently while using a diluted $CO_2$ stream, such as flue gas ($\sim$15% $CO_2$), thus avoiding an energy intensive $CO_2$ concentration step; The use of a pure or highly concentrated $CO_2$ 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 $CO_2$ and $N_2$) are needed. Efforts to further improve catalysts and electrodes for electrochemical $CO_2$ reduction will also help the prospects of using dilute $CO_2$ streams as the feed.

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