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Voltammetric study of CO_2 reduction at Cu electrodes under different $KHCO_3$ concentrations, temperatures and CO_2 pressures

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Abstract

The understanding of the electroreduction pathway of CO_2 over Cu surfaces in $KHCO_3$ solution is very important in the area of electrocatalysis. In this paper, we present linear sweep voltammetry results at different temperatures, different $KHCO_3$ concentrations, and different CO_2 pressures that provide important information about the CO_2 reduction pathway. In experiments under CO_2, at different temperatures, we obtained data that confirm the existence of CO_{ad} as an intermediate of the reduction of CO_2 over Cu surfaces. In addition, voltammetry experiments at $KHCO_3$ concentrations between 0.01 and 2.0 M confirmed the theory that the increased pH created near the electrode surface during the reduction process is being lowered by the neutralization reaction by $KHCO_3$. Also, we present a mechanism in which CO_{ad} is displaced from the Cu surface in solutions pressurized with CO_2 (30–250 psi or 2–17.2 bar). This model is based on voltammetric, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) results of experiments performed under different CO_2 pressures. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cu electrodes; Electrocatalytic reduction of CO_2; Voltammetry; CO_2 pressure

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1. Introduction

Since the world's energy crisis, more people are interested in energy storage processes. The electrochemical reduction of CO_2 is one of these processes since its hydrocarbon products can be used as fuels. In order to study the faradaic yield of the different products of this process, the electroreduction of CO_2 has been done under various conditions such as using different electrode materials, solvents and supporting electrolytes [1–6].

Hori and collaborators observed the formation of methane and ethylene when Cu electrodes were used to reduce CO_2 in aqueous $KHCO_3$ solutions [7–10]. Considerable attention has been given to understanding the mechanism of this reaction in order to increase the yield of hydrocarbons and avoid the passivation of the working electrode [11–16].

Electrolysis, voltammetry, in situ infrared spectroscopy, and real-time mass spectroscopy results indicate that CO adsorbs weakly on Cu surfaces [9,11,17–19]. On the other hand, the electrolysis of CO on Cu electrodes in $KHCO_3$ solution produces hydrocarbons in low yield [9]. These results support the theory that CO is an intermediate in the production of methane and ethylene from CO_2.

The effect of temperature on the electrolysis was one of the experimental conditions studied when CO_2 was reduced in $KHCO_3$ solution over a Cu electrode [8,14]. It was observed that the faradaic yield for methane increased with decreasing temperature. On the other hand, the faradaic efficiency for H_2 increased with increasing temperature. Studies at very low temperature have been presented recently at Au [20] and Cu [21] electrodes. Other metals used to study the effect of temperature include In, Sn, and Pb electrodes [22].

Different products and faradaic yields have been obtained when different supporting electrolytes and concentrations were used in the reduction of CO_2 on

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Cu electrodes [9,10]. High faradaic yields for methane and ethylene were observed when 0.1–0.5 M $KHCO_3$ solutions were used. Hori and collaborators suggested that when a weak acid such as HCO_3^- was used as the supporting electrolyte, the pH near the electrode surface could be maintained lower than if a non-acid was used. This higher H^+ concentration increased the yield of hydrocarbons in the reduction of CO_2.

Various research groups used different CO_2 pressures to increase the CO_2 availability in solution during electrolysis [23–31]. Sakata and coworkers found that when different pressures of CO_2 were used in its reduction, using Cu electrodes in $KHCO_3$ solutions, the yield of the products changed [32]. The authors showed that, as the CO_2 pressure increased, the main product changed in the following order:

$H_2 \rightarrow$ hydrocarbons $\rightarrow$ CO

Although several research groups have studied the electroreduction of CO_2 on Cu surfaces, little voltammetric information has been reported [9,10]. In our laboratory, we used linear sweep voltammetry to study the reduction of CO_2 at different $KHCO_3$ concentrations, different temperatures and different CO_2 pressures. The results at different temperatures and $KHCO_3$ concentrations support the idea of the presence of CO as an adsorbed intermediate and the existence of a region of lower pH near the electrode surface, respectively. The voltammetry done in solutions pressurized with CO_2 indicates a decrease in the passivation of the Cu surface due to the adsorption of CO_2. The results of our studies are useful to understand the CO_2 reduction pathway better.

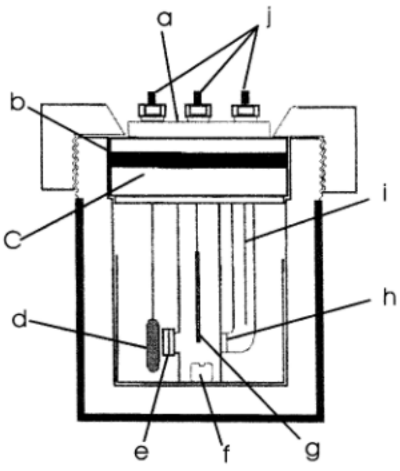

Fig. 1. High pressure electrochemical cell: (a) gas inlet; (b) O-ring; (c) lid; (d) counter electrode; (e) Nafion® membrane; (f) stirrer; (g) working electrode; (h) fritted disk; (i) reference electrode; (j) copper contacts.

2. Experimental

Potassium bicarbonate, $KHCO_3$ (Aldrich, 99.7%), potassium ferricyanide, $K_3Fe(CN)_6$ (Aldrich, 99%) and acetone (Aldrich, 99.5%) were used as received. The water used was distilled first and then purified using a Barnstead Nanopure purification system (17.9 MΩ cm). CO_2 (Air Products, 99.9995%) was run through an Oxy-Trap (Alltech) before being used. A flow bath, constructed in our laboratory and coupled to an ethylene glycol + water circulator (Haake F 3), was used to control the cell temperature. This flow bath was positioned over a magnetic stirrer.

A Princeton Applied Research (PAR) 173 potentiostat/galvanostat coupled to a PAR 175 programmer and to a Soltec XY VP-6424S recorder or a PAR 273 potentiostat/galvanostat controlled with PAR M 270 Research Electrochemistry software, installed in a personal computer (IBM/55 SX), was used to perform the voltammetric experiments.

In all electrochemical experiments, a three-electrode array was used. A Pt foil or gauze was used as the counter electrode whereas Ag|AgCl|KCl (sat) or AgQRE was used as the reference electrode. A 99.999% Cu wire (Johnson Matthey) of 0.25 mm diameter sealed with Torr-Seal epoxy (Varian) inside a glass capillary was used as the working electrode. Before each experiment, the working electrode was polished with 1 μm diamond paste (Buehler) and rinsed with acetone and purified water. Finally, the surface was treated with 10% HCl for 10 s and rinsed using purified water [33].

The experiments at atmospheric pressure were performed in a Pyrex® cell with three compartments separated by glass fritted disks. The gas (CO_2, Ar or N_2) was bubbled into the solution for 15 min before each measurement. The solution was magnetically stirred for 1 min before each voltammogram was recorded. Solutions (0.5 M in $KHCO_3$) were used in the experiments at different temperatures (0–45 °C). Experiments at different $KHCO_3$ concentrations (0.01–0.5 M) were done at 20 °C.

An electrochemical cell was designed for experiments at controlled CO_2 pressures (Fig. 1). The cell body was constructed using 306 stainless steel (SS-316). Three copper wires were used as contacts for the electrodes. The wires were isolated and sealed using Teflon® disks through the SS-316 lid. During the electrochemical experiments, the lid was sealed to the cell body using a Viton® O-ring. A removable Pyrex electrochemical cell fitted into the stainless steel body was used. In this cell, the working electrode compartment was separated from that of the counter electrode by a 0.43 mm cation exchange membrane (Nafion®, Aldrich). A fritted disk separated the reference and working electrode compartments.

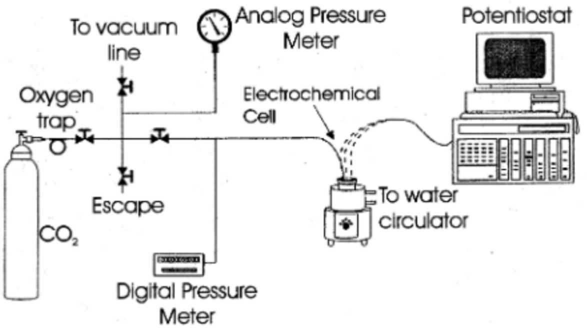

Fig. 2. Setup used for the controlled pressure experiments.

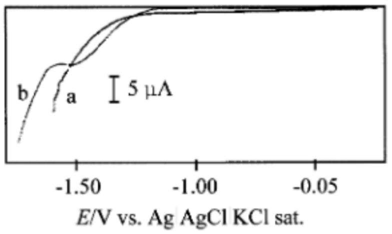

Fig. 3. Voltammograms in a 0.5 M $KHCO_3$ solution saturated with (a) N_2; and (b) CO_2 at 15 °C (20 mV s^{-1}).

The experimental setup is shown in Fig. 2. A valve system was used to control the pressure in the cell. All the valves, connections (Swagelok) and tubings (0.64 and 0.16 cm o.d.) were made of SS-316. A vacuum line was connected to one of the valves to remove oxygen from the system and the solution. A N_2 or CO_2 tank with an oxygen trap was connected to a second valve. The pressure in the cell was monitored using an Omega pressure transducer (PX302-1 KG V) coupled to an Omega transducer indicator (DP-420). Temperature control was achieved by immersing the cell in the flow bath previously described.

Before each experiment, oxygen was removed from the system and the 0.5 M $KHCO_3$ solution for 2 h using the vacuum system. Then, the desired CO_2 pressure (25–250 psi or 2–17.2 bar; 1 psi = 0.0689476 bar) was introduced to the cell over 4 h before doing the voltammetric experiments. In all these experiments, the solution was magnetically stirred for 1 min before recording each voltammogram.

Surface analyses were performed on Cu samples that were exposed to the same conditions of pressure and temperature at which the electrochemical studies were performed. Before exposing the Cu (Johnson Matthey, 99.999%) sample to the experimental conditions, it was subjected to the pretreatment used for the working electrode before each electrochemical experiment. After the preparation, the samples were stored in a desiccator under vacuum until the surface analyses were performed. The samples were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). XPS analyses were performed using the Mg–K_{α} X-ray source of a PHI 5600ci spectrometer at 12.0 kV and 400 W. SEM analyses were performed using a JEOL JSM-5800LV in the high vacuum mode with an acceleration voltage of 15.0 kV.

3. Results and discussion

3.1. Voltammetric experiments at different temperatures

Voltammetric experiments were done at different temperatures with and without CO_2. Fig. 3 shows the voltammetric behavior of a Cu electrode recorded at 20 mV s^{-1} in a 0.5 M $KHCO_3$ solution saturated with (a) N_2 and (b) CO_2 at atmospheric pressure and a temperature of 15 °C. No cathodic peak was observed in the solution saturated with N_2. Only the solvent limit was observed in this solution. On the other hand, a reduction peak ($E_p = -1.5$ V vs. Ag|AgCl) very near to the lower limit was observed when the voltammetry was recorded in the solution saturated with CO_2. In addition, under CO_2, the reduction limit was shifted toward a more negative potential than under N_2.

The electrochemical behavior shown in Fig. 3 was first observed and explained by Hori et al. [9,10]. These authors explained that the lower limit observed in the voltammograms under N_2 is due to hydrogen evolution (see Fig. 3a). As can be seen in Fig. 3b, hydrogen evolution is suppressed under CO_2. The lower limit observed under CO_2 was assigned to both hydrogen evolution and CO_2 reduction using bulk electrolysis results [8,9]. CO_2 is initially reduced to CO and this CO remains adsorbed on the Cu surface. This CO_{ad} causes a partial passivation of the Cu electrode and, hence, decreases the current due to H_2 evolution. After the peak maximum, the CO_{ad} is reduced to secondary products, such as CH_4 and C_2H_4, and the surface becomes 'free' of adsorbed products. Then, hydrogen evolution occurs without any opposition and the lower limit can be observed at more negative potentials.

Voltammetric experiments were done in 0.5 M $KHCO_3$ solutions saturated with N_2 and CO_2 at temperatures between 0 and 45 °C using Cu electrodes. The voltammetric behavior observed at 15 °C (see Fig. 3) in solutions saturated with N_2 and CO_2 is representative of the behavior at temperatures between 0 and 45 °C. Fig. 4 shows the peak current of voltammograms obtained in solutions saturated with CO_2 at atmospheric pressure as a function of temperature. As can be observed, there are two distinct regions in the temperature dependence. Between 0 and 20 °C the reduction current is constant, while the concentration of CO_2 drops by a factor of 2 (see inset in Fig. 4). The inset in Fig. 4 shows the solubility of CO_2 in pure water as a function of temperature [34]. Above 20 °C the current shows a roughly linear increase, by a factor of 4 between 20 and 40 °C, while the concentration decreased by less than a factor of 2. This may be due to a passivation layer of CO being bound below 20 °C, but released above 20 °C. Because the peak current increases and the CO_2 solubility decreases as the temperature increases, the rate-limiting step is not associated with the concentration of CO_2. However, it is obvious that the peak current is related to a CO_2 process on the Cu surface. The only way that the current can increase as the CO_2 concentration decreases is if CO_2, or one of its reduction products poisons or deactivates the Cu surface. It is well known that CO is one of the reduction products of CO_2 [2,8,10,14,35] and that CO adsorbs more strongly than CO_2 on the Cu surface [17]. Therefore, the rate-limiting step is either dissociation of CO or its reduction to give the hydrocarbons, depending on conditions.

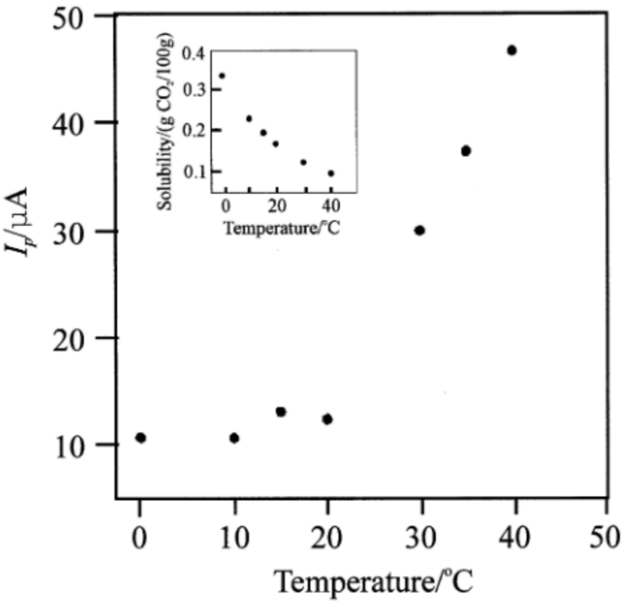

Fig. 4. Cathodic peak current as a function of temperature in the voltammetry (20 mV s^{-1}) of a 0.5 M $KHCO_3$ solution saturated with CO_2. The inset shows the solubility of CO_2 in pure water as a function of temperature [34].

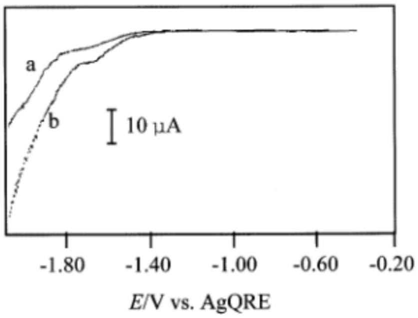

Fig. 5. Voltammetry of CO_2 in a: (a) 0.01; and (b) 0.5 M $KHCO_3$ solution saturated with CO_2 at 20 °C (scan rate 20 mV s^{-1}).

Table 1
$E_{p/2}$ values for $K_3Fe(CN)_6$ in $KHCO_3$ solutions of different concentrations

$[KHCO_3]$/M	E_{pc}/V	E_{pa}/V	$E_{p/2}$/V	◆E_p/V
0.05	ND	ND	ND	ND
0.1	0.184	0.094	0.139	0.090
0.5	0.213	0.122	0.168	0.091
1.0	0.222	0.140	0.181	0.082
2.0	0.241	0.152	0.197	0.089

The concentration of $K_3Fe(CN)_6$ in the solution was 1 mM. A Pt disk and an AgQRE were used as working and reference electrodes, respectively. The scan rate was 100 mV s^{-1}. ND: not determined.

3.2. Voltammetric experiments at different $KHCO_3$ concentrations

Voltammetric experiments of solutions saturated with N_2 and CO_2 were also done at $KHCO_3$ concentrations between 0.01 and 0.5 M at 20 °C. Fig. 5 shows the voltammograms obtained in (a) 0.1 and (b) 0.5 M $KHCO_3$ solutions saturated with CO_2 at atmospheric pressure. In these experiments under CO_2, it can be observed that the lower limit was shifted to more positive potentials as the $KHCO_3$ concentration was increased. This shift in the lower limit was also observed in the voltammograms done under N_2. A possible reason for this shift could be a change in the potential of the quasi-reference electrode (AgQRE) with changes in the $KHCO_3$ concentration. Voltammetric experiments at different $KHCO_3$ concentrations were done using 1 mM $K_3Fe(CN)_6$ as an internal standard to study the stability of the AgQRE. These experiments were done in solutions saturated with N_2 and CO_2 and using a Pt disk electrode as the working electrode. The voltammetry of $K_3Fe(CN)_6$ shows a shift in the peak potentials to more positive values as the supporting electrolyte concentration increases, as shown in Table 1. Therefore, the potential shift of the lower limit is due to the change in the quasi-reference potential that occurs when the $KHCO_3$ concentration is changed.

The importance of these experiments at different $KHCO_3$ concentrations lies in the fact that the peak current increases when the supporting electrolyte concentration is increased. Knowing that the peak current is due in part to H^+ reduction, this increase in current can be assigned to a decrease in pH. However, the pH of solutions previously saturated with N_2 and CO_2 at different $KHCO_3$ concentrations did not show significant differences as can be seen in Table 2. Although the pH in the solutions at different $KHCO_3$ concentrations is nearly the same (pH◆ 7.9), a change in the peak current suggests an increase in the amount of H^+

Table 2
pH of $KHCO_3$ aqueous solutions at different concentrations under N_2 and CO_2

$[KHCO_3]$/M	pH	
	Under CO_2	Under N_2
0.05	7.8	8.9
0.1	7.8	8.6
0.5	7.9	8.7
1.0	7.9	8.7
1.5	7.9	9.1
2.5	8.0	8.6

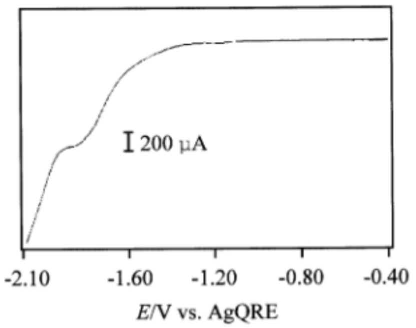

Fig. 6. Voltammogram at 250 psi of CO_2 in a solution of 0.5 M $KHCO_3$ at 20 °C (scan rate 100 mV s^{-1}).

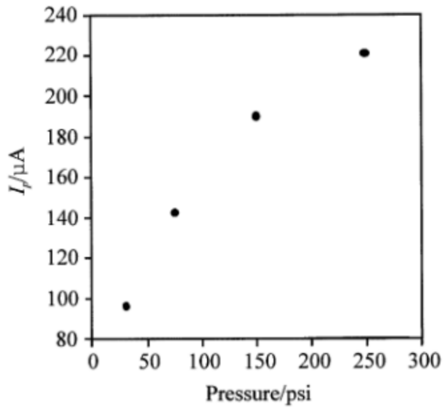

Fig. 7. Cathodic peak current as a function of CO_2 pressure in 0.5 M $KHCO_3$ solution at 20 °C (scan rate 100 mV s^{-1}).

Table 3
Peak currents and peak potentials of voltammograms obtained with Cu electrodes in 0.5 M $KHCO_3$ solutions at 20 °C and CO_2 pressures between 30 and 250 psi

P_{CO_2}/psi	I/•A	E_p/V [a]
30	166.8	− 1.668
75	146.2	− 1.498
150	204.9	− 2.012
250	214.0	− 1.699

[a] vs. AgQRE at 100 mV s^{-1}.

reduced. This can be explained if the pH in the bulk of the solution is neutralizing the OH^- formed at the electrode surface. This has been described by Hori et al. [9,10]. This description considers the reduction of CO_2 in aqueous solution. In this system, each electron used in the reduction of CO_2 to hydrocarbons and water to hydrogen produces one hydroxide ion. For example

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$$

Thus, the reduction of CO_2 increases the pH near the electrode surface. If the supporting electrolyte used in the reduction is a weak acid, such as HCO_3^-, the hydroxide formed near the electrode surface will be neutralized faster than if a non-acid is used as the supporting electrolyte. This neutralization causes a decrease in the pH near the electrode surface that has risen because of the reduction of CO_2 and H_2O. As the concentration of the supporting electrolyte is increased in the solution, the concentration of HCO_3^- available for the neutralization of the hydroxide ions formed near the electrode surface will be higher. Thus, the pH increase resultant of the reduction processes will be neutralized $KHCO_3$ and, then, a higher reduction peak current will be obtained when the $KHCO_3$ is increased. Hence, our results are experimental evidence of the veracity of the theory that $KHCO_3$ lowers the pH that increases near the electrode surface during the reduction process.

3.3. Voltammetric experiments at different CO_2 pressures

Voltammetric experiments were performed in 0.50 M $KHCO_3$ solution at 20 °C pressurizing CO_2 between 30 and 250 psi for 4 h. The voltammograms at different CO_2 pressures show the same behavior as the voltammograms at atmospheric pressure, as can be observed in Fig. 6. Fig. 7 shows the behavior of the reduction peak current as a function of the CO_2 pressure. As can be observed, the reduction peak current increased to a steady state as the CO_2 pressure increased. Table 3 summarizes the information obtained in a typical set of voltammetric experiments in 0.5 M $KHCO_3$ solutions at 20 °C and CO_2 pressures between 30 and 250 psi. Various processes could be the reason for this behavior. As a first possibility, this current increase could be a result of a decrease in the solution pH due to the hydrolysis of CO_2 to HCO_3^-. As was discussed above, an increase in HCO_3^- will cause an increase in the H^+ available for reduction. The second possibility could be that the surface of the Cu electrode suffered changes as the CO_2 pressure was increased. These changes could increase hydrogen evolution or reduce the adsorption of CO. A third possibility is that, due to a higher CO_2

concentration in solution, the CO_2 displaces some CO_{ad} from the Cu surface.

To study the first possibility, voltammetric studies were done in solutions containing 1 mM $K_3Fe(CN)_6$ and 0.5 M $KHCO_3$ at different CO_2 pressures. These studies were done at 20 °C using a Pt working electrode. As can be seen in Table 4, non-significant peak potential changes (10–20 mV) were observed in the voltammetry of $K_3Fe(CN)_6$. As was discussed in the experiments at different $KHCO_3$ concentrations, a shift in the peak potential of $K_3Fe(CN)_6$ is expected when the concentration of the supporting electrolyte is increased. This shift was not observed and, therefore, the increase in peak current was not caused by an increase in the concentration of HCO_3^-.

It may be possible that the Cu surface changes when the CO_2 pressure is increased in the $KHCO_3$ solution over 4 h. These possible changes could favor a weaker adsorption of CO or an increase in hydrogen evolution. To see whether changes occurred on the Cu surface when different CO_2 pressures were introduced to the electrochemical cell, SEM and XPS studies were performed. No appreciable changes in morphology occur when Cu is exposed to 30 and 250 psi CO_2 in 0.5 M $KHCO_3$ solution for 4 h. Table 5 shows some results of the XPS analyses. The ratio of the area of the $Cu2p_{3/2}$ satellite (Cu_{sat}) to the area of the $Cu2p_{3/2}$ peak (Cu_{peak}) is used as a measurement of Cu(II) on the Cu surface [36–38]. As can be observed, the concentration of Cu(II) does not change with different CO_2 pressures. In summary, no significant change of the Cu surface was observed with SEM or XPS techniques. Hence, the observed increase in peak current with increasing pressure was not due to changes on the Cu surface. A more detailed surface analysis study of Cu exposed to different pressures of CO_2 and N_2 in $KHCO_3$ solutions will be published elsewhere.

Table 4
$E_{p/2}$ for $K_3Fe(CN)_6$ [a] in 0.5 M $KHCO_3$ solutions at 20 °C and CO_2 pressures between 30 and 250 psi

P_{CO_2}/psi	$E_{p/2}$/V [b]
30	0.173
75	0.169
150	0.183
250	0.177

[a] $[K_3Fe(CN)_6]$ = 1 mM.
[b] vs. AgQRE at 100 mV s^{-1}.

Table 5
Ratio of the area of the $Cu2p_{3/2}$ satellite to the area of the $Cu2p_{3/2}$ peak (Cu_{sat}/Cu_{peak}) of the XPS signal for a Cu wire exposed to different pressures of CO_2 in a solution of 0.5 M $KHCO_3$

P_{CO_2}/psi	Cu_{sat}/Cu_{peak}
30	0.11
250	0.12

After ruling out the first two possible explanations for the increase in peak current with increasing CO_2 pressure, the third theory is the only explanation for the experimental observations. It is known that CO_2 adsorbs in a weaker form than CO to Cu surfaces in $KHCO_3$ solutions [17]. We believe that an increase in the concentration of CO_2 in the solution will cause an increase in the concentration of CO_2 over the Cu surface by displacement of some CO_{ad}. Sakata and coworkers found the same effect at Ni electrodes [26]. This process will delay the deactivation of the Cu surface and, hence, will lead to an increase in the peak current. If this model is true, an increase in the faradaic yield of CO will be expected as the CO_2 pressure is increased. Sakata and coworkers did bulk electrolysis experiments in $KHCO_3$ solutions with Cu electrodes at different CO_2 pressures [25]. They found an increase in the CO faradaic yield and a decrease in the yield of hydrocarbons as the CO_2 pressure was increased. Hence, their results are in agreement with our model.

Although reproducible peak current results were obtained, we observed poor reproducibility in the reduction peak potential with changes in the CO_2 and N_2 pressures. In an effort to explain this behavior, we did surface analyses (SEM, XPS, and Auger electron spectroscopy) on the working and the quasi-reference electrodes, and voltammetric experiments with an internal standard, to study the stability of the AgQRE at different CO_2 and N_2 pressures. No explanation for the observed behavior has been found yet. We are still working on the solution to this problem before performing bulk electrolysis studies under different experimental conditions.

4. Conclusions

Voltammetric experiments of CO_2 in $KHCO_3$ solutions with Cu electrodes under different conditions offer important information on the electroreduction mechanism. The voltammetry of this system at different temperatures gave us information that is in agreement with the adsorption of CO on the Cu surface as a step in the CO_2 reduction mechanism. In addition, the existence of a neutralization effect of OH^- near the electrode surface by the bulk electrolyte was confirmed by our voltammetric results of solutions at different $KHCO_3$ concentrations.

Using the voltammetric data at different CO_2 pressures at Cu electrodes, we describe the displacement of CO_{ad} from the electrode surface by CO_2 when the electroreduction is done under CO_2 pressure. This explains the increase in the CO faradaic yield when the

CO_2 pressure is increased as observed by Sakata and coworkers [25,26].

Acknowledgements

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