

## Electrochemical Reduction of CO<sub>2</sub> at Polycrystalline Copper in Aqueous Phosphate Buffered Solution: pH and Temperature Dependence

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**Abstract :** The effect of electrolyte solution pH and temperature on the reduction of CO<sub>2</sub> at a copper electrode was investigated using cyclic voltammetry and SNIFTIR spectroscopy. The results indicated that CO<sub>2</sub> was reduced over a wide pH range (2.5 to 9.0); and over a wide temperature range (0 to 80 °C). Reduction products, adsorbed CO and copper carbonyl showed the same pH dependence behavior. CO did not adsorb on the electrode surface at pH less than 3. The results also indicated that the solution temperature shows proportional dependence behavior. Increases of both anodic and cathodic peak currents in the same ratio were observed with increase in temperature. The hydrogen evolution reaction (HER) region was not affected by the change of solution temperature. The probability of soluble CO<sub>2</sub> being reduced electrochemically depended on the amount that reached the copper surface.

**Abstrak :** Kesan pH dan suhu larutan elektrolit ke atas penurunan CO<sub>2</sub> di atas elektrod kuprum telah dikaji dengan menggunakan siklik voltametri dan spektroskopi SNIFTIR. Hasil kajian menunjukkan bahawa CO<sub>2</sub> terturun dalam julat pH yang besar (2.5 – 9.0) dan dalam julat suhu yang luas (0 – 80 °C). Hasil penurunan CO<sub>2</sub>, CO terjerap dan kuprum karbonil menunjukkan sifat kebergantungan ke atas pH yang hampir sama. CO tidak terjerap ke atas permukaan elektrod pada julat pH yang kurang dari 3. Hasil kajian juga menunjukkan bahawa suhu larutan mempengaruhi kadar penurunan CO<sub>2</sub> secara perkadaran terus. Penambahan ke atas kedua-dua puncak arus anodik dan katodik dalam siklik voltametri terjadi dalam kadar yang sama dengan nilai penambahan suhu. Kawasan tindakbalas evolusi hydrogen (HER) juga tidak dipengaruhi oleh suhu. Ini menunjukkan bahawa kebarangkalian untuk CO<sub>2</sub> terlarut mengalami penurunan bergantung kepada amaunnya yang sampai ke atas permukaan elektrod.

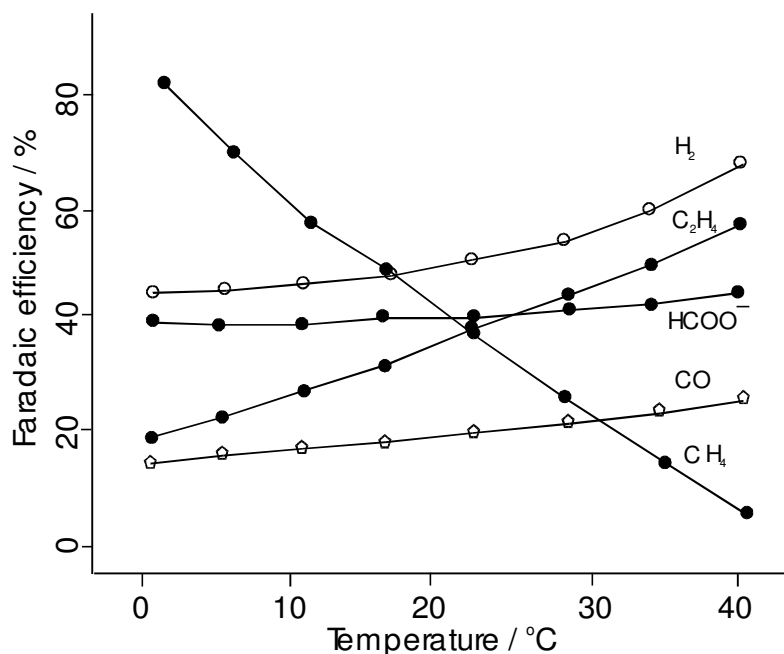
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### Introduction

The electrochemical reduction of CO<sub>2</sub> at transition metal electrodes provides both the means for activating the inert molecule of CO<sub>2</sub> and simultaneously rendering a source of hydrogen. Most electrochemical reductions of CO<sub>2</sub> using metal electrodes indicate that the reduction products depend among others on pH and temperature, which determine the gas solubility [1]. Increasing CO<sub>2</sub> solubility in the electrolyte used for the reduction is important as it increases the surface coverage and the availability of CO<sub>2</sub> to be reduced at the electrode surface. Electrochemical reduction of CO<sub>2</sub> to CH<sub>4</sub> occurs at pH values as high as 9.1 with modest rates and faradaic efficiencies [2]. This indicates that direct reduction of CO<sub>2</sub> occurs even at alkaline pH as a significant partial pressure of CO<sub>2</sub> is present. However, CH<sub>4</sub> can be formed at pH values below 1. Thus the rate of CH<sub>4</sub> formation does depend on pH. In the pH region 9 to 3, the rate increases. This was attributed to an increase in surface hydride coverage which will increase the rate of hydrogenation of CO<sub>2</sub> reduction intermediates, or an increase rate of oxygen removal from the surface, which favors the oxygenation of CO<sub>2</sub> or other intermediates. The increase could also be related to the increasing fraction of soluble carbon in the electrochemically active CO<sub>2</sub> forms such as CO<sub>2(aq)</sub>.

Hori *et al.* [3] reported that the distribution of electrochemical reduction products at metal surfaces was temperature dependent. They found that the faradaic efficiency for the formation of CH<sub>4</sub> at 0 °C was about 65% but dropped significantly with temperature, whereas for C<sub>2</sub>H<sub>4</sub>, the faradaic efficiency rose slowly with temperature as shown in Figure 1. Therefore, depending on the product desired the electrolyte solution temperature could be programmed either to increase or to decrease the less preferred products. However on Ru, the effect of temperature on the rate of CH<sub>4</sub> formation was manifested by the reduction of the faradaic efficiencies if the reduction was carried out at a temperature greater than 80 °C, but no reduction occurred if the electrode was used at 60 °C [4]. This was due to high activation energy for the competing hydrogen evolution reaction (HER) in Ru.

In this work, we report the effect of pH and temperature of the phosphate buffered solution on the reduction of CO<sub>2</sub> at polycrystalline copper. The reduction of CO<sub>2</sub> was investigated spectroscopically and electrochemically by analyzing specific reduction products; the formation of an adsorbed bridge-bonded CO, Cu-CO<sub>B</sub> and copper(I)-carbonyl, Cu(I)-CO at suitable potentials, as these species were the



**Figure 1:** The Faradaic efficiency of products at various temperatures during the electrochemical reduction of CO<sub>2</sub> in aqueous solution [2].

prominent side-reaction products of CO<sub>2</sub> reduction at the copper surface.

### Experimental

Experimental details in the present study have been reported elsewhere [5]. The reduction of carbon dioxide was performed in a water-jacketed three-electrode thermostated cell. Electrochemically polished disc copper electrodes (0.8 cm diameter, 99.95 % purity from RS Components Ltd) used throughout this work were cathodically protected by applying a negative potential immediately after its immersion into the degassed phosphate buffered solution (pH 6.8). A Pt ring and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. A reducing potential close to, or at, the hydrogen evolution potential was applied for a few minutes before the cyclic voltammetry measurements to remove any oxides or hydroxides from the surface. Purified nitrogen gas (99.99%) was bubbled through the solution between the experiments and passed over the electrolyte quiescently during experiments. Purified CO<sub>2</sub> (99.95%) was bubbled for 15 minutes to prepare CO<sub>2</sub>-saturated solutions for the electrochemical reduction experiments. All the electrochemical and IR spectral measurements were performed at the specific temperature in a staircase mode using a fully evacuated FTIR spectrometer (Bruker IFS-113V) fitted with a mercury-cadmium-telluride (MCT) photoconductive detector cooled at 77 K (using liquid nitrogen), *p*-polarizer and Ge/KBr beam splitter.

Operation of the spectrometer was computer-controlled, running under OPUS 3.0 software.

### Results and Discussion

#### *The influence of pH on the reduction of CO<sub>2</sub>*

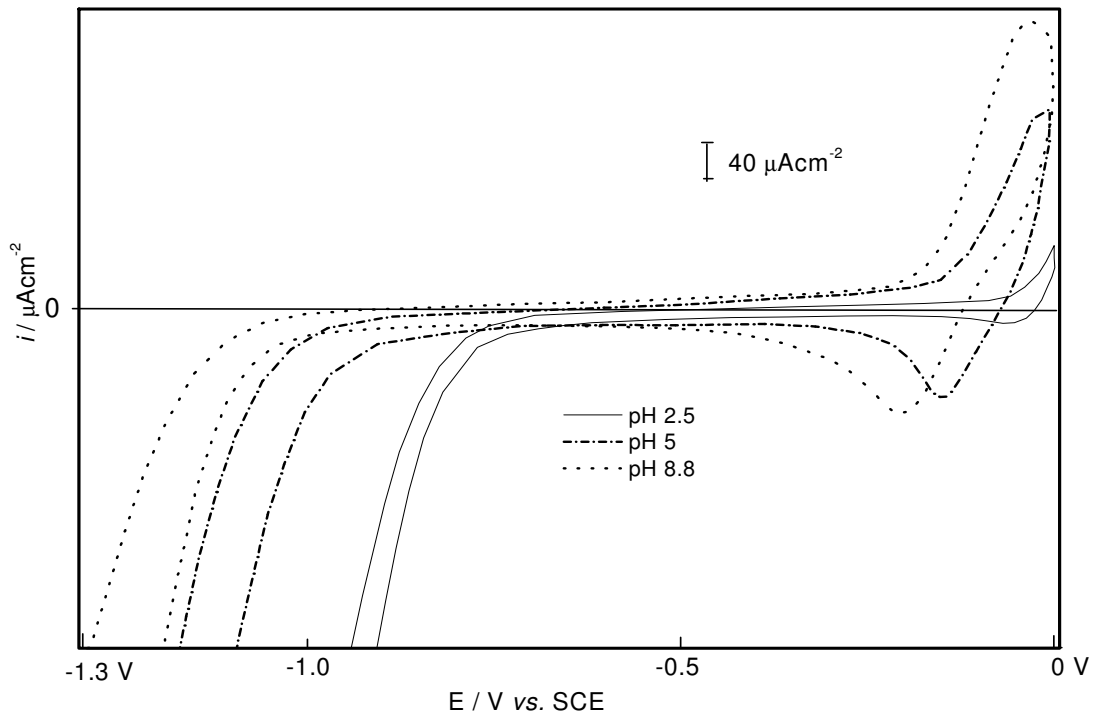
pH obviously affects the copper electrochemical behavior, as shown in the voltammograms for CO<sub>2</sub>-saturated phosphate buffered solutions with varying pH in Figure 2. The effect of solution pH is clearly shown by the anodic peak shifts toward more positive, and cathodic peak shifts toward more negative potentials with increase in pH. The anodic peak current increases with pH due to the fact that the oxidation of copper to oxide or to hydroxide is pH dependent. According to the Pourbaix diagram for copper [6], the formation of cuprous oxide, Cu<sub>2</sub>O, is an intermediate step before dissolution at less negative potential occurs. This process is described by the following equation;



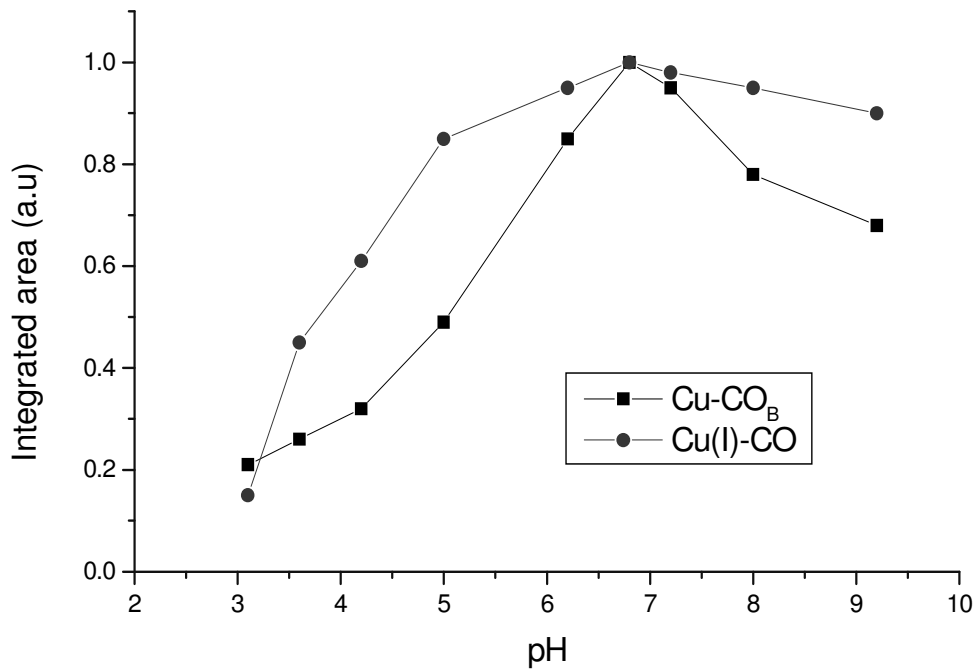
As can be seen this is a pH dependent reaction; the higher the concentration of H<sup>+</sup> the higher the potential is required to oxidize the copper surface.

The same pH dependence was shown for the hydrogen evolution region where hydrogen evolution favorably occurred at low pH, at less negative potential as expected. However, no peaks for the adsorption or the reduction of CO<sub>2</sub> process were observed.

The amount of dissolved CO<sub>2</sub> in aqueous solution that is available for the electrochemical



**Figure 2:** Voltammogram for copper electrode at  $v = 0.05 \text{ Vs}^{-1}$  in CO<sub>2</sub> saturated phosphate buffered solution at different solution pH.



**Figure 3:** Integrated peak area of Cu-CO<sub>B</sub> at  $-0.7 \text{ V}$  and Cu(I)-CO at  $0 \text{ V}$  correspond to the electrolyte pH change, relative to values at pH 6.8 at  $0 \text{ }^\circ\text{C}$ .

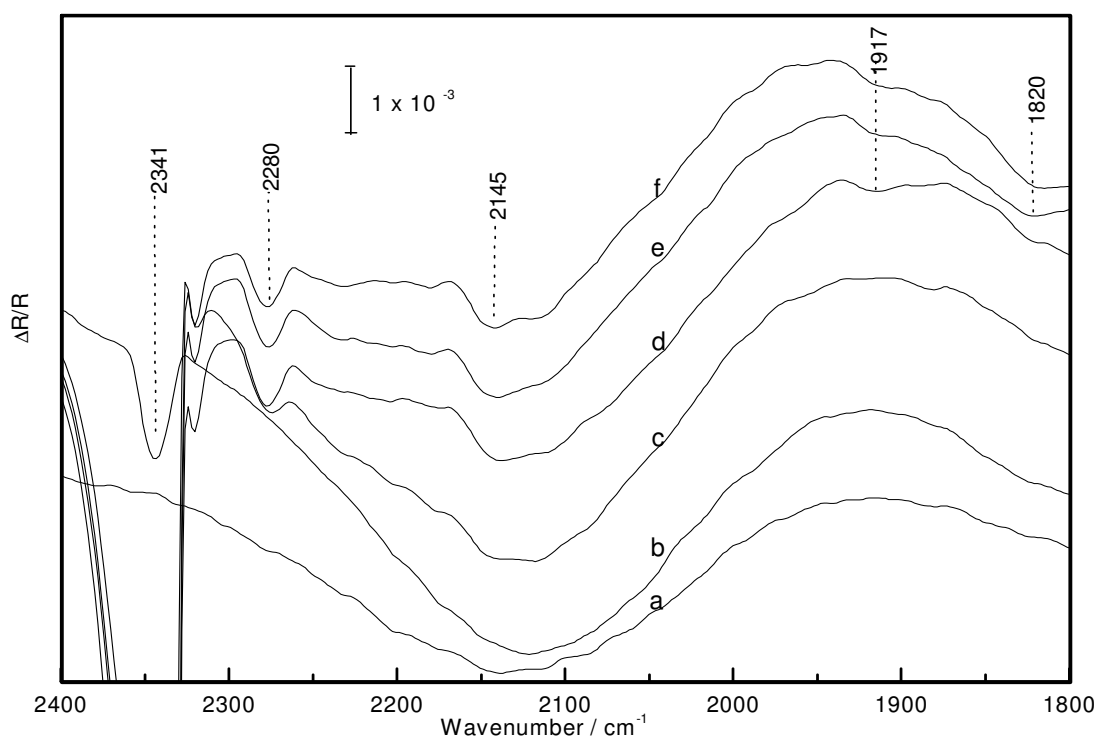
reduction process is pH dependent. Hori *et al.* [7,8] reported that the current response of a Cu electrode at  $-1.3$  V in phosphate buffered solution was due to the reduction of CO<sub>2</sub>. However, others indicated that there was no difference in this particular current response for N<sub>2</sub> and CO<sub>2</sub>-saturated phosphate buffered solution [9]. The only difference was that the current response shifted cathodically by about 0.1 V due to pH changes in solution and this was reconfirmed through the present study (5). To get a clearer picture of these contradictory observations, the effects of pH on the CO<sub>2</sub> reduction were investigated. The pH of the phosphate buffer solution was regulated from 1.5 to 9.2 by adding phosphoric acid or potassium phosphate solution. Figure 3 shows the spectral peak areas of Cu-CO<sub>B</sub> at  $-0.7$  V and Cu(I)-CO at 0 V as the copper surface was polarized at  $-1.5$  V while CO<sub>2</sub> was continuously bubbled into the solution. The SNIFTIR spectra were normalized relative to  $-1.3$  V at each set and then divided by the highest peak area at pH 6.8, 0.15 for Cu-CO<sub>B</sub> and 0.10 for Cu(I)-CO. The figure shows that both Cu-CO<sub>B</sub> and Cu(I)-CO were observed in the pH range 3.1 to 9.2. No Cu-CO<sub>B</sub> or Cu(I)-CO was observed at pH values below 3.1. The amount of Cu-

CO<sub>B</sub> produced increased as the pH increased and peaked at neutral pH after which it slowly decreased.

The results indicated that CO<sub>2</sub> was not electrochemically reduced to CO at pH values lower than 3.1. In acidic electrolyte medium, the solubility of CO<sub>2</sub> decreases with decrease in pH as required by the equilibrium:



However, a weak band at  $2145\text{ cm}^{-1}$  was observed possibly for CO in solution of pH 2.5 (Figure 4). The band was assigned based on the value reported in the literature for CO gas in solution [10,11]. CO that was produced from the CO<sub>2</sub> reduction was not adsorbed on the copper surface at pH 2.5. The amount of both species, Cu-CO<sub>B</sub> and Cu(I)-CO was higher at near-neutral pH compared to those at low or high pH values. At low pH, as expected, the electrode surface became cleaner as the copper oxides or hydroxides were reduced. However the HER was positively shifted and became predominant as the pH of the solution decreases as shown by the voltammogram in Fig 2. Therefore, the reduction of CO<sub>2</sub> process at pH values lower than neutral pH was less favored. At alkaline pH, the reduction of CO<sub>2</sub>



**Figure 4:** SNIFTIR spectra obtained from a CO<sub>2</sub>-saturated phosphate buffered solution (pH 2.5) as the copper was polarized at  $-1.5$  V for 15 minutes. Spectra shown are from (a)  $-1.0$  V to (f)  $0$  V in  $0.2$  V per step.  $E_{\text{ref}} = -1.3$  V.

also decreased due to the loss of dissolved CO<sub>2</sub> from the solution. Increase in pH increased the conversion of CO<sub>2</sub> to carbonate and in turn reduced the probability of CO<sub>2</sub> being reduced. However in the near-neutral pH region, the CO<sub>2</sub> reduction process can directly proceed at high negative polarization potential ( $E_{\text{pot}}$ ). As previously reported, the  $E_{\text{pot}}$  directly influenced the distribution of the electrode surface charge, which reduced the CO<sub>2</sub> [5].

The copper carbonyl, Cu(I)-CO shows the same behavior toward pH responses. Higher band intensity was observed for the near-neutral pH region (pH 6.2-6.8) and low band intensity at lower and higher pH values. As mentioned earlier the oxidation of Cu to Cu(I) either to cuprous oxide, Cu<sub>2</sub>O or cuprous hydroxide, CuOH was pH dependent [6,12,13]. Therefore at low pH, at potentials where the Cu(I)-CO appears, the band intensity reduction is expected. The potential-pH relationship might be a good explanation for this observation as can be seen directly from the formal potential of the couple Cu/CuO and pH which is given by the following equation [14]:

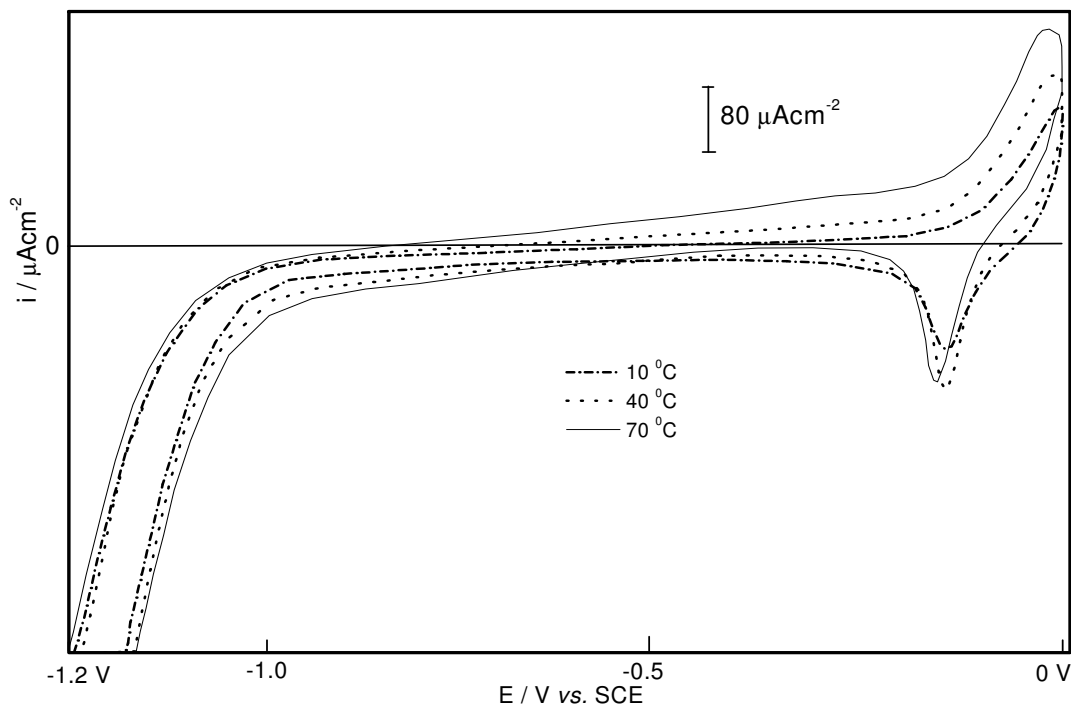
$$E = 0.471 - 0.0591 (\text{pH})$$

At the potentials where Cu(I)-CO was normally observed (-0.1 V) for instance, the electrode surface was probably more negative than it should be, more than -0.1 V. Therefore the formation of Cu(I)-CO

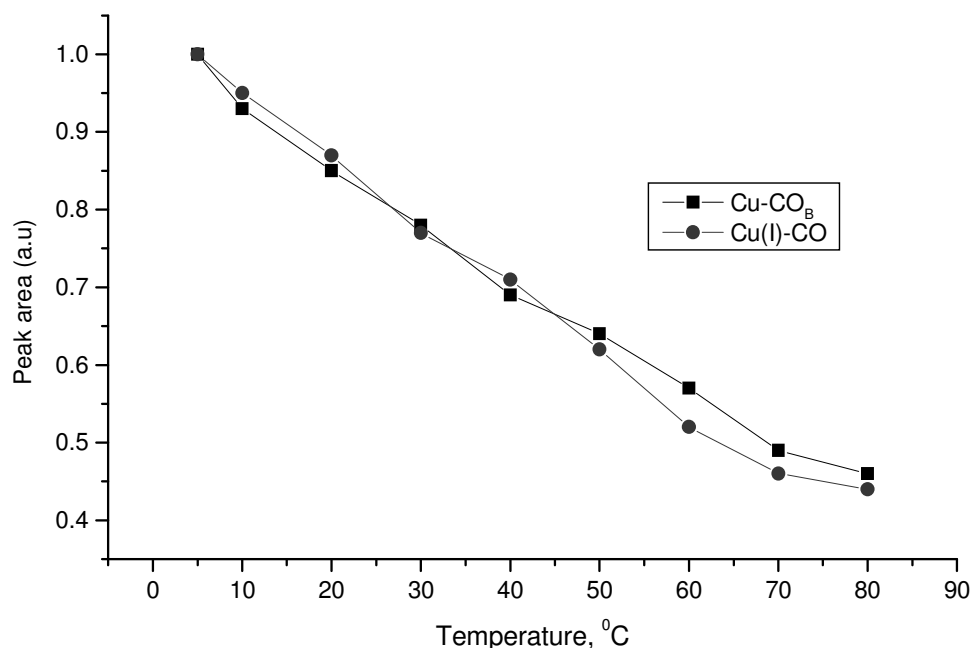
could not fully occur at this potential under alkaline conditions.

It is also worthwhile to note that the band at 2280 cm<sup>-1</sup> was clearly observed at low pH values. The band was associated with isotopic <sup>13</sup>CO<sub>2</sub> [9, 15]. However, no bands can be attributed to the reduction products of <sup>13</sup>CO<sub>2</sub> since the amount present in the solution was far too small compared to <sup>12</sup>CO<sub>2</sub>.

*The influence of temperature on the reduction of CO<sub>2</sub>*  
The temperature of the solution is believed to influence the electrochemical reaction as it can control the amount of soluble CO<sub>2</sub>. As expected the solubility of CO<sub>2</sub> decreases with increasing temperature. However, the effect of temperature on the reduction step may not only affect the concentration of CO<sub>2</sub> but also the kinetics of the reduction process in addition to the redox behavior of Cu. Figure 5 shows the voltammogram of CO<sub>2</sub>-saturated phosphate buffered solution in the temperature range 10 to 70 °C at a sweep rate of 0.05 V/s. The effect of the solution temperature on the electrochemical behavior of copper is shown by the increase of both anodic and cathodic peak currents in the same ratio as the temperature increases. However no peak attributable to the products of the CO<sub>2</sub> reduction was observed as the temperature was increased. HER also was not affected by the change of solution temperature.



**Figure 5:** Voltammogram for copper electrode at  $v = 0.05 \text{ Vs}^{-1}$  in CO<sub>2</sub>-saturated phosphate buffered solution at different solution temperature.



**Figure 6:** Integrated peak area of Cu-CO<sub>B</sub> at  $-0.7$  V and Cu(I)-CO at  $0$  V at different solution temperature relative to values at  $0^{\circ}\text{C}$ . Spectra are normalized relative to  $E_{\text{ref}} = -1.3$  V.

The probability of soluble CO<sub>2</sub> being involved in the reduction process depends on the amount that reaches the copper surface, which is related to the temperature and its solubility in phosphate buffered solutions. The solution temperature effect on the reduction of CO<sub>2</sub> was studied spectroscopically at temperature range from  $0$  to  $80^{\circ}\text{C}$ . Figure 6 shows the integrated spectral peak area of Cu-CO<sub>B</sub> at  $-0.7$  V and Cu(I)-CO at  $0$  V at different temperatures. The SNIFTIR spectra are normalized relative to  $-1.3$  V at each set and divided to the highest values at lowest temperature of  $0^{\circ}\text{C}$ ,  $0.12$  for Cu-CO<sub>B</sub> and  $0.10$  for Cu(I)-CO. The figure shows that the peak areas for both Cu-CO<sub>B</sub> and Cu(I)-CO are highest at lowest temperature ( $0^{\circ}\text{C}$ ) and decrease with solution temperature. A reduction of about 50% of the peak area was observed for solution temperature at  $60^{\circ}\text{C}$  compared to that at  $0^{\circ}\text{C}$ . The reduction in peak area at high temperature was due to the decrease in CO<sub>2</sub> solubility. However no other bands appeared that might be related to other CO<sub>2</sub> reduction products at high temperature. As has been reported, a copper surface tends to stabilize the higher coordination binding sites, e.g. expected 3-fold hollow, at high temperature [16]. However, the temperature under the present study was much higher than the one that has been reported. Rao *et al.* reported the stabilization of higher coordination binding site at

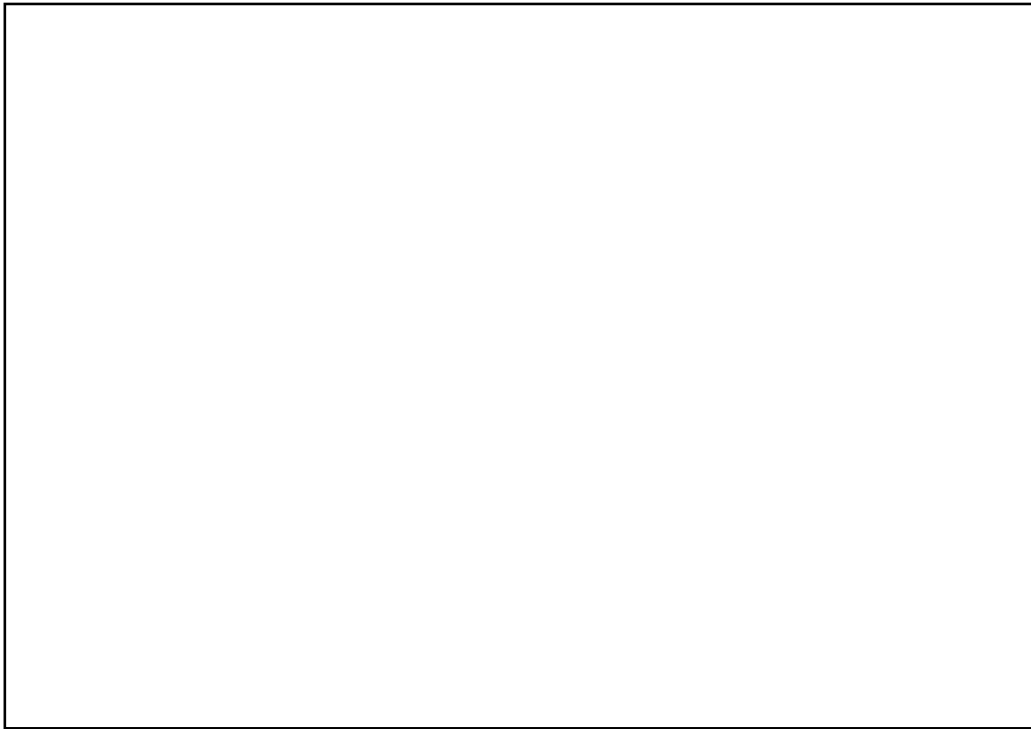
copper surface occurred in the temperature range from  $80$  to  $270$  K.

### Conclusion

Under the present experimental conditions, CO<sub>2</sub> was electrochemically reduced at polycrystalline copper in phosphate buffered solution over a wide pH range;  $2.5$  to  $9.2$  and over a wide temperature range;  $0$  to  $80^{\circ}\text{C}$ . This observation was based on the formation of adsorbed bridge-bonded CO, Cu-CO<sub>B</sub> and Cu(I)-CO at the chosen  $E_{\text{pol}}$  of  $-1.5$  V for a specific polarization time of  $15$  minutes. Both adsorbed CO and copper carbonyl showed the same pH dependence behavior. CO did not adsorb on the electrode surface which is an acidic surface, at pH less than  $3$ . The results also showed that the solution temperature shows a proportional dependence behavior. Increases of both anodic and cathodic peak currents in the same ratio were observed with increase in temperature. No additional peak that can be attributed to the products of the CO<sub>2</sub> reduction was observed at high solution temperature. Furthermore, HER region was affected not only by the changes of the solution temperature, but also by the probability of soluble CO<sub>2</sub> being involved in the electrochemical reduction. Therefore the reduction of CO<sub>2</sub> depends on the amount of CO<sub>2</sub> that reaches the copper surface, which is related to its solubility in phosphate buffered solutions.

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### Captions of Figure

**Figure 1:** Dependence of product distribution on temperature during the electrochemical reduction of CO<sub>2</sub> in aqueous solution [2].

**Figure 2:** Voltammogram for copper electrode at  $v = 0.05 \text{ Vs}^{-1}$  in CO<sub>2</sub> saturated phosphate buffered solution at different solution pH.

**Figure 3:** Integrated spectral peak area of Cu-CO<sub>B</sub> at  $-0.7 \text{ V}$  and Cu(I)-CO at  $0 \text{ V}$  correspond to the electrolyte pH change, relative to values at pH 6.8 at  $0^\circ\text{C}$ .

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