

## Linearly adsorbed carbon monoxide at polycrystalline copper in aqueous phosphate buffered solution: the influence of anions, temperature and pH

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**ABSTRACT** The affects of pre-adsorbed anions; the temperature and pH of the electrolyte phosphate buffered solution on the formation of linearly adsorbed CO at copper surface were investigated in. The results showed that in the region where linearly adsorbed CO, Cu-CO<sub>L</sub> was not observed, an adsorbed surface hydroxide, Cu(OH) band appeared at negative potentials below -0.9V. Inversely the band disappeared at potentials where CO adsorbed on the surface from -1.0 to -1.5V. The surface hydroxide species was likely to form during the cathodic reduction of Cu at potentials negative to the formation of Cu(I) oxide. The results also showed that the formation of Cu-CO<sub>L</sub> was dependent to solution's temperature and pH. It appeared only at low temperatures below 18°C. The highest peak area of Cu-CO<sub>L</sub> band was obtained at pH 6.8. It was likely that the pH influenced the characteristics of the electrode surface and other competing reactions rather than influenced the CO adsorption process itself.

**ABSTRAK** Kesan pra-jerapan anions, suhu dan pH larutan elektrolit tampan fosfat ke atas pembentukan CO terjerap lurus di atas permukaan kuprum telah dikaji. Hasil kajian menunjukkan dalam julat keupayaan dimana CO tidak terjerap pada (kurang dari -0.9V), puncak hidrosil terjerap, Cu(OH) terbentuk. Puncak ini hilang dalam julat keupayaan di mana CO terjerap lurus (-1.0 hingga -1.5V). Spesies hidroksil terjerap boleh terhasil semasa penurunan katod kuprum pada keupayaan negatif dari pembentukan Cu(I) oksida. Hasil kajian juga menunjukkan pembentukan Cu-CO<sub>L</sub> bergantung kepada suhu dan pH larutan elektrolit dan hanya terbentuk pada suhu rendah dari 18°C. Luas puncak terbesar diperolehi pada pH 6.8. pH lebih memberikan kesan kepada kriteria permukaan elektrod berbanding terhadap proses penjerapan CO.

(linear adsorbed CO, copper, adsorbed hydroxide)

### INTRODUCTION

Although many studies on the adsorption of CO on Cu have been reported e.g. by Hayden and coworkers [1-4], Pritchard and coworkers [5-10], Seki and coworkers [11,12], Hori and coworkers [13-16], Eischen *et al.* [17] and Hernandez *et al.* [18], a concordant conclusion about the exact mechanism for CO interaction on polycrystalline copper surfaces is still unclear particularly as a function of anions, temperature, pH and potential polarization time. The latter is of particular importance in the present study, the

electrocatalytic reduction of CO<sub>2</sub> on Cu; the main product was adsorbed CO that involves as an intermediate/product. Therefore, it is important to study the CO adsorption behavior on polycrystalline copper to gain more insight into the mechanism of CO<sub>2</sub> reduction.

The multiplicity of CO binding sites occurring on the electrode surface can be roughly characterized by the  $\nu_{C\equiv O}$  stretching frequency. The adsorption of CO at specific binding sites on metal surfaces will vary with the nature of the surface, the physical condition; such as

smoothness and roughness, the degree of crystallinity, the CO concentration and coverage as well as the temperature. The relative intensities of the CO band at a specific frequency vary mainly with CO coverage and temperature. Moreover, adsorbed CO can be removed from the surface by pumping or evacuation with or without heating process. Camplin *et al.* [19] reported the adsorption of CO at cryogenic temperatures on Cu (100) where the adsorption of CO<sub>L</sub> was affected by temperature and surface coverage,  $\theta_{CO}$ . At a low temperature of 23K, the chemisorbed species at 2083 cm<sup>-1</sup> was observed with 2L CO exposure and an extra band for physisorbed species at 2138 cm<sup>-1</sup> was observed at the same temperature with 4L CO exposure. By increasing the temperature to 40K, the physisorbed CO band disappeared. Moreover, we have reported that the linearly adsorbed CO at copper surface was inversely proportional to the CO concentration in the solution [20].

The presence of anions such as hydroxide, carbonate and phosphate in solution might cause competition for the adsorption sites on the electrode surface. The competition for the adsorption sites between pre-adsorbed anions and CO has been reported. Huber *et al.* [21] rationalized the competition for the adsorption site by emphasizing the charge transfer process, which occurs within desorption of pre-adsorbed anion and the adsorption of CO. Koga *et al.* [22] suggested that the competitive adsorption of CO on Cu(100) and Cu(111) with adsorbed anions such as carbonates and monobasic phosphates occurred at potentials near or below the potential zero charge (pzc). CO displaces specifically adsorbed anions, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> at a certain potential below pzc, and in turn it is reversibly displaced by the anions when the potential is reversed at nearly the same potential [23]. The same argument might explain the behavior of CO adsorption on polycrystalline copper surface.

In this work, the adsorptions of CO on polycrystalline copper were investigated in phosphate buffered solution. The spectroscopic properties of the adsorbed CO on Cu were investigated as a function of polarization potential ( $E_{pol}$ ), pH and temperature. Using the *in situ* IR measurements, we report the behavior of linearly adsorbed carbon monoxide on the polycrystalline

copper is dependent on the existence of pre-adsorbed anions, the temperature and pH of the solution.

## MATERIALS AND METHODS

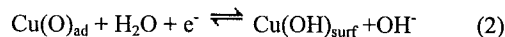
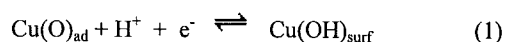
The experimental details for the electrochemistry and the spectroscopic studies have been discussed in detail elsewhere [20]. The copper electrode used was electrochemically polished. The IR spectral measurements were performed in a staircase mode using a fully evacuated FTIR spectrometer (Bruker IFS-113 V) fitted with a mercury-cadmium-telluride (MCT) photoconductive detector cooled at 77°K (using liquid nitrogen), *p*-polarizer and Ge/KBr beam splitter. Substractively Normalized Interfacial Fourier Transform Infrared Spectroscopy, SNIFTIRS experiments were performed by spectra collection at 200 interferograms in a staircase mode. The potential, either generated by Hi-Tek DT-2101 potentiostat and PP-R1 waveform generator, was changed by 100 during each step or from a custom written software for an interface analogue to digital (A/D) converter, which was run under OPUS 3.0, which enables voltage 'steps' to be programmed. A time delay can be introduced after any change in voltage and before the collection of spectra was started, in order to allow the electrochemical system to reach a stable semi-steady state.

## RESULTS AND DISCUSSION

### Anion effect on the adsorption of CO

The influence of the surface charge and the present of surface anions on the adsorption of CO on Cu were performed using the experimental procedure shown in Figure 1. Figure 2 shows the spectra in a wavenumber region of 4000 to 1400 cm<sup>-1</sup>, obtained from seven sets of experiments, from starting applied potential,  $E_{ASP}$  of -1.5 to  $E_{ASP}$  -0.8 V. Each spectrum was calculated by subtracting the spectrum obtained at -0.8V (reference spectrum at reference potential,  $E_{ref}$  = -0.8 V) in each set, from the spectrum collected at  $E_{ASP}$ . The upward or positive bands correspond to increased absorbance at reference potential or decrease absorbance at  $E_{ASP}$ , whereas bands pointing downward or negative bands indicate increased absorbance at  $E_{ASP}$ . The figure shows the appearance of positive band at 2082 cm<sup>-1</sup> for

linearly adsorbed CO on copper, Cu-CO<sub>L</sub> at potential from E<sub>ASP</sub> of -1.5 (a) to E<sub>ASP</sub> of -1.0V (f). This is in agreement with previously report the observation that has been reported previously; the Cu-CO<sub>L</sub> existed at a negative potential range from -1.5 to -1.0 V [20]. On the other hand, a negative band at 3660cm<sup>-1</sup> appears in the region where a positive band at 2082 cm<sup>-1</sup> of CO-CO<sub>L</sub> appears. At E<sub>ASP</sub> lower/below than -1.0 V, the CO-CO<sub>L</sub> band disappears whereas the band at 3660 appears. The results indicate that the band at 3660 cm<sup>-1</sup> may correlate with the band at 2082 cm<sup>-1</sup>. It is possible to conclude that the disappearance of the band at 3660 cm<sup>-1</sup> coincides with the appearance of the CO-CO<sub>L</sub> band at 2082 cm<sup>-1</sup>. At potentials where CO adsorbs on the surface from -1.0 to -1.5 V, the band at 3660 disappears. The band at 3660 cm<sup>-1</sup> can be assigned as νOH, the stretching frequency of adsorbed surface hydroxide [24,25]. Hartinger *et al.* [24] reported the remarkable observation that a Cu(OH) surface species, Cu(OH)<sub>ad</sub> was formed upon cathodic reduction of Cu at potentials negative to the Cu(I) oxide voltammetric wave. The authors explained this in terms of the reaction of surface oxygen with water or protons as follows:



Moreover it has been reported that a decrease in adsorbed CO band intensity on platinum can be attributed to a decrease in adsorbed CO coverage, which is induced by hydroxyl adsorption [26]. Therefore the adsorption of CO is hampered by the surface hydroxide. The same phenomenon might explain the behavior of CO adsorption on polycrystalline copper in phosphate buffered solution. The adsorption of CO will not take place until the hydroxide layer is reduced. However once the electrode surface is reduced, adsorbed hydrogen may also be formed, competing for the hydrogen evolution reaction (HER) to occur. However, at potential below the HER region, the adsorption of CO can be occur. However, at potential less than E<sub>ASP</sub> of -1.0V, CO does not adsorb on the Cu surface due to the competing adsorption process from the hydroxide anions. As been mentioned earlier, the presence of electrolyte anions such as hydroxide, carbonate

and phosphate in solution can cause competition process for the adsorption sites as the electrode surface is polarized, particularly at less negative potential at Cu surface.

#### The influence of temperature on the formation of Cu-CO<sub>L</sub>

In order to investigate the temperature dependency of the CO adsorption on the polycrystalline copper electrode, experiments were carried out at different temperatures ranging from 0 to 20°C. The spectra were measured as the electrode potential was stepped from -1.4 V to -0.8 V at different solution temperatures. Figure 3 shows the SNIFTIR spectra for the appearance of Cu-CO<sub>L</sub> at 2082 cm<sup>-1</sup> at -1.4 V, at different temperatures. The spectra are normalized relative to spectrum taken at -0.8 V of each set. The band at 2082 cm<sup>-1</sup> appears only at low temperatures (0°, 5° and 10°C) and not at higher temperatures (>18°C). This clearly shows that the formation of Cu-CO<sub>L</sub> on Cu is temperature dependent. This explains why studies at room temperature failed to detect Cu-CO<sub>L</sub> on Cu [18]. The adsorption of CO at linear binding sites can only occur at low temperatures due to the effect of the energy transfer between the neighboring CO molecules and between the CO molecules with copper surfaces. This is consistent with the fact that at low temperatures, the low coordination sites (with slightly higher adsorption energy) are stabilized [27], and thus increasing the probability of orbital overlap in Cu-CO<sub>L</sub> and consequently its formation is favored at low temperature. Inversely at high temperatures, the high coordination sites are stabilized and thus no Cu-CO<sub>L</sub> is observed.

#### The influence of pH on the formation of Cu-CO<sub>L</sub>

Figure 4 shows the integrated peak areas of Cu-CO<sub>L</sub> at -1.4 V, obtained at different pH values. The SNIFTIR spectra are normalized relative to the spectrum recorded at -0.4V during the cathodic sweep. The results show that the adsorption of CO on copper surface was observed to optimally occur at a pH value of 6.8. Therefore the integrated peak area were normalized by the highest values (0.37) of which were obtained at pH 6.8. The fact that the optimum pH for the adsorption of CO at Cu is 6.8 may be misleading if one is to assume that the process is, in their own accord, solely pH

dependent. It is more likely that the pH influences the characteristics of the surface and other competing reactions. At low pH values, the adsorption of CO is disfavored by the hydrogen evolution reaction. At high pH values, the electrode is very likely to be covered by hydroxides, which are very difficult to remove even at very negative potentials. Hence, at neutral pH, H<sub>2</sub> evolution is shifted to potentials where it will not dominate CO adsorption, but sufficient enough to reduce the surface.

### CONCLUSION

The results show that the adsorption of CO as Cu-CO<sub>L</sub> on polycrystalline Δ copper depends on various factors such as pre-adsorbed anions on the surface, the temperature and the pH of the solution. The main problem to overcome is the

removing of the pre-adsorbed anions, especially hydroxide from the surface due to its competing reaction with the adsorption of CO. Polarizing the surface at high cathodic potential is one way of removal the pre-adsorbed anions and consequently induces the adsorption of CO. The appearance of an adsorbed CO on copper is also dependent on the applied potential ( $E_{ASP}$ ) and the electrolyte solution temperature and pH. Cu-CO<sub>L</sub> appears immediately after the surface was polarized with the starting applied potential,  $E_{ASP}$  at high negative potential. It appears in a small potentials range from -1.5 to -1.0 V.

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### CAPTIONS FOR FIGURES

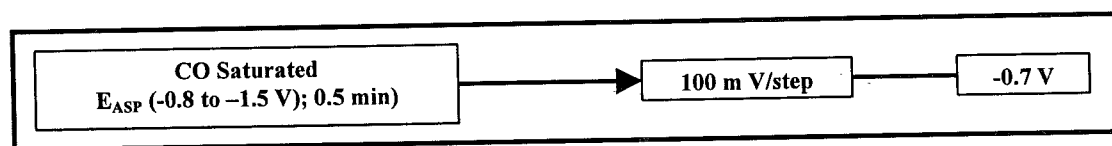


Figure 1. The experimental scheme used to evaluate the adsorption of CO on Cu

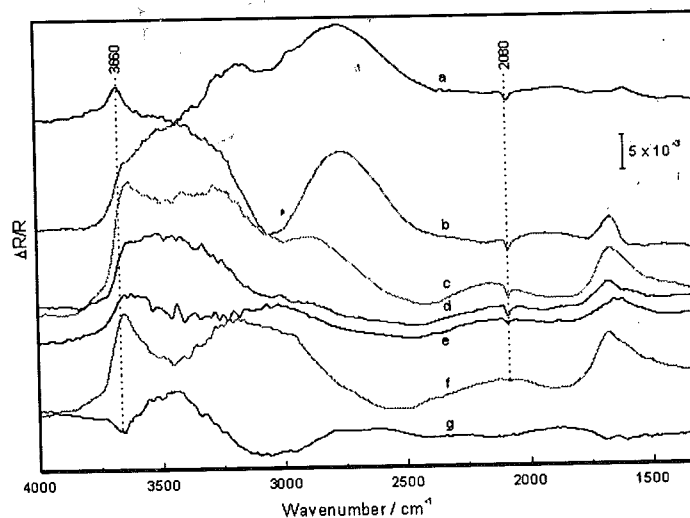
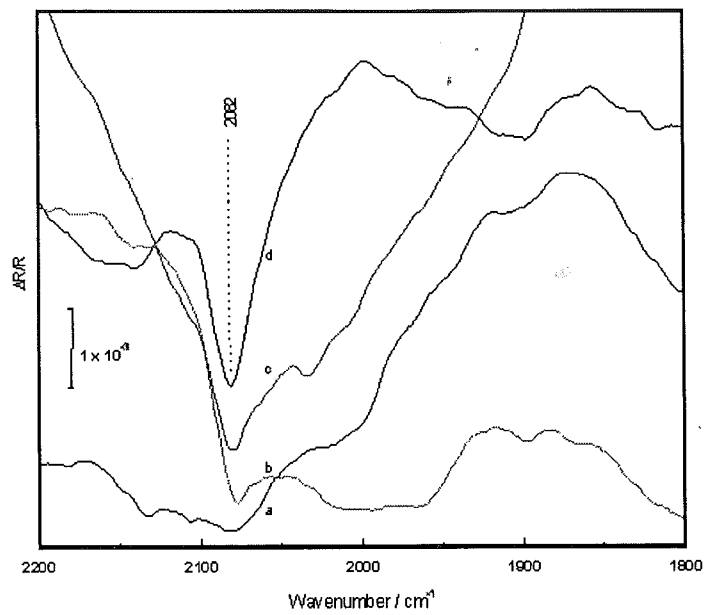
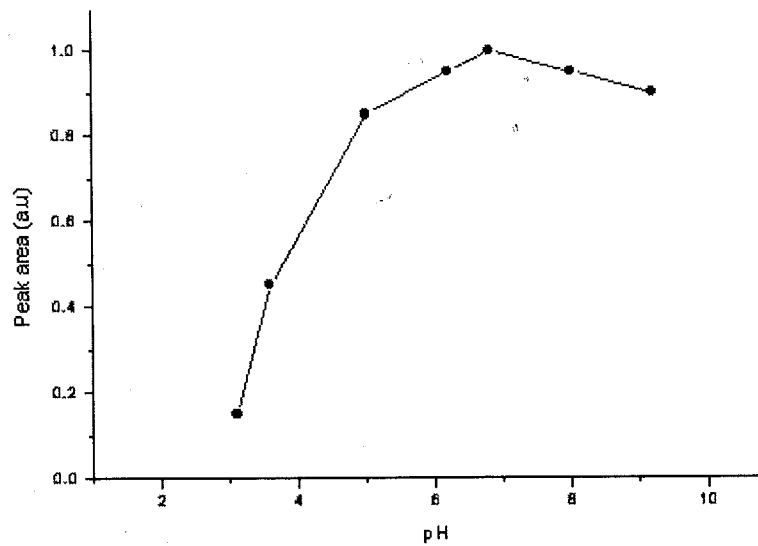


Figure 2. SNIFTIR spectra of a CO-saturated buffered phosphate solution at each  $E_{ASP}$  at 0°C. Spectra shown are at (a)  $E_{ASP} = -1.5V$  to (g)  $E_{ASP} = -0.9V$ ; normalized relative to -0.8V of each set.



**Figure 3.** SNIFTIR spectra at  $-1.4\text{V}$  obtained from  $\text{CO}$ -saturated buffered phosphate solution at different temperature. Spectra shown are obtained at (a)  $18^\circ\text{C}$ , (b)  $10^\circ\text{C}$ , (c)  $5^\circ\text{C}$  and (d)  $0^\circ\text{C}$ ; normalized relative to  $-0.8\text{V}$  of each set.



**Figure 4.** Integrated peak area of adsorbed linear-bonded  $\text{CO}$ ,  $\text{CO}_L$  at  $-1.4\text{V}$  corresponding to  $\text{pH}$  of the solution.

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