ELECTROCHEMICAL BEHAVIOR OF POLYCRYSTALLINE COPPER DURING THE ADSORPTION OF CO

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ABSTRACT

The electrochemical properties of electrode copper in carbon monoxide-saturated phosphate buffered solution were investigated. The electrochemistry of copper surface was sufficiently changed after the supporting electrolyte solution was saturated with CO. The hydrogen evolution region was depressed and shifted cathodically due to the adsorption process of CO on the copper surface in a linear or terminally bonded manner, $Cu\text{-}CO_L$. The oxidation and the reduction peaks of copper were significantly changed with two couple of redox peaks. This is due to the subsequent formation and the corresponding reduction of copper(I) and the copper-carbon manoxides species. Further changed in electrochemical properties occurred when the electrode surface was polarized at high cathodic potential (-1.4 V) for a period of time (15 min). The hydrogen evolution region was further depressed due to the adsorption of CO process in multiple bonding sites as adsorbed bridge bonded CO, $Cu\text{-}CO_B$ that occurred predominantly.

1.   INTRODUCTION

Depending on the metal surface, carbon monoxide may adsorb either in a molecular form or in a dissociative fashion where in some cases both states coexist on particular surface planes and over specific ranges of temperature. On reactive surfaces of metals (the left-hand side of the periodic table, e.g. Na, Ca, T, rare earth metals) the adsorption is almost invariably dissociative, leading to the formation of adsorbed carbon and oxygen atoms. This reaction thereafter leads to the formation of surface oxide and oxy-carbide compounds[1]. By contrast, on surfaces of metals on the right hand side of the d-block, e.g. Cu, Ag, the interaction results in the adsorption

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of the molecular form. The strength of the interaction between the CO molecule and the metal is also much weaker, so that the metal-carbon monoxide, M-CO bond may be readily broken and the CO desorbed from the surface by raising the surface temperature without inducing any dissociation of the molecule. For the majority of the transition metals, however, the nature of the adsorption (CO molecular or dissociative) is very sensitive to the surface temperature and surface structure; for example the Miller crystal index plane, the presence of any lower coordination sites such as step and defects sites, and a mixture of a variety of surface structure as in polycrystalline surfaces[1,2] and the surface pre-treatment[3].

Although many studies have addressed the adsorption on Cu of CO from the gas phase[4,5,6] and from electrolyte solutions[7,8,9], a concordant conclusion about the exact mechanism for the interaction of CO with copper surfaces is still unclear, particularly in the latter case and especially as a function of the potential polarization time. The latter is of particular importance in the supposedly electrocatalytic reduction of CO_2 on Cu; this process involves the polarization of potential for prolonged periods and involves CO as an intermediate and product[10].

In this paper, we report the change of the electrochemical behavior of polycrystalline copper during the adsorption of carbon monoxide in phosphate buffered solution. *In situ* infrared spectra were also measured to confirm the electrochemical properties change. The Substractively Narmalized Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIRS) techniques were used to detect any interfacial changes during the adsorption of carbon monoxide on the polycrystalline copper surface.

2.   EXPERIMENTAL

Experimental details in the present study have been reported elsewhere[10]. Electrochemically polished copper electrodes used throughout this work were cathodically protected by applying a negative potential immediately after its immersion into degassed phosphate buffered solution (pH 6.8). A cathodic potential, which is close to or at the hydrogen evolution potential was applied for few minutes before the cyclic voltammetry measurements in order to remove any oxides or hydroxides from the surface. Nitrogen gas was bubbled through the solution between the experiments and passed over the electrolyte quiescently during experiments. Carbon monoxide was bubbled for 15 minutes to prepare CO-saturated solutions for both the electrochemistry and the CO adsorption experiments. The starting applied potential, E_{SAP} at high negative potential, -1.4 V is immediately applied after its immersion into CO-saturated solution. The IR spectra were measured using a fully evacuated FTIR spectrometer (Bruker IFS-113V) fitted with a mercury-cadmium-telluride (MCT) photoconductive detector. The *in situ* infrared spectral collection was performed in the positive direction to 0 V then backs to the initial potential of -1.4 V. The experimental set up is shown in Figure 1. The same procedure is applied to the polarized surface electrode (E_{POL} at -1.4 V) at which the applied potential was hold for 15 minutes before the electrochemical and the infrared spectrum were measured.
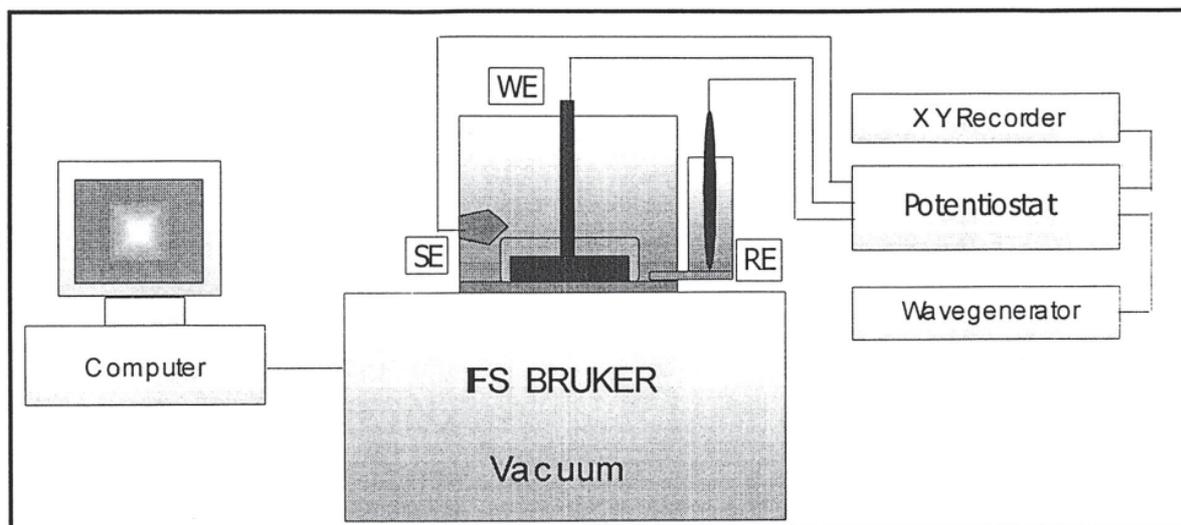
Figure 1 : *Schematic diagram of IR in situ measurement*

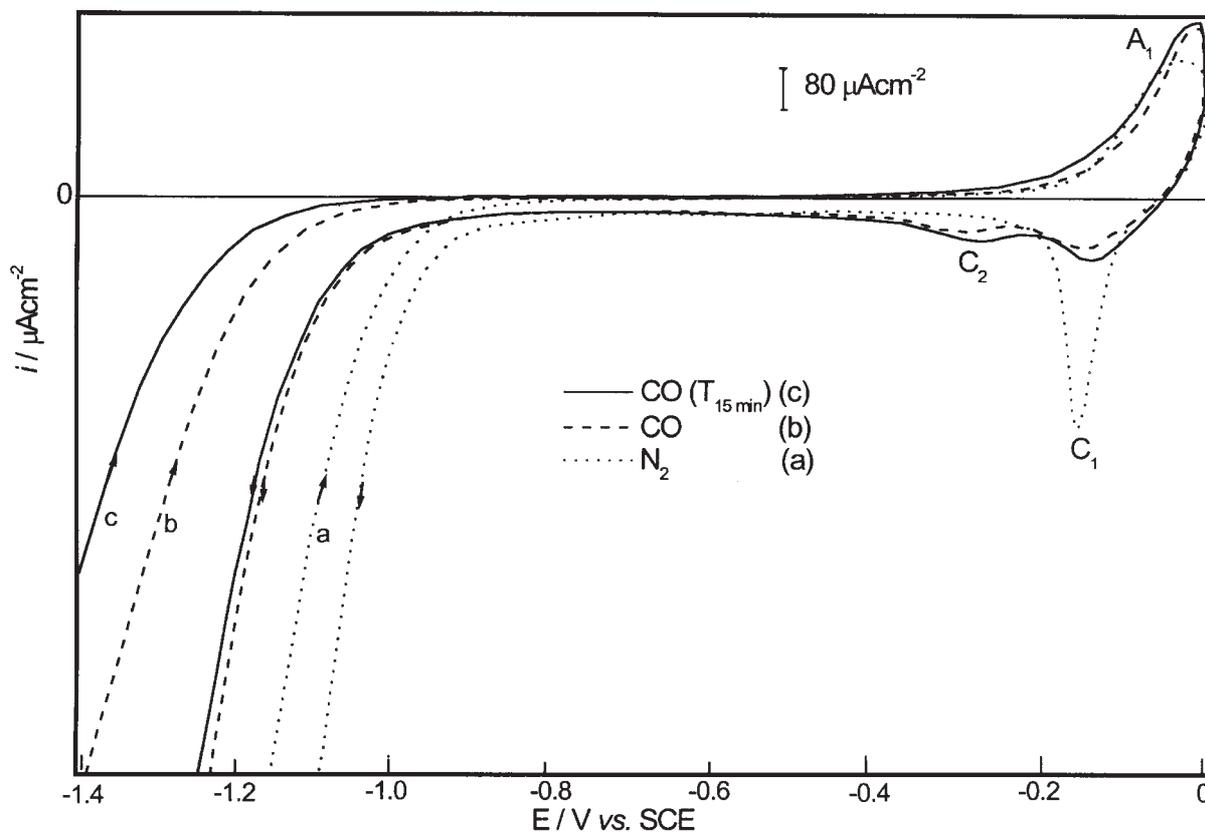# 3. RESULT AND DISCUSSION

Cyclic voltammetry

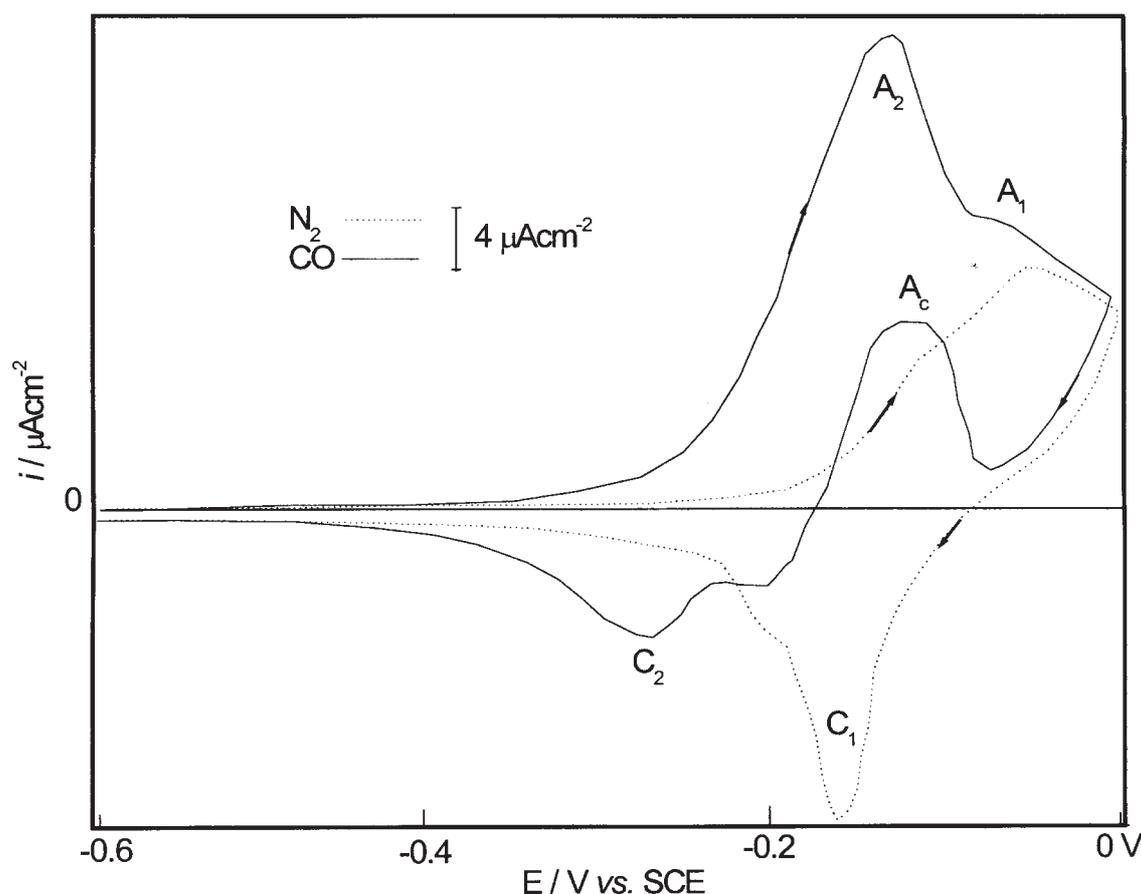*Figure 2 :* *Voltammogram of copper electrode at $v = 0.05\ Vs^{-1}$ in (a) N_2 and (b) CO-saturated phosphate buffered solution (pH 6.8) at 18°C and (c) CO-saturated with polarized electrode at $E_{POL} = -1.4\ V$ for 15 min.*

The voltammetric response of Cu in N_2 and CO saturated phosphate buffer solution at 0.05 V/s is shown in Figure 2. The voltammogram are in agreement with the observations at faster sweep rate of 0.1 V/s reported in the literature[9]. In N_2 saturated solution, the formation and the reduction of copper oxides or/and hydroxides peak, A_1 is evident on the forward and reverse sweeps (Fig 2a). On the reverse sweep, the reduction of such species is observed around -0.15 V, C_1. When the solution was saturated with CO, two reduction waves are observed, C_1 and C_2 at -0.15 V and -0.25 V respectively. It is plausible to conclude that the reduction of copper-carbon monoxide species occurs at latter peak, C_2. However no clear corresponding oxidation peak was obserbed. The onset of hydrogen evolution reaction (HER) region is shifted cathodically upon saturation with CO (Fig 2b). The data clearly indicate that CO has a profound influence on the electrochemical behavior of Cu. The hydrogen evolution is depressed cathodically due to the competing reaction between the adsorption of hydrogen and the reaction of CO on the electrode surface. When the electrode was polarized at -1.4 V for 15 min prior the voltammogram measurement, the onset of hydrogen evolution is further shifted cathodically (Fig 2c). It is due to the effect of the adsorption of CO on the electrode surface with more negatively charged surface and will be supported in detail spectroscopically.
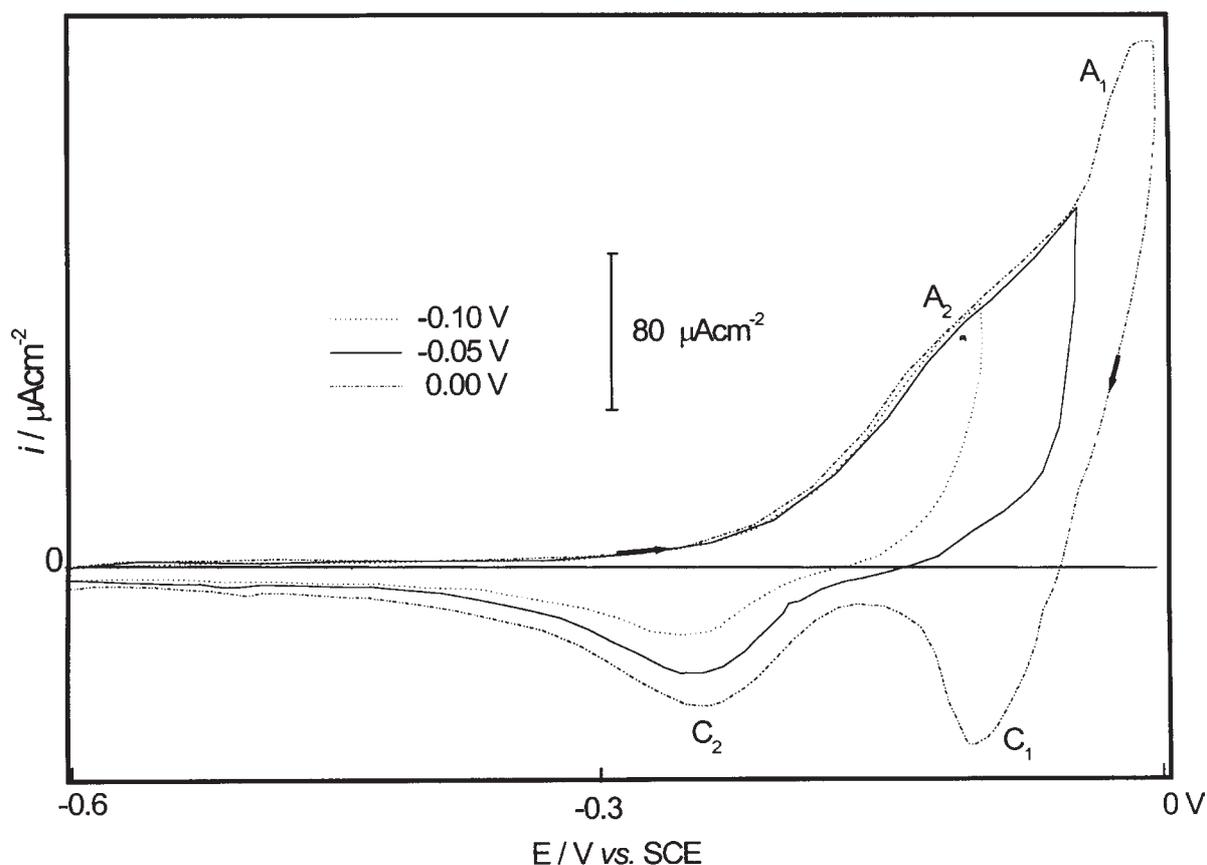
Figure 3 : *Voltammogram of copper electrode at ν = 0.01 Vs^{-1} in CO-saturated phosphate buffered solution at 18°C with different anodic potential limit.*

Figure 3 shows of the effect of positive limit on the voltammetric behavior of Cu in a CO-saturated solution. At least two redox peaks couples can be observed: A_2/C_2 at -0.120/-0.245 and A_1/C_1 at -0.1/-0.098 V. The voltammograms were recorded at 10 mV/s, which clearly indicates that the reduction in slow sweep rate results in a better resolution of the redox peaks (compared to Figure 2). The first couple, A_2/C_2 is most likely to be associated with the oxidation of Cu to Cu(I) and the subsequent formation of the oxides or hydroxide of Cu(I) and their corresponding reduction. Furthermore the discussion below will show that CO is also involved and interacted at these potentials.


Figure 4 : *Voltammogram of copper electrode at v = 0.001 Vs⁻¹ in N₂ (dot) and CO (solid) saturated phosphate buffered solution (pH 6.8) at 18˚C.*

A_1/C_1 on the other hand, corresponds to the oxidation of the surface Cu(I) to Cu(II) and the reduction back to Cu(I). Further evidence for this can be obtained when analysing the voltammograms at a very slow sweeps rate, 1 mV/s. Figure 4 shows that the voltammogram of the degassed solution is similar to that obtained at faster sweep rates. However, for the CO saturated solution, the ratio of the anodic current density relative to the N_2-saturated solution is much higher at low sweep rates. The charge consumed during the oxidation process at 1 mV/s when the solution is saturated with CO is at least 4 times larger than the N_2-saturated solution.

Another interesting feature is that the anodic current is observed during the negative sweep (A_c), which was also observed by Hernandez and Kalaji[9] using mechanically polished electrode. Dragowska *et al.*[11,12] observed a similar behavior when copper surfaces were corroded in solutions containing chloride anions. The authors attributed this to the dissolution of the metal. Hernandez and Kalaji[9] showed using spectroscopic and chronoamperometric measurements that the anodic current on the negatives sweep coincides with the formation of Cu(I) carboxyl species either by direct reaction of CO with Cu(I) or by the reductive reaction of CO with CU(II) species. However, the authors failed to observe any adsorbed linear bonded CO on Cu in the potential range 0 to -1.15 V. On the other hand, the present results show that the appearance of adsorbed linear bonded CO in the potential range more negative than -1.1 V (spectrum not shown). Moreover, the results reported previously indicate that the appearance of adsorbed linear bonded CO during the reduction of CO_2 can only be observed if the potential is polarized for a minimum of 10 minutes at potential values more negative than -1.1 V[10]. Hence, similar experimental procedure as those utilized previously, were repeated for CO saturated solutions in order to ascertain the origin of the bands observed during the reduction of CO_2.

In situ FTIR
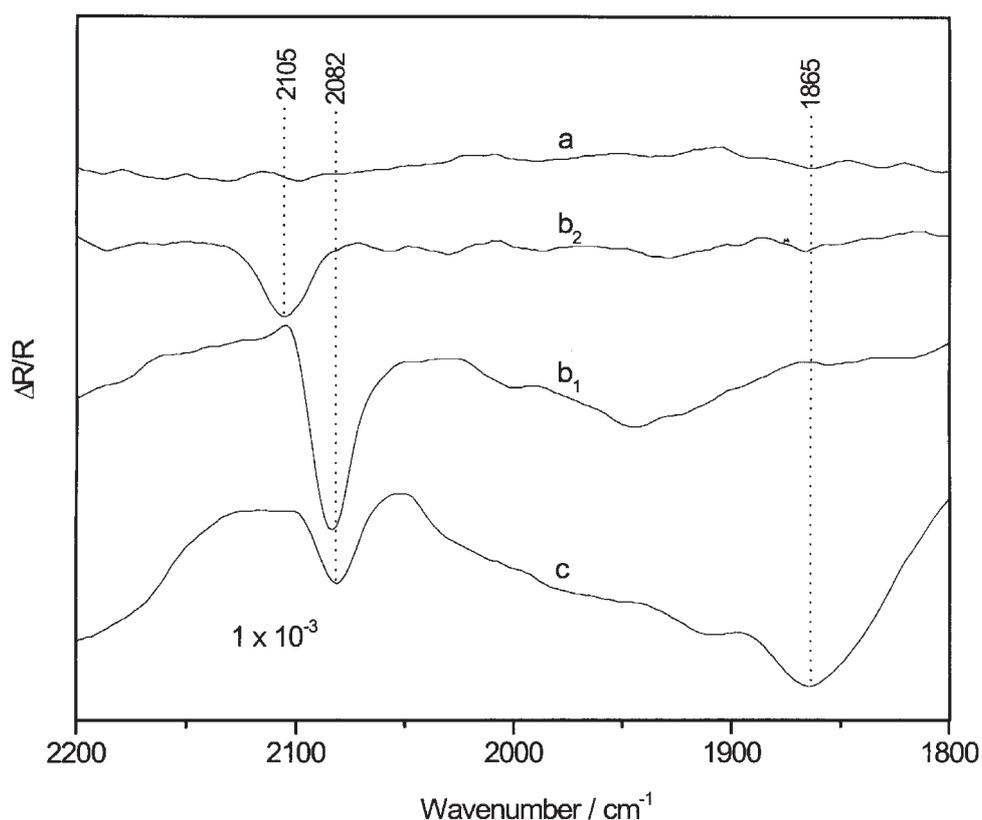
Figure 5 : SNIFTIR spectra of copper electrode for the same experimental condition as in Fig. 1. Spectrum (a) for N_2-saturated, b_1 and b_2 (at -0.1 V) for CO-saturated and c for CO-saturated with polarized electrode at E_{pol} = -1.4 V for 15 min at 18°C in phosphate buffered solution (pH 6.8). Spectra shown at -1.3 V (a,b_1,c) and -0.1 V (b_2); normalized to spectrum obtained at -0.4 V (reverse sweep).

Figure 5 shows the SNIFTIRS measurement for the same experimental condition as shown in Figure 2. The spectrum was calculated by subtracting the spectrum obtained at -1.3 V (reference spectrum at potential of -0.4 V, E_{REF} = -0.4 V of reverse sweep) in each set, from the spectrum collected at E_{SAP}. In CO-saturated solution (b_1), a monopolar band is observed at 2082 cm^{-1} that occasionally shifts with potential (not shown). This band is neither observed in N_2-saturated solution under the same conditions (a) nor in CO-saturated solution when s-polarized radiation was used. From the surface selection rules, it is clear that the species responsible for this absorption is an adsorbed species and as expected it is assigned to linear bonded CO, Cu-CO_L. The band position is in agreement with vC=O stretching frequency of adsorbed CO on Cu, which lies in the frequency range of 1990 to 2100 cm^{-1} for linearly adsorbed CO on thin Cu films[7,13,14] and on Cu(100) at 2070 to 2090 cm^{-1} [2,15]. The adsorption of CO must be responsible for the observed negative shifts in the onset of HER as indicated by voltammogram in Figure 2. At anodic potentials of -0.1 V, a new band appears at 2105 cm^{-1} (spectrum b_2) which as previously reported, is due to the formation of copper (I)-carbonyl, Cu(I)-CO, as the copper surface is oxidized. It indicates that as copper(I) forms, it reacts with CO to form Cu(I)-CO. This is consistent with the same observation obtained when the reduction of CO_2 occurs in the CO_2-saturated solution[10].

An interesting observation when the electrode surface was polarized at -1.4 V for 15 minutes in the CO-saturated solution. The same band at 2082 cm^{-1} appears for the linearly bonded adsorbed CO with less band intensity. Another negative band at 1865 cm^{-1} appears at lower wave number (spectrum c). The band shows shifting in wave number as the potential is changed (not shown). The latter band was briefly discussed previously and its assignment is in agreement with values reported in the literature[9,16-18]. The appearance of a new band at lower wave number is due to the formation of adsorbed bridge bonded carbon monoxide[2], Cu-CO_B. The results show that the adsorption of CO depends on the state of the copper surface either without or with polarization process. The results can be simplified as follows where Cu-CO_L appears immediately after the electrode surface is applied with the starting applied potential, E_{SAP} at high negative potential. Adsorbed bridge bonded CO, Cu-CO_B on the other hand, appears as a time function of polarization potential, E_{POL}. A reduction in band intensity of Cu-CO_L during the polarization of the electrode surface seems to have a correlation with the appearance of Cu-CO_B band. This will be discuss in detail elsewhere.

4. CONCLUSION

The cyclic voltametric results show that the electrochemical behavior of copper surface is changed when the solution is saturated with CO. The hydrogen evolution region is shifted cathodically and the charge consume during the oxidation of copper increases. This is due to the adsorption of CO on the copper surface (Cu-CO_L). Further dramatic change in electrochemical behavior occurs when the copper surface is polarized at high cathodic potential for a period of time. Through the polarization process the adsorption of CO on polycrystalline occurs at two binding sites, linearly bonded CO and bridge bonded CO. It suggests that the main problem need to overcome prior the CO adsorption on the electrode surface is the removal of the pre-

adsorbed anions, especially hydroxide from the surface due its competing reaction with the adsorption of CO. Polarizing the electrode surface at high cathodic potential is one way of removing the pre-adsorbed anions. No higher 3-fold hollow multiple bonded CO was observed under the experimental conditions.

ACKNOWLEDGMENT

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