

Electrochemical Behavior of Polycrystalline Copper in Aqueous Phosphate Buffered Solution During CO₂ Reduction

Jumat Salimon* & Maher Kalaji**

* *School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

** *Department of Chemistry, University of Wales, Bangor, UK LL57 2UW*

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ABSTRAK

Proses redoks yang terjadi di permukaan elektrod kuprum dalam larutan tampan fosfat telah dikaji. Hasil kajian menunjukkan bahawa proses pengoksidaan dan penurunan yang terjadi di permukaan kuprum terjadi dengan perlahan dengan proses evolusi hidrogen terjadi pada nilai keupayaan yang lebih negatif dari -1.0 V. Proses evolusi hidrogen ini didapati tidak dipengaruhi oleh tahap keupayaan anodik yang dikenakan. Lapisan filem tipis yang terbentuk di permukaan kuprum mengalami tindak balas penurunan secara proses berbalik-quasi. Dalam larutan yang ditepukan dengan gas CO₂, kehilangan kuprum ke dalam larutan terjadi disebabkan oleh pembentukan spesies terlarut. Proses kehilangan ini meningkat melalui proses pempolaran permukaan elektrod di mana kuprum(I)-karbonil terbentuk dan larut ke dalam larutan. Hasil kajian juga menunjukkan sifat-sifat elektrokimia elektrod kuprum berubah secara dramatik melalui proses pempolaran. Melalui proses ini, kawasan evolusi hidrogen terhalang dengan jayanya disebabkan proses penurunan CO₂ terjadi. Proses penurunan ini meningkat dengan hanya menggunakan elektrod kuprum yang telah dipolarakan pada keupayaan katod yang tinggi untuk jangka masa tertentu.

ABSTRACT

The redox processes occurring on the copper surface in phosphate buffered solution were investigated. The results show that the oxidation and the reduction of copper surface occur in a slow process with hydrogen evolution region proceeding at potential more negative than -1.0 V. It is found that the hydrogen evolution region was not affected by the anodic potential limits. The anodic film forms on the copper surface are reduced possibly in quasi-reversible manner. In CO₂-saturated solution, the loss of copper to the solution increases due to the formation of copper soluble species. This process is further enhanced with the polarization process, where copper(I)-carbonyl forms to the bulk solution. The results also show that the electrochemical behavior of copper electrode is dramatically changed by the polarization process. The hydrogen evolution region is greatly depressed due to the CO₂ reduction process. Consequently, the reduction of CO₂ is not pronounced on the copper surface except for the electrode surface has which been polarized at high cathodic potential for a period of time.

Keywords: Electrochemical, polycrystalline copper, CO₂ reduction

INTRODUCTION

It is a well-known fact that gaseous CO_2 dissolves in water in an amount that depends on a series of equilibrium steps (Aurian-Blajeni 1992). On dissolution, the species formed are: aqueous carbon dioxide, carbonic acids, hydrogen carbonates and carbonates; the quantity of each depends, amongst other factors, on the pH of the solution. Therefore, the need for monitoring this process in aqueous media such as phosphate buffered solution becomes important, as the nature of the reduction products depends on a variety of experimental conditions.

It is clear from the previous report that the control of pH is an important issue when discussing the reduction of CO_2 (Jumat 2001). The loss of CO_2 through the carbonate route is a consequence of pH change. This was due to the very basic conditions appearing across the double layer as a consequence of the onset of hydrogen evolution. This leads to a substantial decrease in the CO_2 available for the reduction process. This result agrees with the general fact that no reduction products are obtained in nitrogen-saturated hydrogen carbonate or carbon dioxide-saturated solution (Jumat and Kalaji 2002) and with the general low faradaic yields observed for the process. However pre-treatment such as the removal of the species that enhance the basic environment of the electrode surface such as "hydroxide" ions may increase the faradaic yields. Polarization of the electrode surface at high cathodic potential is one of the novel ways (Jumat and Kalaji 2002a). In this report, we discuss the results of our study of the processes occurring at and near the surface of Cu electrode in phosphate buffered solution. The use of buffer solution such as phosphate buffer that can maintain the pH of the electrolyte solution, also in the thin layer during the electrochemical reduction is worth trying. Beside its better pH control, phosphate buffers do not exhibit any absorbance that may overlap with the carbonate-hydrogen carbonate system during Substratively Normalized Infrared Fourier Transform Spectroscopy, SNIFTIRS measurements.

MATERIALS AND METHODS

Experimental details in the present study have been reported elsewhere (Jumat and Kalaji 2002). 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 reducing potential 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. CO_2 was bubbled for 15 min to prepare CO_2 -saturated solutions for the electrochemical reduction experiments.

The electrolyte solution at low temperature $\sim 5^\circ\text{C}$ was first degassed with N_2 and then either saturated with CO_2 for 15 min or CO_2 -saturated while the admission potential at high negative of -1.5 V was employed as soon as the

electrode was immersed in the solution. The admission potential holding time was varied prior to the spectra measurement. The *in situ* IR spectra measurements were performed 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. The spectrometer was fully computer controlled running under OPUS 3.0 software. SNIFTIRS spectra collection was performed with 200 scans at a resolution of 4. The potential either generated by Hi-Tek DT-2101 potentiostat and PP-R1 waveform generator or controlled by an ADC converter interface to a PC that controlled the spectrometer, was stepped by 100 mV during each step. The spectral collection was performed first in the negative direction (from -0.7 V) towards a potential of -1.5 V then towards positive potential of 0.0 V, then back to the initial potential of -1.5 V.

RESULTS AND DISCUSSION

Voltammetry of Copper in Buffered Phosphate Solution

The electrochemical behavior of copper in phosphate solution has been reported elsewhere (Osamu and Hori 1993; Hernandez and Kalaji 1996; Drogowska *et al.* 1992; Ribotta *et al.* 1995; Alhaji and Reda 1996). In general, in N₂-nitrogen saturated buffered phosphate solution (*Fig. 1*) an anodic wave corresponding to the formation of copper oxides and/or hydroxides of Cu(I) and Cu(II) is observed at about -0.12 V during the forward sweep from -1.1 V to 0 V. However there is no clear peak separation between the formation of oxide and hydroxide of Cu(I) and Cu(II) as was observed in the hydrogen carbonate solution (Jumat and Kalaji 2002; Hernandez and Kalaji 1996). On the reverse sweep from 0 V to -1.1 V, it is clear that the reduction of such oxides occurs at about -0.23 V. At low sweep rate, 0.005 V/s, the oxidation and the reduction peaks are much sharper than that at 0.05 V/s. The result shows that the oxidation and the reduction of copper surfaces may be a slow process. Hydrogen evolution reaction, HER commences at potentials more negative than -1.0 V.

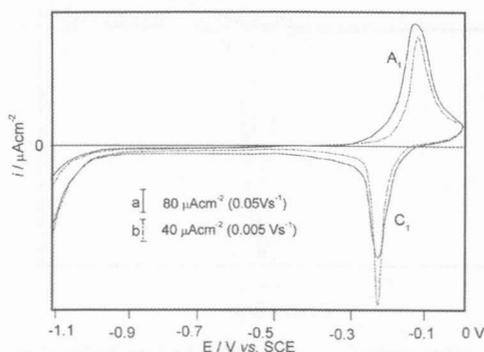


Fig. 1: Voltammogram for copper electrode at (a) $v = 0.05$ and (b) 0.005 Vs^{-1} in N₂ saturated phosphate buffered solution (pH 6.8) at 18°C

The effect of the anodic limit on the shape of the voltammograms is illustrated in Fig. 2. The onset of the hydrogen (not shown) was not affected by the positive potential limit. The current profiles in the positive direction (from -0.6 V) show a broad region with only one noticeable current peak, A_1 at -0.04 V, whereas during the negative sweep, one cathodic peak, C_1 at -0.16 to -0.18 V is observed. The broad anodic peak is due to the copper dissolution and anodic film growth (Alhaji and Reda 1996). The position and the charge of anodic current peak A_1 were maintained for several successive runs whereas the structure and the position of the cathodic peak depended on the positive potential limit. As the positive potential limit became more positive, the charge of the cathodic current increased, whereas the peak potentials shifted in the negative direction. The difference in shape between the anodic and cathodic peaks is most likely due to different reaction mechanisms. Therefore the oxidation is most likely to be diffusion controlled and will be discussed in detail elsewhere, whereas the reduction step is kinetically controlled. Such behavior is known in electrochemical system such as the reversible conversion of Pb to $PbSO_4$ in sulphuric acid (Jumat 2001).

The charge density associated with the cathodic wave, Q_{red} (0.82 mC) was always smaller than the one associated with the anodic peak, Q_{ox} (0.95 mC). This indicates a loss of copper species into the solution, possibly through copper species such as CuO or $CuHPO_4$. It is possible but unlikely that the difference in this value could be due to the accumulation of unreduced anodic film on the copper surface. However, since the voltammograms show a good reproducibility on all subsequent anodic sweeps under repetitive cycling conditions with cathodic and anodic peaks separation value of 120 mV, it can be concluded that any anodic film formed on the copper surface was easily reduced, possibly in quasi-reversible manner (Pyun and Park 1986).

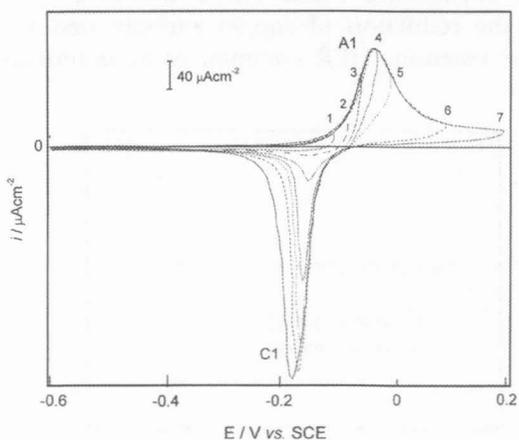


Fig. 2: Voltammogram of copper electrode at $v = 0.005$ Vs-1 in buffered phosphate solution (pH 6.8) at 18°C. Potential range from (1) -0.6 to -0.1 V; (2) -0.6 to -0.075 V; (3) -0.6 to -0.05 V; (4) -0.6 to 0.025 V; (5) -0.6 to 0 V; (6) -0.6 to 0.1 V and (7) -0.6 to 0.2 V

Voltammetry of Copper in CO₂ Saturated Phosphate Buffer Solution

The introduction of CO₂ into phosphate buffer solution has an impact on HER as well as the redox behavior of copper. Fig. 3 shows the difference in voltammetric behavior between N₂-saturated and CO₂-saturated solution (Figs. 3a and 3b respectively). It is interesting to note that HER occurs at very similar potential in the two solutions, which is in contrast to hydrogen carbonate solutions. This is due to the buffering effect of the phosphate solution, in which the pH drops by only 0.6 units upon saturation with CO₂. The oxidation of the Cu surface and the corresponding reduction of solution species and deposits is similar to that observed in hydrogen carbonate solutions; however, an asymmetry was observed here between Q_{red} and Q_{ox}; indication of a loss of soluble species to the bulk solution.

The average of the Q_{red}/Q_{ox} efficiency is about 70% (Fig. 3b). It is possible and likely that the difference in this value could be due to the accumulation of unreduced anodic film on the copper surface, which is related to the formation of species that are related to the oxidation of copper species at anodic potential region. The formation of oxidized copper film (oxides and/or hydroxides) and soluble copper species result from the interaction of reduced-CO₂ species such as CO with oxidized copper also believed to occur at this potential. It is interesting to highlight that once the electrode was first polarized at negative potential, E_{pol} of -1.5 V for 15 min prior to the voltammogram measurement, the average of the Q_{red}/Q_{ox} efficiency decreases dramatically to about 30% (Fig. 3c). It indicates that the formation of soluble copper species increased at anodic potential dramatically due to the polarization of the electrode surfaces at high negative potential.

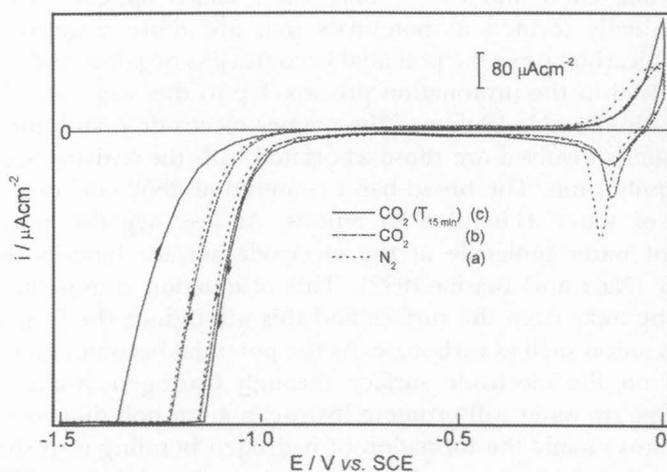


Fig. 3: Voltammogram for copper electrode at $v = 0.05 \text{ Vs}^{-1}$ in (a) N₂ saturated phosphate buffered solution, (b) CO₂ saturated without and (c) with polarization at polarization potential of -1.5 V for 15 min

In situ FTIR*SNIFTIR Spectra of N₂-saturated Buffered Phosphate Solution*

The use of phosphate buffers has some advantages when compared with bicarbonate solution in that it allows a better pH control and reduces to a certain extent the interference from the hydrogen carbonate ions. However, the strong absorbance exhibits will mask the spectral range from 1300-900 cm⁻¹, by phosphate buffers. It is important to be able to distinguish the background spectrum of the electrolyte from that of the electroactive species. Therefore the SNIFTIR spectra of the phosphate solution in responses to potential changes were recorded. *Fig. 4* shows the SNIFTIR spectra of the phosphate buffered solution, which has been saturated with pure N₂ gas. The positive bands at 1160 cm⁻¹ (ν_{as}-PO₂), 1076 cm⁻¹ (ν_s-PO₂) and 943 cm⁻¹ (ν_{as}-P(OH)₂) correspond to the depletion of monobasic phosphate, H₂PO₄⁻; whereas negative bands at 1061 cm⁻¹ (ν_s-PO₂) and 991 cm⁻¹ (ν_s-P(OH)₂) correspond to the formation of dibasic phosphate, HPO₄²⁻ as the potential becomes more negative (Chapman and Thirlwell 1964, Weber and Nart 1996). The main negative band at 1010 cm⁻¹ (ν_s-PO₃) can be assigned to the formation of tribasic phosphate, PO₄³⁻ as HPO₄²⁻ is deprotonated, as the potential is made more negative. Consequently, a broad negative band at 2720 cm⁻¹ appears as the potential becomes more negative. It is attributed to the OH stretching for the hydrogen bonding that forms between H₂O molecule and PO₄³⁻ (Weber and Nart 1996).

Fig. 5 shows SNIFTIR spectra of copper in CO₂-saturated phosphate buffered solution as the initial potential at -1.5 V is stepped towards positive values as shown in scheme A (*Fig. 6*). The spectra are normalized relative to E_{ref} -0.6 V. The spectra obtained are similar to those obtained in CO₂-saturated hydrogen carbonate solution, except for the bands due to the phosphate species. HCO₃⁻ (1356 and 1302 cm⁻¹) and CO₃²⁻ (1401 cm⁻¹) bands appear with potential. Carbonate initially formed at potentials that are more negative and then converted to bicarbonate as the potential becomes less negative, as the carbonate ions are involved in the protonation process. Up to this stage, the fate of CO₂ during the cathodic polarization of the copper electrode is still unclear as the main compounds involved are those associated with the hydrogen carbonate/carbonate equilibrium. The broad band centered at 2852 cm⁻¹ corresponds to OH stretch of water H-bonded to anions. At less negative potential, the orientation of water molecule at the electrode surface bounds through an oxygen atom (Nart and Iwasita 1992). This orientation causes the hydrogen atoms pointing away from the surface and this will induce the formation of H bonding with anion such as carbonate. As the potential becomes more negative, water bonds on the electrode surface through hydrogen atoms. An excess negative charge on water will promote hydrogen atom pointing away from the surface and thus enable the formation of hydrogen bonding with surrounding anions containing hydrogen such as phosphate. The band at 2756 cm⁻¹ is consistent with the band observed for OH stretch of hydrogen bond of water-phosphate couple, as compared to that spectra in N₂-saturated solution where a broad band centered at 2720 cm⁻¹ as shown by insert figure in *Fig. 4* which is

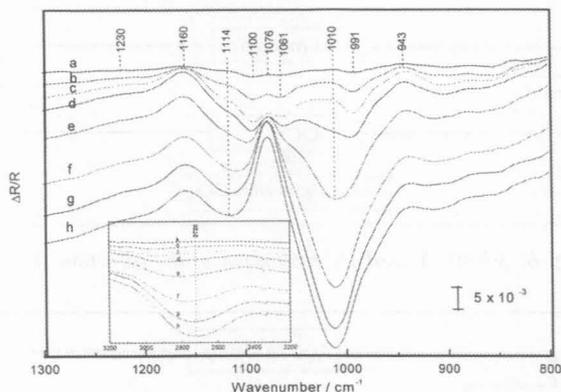


Fig. 4: SNIFTIR spectra obtained from N_2 -saturated phosphate buffered solution as the potential was carried in staircase mode. Spectra shown are from (a) -0.8 V to (h) -1.5 V in 0.1 V per step. $E_{ref} = -0.7$ V

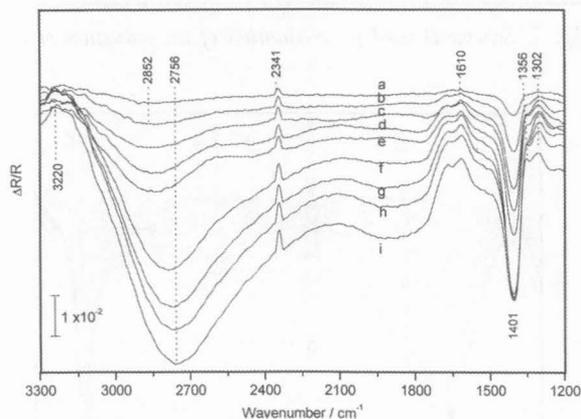


Fig. 5: SNIFTIR spectra obtained from copper in CO_2 -saturated phosphate buffered solution as the potential was varied in staircase mode. Spectra shown are from (a) -0.7 V to (i) -1.5 V in 0.1 V per step. $E_{ref} = -0.6$ V

associated with OH stretch of hydrogen bonded water-phosphate couple (Chapman and Thirlwell 1964). The 2852 cm^{-1} band shifts toward lower frequency as the potential becomes more negative. This may indicate that the OH stretch of hydrogen bonded in water-phosphate couple is more predominant than water-carbonate couple at more negative potentials due to the predominant water orientation (Nart and Iwasita 1992).

As the electrode surface is polarized while bubbling CO_2 in the solution according to the scheme shown in Fig. 7, an interesting electrochemical behavior (Fig. 3c) and SNIFTIR spectra were observed. As shown in Fig. 8, several new bands were observed at 1881 , 1955 and 2107 cm^{-1} . The band at 1881 cm^{-1} (at -1.4 V) shifts to 1955 cm^{-1} (at -0.2 V), as the potential is made more

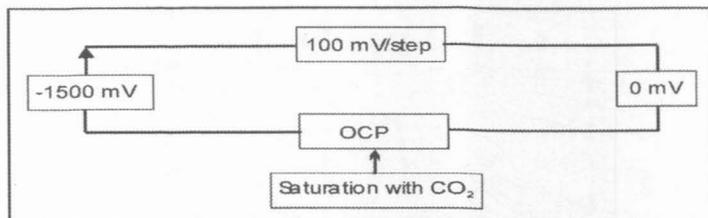


Fig. 6: Scheme A used for evaluation of the reduction of CO₂

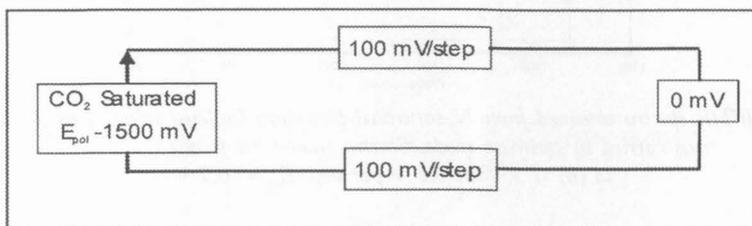


Fig. 7: Scheme B used for evaluation of the reduction of CO₂

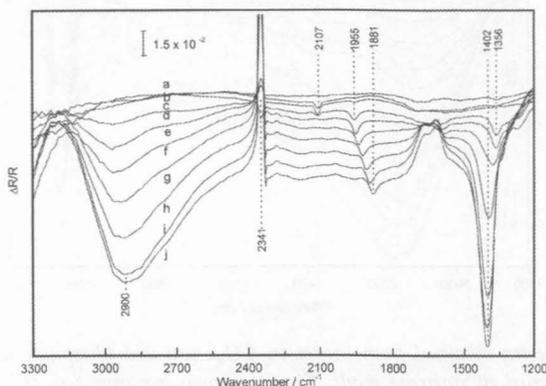


Fig. 8: SNIFTIR spectra obtained from continuous CO₂-saturated buffered phosphate solution as the copper was polarized at -1.4 V for 15 minutes at 0°C. Spectra shown are from (a) -0.3 V, (b) -0.1 V of reverse sweep, (c) 0 V to (j) -1.4 V of forward sweep in 0.2 V per step. E_{ref} = 0.4 V of reverse sweep

positive. This shifting band proves that the band is associated with adsorbed species (Dovydov 1990; Nakamoto 1986). As reported earlier the band at 1881 cm⁻¹ is assigned to adsorb bridge-bonded CO (Jumat and Kalaji 2002). A shift in band position for adsorbed CO has been rationalized by the p-back donation process, which is well documented (Blyholder 1964). The shift to higher frequency as the potential is made more positive indicates an increase in the

C-O bond order/strength. At high negative potential, p-back donation from copper dp orbital to CO antibonding $2\pi^*$ is believed to decrease the C-O bond order which consequently lowers the C-O stretch frequency. On the other hand, at less negative potentials (-0.2 V), the π -back donation becomes less, thus increasing the C-O bond strength. Increases in C-O bond order will therefore increase the C-O stretch frequency. The band at 2107 is assigned to soluble species, copper(I)-carbonyl which appears at anodic region where copper is oxidized to copper(I) (Hernandez and Kalaji 1996).

The existing of these bands proves that the reduction of CO_2 can only occur on the polarized electrode surface. This might be due to the electrode surface turn to be cleaned after the removal of specific pre-adsorbed ions such as hydroxide, electrolyte anions and oxides from the surface, thus leaving the clean surface to allow the reduction process. The electrochemical properties change on the copper surface is clearly shown in *Fig. 3c* where the hydrogen evolution region is depressed and shifted toward more negative potential, implying that some other process occurred in this region. This is consistent with the appearance of new bands of adsorbed CO and copper(I)-carbonyl in the same experimental condition.

CONCLUSION

It is clearly shown that the electrochemical behavior of copper electrode in phosphate buffered solution is dramatically changed by the polarization process. The hydrogen evolution region is depressed greatly compared to what has been reported in hydrogen carbonate solution. The oxidation and the reduction processes occur slowly on the copper surface as clearly shown by the cyclic voltammogram. The hydrogen evolution region occurs at potential more negative than -1.0 V and not affected by the anodic potential limits. The anodic film forms on the copper surface are reduced in quasi-reversible manner. In CO_2 -saturated solution, the loss of copper to the solution increases due to the formation of copper soluble species. The rate of copper dissolution to the solution is enhanced through the polarization process, where copper(I)-carbonyl forms at anodic potentials. The reduction of CO_2 will not proceed on the copper surface unless the electrode surface has been polarized at high cathodic potential for a period of time. This might be due to the competing process between the CO_2 reduction and the specific pre-adsorption of anions processes occurring on the electrode surface.

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REFERENCES

- ALHAJI, J. N. and M. R. REDA. 1996. Role of solution chemistry on corrosion of copper in synthetic solution: Effect of bicarbonate ion concentration on uniform and localized attack. *British Corr. J.* **31(2)**: 125-131.
- AURIAN-BLAJENI, B. 1992. Electrochemical reduction of carbon dioxide. In *Electrochemistry in Transition*, ed. O. J. Murphy. p. 381-396. New York: Plenum Press.
- BLYHOLDER, G. 1964. Molecular orbital view of chemisorbed carbon dioxide. *J. Phys. Chem.* **68(10)**: 2772-2778.
- CHAPMAN, A. C. and L. E. THIRLWELL. 1964. Spectra of phosphorous compounds – I: The infra-red spectra of orthophosphates. *Spectrochim. Acta* **20**: 937-947.
- DOVYDOV, A. A. 1990. *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides*. New York: John Wiley & Sons.
- DROGOWSKA, M., L. BROSSARD and H. MENARD. 1992. Effect of phosphate ions on copper dissolution and passivation. *J. Electrochem. Soc.* **139(10)**: 2787-2793.
- HERNANDEZ, R. M. and M. KALAJI. 1996. Use of isotopically labeled compounds for the in situ IR study of the electroreduction of CO₂ in aqueous hydrogen carbonate and buffered phosphate solutions. *J. Chem. Soc., Faraday Trans.* **92**: 3957-3962.
- JUMAT, S. 2001. Electrocatlytic activity of copper towards the reduction of carbon dioxide. Ph.D thesis, University of Wales, Bangor.
- JUMAT, S. and M. KALAJI. 2002. *In situ* FTIR observation of the intermediate species from the electrochemical reduction of carbon dioxide on polycrystalline copper. *Malay. J. of Anal. Sci.* (in press).
- JUMAT, S. and M. KALAJI. 2002a. Surface pretreatment effect on the electrochemical reduction of CO₂ at polycrystalline copper in aqueous hydrogen carbonate solution. *Sains Malaysiana* **31(1)** (in press).
- NAKAMOTO, K. 1986. *Infrared Spectra of Inorganic and Coordination Compounds*. 4th edition. New York: John Wiley & Sons.
- NART, F. C. and T. IWASITA. 1992. On the adsorption of H₂PO₄⁻ and H₃PO₄ on platinum: An in situ FT-ir study. *Electrochim. Acta* **37(3)**: 385-391.
- OSAMU, K. and Y. HORI. 1993. Reduction of adsorbed CO on a Ni electrode in connection with the electrochemical reduction of CO₂. *Electrochem. Acta* **38(10)**: 1391-1394.
- PYUN, C. H. and S. M. PARK. 1986. *In situ* spectroelectrochemical studies on anodic oxidation of copper in alkaline solution. *J. Electrochem. Soc.* **133(10)**: 2024-2030.
- RIBOTTA, S. B., M. E. FOLQUER and J. R. VILCHE. 1995. Influence of bicarbonate ions on the stability of prepassive layers formed on copper in carbonate-bicarbonate buffers. *Corr. Sci.* **51(9)**: 682-688.
- WEBER, M. and F. C. NART. 1996. On the adsorption of ionic phosphate species on Au(111) – An in situ FTIR study. *Electrochim. Acta* **41(5)**: 653-659.