Comparative study of copper behaviour in bicarbonate and phosphate aqueous solutions and effect of chloride ions

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Copper oxidation in aqueous solutions of pH 8 showed some differences in the presence of bicarbonate and phosphate ions. The bicarbonate ions did not interfere with Cu_2O film formation but the Cu^{2+} ions were stabilized by the complexing action of CO_3^{2-} anions. In phosphate solutions, copper dissolved in the range of potentials associated with the Cu(I) oxidation state and the Cu(II) compound on the surface resulted in an extensive passivation region. In both solutions, a higher ion concentration caused an increase in the anodic current, suggesting that the copper ions were stabilized by the complexing action of the electrolyte. The copper oxidation current in a bicarbonate solution was higher than that observed in a phosphate solution of the same concentration. The thickness of the Cu(II) film rather than the Cu(I) layer appears to be the important factor related to the stability of the passive layer on the copper surface. The shift in the breakdown potential toward more positive values indicates that both bicarbonate and phosphate ions inhibit localized corrosion due to the presence of chloride ions. Their protective effect depends on the concentration of each anion, although the concentration of chloride ions necessary for pitting is larger in phosphate solutions than in bicarbonate solutions. In both solutions, long-term immersion of copper under anodic polarization results in the precipitation of a protective coating.

1. Introduction

Bicarbonate, phosphate and chloride ions are usually found in natural waters where their ability to form soluble complexes and their buffering capacity affect the corrosion or protection of copper. Each ion plays a different role depending on the ambient conditions, in particular, the ion concentration, potential, pH range and temperature. The effect of anions on the electrochemical behaviour of copper in alkaline and neutral solutions has been described in several papers [1–17]. There is general agreement that the anodic film on copper presents a simple Cu_2O or a duplex Cu_2O/CuO, $Cu(OH)_2$ structure, depending on the electrode potential. The passive film of Cu(II) compounds has a double structure: a lower layer grown via a solid-state mechanism, and an upper layer formed by nucleation and growth from the solution.

Recently, the electrochemical oxidation of copper in the presence of bicarbonate or phosphate ions plus chloride or sulphate ions in aqueous solutions at pH 8 has been studied in our laboratory [14–17]. An increase in the bicarbonate or phosphate concentration, electrode potential or exposure time contributes to the formation of a stable layer consisting of the precipitated Cu(II) oxidation product. This Cu(II) layer is essential for copper passivity.

This paper presents a comparative study of copper oxidation in bicarbonate and phosphate solutions of pH 8 and their inhibiting effect against attack by chloride ions.

For the ternary $Cu-CO_2-H_2O$ system [18, 19], the passivity of copper has been interpreted in terms of the formation of a protective malachite $(CuCO_3 * Cu(OH)_2)$ or azurite $(2CuCO_3 * Cu(OH)_2)$ film. Some high solubility aqueous copper carbonate complexes are known: $CuCO_3(aq)$, $Cu(CO_3)_2^{2-}$ and $CuCO_3(OH)_2^{2-}$. The values of the solubility products indicate that the formation of copper oxides is favoured and the basic copper carbonate is less soluble than the chloride compounds. In the 6–9 pH range, carbonic acid is present mostly in the form of HCO_3^- ions.

Phosphate is an inorganic anodic corrosion inhibitor which acts as a buffering agent. The calculations of the buffer capacities of 0.1 M of phosphate, borate and carbonate solutions at pH 8 give the highest value for phosphate solution: 2.7×10^{-2} mol (pH unit)$^{-1}$ for phosphate ions $> 1.5 \times 10^{-2}$ mol (pH unit)$^{-1}$ for borate ions $> 4.9 \times 10^{-3}$ mol (pH unit)$^{-1}$ for carbonate ions.

The individual phosphate species are present in a 0.1 M Na_2HPO_4 solution at pH 8 in the following concentration: $[H_2PO_4^-] = 1.39 \times 10^{-2}$ M, $[HPO_4^{2-}] = 8.61 \times 10^{-2}$ M, $[PO_4^{3-}] = 4.13 \times 10^{-5}$ M. By compar-

ing the solubility constants [19] for $Cu_2O\ K_{so} = [Cu^+]$ $[OH^-] = 10^{-14}$, $CuO\ K_{so} = [Cu^{2+}]\ [OH^-]^2 = 10^{-20}$, $Cu_3(PO_4)_2\ K_{so} = [Cu^{2+}]^3[PO_4^{3-}]^2 = 10^{-37}$, it was possible to obtain a value for the minimum copper concentration necessary for precipitation: $[Cu^+] = 10^{-8}$ M for Cu_2O, $[Cu^{2+}] = 10^{-7}$ M for CuO, $[Cu^{2+}] = 10^{-9}$ M for $Cu_3(PO_4)_2$. The formation of phosphate may predominate.

2. Experimental details

The measurements were performed in a conventional two-compartment, three-electrode electrochemical cell. The working electrode was either a copper-disc electrode rotated at 1000 r.p.m. or a stationary disc electrode (surface area of $0.13\,cm^2$), cut from a polycrystalline copper rod (Johnson Matthey, grade 1) and set in a Kel-F holder. Before each experiment, the electrode surface was mechanically polished with an alumina suspension and rinsed with distilled water. At the beginning of each experiment, the copper electrode was immersed in the solution with the potentiostat set at -0.9 V to remove all traces of surface oxides.

The auxiliary electrode was a platinum grid separated from the main compartment by a Nafion® membrane. A saturated calomel electrode (SCE) connected to the cell by a bridge with a Luggin capillary served as the reference electrode for all potentials quoted in this paper. The potential was corrected for the iR drop, which was measured by the a.c. impedance technique.

Each solution was prepared with Baker analytical grade reagent and deionized water. The solutions were brought to pH 8 and were free of any buffer and other supporting electrolytes. The cell capacity was $\sim 600\,cm^3$, which ensured that the Cu^{2+} build up in the bulk of the solution during the experiment was negligible. Each solution was deaerated with nitrogen prior to and during the measurements. All results represent average values of three to five data sets.

The potential was applied to the working electrode by an EG&G PAR 273A potentiostat and controlled by computer using an EG&G PAR Model 270 Electrochemical Analysis System or, for microsecond records, a Computerscope interface (R.C. Electronic Inc.). The charge associated with the oxidation or reduction processes was obtained by integrating voltammetric or chronopotentiometric curves. Electrode rotation was performed using an analytical rotator (Pine Instrument Company).

3. Results and discussion

A copper electrode was oxidized and reduced voltammetrically under a number of variables including the electrolyte concentration, potential sweep limit, sweep rate and solution temperature.

3.1. Electrolyte concentration

The effect of ion concentrations on voltammetric curves for a copper-disc electrode in 0.1 M and 0.05 M bicarbonate and 0.1 M and 0.2 M phosphate solutions (pH 8, 25° C) is presented in Fig. 1. The electrode was rotated at 1000 r.p.m. with a scan rate $0.005\,V\,s^{-1}$. For both electrolytes, the higher concentration causes an increase in anodic current, although the cathodic current remains almost independent of ion concentration. Both ions interfere with the copper electrooxidation process, but the current density was always higher in $NaHCO_3$ than in a Na_2HPO_4 solution of the same concentration.

For both bicarbonate and phosphate solutions, two well-defined reduction current peaks are observed on the negative potential sweep, their presence suggesting that two distinct films or phases were formed on the anodic potential scan.

3.2. Positive potential sweep limit

A series of voltammograms reversed at various positive potential sweep limits is illustrated in Fig. 2. The copper disc electrode was rotated at 1000 r.p.m., with a scan rate of $0.005\,V\,s^{-1}$ in 0.1 M $NaHCO_3$ and 0.1 M Na_2HPO_4 solutions at 5° C and pH 8.

For the bicarbonate solutions (5 to 60° C) primary passivation of the electrode surface was observed when the potential sweep limit was set between the two anodic current peaks [14, 16]. It was associated with the formation of a Cu_2O layer which was reduced with 100% Q_{red}/Q_{ox} efficiency in cathodic
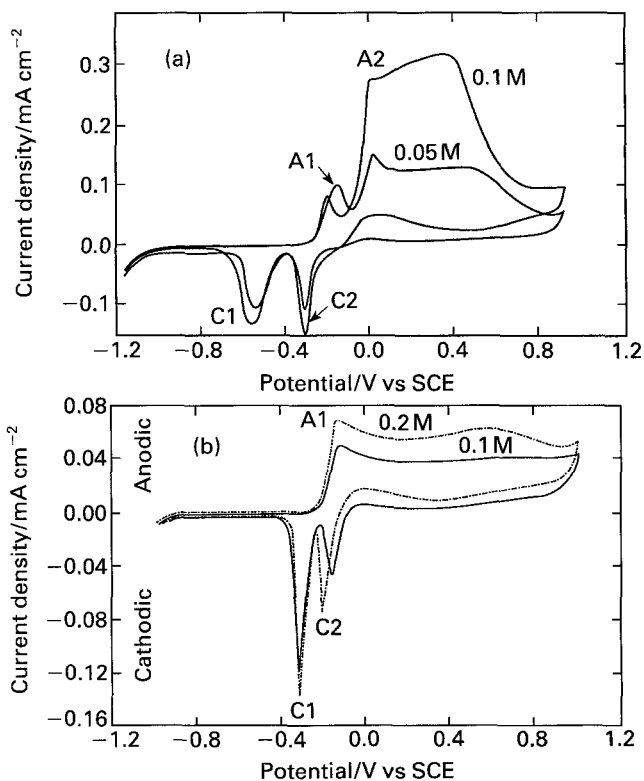

Fig. 1. Voltammograms for a copper disc electrode rotated at 1000 r.p.m., $dE/dt = 0.005\,V\,s^{-1}$, in (a) 0.05 M and 0.1 M $NaHCO_3$, and (b) 0.1 M and 0.2 M Na_2HPO_4 solutions (pH 8, 25° C).
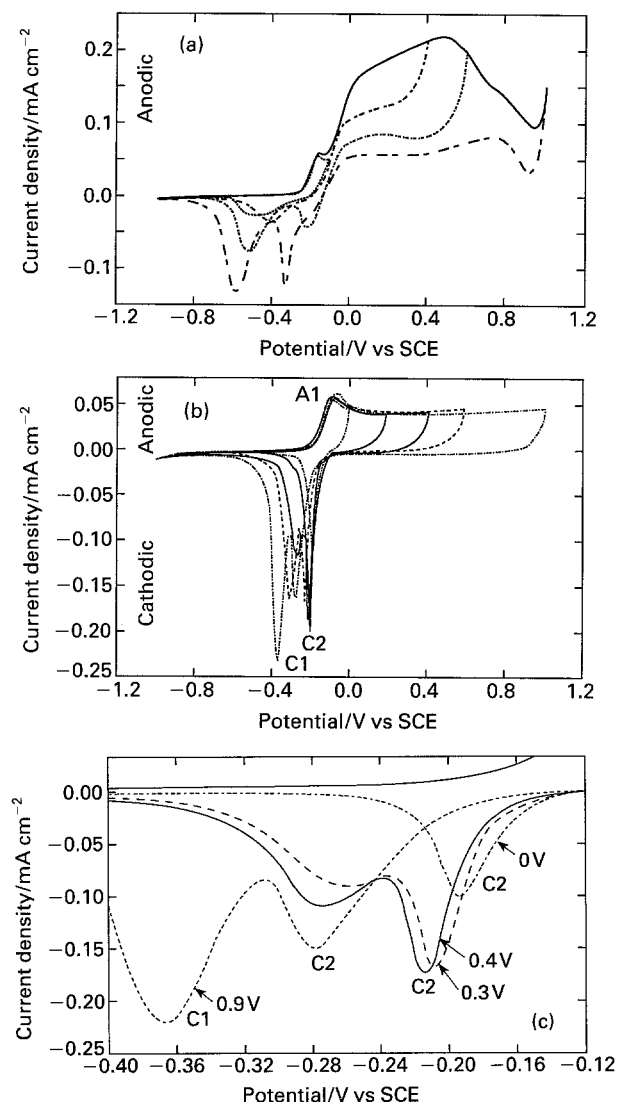
Fig. 2. Voltammograms for a copper disc electrode rotated at 1000 r.p.m., $dE/dt = 0.005\,V\,s^{-1}$ and reversed at progressively increasing potentials in (a) 0.1 M $NaHCO_3$ and (b) and (c) 0.1 M Na_2HPO_4 solution (5° C, pH 8).

peak during the negative potential scan. At a more positive potential scan limit, the anodic current increased sharply, followed by a broad oxidation area. An oxidation current was also recorded on the reverse (negative) scan, indicating that copper was highly soluble despite the fact that the electrode surface remained covered by a film of Cu(I) oxidation product.

The passivity of the oxide film broke down for $NaHCO_3$ concentrations smaller than 0.05 M and at potentials higher than that of the first anodic current peak [14, 16]; this breakdown was manifested by a rapid rise in the anodic current at a given potential on the voltammograms, suggesting that CO_3^{2-} ions were interacting with the $CuO/Cu(OH)_2$ film rather than with the Cu_2O layer. For bicarbonate concentrations above 0.05 M, the surface layer did not break down but, during the potential sweep in the negative direction, the electrode was reactivated and an anodic current related to copper dissolution was recorded.

For the phosphate solutions (5 to 30° C) only one

anodic current peak was observed. It was followed by an extensive passivity region until the onset of oxygen evolution. A small oxidation current of a few $\mu A\,cm^{-2}$ recorded during the reverse potential sweep is consistant with the formation of a passive layer in the passive region.

At the positive potential scan limit of 0 V, only one reduction current peak C2 was recorded, at $-0.2\,V$, with only 15% reduction efficiency, Q_{red}/Q_{ox}. As the positive potential sweep limit or oxidation time increased, a second reduction current peak, C1, appeared at a more negative potential than C2 (Fig. 2). A similar effect was observed for higher scan rates in the positive direction: upon a reverse sweep in the negative direction, only one current peak, C2, was recorded but for a longer arrest time at an anodic potential of 0 V, two reduction current peaks, C1 and C2, were present on the voltammetric curve. The anodic and cathodic processes were both time-dependent, though the oxidation reaction was slower.

That the anodic product formed at a potential below 0 V was reduced with only 15% Q_{red}/Q_{ox} efficiency, combined with the absence of a current peak for Cu_2O reduction, suggests that the Cu(I) species is highly soluble in the phosphate solutions. The Cu(II) compound appeared first on the copper surface, followed by the formation of Cu(I) products. This time delay could be due either to the precipitation of Cu(I) compound from the supersaturated solution at the electrode surface or to disproportionation of Cu(II) ions or compounds with copper metal.

3.3. Temperature effect

The differences in the copper behaviour for carbonate and phosphate solutions are more pronounced at higher temperature. Figure 3 shows voltammetric curves recorded at 5° C and 60° C in a solution with either 0.1 M $NaHCO_3$ or 0.1 M Na_2HPO_4 (pH 8) on a rotating copper disc electrode (1000 r.p.m.) at a scan rate of $0.005\,V\,s^{-1}$.

The effect of temperature in bicarbonate solutions was barely noticeable at the first anodic current peak and in the primary passivity region, but intensified considerably in the broad oxidation region (Fig. 4). From 5° C to 60° C, the anodic current increased sharply as the potential reached the broad oxidation region, and the reduction efficiency, Q_{red}/Q_{ox}, fell from 100% to 11%. Furthermore, the potential range of the second oxidation region narrowed, and the secondary passive region expanded as the temperature rose. This effect is associated with the increase in the copper dissolution–precipitation rate with temperature. The protective characteristics of the passive layer were well defined in the large range of potentials at 60° C and only slightly noticeable at 5° C. Clearly, the barrier offered by the passive film to the current is stronger at higher temperatures.
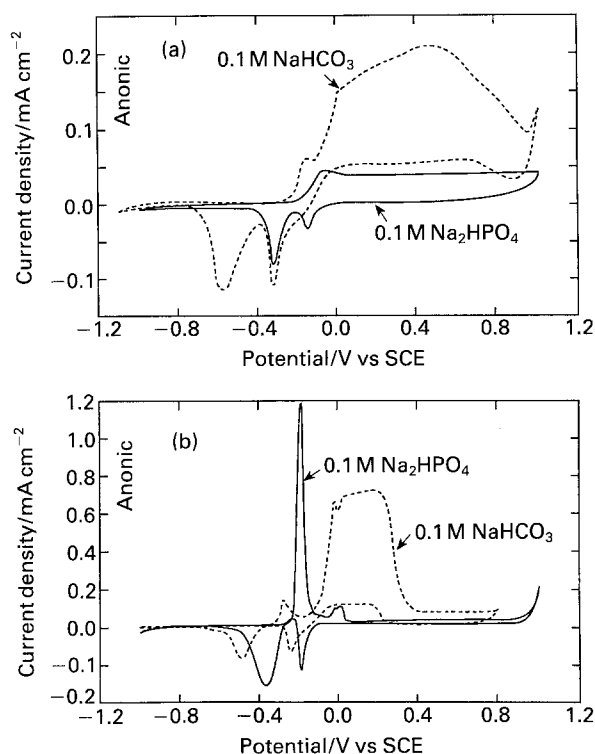
The oxidation kinetics were faster at higher tem-

Fig. 3. Voltammograms for a copper disc electrode rotated at 1000 r.p.m., $dE/dt = 0.005\,V\,s^{-1}$ in 0.1 M NaHCO$_3$ and 0.1 M Na$_2$HPO$_4$ solutions (pH 8) at (a) 5° C and (b) 60° C.

peratures and the Cu^{2+} species were stabilized by the complexing action of carbonate anions. The breadth of the second oxidation region indicates the potential limits for copper solubility. Copper carbonate, CuCO$_3$, does not exist naturally, nor does it seem to have been isolated. The existence of cupric ion–carbonate ion complexes has been postulated by several authors [18–23]. In solutions of constant ionic strength 0.1 M NaHCO$_3$, the following concentrations of soluble Cu(II) species exist in equilibrium with malachite: $[Cu^{2+}] = 4.3 \times 10^{-9}\,M$, $[CuCO_3(aq)] = 1.5 \times 10^{-5}\,M$, $[(CuCO_3)_2^{2-}] = 5.1 \times 10^{-7}\,M$ and $[CuCO_3(OH)_2^{2-}] = 2.3 \times 10^{-9}\,M$. The species CuHCO$_3^-$ should not be considered [19] and the Cu(I) carbonate complexes are not known. The interaction between Cu(II) and CO$_3^{2-}$ ions resulting in soluble complexes may explain the different anodic behaviour of copper in solutions containing bicarbonate [14, 16, 17] compared to that of other aqueous electrolytes. In the presence of electrolytes such as phosphate [5, 15], borate [5, 24] and phthalate [5], the copper dissolved in the range of potential associated with the Cu(I) oxidation state while the Cu(II) compounds on the copper surface provided an extensive range of passivity.

For the phosphate solution, the effect of temperature was evidenced in the potential region of the anodic current peak (−0.2 to 0.2 V). From 5° C to 30 °C (Fig. 4), only one anodic current peak, at around −0.08 V, was recorded. The Cu(II) oxidation compounds formed first on the electrode surface. From 30° C to 60° C, the first well-defined oxidation current peak became dominant, its maximum corresponding to −0.19 V, and a second anodic
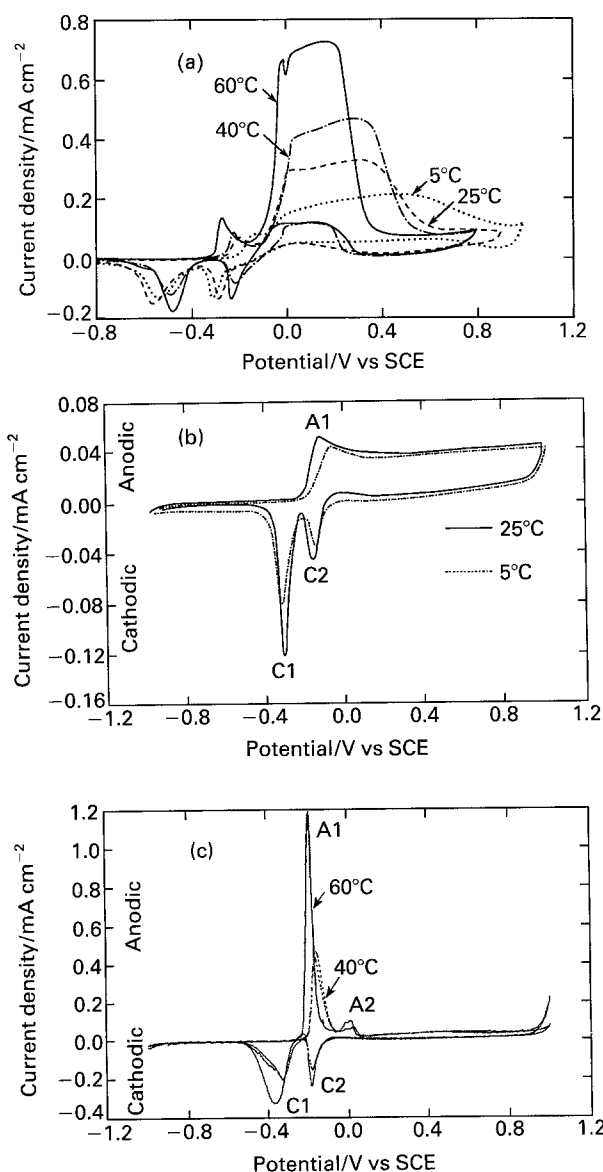

Fig. 4. Voltammograms for a copper disc electrode rotated at 1000 r.p.m., $dE/dt = 0.005\,V\,s^{-1}$ in (a) 0.1 M NaHCO$_3$ and (b) and (c) 0.1 M Na$_2$HPO$_4$ solutions (pH 8) at 5, 25, 40 and 60° C.

current peak, at 0.005 V, appeared. The copper oxidation rate increased, resulting in the formation of a Cu$_2$O layer, and copper was dissolved through this layer at more positive potenitals. However, both the charge and the current density in the passive region were independent of the temperature.

The activation energy was calculated with the current density values at the potential of the first anodic current peak, and was estimated to equal the activation energy of the Cu$_2$O passive film formation. The current density values for various temperatures in 0.1 M NaHCO$_3$ and 0.1 M Na$_2$HPO$_4$ solutions were plotted as a function of $1/T$ in Fig. 5. One slope in the Arrhenius plot in the case of carbonate solutions and two slopes for phosphate and borate [24] solutions were obtained. In carbonate solutions an activation energy of $\sim 10\,kJ\,mol^{-1}$ was calculated. In phosphate solution a transition was observed at around 30° C with a low $\sim 8\,kJ\,mol^{-1}$ activation energy for the product formed below 30° C
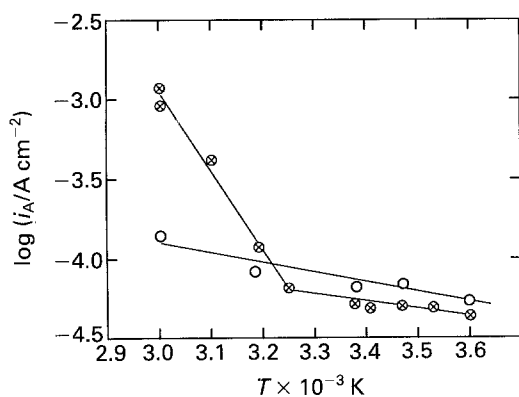
Fig. 5. Arrhenius plots of $\log i_{A1}$ against $1/T$ for (○) 0.1 M NaHCO$_3$ and (×) 0.1 M Na$_2$HPO$_4$ solutions (pH 8).

and the other, from 30 to 60° C, attaining a value of $\sim 90 \text{ kJ mol}^{-1}$, compared to 19 kJ mol^{-1} below 25° C and 48 kJ mol^{-1} at higher temperatures in borate solutions [24].

The low activation energy is compatible with a poorly structured thin passive layer where the metal electrodissolution process becomes energetically close to a diffusion controlled process in solution [24]. From this it may be concluded that the process occurs through a passive layer containing large amounts of water. However, as the Cu(II) dissolution rate increases, a new passive film containing Cu(II) compounds is formed by a dissolution–precipitation mechanism. The protective characteristics of the film improve at higher temperature, as demonstrated by an expanded secondary passive region and a shift of the breakdown potential values in a positive direction. This effect can be explained in terms of the structural modifications as the passive film loses its water molecules and becomes more compact.

3.4. Oxidation and reduction charge

The total copper oxidation charge, Q_{ox}, is associated with the charge involved during the positive potential scan and, also, the anodic charge involved during the negative going scan. The value of Q_{ox} for an anodic scan limit of 0.8 V and $dE/dt = 0.005 \text{ V s}^{-1}$ was 69 mC cm^{-2} at 60 °C and 49 mC cm^{-2} at 5 °C in the case of the bicarbonate solutions, compared to 17 mC cm^{-2} and 10 mC cm^{-2} at 60° C and 5° C, respectively, for the phosphate solutions. It should be noted that the Q_{ox} values were higher in NaHCO$_3$ than in Na$_2$HPO$_4$ solutions. The charge associated with the cathodic sweep was always smaller than that associated with the anodic scan, which implies a loss of copper species in the solution. The ratio between the total cathodic and anodic charges, $Q_{\text{red}}/Q_{\text{ox}}$, in bicarbonate solutions (0.09 at 60° C and 0.13 at 5° C) is smaller than in phosphate solutions (0.17 and 0.26, respectively), although in all cases both Q_{ox} and Q_{red} decrease as the scan rate increased. This can be attributed to a decrease in both the extent of the dissolution and the thickness of the surface layer. At higher scan rates, a shorter time was spent in the potential region

where dissolution occurs, and consequently, less dissolution and precipitation were induced. This simultaneous reduction in the film thickness and copper dissolution suggest that the two processes are interrelated. It is possible that the extent of the dissolution determines the thickness of the passive layer, which would confirm that the film is formed by the precipitation of dissolved Cu(II) species.

3.5. Effect of chloride anion

The presence of chloride anions affects the behaviour of copper in both bicarbonate and phosphate solutions [14–16]. The voltammograms for copper electrode in 0.1 M NaHCO$_3$ and 0.1 M Na$_2$HPO$_4$ solutions with and without chloride ions are presented in Figs 6 and 7. In phosphate solutions (Fig. 7), the chloride ions caused the anodic current to increase, particularly in the potential region from -0.2 to 0.2 V, which was the location of the first anodic current peak related to the Cu(I) oxidation state. In 0.1 M Na$_2$HPO$_4$ + 0.1 M NaCl solution at temperature between 5 to 60° C, the electrode surface remained passive without any visible traces of corrosion but in 0.1 M Na$_2$HPO$_4$ + 0.7 M or 1 M NaCl solutions, the high anodic current for a potential range of -0.2 to 0.2 V was followed by electrode passivation and the electrode surface presented different zones of corrosion.

In 0.1 M NaHCO$_3$ + 0.1 M NaCl solution (Fig. 6), chloride ions have little effect on the anodic polarization curves at low potentials and at the potential of formation of the Cu(II) oxidation layer until the film broke down. In both solutions, the reduction efficiency, $Q_{\text{red}}/Q_{\text{ox}}$, decreased as the chloride ion concentration increased indicating that a large part of the anodic current was linked to the formation of soluble copper species.

Both bicarbonate and phosphate ions inhibited the localized attack on copper induced by chloride ions [14–16]. This protective effect is due to the shift in breakdown potential and corrosion potential towards more positive values than those obtained in pure chloride solutions. These potentials depended on the concentration of each anion, although, the con-
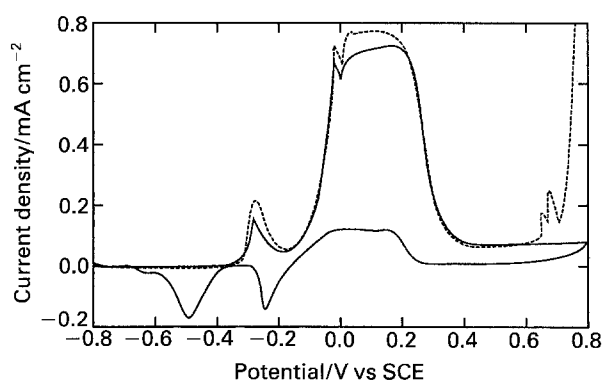

Fig. 6. Voltammograms for a copper disc electrode rotated at 1000 r.p.m., $dE/dt = 0.005 \text{ V s}^{-1}$ in (———) 0.1 M NaHCO$_3$ and (- - - -) 0.1 M NaHCO$_3$ + 0.1 M NaCl solutions (pH 8, 25 °C).
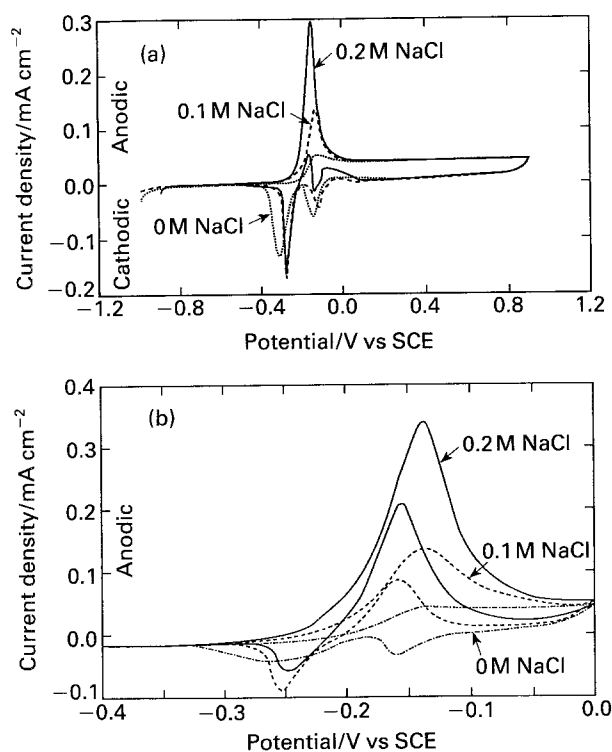
Fig. 7. Voltammograms for a copper disc electrode rotated at 1000 r.p.m., $dE/dt = 0.005\,V\,s^{-1}$ in 0.1 M $Na_2HPO_4 + x$M NaCl solution (pH 8, 25° C); $x = 0$, 0.1 and 0.2.

centration of chloride ions necessary for pitting initiation was larger in the phosphate solutions. The critical concentration of chloride ions is related to various parameters, such as the electrochemical conditions, temperature, exposure time, agitation, etc. Under anodic polarization, long-term immersion of copper in the solutions caused the precipitation of a protective coating. A high [phosphate]/[chloride] ratio favours the formation of a thin compact passive film, while a high [chloride]/[phosphate] ratio led to the precipitation of a thick porous protective deposit on the copper surface.

4. Conclusion

In both bicarbonate and phosphate solutions, a higher ion concentration caused an increase in the anodic current, suggesting that the anions interfere in the copper electrooxidation process. The copper oxidation current in a bicarbonate solution was always higher than that observed in a phosphate solution of the same concentration.

Bicarbonate solutions favour the formation of a Cu_2O layer both thermodynamically and kinetically, and the bicarbonate ions do not interfere with the first electrooxidation process. General dissolution of the copper surface results from the complexing action of CO_3^{2-} anions towards Cu(II).

In the phosphate solutions, the copper dissolves in the range of potentials associated with the Cu(I) oxidation state. Cu(II) compounds on the copper surface resulted in an extensive passivity region. Homogeneous dissolution of the copper surface occurs in both solutions, but the presence of chloride ions is

necessary for pitting initiation. The increase in the corrosion-breakdown potential difference provides information on the surface film stability and indicates that both bicarbonate and phosphate ions inhibit localized corrosion. The magnitude of this protection depends on the concentration of each anion, although the phosphate solutions have a stronger protective effect.

In both the bicarbonate and the phosphate solutions, at a sufficiently positive potential, a higher temperature or longer exposure time resulted in a large accumulation of Cu(II) compounds on the electrode surface. The Cu(II) film rather than the Cu(I) layer was necessary for a stable protective layer to form on the surface and slow down the copper dissolution.

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