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The Effects of Temperature and pH on the Dissolution and Passivation Processes of Copper in Carbonate-Bicarbonate Solutions

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Foram feitos estudos eletroquímicos de eletrodos de cobre policristalino em soluções de carbonato-bicarbonato, analisando os efeitos da temperatura e do pH, cobrindo uma extensa faixa de composições eletrolíticas num intervalo de 5-65 °C. As condições hidrodinâmicas do sistema também foram consideradas. Os resultados são explicados com base numa modificação das características do filme decorrente dos efeitos de agitação da solução e das temperaturas elevadas. Nestas situações, forma-se uma camada menos hidratada, reduzindo o processo de dissolução. A força iônica torna-se um fator adicional que afeta o estado geral do sistema.

Electrochemical studies of polycrystalline copper electrodes in carbonate-bicarbonate solutions analyzing both temperature and pH effects were carried out, covering a wide range of electrolyte composition in the 5-65 °C range. Hydrodynamic conditions were also considered. The results are explained on the basis of a modification of the characteristics of the film through solution stirring and high temperature. In this situation, a less hydrated passive layer is obtained, reducing the dissolution process. The ionic strength becomes an additional factor that affects the general state of the system.

Introduction

The behavior of copper in neutral and alkaline solutions has been studied by several authors[1-11]. There exists a general agreement about the structure and composition of prepassive and passive films, although the kinetics of complex anodic processes can change depending on potential perturbations, the nature of ions in solution[4-7,9,11], ionic strength, pH, and hydrodynamic conditions[5-8].

The aim of this study was to attain information about the potentiodynamic behavior of copper in solutions containing carbonate/bicarbonate ions, covering wide ranges of electrolyte pH, temperature, and ionic strength, in order to establish their contributions to the metal dissolution and passivation processes.

Materials and Methods

The electrochemical equipment, experimental details and electrode treatment have been previously described in detail[7,12]. "Specpure" copper rotating disks (Johnson Matthey Chemicals., 0.15 cm^2 apparent area) embedded in PTFE holders were used as the working electrodes.

The potentials were measured against a saturated calomel electrode (SCE), but in the text the potential are referred to the NHE scale, taking into account the corrected potential values of SCE according to a suitable equation[13]. A large-area platinum plate was employed as the counter electrode.

The electrolyte solutions consisted of a mixture of $xM\ KHCO_3 + yM\ K_2CO_3$ ($0.0075 \le x \le 2.25$; $0.0005 \le y \le 1.5$), covering the 8.3-11.6 pH range. They were prepared from analytical grade reagents and triple-distilled water previously boiled to remove carbon dioxide. At each pH, the values of x and y were set to cover a wide range of

ionic strength by keeping the HCO_3^- - CO_3^{2-} concentration ratio constant. Electrochemical measurements were performed at 5, 25, 45, and 65 °C under purified nitrogen gas saturation using single and repetitive triangular potential sweeps, between preset cathodic ($E_{s,c}$) and anodic ($E_{s,a}$) switching potentials at potential scan rates (v) in the 0.002 V/s ≤ v ≤ 0.300 V/s range. The working electrode was maintained either at rest or under rotation at speed ω, which was varied in the range of 600 rpm ≤ ω ≤ 2500 rpm.

After electrochemical measurements, some specimens were examined by scanning electron microscopy (SEM).

## Results and Discussion

The voltammograms of copper in still 0.75M $KHCO_3$ + 0.05M K_2CO_3 solution at pH 8.9 run at different v, at 25 °C, between $E_{s,c}$=-0.95 V and $E_{s,a}$=0.55 V (Fig. 1), show three anodic current contributions, at ~ 0.03 V (Peak 1), 0.18 V (Peak 2), and 0.40V (Region 3). Peak 1 is related to the Cu_2O electroformation (first passivating layer)[1,4], while Peak 2 was attributed to the formation of a $Cu(OH)_2$-CuO complex layer through a nucleation and growth mechanism under diffusion control[1,4,10]. The broad current contribution corresponding to Region 3 may be related to the presence of a protective composite $CuCO_3$-$Cu(OH)_2$ layer (second passivating layer)[5-7]. Peaks 1 and 2 overlap at v > 0.025 V/s, so Peak 1 can not be clearly distinguished. At v < 0.025 V/s, reverse scans show a reactivation of the electroxidation process in the potential region corresponding to Peak 2 and Region 3, suggesting a decrease in the passive film stability. The reverse scan shows three cathodic contributions, which exhibit complex contours (Peaks 4, 5, and 6), whose relative heights and locations depend on temperature, v, $E_{s,a}$, electrolyte composition, and solution pH. Peak 4 involves two contributions, Peak 4' and 4'', which were associated with the electroreduction of Cu(II) to the Cu(I) species, in the -0.07 to -0.06 V potential range[9]. Peaks 5' and 5'' have been related to the electroreduction of the composite $CuCO_3$-$Cu(OH)_2$ layer in the -0.28 to -0.43V region[6,11], and Peak 6, in the -0.60 to -0.80V region, has been assigned to the electroreduction of the Cu(I) species to Cu(0)[6] (Fig. 1). Peak 1 is better defined when either temperature or ionic strength increases, but its relative contribution diminishes; also, it appears at more negative potentials, so a lower overpotential is required for the Cu_2O electroformation reaction (Fig. 2). As temperature rises, the height of Peak 2 increases, Peak 1 occurs at more negative potentials, and the changes corresponding to Region 3 indicate greater stabilization of the passive layer. In dilute solutions, a significant temperature effect is not observed.

A linear log j_{p2} *vs.* log v relationship is obtained in still carbonate/bicarbonate solutions covering the 5-65 °C range, with the corresponding slope being ~0.45 (0.08, indicating a diffusional process. At constant v, j_{p2} increases as temperature and ionic strength are raised (Fig. 3).

At 25 °C, in the 8.3-9.5 pH range, at constant bicarbonate concentration, j_{p2} is independent of pH, whereas a linear log j_{p2} *vs.* pH is observed at pH > 9.5 (see Fig. 9 in Ref. 7). These data, together with the analysis of the corresponding stoichiometric equations and the associated reaction orders, show that in the first pH region HCO_3^- behaves as the
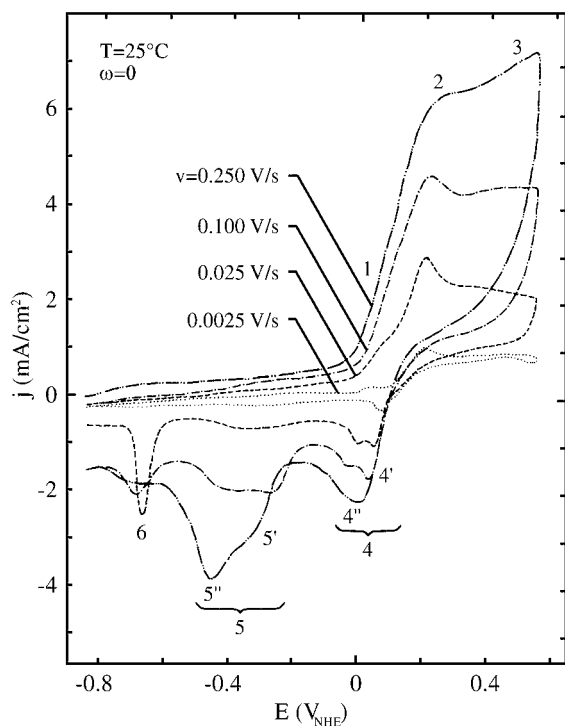
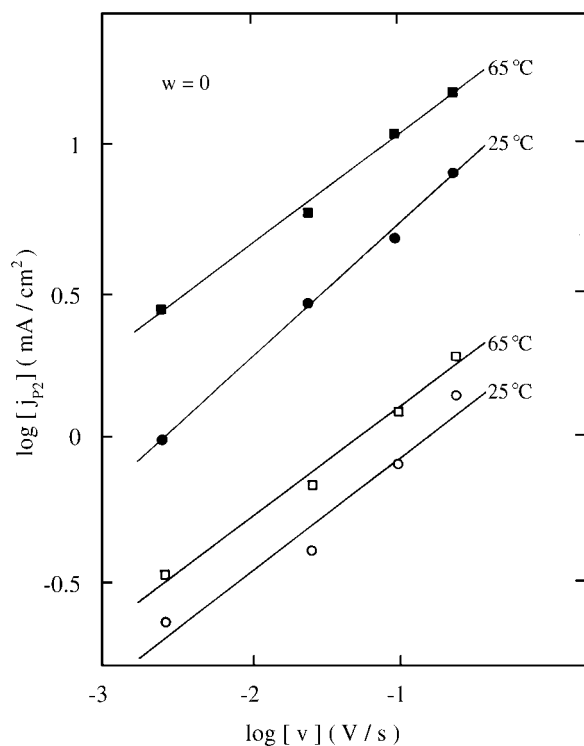**Figure 1.** The influence of v on the voltammograms run with STPS in still 0.75 M $KHCO_3$ + 0.05 M K_2CO_3, pH 8.9 at 25 °C.
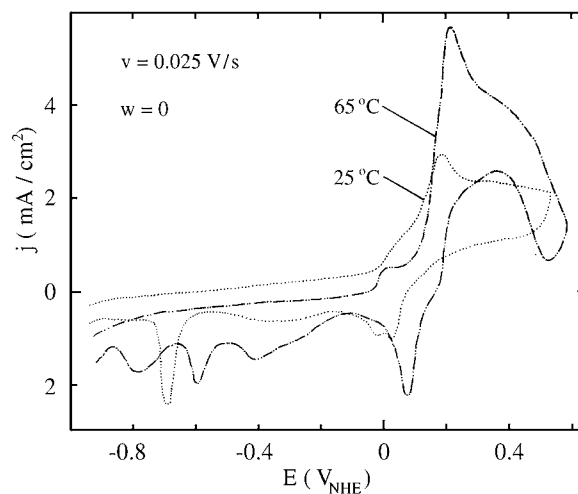
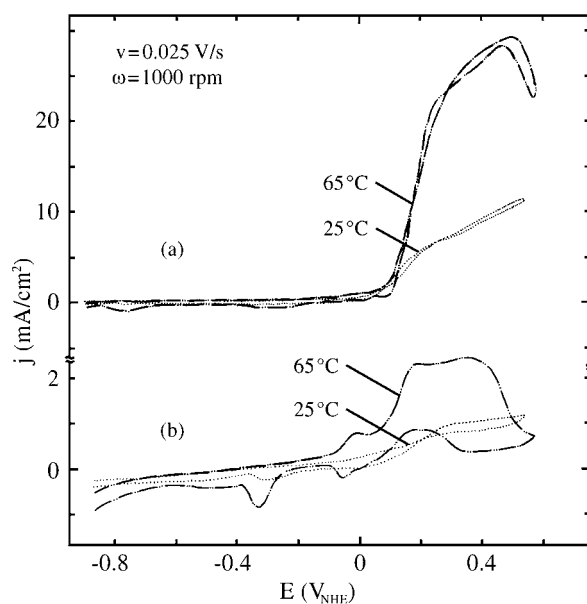**Figure 2.** The influence of Ts on the voltammograms run at v = 0.025 V/s in still 0.75 M $KHCO_3$ + 0.05 M K_2CO_3, pH 8.9, ω = 0.

aggressive anion, but in the second pH region the local pH

Figure 3. The dependence of j_{p2} on v at different Ts in still solutions.($\square$,•) 0.75 M KHCO$_3$ + 0.05 M K$_2$CO$_3$, pH 8.9; ($\square$,O) 0.075 M KHCO$_3$ + 0.15 M K$_2$CO$_3$, pH 10.5.
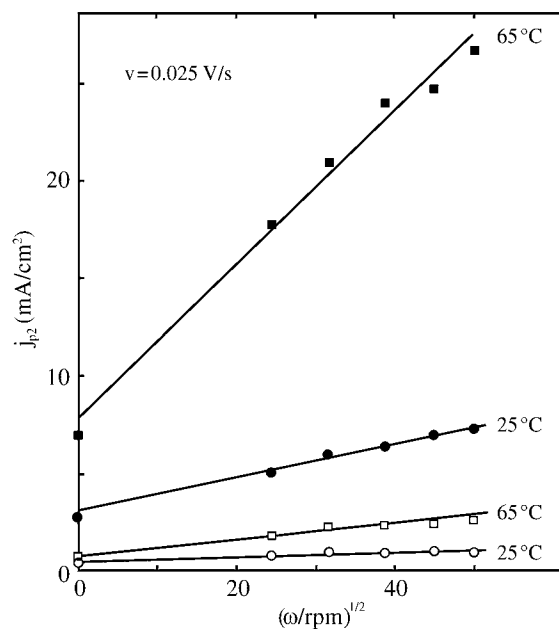
value at the region interface becomes an additional factor[7]. Similar results are obtained under stirring.

Under stirring, anodic current peaks and the reactivation process during the backward potential scan increase with temperature, ionic strength, and ω (Fig. 4). This effect is associated with the increment of soluble Cu(II) species obtained from the dissolution of the CuO-Cu(OH)$_2$ film and basic copper carbonates. This situation improves the dissolution-precipitation mechanism involved in the formation of the protective second passivating layer constituted by Cu (II) compounds. A significant effect of hydrodynamics on Peak 1 is not observed. In general, cathodic peaks decrease under stirring, but they increase with T.

Linear dependence of j_{p2} *vs.* $\omega^{1/2}$ at a constant v are observed, whose slopes increase with temperature. Greater slope changes are obtained with increasing ionic strength (Fig. 5).

In still solutions the activation energy (E$_a$) for the CuO-Cu(OH)$_2$ electroformation is ~15 kJ/mol at pH 8.9 and ionic strength 1, but diminishes to 6.5 kJ/mol when the ionic strength is 0.1 at the same pH. In general, E$_a$ increases with increasing ionic strength, but a clear relation between E$_a$ and pH does not exist.

Under stirring (ω = 1000 rpm), E$_a$ attains higher values, thus, at pH 8.9 and ionic strength 1, E$_a$ is 25 kJ/mol, suggesting changes in the passivating layer composition, particularly in its water content, which is reduced.

Figure 4. The influence of T on the voltammograms run at 0.025 V/s, ω = 1000 rpm. (a) 0.75 M KHCO$_3$ + 0.05 M K$_2$CO$_3$, pH 8.9; (b) 0.075 M KHCO$_3$ + 0.15 M K$_2$CO$_3$, pH 10.5.

Figure 5. The dependence of j_{p2} on ω at different Ts, v= 0.025 V/s. ($\square$,•) 0.75 M KHCO$_3$ + 0.05 M K$_2$CO$_3$, pH 8.9; ($\square$,O) 0.075 M KHCO$_3$ + 0.15 M K$_2$CO$_3$, pH 10.5.
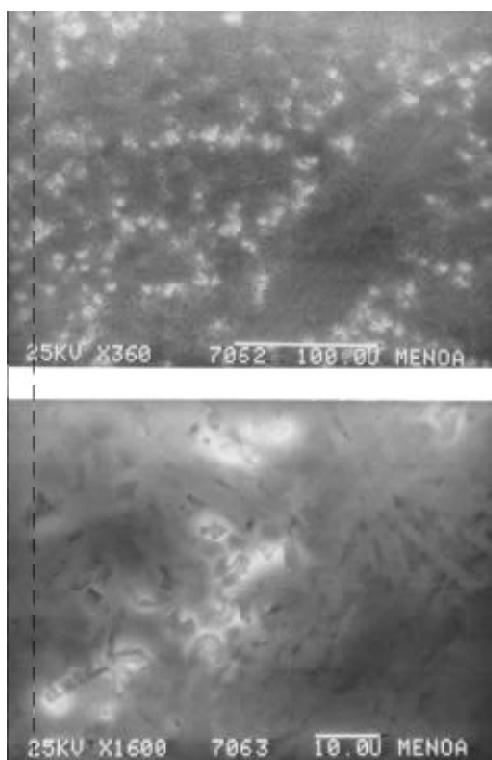
Figure 6. SEM micrographs of polycrystalline Cu specimens after potential holding for 10 min in the region of Peak 2, in 0.075 M $KHCO_3 + 0.15$ M K_2CO_3 solution pH 10.5, $\omega = 1000$ rpm, at 25 °C.

The influence of both T and ω on the surface layers was analyzed through SEM micrographs in carbonate-bicarbonate buffers at different pHs and ionic strengths. Considerable differences can be observed when T, ω, or ionic strength are changed.

At 25 °C and $\omega = 1000$ rpm, the copper surface is completely covered with the corrosion products, the appeara When T rises to 65 °C the film seems to be less hydrated (Figs. 6 and 7). This is an indication that protective characteristics of the film are better observed under stirring and at high temperature through a loss of water molecules. Also, these observations are in agreement with the E_a values obtained.

Conclusions

The electrochemical response of copper in HCO_3^- - CO_3^{2-} solutions ($8.3 \leq pH \leq 11.6$) depends on T, pH, ionic strength of the electrolyte, and hydrodynamic conditions.

Solution stirring and high temperature change the characteristics of the passivating layer, making it more protective; this situation is obtained through a decrease of the water content, so the film becomes less hydrated.

The activation energy obtained for the $CuO-Cu(OH)_2$ electroformation depends on ionic strength. This result is
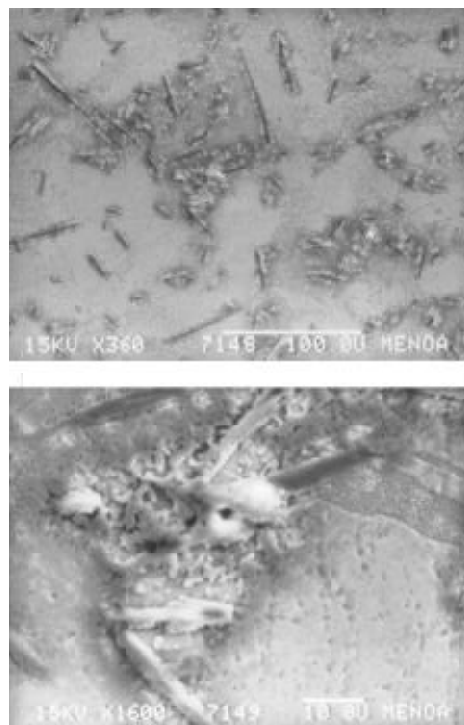
Figure 7. SEM micrographs of polycrystalline Cu specimens after potential holding for 10 min in the region of Peak 2, in 0.075 M $KHCO_3 + 0.15$ M K_2CO_3 solution pH 10.5, $\omega = 1000$ rpm, at 65 °C.

also obtained under stirring, therefore the electrodissolution process is hindered by films containing less water.

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