

Corrosion and Passivity of Copper in Basic Solutions of Acetate Ions

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The anodic oxidation of copper in sodium acetate aqueous solutions is studied in relation to the anodic films formed, in order to elucidate the role of acetates to the corrosion of copper. At open circuit conditions a cuprous oxide layer is formed having a thickness of few monolayers. At low anodic potentials, a composition with a single component which is cuprous oxide, is observed for the thin anodic film, whereas at relatively high anodic potentials a cuprous oxide and cupric hydroxide film is formed, accompanied by extensive dissolution of anodic products. At intermediate potentials, a duplex oxide film formation is not able to explain the electro-oxidation/reduction processes on copper in acetate solutions but the presence of the conducting hydrated layer, which may be probably basic copper acetate on top of cuprous oxide layer, has to be considered.

1. Introduction

The importance to study copper oxides is high both from the point of view of copper corrosion as well as of the semiconducting and photochemical properties of the oxides themselves (Abrantes et al. 1984, Aruchamy and Fujishima, 1989). Thermodynamic data suggest that two types of copper oxides can be formed on copper, cuprous oxide Cu_2O and cupric oxide CuO (or copper hydroxide, $\text{Cu}(\text{OH})_2$), at low and high anodic potentials, respectively, within the range of neutral to basic pH values (Jones, 1992). On the other hand, at low and high pH values, dissolution may occur resulting in the formation of Cu^{2+} and HCuO_2^- ionic species. Due to the significance of copper oxides and the copper metal in technological applications, a large amount of experimental work has been performed in the past in order to elucidate the mechanism of copper electro-dissolution and anodic film formation in basic media. As a basic medium, solutions of alkali metal hydroxides have been widely used thus eliminating the effect of anion to the process mentioned above (Marchiano et al. 1980, Burke et al. 1990). In spite of the extensive investigation of this system, copper oxide growth is still an open topic studied by both electrochemical and modern optical techniques (Strehblow et al. 2001, Kunze et al. 2004, He et al. 2006, Procaccini et al. 2013). A relatively small amount of work has been performed in acetate environment (Sutter et al. 1993, Kiliñçeker and Galip 2008, Gil et al. 2009), mainly in relation to atmospheric corrosion studies (Cano et al 2001, Gil and Leygraf 2007). It is interesting to notice that most studies of this type claim the existence of cuprous and cupric acetate salts on the corroded copper surface. A discussion of the existence and the role of such salts on the anodic oxidation of copper is usually absent in papers studying the phenomena in aqueous solution, thus considering the role of anion as insignificant. Acetate anions adjust the pH to basic values but also determine to some extent the stability (Dewald et al. 1993) and possibly the photochemical activity of anodic films on Cu.

The aim of the present study is to explore the anodic oxidation of copper in acetate solutions, i.e. anodic film formation and (electro)dissolution, as well as the role of acetate ions in the oxidation mechanism in order to elucidate the process of oxide growth during corrosion in such environment. For this task cyclic voltammetry, chronoamperometry, cathodic stripping voltammetry, quartz crystal microbalance and capacitance measurements are employed. The understanding of this relatively simple system may serve as a first step for the elucidation of more complex processes taking place during copper electro-dissolution

such as the oscillatory electrodisolution in buffered acetate solutions (Dewald et al. 1993) and solutions of trichloro- and trifluoro-acetates (Li et al. 2004, Potkonjak et al. 2010, Karantonis et al. 2010).

2. Experimental

Experiments were performed in a single compartment three-electrode cell. A copper (99.99 % Sigma-Aldrich) disk of 0.00785 cm² geometrical surface area was used as a working electrode. This surface area value was used for the normalization of current, capacitance and charge of this copper electrode. The working electrode was constructed by embedding copper wire of 1 mm diameter in acrylic resin. A saturated calomel electrode (SCE) was used as a reference electrode and a carbon rod as a counter electrode. Sodium acetate solutions were prepared by dissolving anhydrous sodium acetate (NaOAc) in deionized water (Sigma-Aldrich). Dissolved oxygen was removed from the solution by purging purified nitrogen gas for about 20 min.

Prior to each measurement the copper electrode was polished by a series of wet sandings (Struers 500, 800, 1200, 2400, 4000) and washed by deionized water. The copper electrode was pretreated by continuous potential cycling from -1.3 to 1 V with a scan rate of 100 mVs⁻¹ in the sodium acetate solution. A roughness $r = 4.8$ of the pretreated copper electrode was estimated by capacitance measurements.

Potentiostatic electrolyses, cathodic stripping measurements, and cyclic voltammetry were performed by a PAR EG &G 263A potentiostat. Capacitance measurements were performed by a SI1260 Solartron impedance/gain-phase analyser at $f = 1$ kHz and amplitude of 10 mV. For electrochemical quartz crystal microbalance measurements (EQCM), a PAR QCM922 microbalance was utilized, equipped with a 0.198 cm² active area gold resonator of 9.98 MHz base frequency. The gold surface was covered by electrodeposited copper. Electrodeposition was performed under periodic potential pulse conditions (10 s at -0.4 V followed by 5 s at 0.2 V) in a 0.1 M CuSO₄ solution. The geometric area of the gold substrate was used for the normalization of the mass difference when Cu deposited on Au was implemented as a working electrode.

3. Results and Discussion

It is known that upon immersion of the copper electrode in alkaline solutions, a thin oxide layer forms spontaneously, according to the reaction:



with equilibrium potential $E = -0.293$ V at pH 8.8. Indeed, this seems to be the case of Cu in 2 M NaOAc solution, as shown in the potentiodynamic reduction curve recorded upon immersion (full curve in Figure 1a), with a scan rate of 10 mVs⁻¹. It is obvious that the reduction peak occurred at -0.59 V can be associated to the reverse of the reaction of the Eq (1). The determined charge corresponding to this peak was $Q = 3.65$ mCcm⁻².

An estimate of Cu₂O thickness, d , can be obtained through the Faraday's law, $d = QV_m/2Fr$. For molar volume $V_m = 23.84$ cm³mol⁻¹ the cathodic charge corresponds to a thickness of $d = 0.94$ nm, a value close to the that proposed for the cuprous oxide film in sodium hydroxide solutions (Kunze et al. 2004). After the reduction scan the system was allowed to rest at open circuit and then a second cathodic scan was performed (dashed curve in Figure 1a). A cathodic peak is also recorded at -0.59 V corresponding to the same Q . It can be concluded that upon immersion of Cu in a 2 M NaOAc solution, a Cu₂O layer forms spontaneously having a thickness of few monolayers.

The influence of the anodic potential to the formation of oxide layers can be seen by cyclic voltammetry using different anodic potential limits E_a , Figure 1b. When $E_a = 0$ V, a single reduction peak is observed at -0.6 V, corresponding to the reduction of Cu₂O. Increasing of the anodic limit this cathodic peak shifts at -0.7 V and in a new sharp cathodic peak at -0.05 V appeared, followed by an apparent diffusion current region. The first discussed peak can be associated to the reduction of Cu₂O whereas the later corresponds to the reduction of a Cu(II) compound layer. As E_a is increased both cathodic peaks are shifted cathodically with a simultaneous increase of their amplitude. Integration of the cyclic voltammograms reveals that the net charge $Q = Q_a - Q_c$ becomes positive when E_a is more positive than 0.250 V. This is an evidence that the rate of electrodisolution is higher than the rate of oxide growth for relatively high anodic potentials.

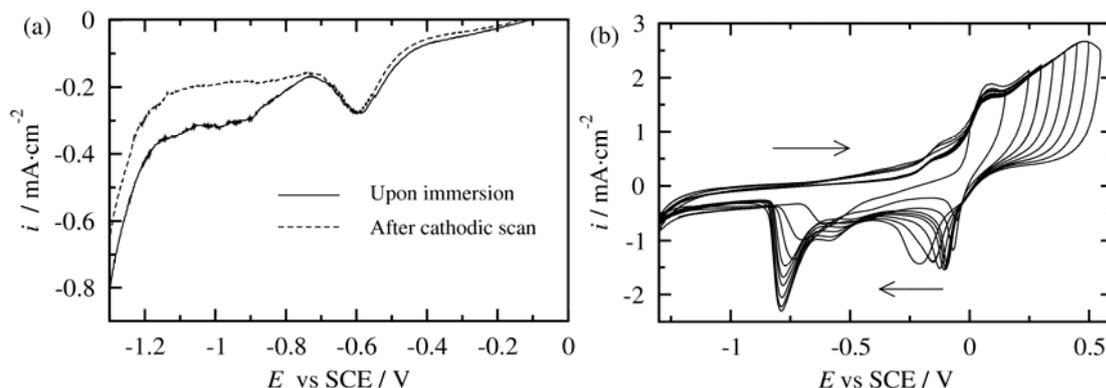


Figure 1: (a) Cathodic scan (10 mVs^{-1}) of a Cu electrode in 2 M NaOAc solution upon immersion and just after the first cathodic scan. (b) Cyclic voltammograms (100 mVs^{-1}) for different anodic potential limits.

The formation of oxides on the Cu electrode surface under potentiodynamic conditions is confirmed by recording the cyclic voltammogram together with the capacitance vs. electrode potential curves, Figure 2a. At $E_c = -1.3 \text{ V}$, the electrode is free of surface species and the capacitance (dashed curve) has a high value due to high electrical permittivity of aqueous solution and the small thickness of the electrochemical double layer. Moving toward the anodic direction the capacitance decreases, and at about -0.27 V the electrode starts to oxidize. The capacitance attains an almost constant value of $16 \mu\text{Fcm}^{-2}$ in the region from 0.15 to 0.5 V . The decrease of the capacitance due to the formation of a thin surface layer with small relative permittivity (about 12 for Cu_2O) confirms the existence of surface oxides. Further increase of the electrode potential results in a gradual increase of the capacitance. This increase can be an indication of either a thinning of the surface layer or the formation of conductive (hydrated) surface species on top of the insulation layer (Schultze et al. 1983). During the backward scan, Fig. 2a shows that the capacitance attains a value of about $10 \mu\text{Fcm}^{-2}$ in the region from 0.25 to -0.2 V , but further shift cathodically of the potential results in a capacitance peak directly associated with the voltammetric cathodic peak at -0.38 V . Therefore, it can be concluded that at this potential CuO or $\text{Cu}(\text{OH})_2$ is reduced. Moving to more cathodic potentials, the capacitance increases again while the Cu_2O layer is reduced to metallic copper (the process showed at second cathodic peak at -0.7 V). In Figure 2b a cyclic voltammogram of Cu deposited on Au in 2 M NaOAc solution with a scan rate of 100 mVs^{-1} is presented (full line) together with the mass change recorded by EQCM by scanning the potential (dashed line). Starting from $E_c = -1.3 \text{ V}$ a small increase of the mass is observed due to the formation of a surface layer from -0.25 to 0.1 V . Further increase of the potential results in a dramatic decrease of the mass which must be attributed to a dissolution of the surface layer, in agreement with charge estimations from cyclic voltammograms. During the cathodic scan (reverse scan) the mass of the electrode remains constant until the potential value of -0.05 V . Further shift of the potential results in a continuous increase of the mass, which can be associated only to the formation of surface products due to the reduction of solution species. The mass increases up to potential of -0.7 V and then gradually decreases due to the transformation of Cu_2O to metallic copper.

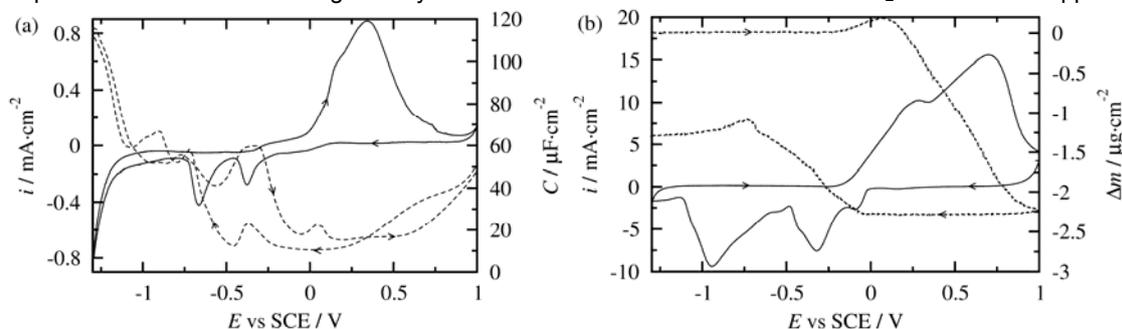


Figure 2: (a) Cyclic voltammogram of Cu in 2 M NaOAc solution (full line) and electrode capacitance vs. electrode potential (dashed line) with scan rate 10 mVs^{-1} . (b) Cyclic voltammogram of Cu deposited on Au in 2 M NaOAc solution (full line) and mass change vs. electrode potential (dashed line) with a scan rate of 100 mVs^{-1} .

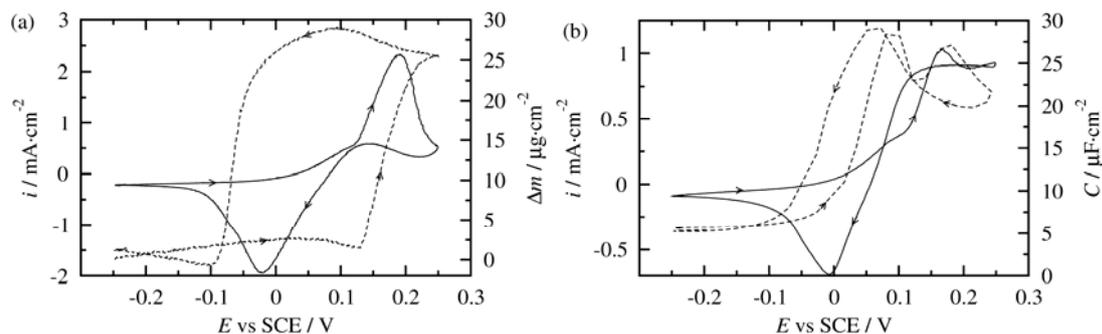
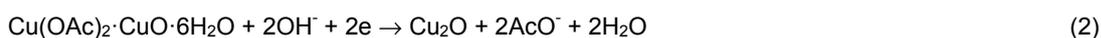


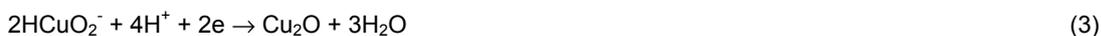
Figure 3: (a) Cyclic voltammogram of Cu deposited on Au in 2 M NaOAc solution (full curve) and corresponding mass changes by potential scanning (dashed curve). (b) Cyclic voltammogram of Cu in 2 M NaOAc solution (full curve) and corresponding capacitance vs. electrode potential curve (dashed curve). Scan rate: 10 mVs⁻¹.

The nature of the Cu(II) compound layer formed at moderate anodic potentials can be elucidated by recording the cyclic voltammogram, together with the mass change and the capacitance, by potential scanning in the region from $E_c = -0.25$ V to $E_a = 0.25$ V, Figures 3a and 3b. During the anodic scan, the voltammogram shows the formation of an oxidation shoulder together with an oxidation peak (full curve). A small amount of mass increase (approximately, a plateau) up to 0.05 V and then a large increase of Δm for potentials more positive than 0.12 V (dashed curve) are observed. The mass increase is still observed during the reverse (cathodic) scan and then is followed by a large decrease of Δm , corresponding to the voltammetric reduction peak at 0 V. Certainly, the reduction peak is associated to the species created by oxidation at potentials more positive than 0.1 V. The reduction peak at about 0 V can be associated to either the reduction of solution species (corrosion products), or the reduction of a surface layer. Since the reduction peak is accompanied by a mass decrease, the first case is eliminated. The mass difference due to the reduction of a surface layer is expected to be $\Delta m = Q(M_{\text{ox}} - sM_s)/2F$ where M_{ox} is the molar mass of cuprous oxide, M_s is the molar mass of the Cu(II) layer, and s is the stoichiometric coefficient. The charge corresponding to the reduction peak is 20 mCcm⁻², therefore the expected mass decrease is 26.4 μgcm^{-2} in the case of copper acetate and 23.4 μgcm^{-2} in the case of basic copper acetate layer. The experimental value of 29.54 μgcm^{-2} confirms the anodic formation of a hydrated copper salt at that potential and excludes the presence of copper hydroxide, i.e.,



In Figure 3b the cyclic voltammogram of Cu in 2M NaOAc (full curve) is presented together with the capacitance variation (dashed curve) for 10 mVs⁻¹ scan rate. During the anodic scan the capacitance increases and exhibits a maximum corresponding to the voltammetric oxidation shoulder at 0.1 V. A second maximum of the capacitance is recorded at more anodic potentials, directly associated to the oxidation peak at 0.2V. This trend of the capacitance variation cannot be interpreted in terms of a decrease of the film thickness, since the mass of the electrode increases in this potential region. Thus, it has to be assumed that a conductive (hydrated) surface layer is formed on top of the insulating cuprous oxide film (Schultze et al. 1983) such as $\text{Cu}(\text{OAc})_2 \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$ compound. A small increase of capacitance is observed up to 0.05 V and then it has a large increase for potentials greater than 0.12 V. High values of capacitance are still observed during the cathodic scan, followed by a large decrease, corresponding to the voltammetric reduction peak for potential values close to 0 V. It is evident that the reduction peak is associated to the species created by oxidation at potentials greater than 0.1 V. During the cathodic scan it seems reasonable to assume that this conductive layer is reduced at about 0 V, since the electrode capacitance becomes very small when the reduction peak is completed.

An example of a chronoamperometric curve together with cathodic stripping in the time domain is presented in Figure 4a for Cu deposited on Au in 2 M NaOAc solution, together with the mass change. The anodic potential step was applied for 120 s and the cathodic scan rate was 10 mVs⁻¹. When $E_a = 0.2$ V, a chronoamperometric peak is observed which is related to a mass increase of the electrode. The peak is followed by a gradual decrease of the current and the mass. During the cathodic scan the typical stripping curve is recorded consisting of two reduction peaks separated by a diffusion current region. If it is assumed that at the diffusion region corrosion products are reduced according to the reaction,



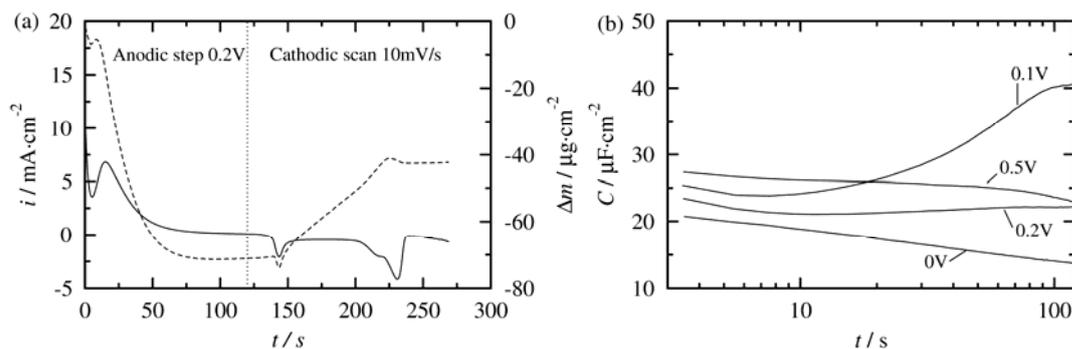


Figure 4: (a) Chronoamperometry and cathodic stripping at reverse scan (full curve) and mass change in time (dashed curve) of Cu deposited on Au in 2 M NaOAc solution for $E_a = 0.2$ V. Scan rate: 10 mVs^{-1} . (b) Capacitance at various anodic potentials as a function of polarization time (logarithmic abscissa).

the increase of Δm should be linear with slope $i_{\text{diff}} M_{\text{ox}} / 2F$. Taking a value of $i_{\text{diff}} = -0.463 \text{ mAcm}^{-2}$ the predicted slope is $0.34 \text{ } \mu\text{gcm}^{-2}\text{s}^{-1}$, which is very close to the observed one, $0.32 \text{ } \mu\text{gcm}^{-2}\text{s}^{-1}$. When $E_a = 0.3$ V (not shown) the diffusion current is $i_{\text{diff}} = -0.407 \text{ mAcm}^{-2}$. The predicted slope of $0.31 \text{ } \mu\text{gcm}^{-2}\text{s}^{-1}$, is in good agreement with the value determined experimentally, which is $0.27 \text{ } \mu\text{gcm}^{-2}\text{s}^{-1}$. The mass change corresponding to the less pronounced cathodic peak is also in good agreement in this case (if $\text{Cu}(\text{OAc})_2$ or basic copper acetate is considered as the oxidant) where the reduction charge of 21.49 mCcm^{-2} corresponds to $\Delta m = -27.4 \text{ } \mu\text{gcm}^{-2}$ (experimental value $-31.3 \text{ } \mu\text{gcm}^{-2}$).

Finally, in Figure 4b the capacitance variation in time, t , is presented during amperometric measurements for different E_a values. As can be seen, for $E_a = 0$ V, the capacitance decays linearly with $\log t$ and exhibits the lowest values, as expected for an electrode covered by an insulating film. For $E_a = 0.1$ and 0.2 V the capacitance increases in time after an initial decay. This peculiar response can be attributed to the existence of a conductive (hydrated) layer on top of the insulator layer (Schultze et al. 1983). For more anodic values of potential, the capacitance is decreasing with time, most probably due to the growth of a thin layer with dual composition.

4. Conclusions

Immersion of copper in sodium acetate solution results in the growth of a cuprous oxide layer, having a thickness of few monolayers. This can be attributed to the mild basic pH of electrolyte. Anodic oxidation of copper results in the formation of cuprous oxide and cupric oxide or hydroxide on the electrode surface. A cuprous oxide layer with thickness of the order of nm is formed at relatively low anodic potentials, whereas a duplex film ($\text{Cu}_2\text{O}/\text{CuO}$ or $\text{Cu}(\text{OH})_2$) is formed at higher anodic potentials. Oxide and hydroxide growth is accompanied by extensive dissolution, mainly in the potential region where $\text{Cu}(\text{II})$ monoxide layers are formed. The role of acetate ions is not limited to the adjustment of the pH. Acetates participate to the formation on the oxidized electrode surface of a hydrated $\text{Cu}(\text{II})$ salt, which is most probably basic copper acetate $\text{Cu}(\text{OAc})_2 \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$. Combined potentiodynamic, capacitance and EQCM measurements revealed that, in contrast to copper oxidation in NaOH solutions, a duplex oxide film formation is not able to explain the electrochemical processes during oxidation and reduction of copper in NaOAc solutions. The presence of the conducting hydrated layer on top of Cu_2O has to be taken into account as a precursor for copper oxide or hydroxide formation.

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