Portugaliae Electrochimica Acta 22 (2004) 81-91

PORTUGALIAE ELECTROCHIMICA ACTA

Cuprous Oxide Layers Grown on Copper. Effect of CO Adsorption

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Received 31 December 2002; accepted in revised form 26 May 2003

Abstract
The semiconducting properties of anodic passive films formed on polycrystalline copper in aqueous borax solutions, pH 9.2, are studied using electrochemical impedance spectroscopy (EIS) and voltammetry. The semiconducting nature of the cuprous passive layer is analysed in the potential region near de rest potential as a function of the electrode potential and the presence of CO dissolved in the electrolyte. The oxide formation is explained as a sequence of Cu_2O growth, cation adsorption, Cu(II), and dissolution steps similarly to previous reported investigations for the metal in CO free solutions. The different growth conditions change the defect or excess of cations accumulated in the outer side of the cuprous layer/electrolyte interface leading to different semiconducting properties.

Keywords: copper oxide, carbon monoxide, EIS, isoelectric point, semiconducting properties.

Introduction

The interface copper/CO plays a critical role in catalysis and corrosion. Copper electrodes show catalytic effects for CO_2 reduction with formation of adsorbed CO as reaction intermediate and the selective production of methane, ethylene and alcohols [1-3]. CO adsorption causes at cathodic potentials a partial passivation decreasing the H_2 evolution current [1]. Various theoretical adsorbate/substrate interaction models are developing that include both CO/CO and CO/substrate coupling phenomena [4-7].

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Recently published articles [8-9] investigate the passive films formed on copper in borax at pH 9.2 for cathodic potentials to that corresponding to the bulk formation of CuO. Variations in the Cu_2O structure and film growth rate are observed in the case of the addition of millimolar concentrations of different ions in electrolytes (SO_4^{-2}, CO_3^{-2}). The presence of either Cu(II) adsorbed on the Cu_2O/electrolyte interface or the formation of a $CuO_{0.67}$ phase is reported at cathodic potentials not far from the Cu_2O/CuO redox potential. In a last publication [10] the effect of CO on the formation of incipient copper oxide is investigated using ellipsometry and isoelectric point measurements.

In this paper electrochemical impedance spectroscopy (EIS) and voltammetry are used investigating the structure of the oxide layers formed under different growth conditions in saturated CO aqueous solutions.

Experimental

The experimental set-up has been described in previous works [8-9]. Polycrystalline copper rods (99.99% purity, area 0.4 cm^2) were used as working electrodes. Prior to each experiment, the electrodes were mechanically polished to a mirror finish with fine grade alumina powder of 0.3 and 0.05 μm.

The experiments were performed at room temperature and in borate buffer solutions ($Na_2B_4O_7$ 0.05 M) under either N_2 bubbling or the same solution saturated with CO. All experiments were performed using calomel reference electrode (SCE).

Electrochemical impedance measurements were carried out using an Analyzer "Zahner IM6" Impedance Spectrum (Zahner Messtechnik GmbH & Co KG, Kronach, Germany) [9] . Before each experiment, the polished electrode was cathodized at E_c= -1.3 V during 1 minute and scan at v= 0.5 mV/s up to E_a: -140 mV < E_a <-60 mV. Then, it was pre-anodised at E_a for 1 h to establish a quasi-steady state corresponding to almost constant thickness and passive layer composition according to the fixed E_a value. The impedance measurements in the 65 kHz ≤ f ≤ 1 mHz frequency range were started at this upper E_a potential limit

and proceeded in steps of 0.02 V towards lower E potentials within the passive region.

Isoelectric point (*iep*) determinations were performed by means of diffusion potential measurement and the transport number value was obtained in the same way as described elsewhere [11-14]. Copper powder (Arqimex, Wolstenholme) was used, mean particle diameter 8.5-10.5 micrometres, and CuO Merck analytical grade, surface area 14.6 m^2/g. Previous to each experiment the metal powder was washed with acetone/water solutions. The oxide particles were used without further treatment.

Results and Discussion

Voltammetric Data

Fig. 1 shows the current potential, *i vs. E,* plot during the reduction of the spontaneously formed oxide layer and the hydrogen evolution. When fresh polished copper electrodes are immersed in aqueous solution the open circuit potential, E_{oc}, is about –0.3 V, and this value shifts anodically with the immersion time. After 5 min of immersion E_{oc} is equal to –0.16 V and =-0.25 V in solution free from CO and saturated with CO, respectively (Fig. 1a). During the first cathodic scan the peaks Ia, Ib, Ic and II are observed. The second cycle obtained between E_c= –1.3 V and E_a= -0.48 V shows only one cathodic peak at –0.63 V (peak I), which corresponds to the reduction of the Cu_2O layer formed during the first anodic scan. The I and II peak potentials depend on the preparation conditions and may be related to Cu_2O clusters of different thickness and different cationic defect. Furthermore, at potentials lower than –1.1 V it is reported that the CO adsorbed decreases the current corresponding to the H_2 evolution. At more cathodic potentials the surface becomes free of adsorbed products [1].

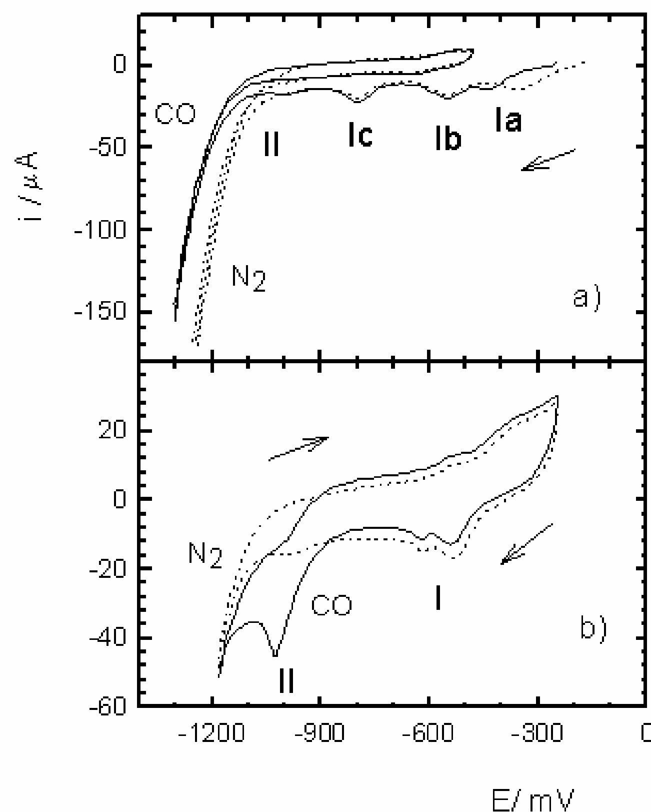

Figure 1. Current/potential plot corresponding to: a) First cathodic scan between the open circuit potential and the cathodic limit E_c = -1.3 V, followed by a potential cycle with anodic limit E_a = -0.48 V. b) Cyclic voltammogram recorded between E_c = -1.2 V and E_a = -0.25 V. Dashed lines: CO free solutions, full lines: CO saturated solutions. Solution pH= 9.2, v = 0.5 mV s^{-1}.

Electrochemical and optical studies show that the oxide is composed of Cu_2O with a surface excess of Cu(II) ions. The oxide/electrolyte structure of a multilayer Cu_2O film may be similar to the previously reported $CuO_{0.67}$ layers [9,15]. The thickness of the different layers depends on the potential, time and stirring conditions.

In the presence of CO several experiments show a very high faradaic current contribution at –1.0 V (Fig. 1b, Peak II) during the cathodic scan previous to the H_2 evolution current. After bubbling N_2 the dissolved CO is removed, peak II decreases and a very small peak is observed at –0.98 V in the CO free solution. In previous articles this small peak was already reported and it may be attributed

to oxide species formed on high active metal sites, like kink sites and step edges. These aging Cu_2O species are more stable under cathodic polarization than that corresponding to the peaks observed at –0.6 V (Peak I). The current intensity of peak Il in CO saturated solutions shows very high dispersion and in many experiments peak II is absent. However in all the experiments there is correspondence between the developed catalytic surface which shows the peak II in CO saturated solutions and the presence of the small peak observed at nearly the same potential in CO free solutions. This indicates CO adsorbed on the oxides monolayer patches formed on the recently polished and cathodized electrode that show high catalytic activity for the reduction of CO to methane and alcohols [1,16-18]. Peak Il charge in CO free solution corresponds to less than 5 % of a monolayer. The adsorption of CO on copper may involve several phenomena as long range attractive interactions and coupling between the adsorbate and lattice phonons. Therefore, the formation of CO/Cu_2O clusters may explain the probable catalytic effect of these fractional oxide monolayers [5,6,16].

Isoelectric point measurements

Through *iep* measurements is investigated the diffuse layer formed on both copper and copper oxide particles after immersion in CO saturated and CO free solutions. There are not changes observed in the iep_{pH} value (pH 10.8) for CuO particles dipped during 20 minutes in solutions in presence or in the absence of CO. The similar *iep* measured on Cu in CO free solutions and CuO particles in solutions with and without CO indicates similar OH^-/O^{2-} ratio for these diffuse layers.

On the other side, a significant decrease of around one pH unit is observed for Cu particles in solutions saturated with CO related to the iep_{pH} value obtained in free CO solutions. The adsorption of CO on the Cu/Cu_2O interface decreases the isoelectric point from 10.8 to 10.1 indicating lower surface cationic defect in the presence of CO [10,19].

Electrochemical Impedance Spectroscopy Data

The presence of either CO or millimolar concentration of CO_3^{2-} and SO_4^{2-} produces detectable changes in the oxide structure and the oxide growth kinetic when the oxide layer is formed using low sweep rate, v= 0.5 mV s^{-1} [9,20].

For the oxide grown after anodization at E_a, –140 mV < E_a < 60– mV the impedance diagram exhibits slightly distorted capacitive semicircle at high frequencies followed by a not well defined second contribution. The time constant at high frequencies could be related to the Cu_2O electronic properties.

The whole set of experimental data can be well described by the following transfer function:

$$Z(j\omega)= R_\Omega + 1 / ([CPE] + (R_t + Z_w)^{-1}) \qquad (1)$$

where $\omega = 2\pi f$, R_Ω corresponds to the ohmic resistance of the electrolyte, [CPE] is the constant phase element given by $[CPE] = [C\ (j\omega)^{\alpha}]^{-1}$, C is the high frequency capacitance, α takes into account the distribution of time constants due to surface in-homogeneities, R_t is the charge transfer resistance associated with the couple Cu/Cu_2O and Z_w could be associated with a finite-length diffusion process.

The analysis of the impedance parameters associated with the lowest frequencies denotes a complex process [21]. More work is in progress to correlate the low frequency response and the time constants involved [20-23]. The measured capacitance values associated with the high frequencies, $C \approx 18$ and 10 $\mu F\ cm^{-2}$ and $\alpha \approx 1$, are typical of a metal covered with a passive film [23] and may be considered as the passive film and double layer capacitance, $C_{H,}$ connected in series. The capacitances have lower values than the typical C_H and are associated to the space-charge capacitance of a semiconducting film, C_{SC} [9]. The potential dependence of C_{SC} should obtain the Mott-Schottky relation:

$$C_{SC}^{-2} = (2 / e\ N_{sc}\ \varepsilon\varepsilon_0)\ [(-E + E_{FB} - (kT / e)] \qquad (2)$$

where N_{SC} and E_{FB} are the carrier concentration and the flat band potential of the oxide, respectively. The other symbols have the usual meanings.

Similar to previous studies, the resulting Mott-Schottky plots show two relatively well defined linear regions with both positive and negative slopes corresponding to the Cu/Cu_2O and the Cu/CuO flat band (*FB*) potential domains, -0.41V and – 0.05 V respectively (Fig. 2) . The α vs. E dependencies are $0.78 < \alpha < 0.84$, $0.798 < \alpha < 0.82$, and $0.68 < \alpha < 0.74$ for $E_a =$ -60 mV, -100 mV, and -140 mV respectively. The fitted α are practically independent on the presence of CO. The α variation indicates a progressive compactness of the Cu_2O layer in the region dominated by the Cu/CuO *FB* potential and a decrease in compactness in the Cu_2O/Cu *FB* potential region. The change is related to a first small decrease followed by an increase of either inter-grain or surface cation defect domains in the growing Cu_2O layer.

The oxidation of Cu to Cu_2O proceeds by a hole mechanism and an accumulation of holes in Cu_2O is required for the oxidation process and likewise depletion conditions are necessary for its reduction. For potentials E_a, anodic to the Cu/CuO couple, $(E_{fb})_2 \cong$ - 50 mV, a limit thickness is observed [8,9]. For $E_a <$ -50 mV enough electrons are available to reduce the adsorbed Cu(II) to Cu(I), and the film thickness increases for increasing E. The results indicate that the Cu_2O growth depends on the electric potentials developed both at the metal/oxide, E_{MO}, and at the Cu_2O/electrolyte interface, E_{OE}. The E_{OE} depends on the hydrate complexes formed on the Cu_2O/electrolyte boundary and the presence of adsorbed CO.

The rest potential, E_{oc}, in the presence of CO shifts cathodically about 50 or 100 mV with respect to the E_{oc} in CO free solutions. This shift indicates a decrease *of* the cationic defect with respect to that corresponding to free CO solution. For potentials lower than – 60 mV, decreasing polarization potential E_a decreases the E_{MO} value and the film thickness decreases [9].

For E_a= -60 mV (Fig. 2a), the Mott-Schottky plots show data practically independent on the presence of CO for the relatively thicker formed Cu_2O films ($d \cong 30$ nm) [10].

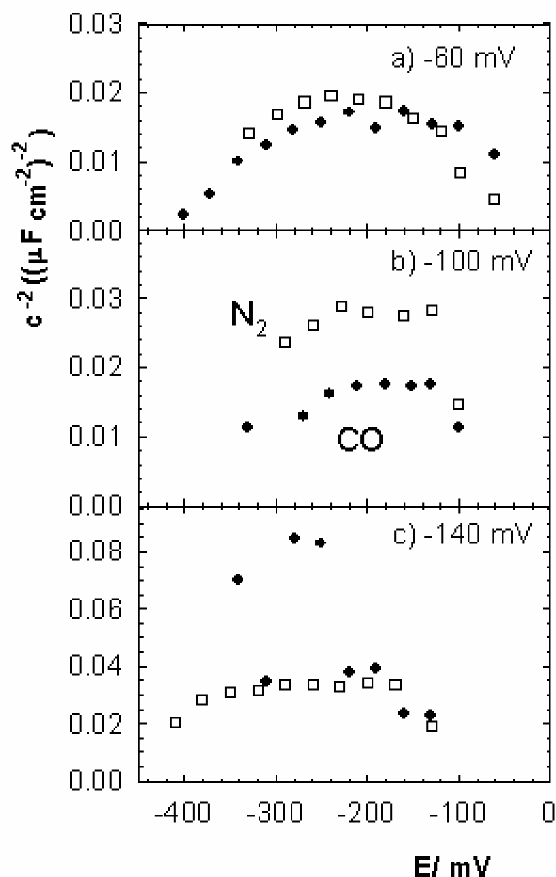

Figure 2. Mott-Schottky plots, C_{SC}^{-2} vs. E, of the oxide formed at pH 9.2 using different E_a. a) $E_{a=}$ -60 mV, b) $E_{a=}$ -100 mV, c) $E_{a=}$ -140 mV. (●) CO saturate solution and (□) N_2 saturated solution.

For E_a= -100 mV (Fig. 2b), the films result more isolating in the presence of CO and this effect is related to the formation of thicker films in CO solution ($d \cong 40$ nm) related to CO free solution [8-10,21]. The higher thickness is related to a decrease of the cationic defect. The E_{OE} variation allows that more electrons are available to reduce the interfacial Cu(II) to Cu(I) and therefore the thickness increases.

For E_a= -140 mV (Fig. 2c), the films are thinner ($d \cong 25$ nm) and the Mott-Schottky plot shows higher slops in the presence of CO. These films have high conductivity, which is related to CO adsorbed on Cu_2O clusters. The adsorption of CO (a weak base) occurs on strong Lewis acid, highly co-ordinated, metal sites [24]. Besides chemisorbed oxygen coordinated with Cu(0) and Cu(I) may

stabilize a CO cluster [25], while Cu(II) with co-ordination number six seems unstable relative to the CO adsorbed on oxides in which copper ions are found in square planar oxygen coordination [26].

The present results indicate that low coverage Cu(0) and Cu(I) species, coordinated with CO, may promote with anodic polarization an initial increase in the rate growth of the Cu_2O multilayer. On the other side, CO adsorption may stabilize cathodically polarized Cu(I) oxide patches showing catalytic effects in the CO and CO_2 reduction process.

Conclusion

The adsorption of CO on the Cu/Cu_2O interface decreases the isoelectric point from 10.8 to 10.1 and the surface cationic defect in the Cu_2O/electrolyte interface. The CO adsorbed on Cu_2O increases the oxide growth rate for $E > -0.1$ V . For more cathodic potentials, $E < -0.1$ V, the oxide multilayer grown in CO aqueous solutions shows higher conductivity and higher number of carriers than the CO free oxide. The catalytic reduction of CO on cathodically polarized copper electrodes may involve adsorbed CO on oxide monolayer cluster sites.

Acknowledgements

This research project was financially supported by the "Comisión de Investigaciones Científicas de la Provincia de Buenos Aires", CIC, the "Consejo Nacional de Investigaciones Científicas y Técnicas", CONICET, the "Universidad Nacional de La Plata", and the "Fundación Antorchas". Part of the equipment used in the experimental work was provided by DAAD. J.O.Z and A.M.CL. are members of the Research Career of CIC. The authors thank the Organising Committee of SIBAE XV (Évora, Portugal, 8-13 September 2002) for the helpful discussions.

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