Surface reconstruction during the adsorption/desorption of OH⁻ species onto Cu(111) and Cu(100) in 0.1 M NaOH solution

V. D. JOVIĆ[a#] and B. M. JOVIĆ[b#]

Department of Materials Engineering, Drexel University, Philadelphia, PA 19104, USA

The process of adsorption/desorption of OH⁻ species onto Cu(111) and Cu(100) in 0.1 M NaOH solution has been investigated by cyclic voltammetry and the potentiostatic pulse technique. Investigation of the electrochemical behavior of the Cu(100) face in 0.1 M NaOH solution was performed for the first time in this work. It was shown that the adsorption/desorption of OH⁻ species occurs in the potential range between –1.13 V *vs.* SHE and – 0.83 V *vs.* SHE forming an adsorbate of low coverage. It was shown that in 0.1 M NaOH solution irreversible surface reconstruction of the Cu(111) face occurs as a consequence of the adsorption/desorption of OH⁻ species. The original surface cannot be restored even if the electrode is exposed to potentials more positive than – 0.53 V *vs.* SHE for some time. If this time is, in the case of repetitive pulse experiments, equal or smaller than 10 s reconstruction does not occur. Adsorption of OH⁻ species takes place in the potential range more negative than – 0.6 V *vs.* SHE only on reconstructed surfaces. For this process to occur onto non-reconstructed, original Cu(111) surfaces, higher overpotentials are needed.

Keywords: Cu(111), Cu(100), OH⁻ adsorption, surface reconstruction.

INTRODUCTION

Although the anodic oxidation of copper in alkaline solutions has been extensively studied (review of these papers is given in the paper of Droog *et al.*[1]), the initial stage of the oxidation process has received little attention. A small anodic peak on the voltammogram, preceding the peak of Cu_2O formation was first observed by Ambrose *et al.*[2] after careful examination at high sensitivity and high sweep rates. This peak has been tentatively assigned to the formation of soluble $Cu(OH)_2^-$ species. Investigating the initial stages of the anodic oxidation of polycrystalline[1] and single crystal[3] copper surfaces in 1 M NaOH solution, Droog *et al.*[1,3] concluded that electrosorption of oxygen species occurs at potentials more

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a   On the leave of absence from the Center for Multidisciplinary Studies University of Belgrade, P. O. Box 33, 11030 Belgrade, Yugoslavia.
b   On the leave of absence from the Institute of Technical Sciences SASA, P. O. Box 745, 11001 Belgrade, Yugoslavia.
Serbian Chemical Society active member.

negative than the potential of Cu_2O formation. It is important to note that they were the first to detect the change of the voltammogram during the initial stage of copper oxidation[1] after prolonged polarization of the copper electrode at a potential of about – 0.6 V *vs.* SHE.

With the introduction of *in situ* Raman spectroscopy,[4–6] infrared spectroscopy[7] and *in situ* atomic force microscopy (AFM)[8] and scanning tunneling microscopy (STM)[9] it was possible to obtain evidence of the state of Cu surfaces immersed in different electrolytes in the underpotential region of Cu_2O formation.

Cruickshank *et al.*[10] investigated the state of a Cu(100) surface in 0.1 M $HClO_4$ and in 0.1 M H_2SO_4 solutions as a function of the potential by cyclic voltammetry and the *in situ* AFM technique. They concluded that at potentials close to hydrogen evolution a square lattice with the atomic spacing of 0.26±0.02 nm corresponded to bare Cu(100), while the same lattice with the atomic spacing of 0.36±0.02 nm, recorded at potentials more positive than – 0.1 V *vs.* SHE, corresponded to the $(\sqrt{2}\times\sqrt{2})R45^\circ$ adlattice, in which O or OH^- is chemisorbed in the 4-fold hollow site.

Wilms *et. al.*[11,12] performed *in situ* STM measurements of a Cu(111) surface immersed in 5 mM H_2SO_4 soltuion in a special STM flow cell providing no contamination of the electrolyte with oxygen. They found that sulphate anions adsorb forming a long-range Moiré pattern and a short-range distorted hexagonal pattern with nearest-neighbour distances of (0.43±0.04) nm and (0.70±0.04) nm.[11,12] The Moiré pattern was suggested to be the consequence of a mismatch of the structure that consists of a $(\sqrt{3}\times\sqrt{7})SO_4^{2-}$ with the (111) structure of a second Cu layer.[12] These structures were found to be stable at potentials more positive than 0.05 V *vs.* SHE, with a well defined peak of their adsorption between 0.05 V and 0.15 V *vs.* SHE.

Härtinger and Doblhofer[13] investigated the electrochemical interface between Cu(111) and aqueous electrolytes containing fluoride and sulphate anions at various pH values. The differential capacitance measurements were characterized with a well defined peak at a potential of about –0.46 V *vs.* SHE which was ascribed to the adsorption of OH^- species in all the investigated electrolytes as a consequence of an electrosorption process of the following type:

$$Cu + H_2O \underset{k_{des}}{\overset{k_{ads}}{\Longleftrightarrow}} Cu(OH)_{ads} + H^+ + e^- \qquad (1)$$

They proposed an equaivalent circuit for the adsorption of OH^- species which had already been proposed by other authors[14,15] for anion adsorption, which was composed of a charge transfer resistance (R_{ct}) and an adsorption pseudo-capacitance (C_{ads}) connected in series which were both connected in parallel with the double layer capacitance (C_{dl}). Using a non-linear least-squares fit procedure, they found that the predicted equivalent circuit satisfies the impedance behavior in the potential region of the peak appearing on differential capacity *vs.* potential curves.

The formation of a hydroxide adsorbate on Cu(111) surfaces in 0.1 M NaOH at potentials negative with respect to the potential of Cu_2O formation has been investigated by Härtinger *et al.*[16] using cyclic voltammetry and surface-enhanced Raman spectroscopy

(SERS). The experiments were performed in deaerated solutions. The presented voltammograms were recorded on a relatively low sensitivity scale and showed only peaks of Cu_2O and CuO formation and reduction. The SERS spectra recorded at potentials negative with respect to the potential of Cu_2O formation exhibited a remarkable Raman band located at around 700 cm^{-1}. The intensity of this band was found to depend on potential as well as on the time of holding the electrode at a given potential. It was concluded that this band corresponds to CuOH-surface species, which were formed upon cathodic reduction of the oxidized Cu(111) electrode. The process leading to $CuOH_{surf}$ formation was formulated in terms of proton (water) reduction on the oxidized copper surface

$$Cu^*(O)_{ad} + H^+ + e^- = CuOH_{surf} \tag{2a}$$

$$Cu^*(O)_{ad} + H_2O + e^- = CuOH_{surf} + OH^- \tag{2b}$$

assuming that the species $Cu^*(O)_{ad}$ exists at potentials more negative than Cu_2O reduction. It is interesting to note that after stepping the potential from – 0.25 V *vs.* SHE (just before the peak of Cu_2O formation) to – 0.85 V *vs.* SHE, the intensity of the band at 700 cm^{-1} started to increase with time of holding the electrode at that potential, reaching its maximum after about 10 min.

The initial stages of the oxidation of Cu(111) in non-deaerated 0.1 M NaOH solution were recently studied by cyclic voltammetry and the *in situ* STM technique in the underpotential range of Cu_2O formation by Maurice *et al.*[17] It was shown that the adsorption/desorption process occurs in this potential region (with a reversible potential of – 0.675±0.02 V *vs.* SHE), being initiated preferentially at the step edges on the upper terrace side inducing the lateral growth of terraces. The adlayer was found to form an ordered structure with an hexagonal lattice having a unit vector of 0.6±0.02 nm and two coincidence cells: $(\sqrt{21}\times\sqrt{21})R10°$ and $(\sqrt{49}\times\sqrt{49})R20°$. Charge transfer measurements indicated the adsorption of hydroxide or hydroxyl groups with one adsorbate per unit cell, *i.e.,* a coverage of *ca.* 0.2 ML. The adlayer lattice parameters indicated that the reconstructed outermost Cu plane has the close-packing density and symmetry of the Cu planes in $Cu_2O(111)$, with the adlayer forming a (2 ×2) lattice of OH_{ads}. It was also stated in this paper that surface reconstruction at large values of the overpotential of adsorption or desorption was very fast (under the given experimental conditions).

According to the results presented so far it seems that the adsorption/desorption of OH⁻ species takes place in alkaline solutions[1–3,11–13,16,17] on copper single crystal surfaces in the underpotential range of Cu_2O formation. In the case of acidic solutions, adsorbed OH⁻ species were detected only in the AFM cell, which was exposed to air,[10] while in specially designed flow cell, where contamination of the electrolyte with oxygen was avoided, no adsorption of OH⁻ species has been reported.[11,12]

In this study an attempt was made to investigate the electrochemical behavior of Cu(111) and Cu(100) faces in deaerated 0.1 M NaOH solution by using cyclic voltammetry and the potentiostatic pulse technique, in order to determine the parameters of the process of OH⁻ spe-

cies adsorption/desorption and its influence on the state of copper single crystal surfaces in the potential range negative with respect to the potential of Cu_2O formation.

<div align="center">EXPERIMENTAL</div>

All experiments were carried out in a two-compartment electrochemical cell at 25 ± 1 ºC in an atmosphere of purified (99.999 %) nitrogen. The Cu(111) and Cu(100) electrodes ($d = 2.54$ cm) were sealed in epoxy resin (resin EPON 828 + hardener TETA) in such a way that only the (111), or (100) disc surface was exposed to the solution. The surface area of the electrode exposed to electrolyte was 5.05 cm^2. The counter electrode was a platinum sheet which was placed parallel to the working electrode. The reference electrode was a mercury/mercury-oxide electrode (Hg|HgO) in 0.1 M NaOH. The reference electrode was placed in a separate compartment and connected to the working compartment by means of a Luggin capillary. All solutions were made from supra pure chemicals (50 % NaOH solution – Fischer) and EASY pure UV water (Barnstead). All potentials are given *vs.* SHE.

The copper single crystals (Monocrystals Comp.) were mechanically polished on fine grade emery papers (1200, 2400 and 4000) with subsequent polishing on polishing clothes impregnated with a suspension of polishing alumina with particles dimension of 1 μm, 0.3 μm and 0.05 μm. After mechanical polishing, the electrodes were electrochemically polished in a solution of 85 % phosphoric acid at a constant voltage of 1.7 V (*vs.* Pt counter electrode) until the current density dropped to a value of about 10 mA cm^{-2}. The electrodes were then thoroughly washed with pure water (Barnstead - EASY pure UV), cleaned for 30 s in 10 vol.% H_2SO_4, again washed with pure water and transferred into the electrochemical cell. Before each experiment the electrolyte was purged with high purity nitrogen (99.999 %) for 45 min while during the experiment a nitrogen atmosphere was maintained over the solution to prevent contamination with oxygen.

Using a universal programmer PAR M-175, a potentiostat PAR M-173 and a X-Y recorder (Houston Instrument 2000R), cyclic voltammetry experiments were performed. The universal programmer and potentiostat in conjunction with a computer were also used for recording cyclic voltammograms and potentiostatic pulse transients.

<div align="center">RESULTS</div>

Cyclic voltammetry

The cyclic voltammograms recorded on Cu(111) and Cu(100) faces at a sweep rate of 100 mV s^{-1} in 0.1 M NaOH solution are shown in Fig. 1a and 1b, respectively. After immersion of the electrodes into the solution, the initial potential (negative with respect to the open circuit potential by about 0.3 V – marked on the Figure) was immediately applied and electrodes were cycled in the given potential range with the first sweep going towards the positive potential limit. As can be seen the voltammogram of Cu(111) (Fig. 1a) is characterized by one anodic peak at about – 0.65 V *vs.* SHE and a shoulder at about – 0.70 V and two cathodic peaks at about – 0.85 V and – 0.73 V. The shape of this voltammogram was found to depend on the time of holding the electrode at the initial potential and it changed slightly with the number of cycles. The voltammogram obtained on Cu(100) (Fig. 1b) was established after 2–3 cycles and did not change with further cycling. As can be seen this voltammogram is characterized by the presence of one pair of voltammetric peaks, an anodic one at about – 1.0 V and a corresponding cahtodic peak at about – 1.02 V. The beginning of Cu_2O oxide formation (anodic current density starts to increase) on the (111) face of copper (Fig. 1a) was detected at about – 0.45 V while for the (100) face of copper (Fig. 1b) this potential was about 0.10 V more negative (about – 0.55 V).
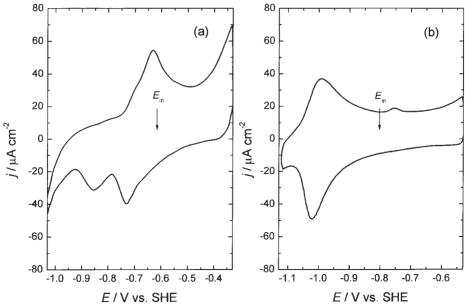
Fig. 1. (a) Cyclic voltammogram of Cu(111) in a solution of 0.1 M NaOH recorded at a sweep rate of 100 mV s^{-1} after setting the initial potential (marked with the arrow) at – 0.63 V. (b) Cyclic voltammogram of Cu(100) in a solution of 0.1 M NaOH recorded at a sweep rate of 100 mV s^{-1} after setting the initial potential (marked with the arrow) at – 0.83 V.

Since the voltammogram of Cu(111) changed with the time of holding the electrode at the initial potential, a new set of experiments was performed on this surface. The initial potential was set at – 1.03 V and the electrode was cycled at a sweep rate of 100 mV s^{-1} with changing of the anodic limit of cycling. When the anodic limits were set at – 0.73 V and – 0.63 V, no changes on the voltammogram were recorded, as can be seen in Fig. 2a. After setting anodic limit at – 0.53 V, the shape of the voltammogram started to change with the number of cycles. A stable voltammogram, marked in the Figure with the *n*-th cycle, was established after about 10 cycles (Fig. 2a). A similar behavior was recorded after the anodic limit was set at – 0.43 V, as can be seen from Fig. 2b. After adjusting the anodic limit to a potential of – 0.33 V (beginning of Cu(111) oxidation) a significant change took place during cyding of the electrode. A stable voltammogram (*n*-th cycle in Fig. 2c) was established after about 30 cycles. This voltammogram is the same as the one shown in Fig. 1a. Hence, it seems that the reconstruction of Cu(111) surface takes place in the underpotential range of Cu$_2$O oxide formation and that this phenomenon starts to be visible on the voltammograms recorded at the sweep rate of 100 mV s^{-1} already at an anodic potential limit of about – 0.53 V.

The cyclic voltammograms of Cu$_2$O oxide formation on both copper faces at the sweep rate of 100 mV s^{-1} are shown in Fig. 3. For the Cu(111), Fig. 3a, two voltammograms are presented. The first voltammogram was recorded after holding the electrode at a potential of – 0.93 V for 5 min (curve 1-st, dashed line) and the *n*-th
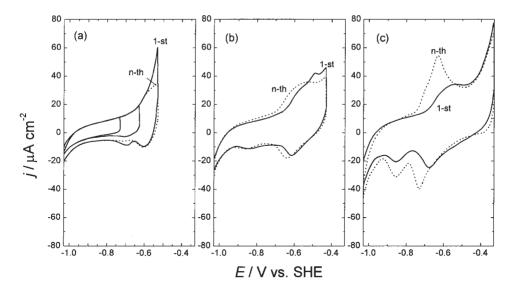
Fig. 2. Cyclic voltammograms of Cu(111) in a solution of 0.1 M NaOH recorded at a sweep rate of 100 mV s^{-1} after setting the initial potential and cathodic limit at – 1.03 V and the anodic potential limit at: (a) – 0.73 V, – 0.63 V and – 0.53 V; (b) – 0.43 V and (c) – 0.33 V.
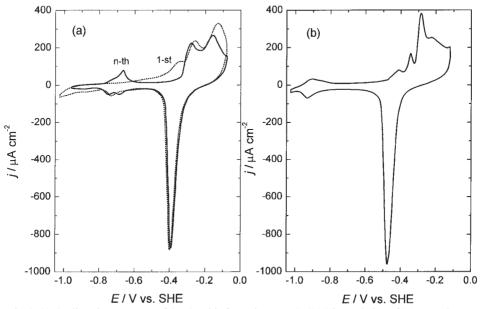

Fig. 3. (a) Cyclic voltammogram of Cu$_2$O oxide formation onto Cu(111) in a solution of 0.1 M NaOH recorded at a sweep rate of 100 mV s^{-1} after setting the initial potential at –0.93 V (dashed line – first cycle, full line – n-th cycle). (b) Cyclic voltammogram of Cu$_2$O oxide formation onto Cu(100) in a solution of 0.1 M NaOH recorded at a sweep rate of 100 mV s^{-1} after setting the initial potential at –1.03 V.

voltammogram (curve *n*-th, full line) was recorded after cycling the electrode within the given potential limits until a stable voltammogram was obtained (the heights of the peaks stopped changing). Once a stable voltammogram was established, no further changes were detected while cycling the Cu(111) electrode in the region of Cu_2O oxide formation. In the case of the Cu(100) face there was no change in the peak heights with cycling and a reproducible voltammogram was obtained after a couple of cycles (Fig. 3b) under the given conditions of cycling ($v = 100$ mV s^{-1}).

Potentiostatic pulse experiments

During the repetitive potentiostatic pulse experiments, both single crystals were exposed to the same pulsing procedure. Repetitive pulsing was continuously performed between the lower potential limit (LPL) and the upper potential limit (UPL) without switching to the initial potential limit until the experiment was finished. If the initial potential limit was set at the MLPL (maximum lower potential limit), the electrodes were continuously pulsed with changing UPL in the sequences of 25 mV, 50 mV or 100 mV until the maximum UPL (MULP) was reached. The same procedure was used in the opposite way, while setting the initial potential at the MUPL and pulsing between the MUPL and the LPL until the MLPL was reached. The duration of the pulses was changed from 20 ms to 10 s. The *j*–*t* transients recorded during pulsing between the LPL and the UPL are labeled as P pulses, while the *j*–*t* transients recorded during pulsing between the UPL and the LPL are labeled as R (reverse) pulses. In all the Figures P pulse was shown as a first pulse, while the R pulse was shown as the second pulse. The MUPL for the Cu(111) electrode was set at -0.33 V, while for Cu(100) this potential was set at -0.63 V (before the beginning of oxide formation). For each set of potential limits, at least five anodic and five cathodic *j-t*– transients were recorded by the computer. All the recorded *j*–*t* transients for one set of potential limits were identical.

(i) Cu(100) surface

Anodic and cathodic *j*–*t* transients recorded for Cu(100) were found to be identical and very fast, so that both the adsorption and desorption processes were finished within 10 ms with the current density dropping to zero.

The set of anodic *j*–*t* transients recorded for Cu(100) is shown in Fig. 4a. The corresponding charge (Q_p), obtained by integration of the area under these transients, is shown in Fig. 4b as a function of the applied potential. Considering the CV curve shown in Fig. 1b, it seems as though the adsorption process was finished at about -0.85 V with the amount of charge recorded under the anodic peak (without correction for the double layer charge) being about 40 μC cm^{-2}. However, the Q_{CV} *vs. E* curve obtained by integration of the area under the anodic part of the voltammogram up to -0.63 V also shown in Fig. 4b, although somewhat different from the Q_p *vs. E* curve, indicates a further increase of charge at more positive potentials. In both cases (pulse experiment and CV analysis) the Q *vs. E* curve are not characterized by the presence of a plateau at potentials more positive than -0.85 V.
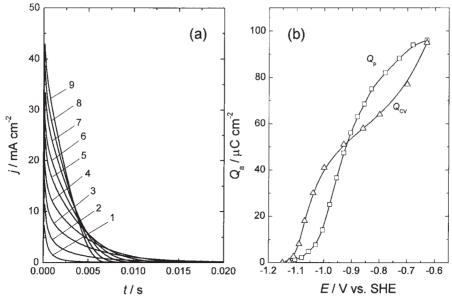
Fig. 4. (a) Anodic j–t transients recorded in 0.1 M NaOH solution onto a Cu(100) face at different UPLs (E_{in} (MLPL) $=-1.13$ V): 1. -1.03 V; 2, -0.98 V; 3, -0.93 V; 4, -0.88 V; 5, -0.83 V; 6, -0.78 V; 7, -0.73 V; 8, -0.68 V; 9, -0.63 V. (b) Charge (Q_p) vs. potential dependence obtained by integration of the area under the anodic j–t transients of Fig. 4a and charge (Q_{CV}) vs. potential dependences obtained by integration of the area under anodic part of the voltammogram shown in Fig. 1b.

(ii) Cu(111) surface

If the electrode would be cycled for some time between –1.03 V and – 0.83 V after being immersed in the solution, a stable voltammogram, characteristic for double layer behavior, would be obtained after a couple of cycles (like the one shown in Fig. 2a). The zero current density in such a case was maintained at a potential of about – 0.93 V. By applying repetitive pulses of duration no longer than 10 s onto such a surface from a MLPL $=-0.93$ V and a UPL $=-0.43$ V, reproducible anodic and cathodic j–t transients of the shape shown in Fig. 5 were obtained. As can be seen, both processes, adsorption and desorption, were very fast, with the current density dropping to zero after a maximum of 20 ms. The charge under both transients was found to be almost identical and was found to increase with increasing UPL of pulsing. The charge (Q_p) under the anodic j–t transients recorded in the potential range between LPL $=-0.93$ V and UPL $=-0.43$ V, obtained by integration of the area under the corresponding transients, is plotted as a function of potential in Fig. 6. As can be seen, on a non-reconstructed surface, a linear $Q_p - E$ dependence was recorded in the potential range from – 0.93 V to about – 0.63 V, while at more positive potentials a much sharper increase in the anodic charge was detected. For comparison, the charge obtained by integration of the area under the anodic part of the voltammogram recorded on a non-reconstructed (first sweep in Fig. 3a $- Q_{CV-1}$) and on a reconstructed surface (Fig. 1a) at a sweep rate of 100 mV s^{-1} (Q_{CV}) are also shown in this Figure.
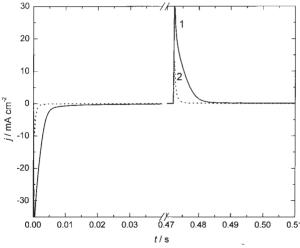
Fig. 5. Cathodic and anodic *j–t* transients recorded during repetitive pulsing of a freshly prepared (non-reconstructed) Cu(111) surface in 0.1 M NaOH with P and R pulse duration of about 0.47 s: 1. Repetitive pulsing between LPL = – 0.93 V and UPL = – 0.43 V; 2. Repetitive pulsing between LPL = – 0.93 V *vs*. SHE and UPL = – 0.67 V.

After the electrode had been cycled between – 1.03 V and – 0.33 V for about 30 cycles, the voltammogram shown in Fig. 1a was obtained, indicating that the electrode surface had been reconstructed. Again, if the initial potential was set at –1.03 V and the electrode was cycled for some time between –1.03 V and – 0.83 V the same voltammograms as the ones presented in Fig. 2a would be obtained and again the zero current density in such a case would maintain at a potential of about – 0.93 V indicating that the electrode surface had returned to its original (non-reconstructed) state. However, application of repetitive pulses on such a surface resulted in completely different transients. The transients were sensitive to the duration of the pulses, especially the cathodic pulses. In Fig. 7 are shown only one anodic and one cathodic transient recorded during repetitive pulsing between LPL = – 0.93 V and UPL = – 0.83 V (the initial potential was set at – 0.93 V). As mentioned earlier, at least five pairs of anodic and cathodic transients were recorded at each potential limit sequence and they were all identical to the ones shown in Fig. 7. As can be seen, the anodic current density recorded dur-
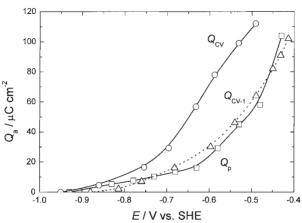

Fig. 6. Charge (Q_p) *vs*. potential dependence obtained by integration of the area under the anodic *j–t* transients recorded during repetitive pulsing of freshly prepared (non-reconstructed) Cu(111) surface in 0.1 M NaOH with P and R pulse duration of about 0.47 s. Q_{CV} represents the charge obtained by integration of the area under the anodic part of the voltammogram shown in Fig. 1a. Q_{CV-1} represents the charge obtained by integration of the area under the anodic part of the voltammogram representing the first sweep (dashed line) shown in Fig. 3a.
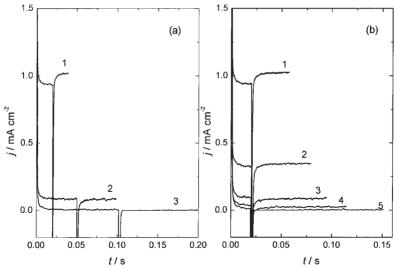
Fig. 7 (a) Anodic and cathodic *j–t* transients recorded during repetitive pulsing of a reconstructed Cu(111) surface in 0.1 M NaOH between LPL = – 0.93 V and UPL = – 0.83 V with different P and R pulses durations: 1. 20 ms; 2. 50 ms and 3. 100 ms. (b) Anodic and cathodic *j–t* transients recorded during repetitive pulsing of a reconstructed Cu(111) surface in 0.1 M NaOH between LPL = – 0.93 V and UPL = – 0.83 V with different durations of the R pulse: 1. 40 ms; 2. 60 ms; 3. 80 ms; 4. 100 ms and 5. 140 ms. Duration of the P pulse was 20 ms.

ing the R pulses was found to decrease with increasing duration of both pulses (a), as well as with increasing duration of the R pulses only (b).

Similar *j-t* transients to the ones shown in Fig. 7b were obtained during repetitive pulsing between LPL = – 0.93 V and MUPL = – 0.43 V, with the anodic current density during the P pulse being somewhat smaller, as shown in Fig. 8. The duration of the R pulse needed for the anodic current density recorded during that pulse to reach zero was shorter (60 ms) than the one recorded in Fig. 7b (140 ms).
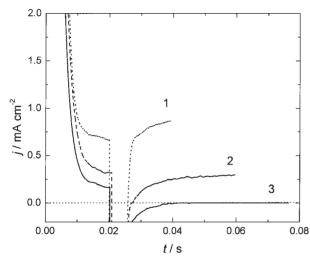

Fig. 8. Anodic and cathodic *j–t* transients redorded during repetitive pulsing of a reconstructed Cu(111) surface in 0.1 M NaOH between LPL = – 0.93 V and UPL = – 0.43 V with different durations of the R pulse: 1. 20 ms; 2. 40 ms and 3. 60 ms. Duration of the P pulse was 20 ms.
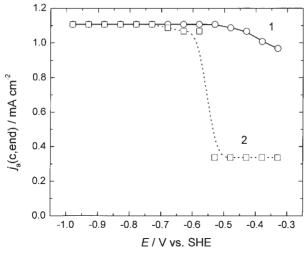
Fig. 9. Dependence of the anodic current density recorded during the R pulse (j_a(c,end) – recorded at the end of the R pulse) on the potential of repetitive pulsing of a reconstructed Cu(111) surface in 0.1 M NaOH with a P pulse duration of 20 ms. Curve 1 was obtained while pulsing from MLPL towards MUPL. Curve 2 was obtained while pulsing from MUPL towards MLPL.

If the repetitive pulsing started from MLPL = –1.03 V and the UPL was changed in steps of 50 mV towards more positive values, the anodic current density recorded during the R pulses (j_a(c,end) – recorded at the end of the R pulse) maintained a constant value of about 1.1 mA cm^{-2} up to about – 0.53 V and then started to decrease slightly (curve 1 of Fig. 9). If the repetitive pulsing started from the most positive potential MUPL = – 0.33 V and the LPL was changed in steps of 50 mV towards more negative values (MLPL = – 0.93 V) a sudden increase of j_a(c,end) from about 0.3 mA cm^{-2} to about 1.1 mA cm^{-2} was detected at a potential of – 0.53 V (curve 2 of Fig. 9).

The dependence of different charges, obtained by integration of the area under the corresponding j–t transients presented in Fig. 7b, as a function of the duration of the R
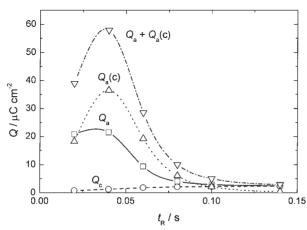

Fig. 10. Dependence of different charges, obtained by integration of the area under the corresponding j–t transients presented in Fig. 7b, as a function of the duration of the R pulse (t_R): Q_a represents the charge under the P pulse, anodic transient (first transient), Q_c represents the cathodic charge under the R pulse (second transient), Q_a(c) represents the anodic charge under the R pulse (second transient) and $Q_a + Q_a$(c) represents the total anodic charge under both the P and R pulses (first and second transient).

pulses is shown in Fig. 10, Q_a represents the charge under the P pulse (anodic transient), Q_c represents the cathodic charge under the R pulse (second transient), $Q_a(c)$ represents the anodic charge under the R pulse (second transient) and $Q_a + Q_a(c)$ represents the total anodic charge under both the P and the R pulses (first and second transient). As can be seen, all these charges became very small when the duration of the R pulse (t_R) reached 140 ms, with $Q_a + Q_a(c)$, Q_a and Q_c being identical while $Q_a(c)$ dropped to zero.

<div align="center">DISCUSSION</div>

Cyclic voltammetry

The systematic investigation of the electrochemistry of Cu(111) in 0.1 M NaOH solution in the underpotential range of Cu_2O formation has practically been the subject of only two papers.[16,17] In both papers the formation of an adsorbed layer of OH⁻ species was confirmed. Considering the voltammograms for Cu(111) presented in Figs. 1a, 2 and 3a, it seems that the process of OH⁻ species adsorption is more complex, involving a reconstruction of the original Cu(111) surface. As can be seen in Fig. 2, if the initial potential is set at the most negative values of –1.03 V, a typical and reproducible "double layer" voltammogram can be obtained by cycling the electrode up to – 0.63 V. A change of the shape of the voltammogram with the number of cycles can be detected already at an anodic limit of – 0.53 V (Fig. 2a), while at more positive potential limits a significant change in the shape of the voltammogram shape occurs, as seen in Fig. 2b and c. After reaching the potential of the beginning of Cu_2O formation (about – 0.45 V), a well defined anodic peak at about – 0.63 V developed, while two cathodic peaks appeared at potentials of – 0.72 V and – 0.85 V. Such a behavior is in accordance with the finding of Maurice *et al.*[17] that the adsorption of OH⁻ species modifies the step edges corresponding to the lateral growth of terraces and also to the formation Cu islands on top of the terraces. It is interesting to note that the cyclic voltammogram obtained in a STM cell containing non-deaerated solution[17] differs significantly from the one obtained in our work in deaerated solution, indicating that the presence of dissolved oxygen in the solution causes some changes of the original single crystal surface (see Fig. 1 of Ref. 17). It is quite difficult to explain the origin of the two cathodic peaks on the voltammograms presented in Figs. 1a and 2. The first cathodic peak at a potential of about – 0.72 V most probably corresponds to the desorption of adsorbed OH⁻ species, while the second peak at about – 0.85 V could be either the consequence of oxygen (traces) reduction[a], or reconstruction of the Cu(111) surface. It should be mentioned here that these two cathodic peaks start to appear with the beginning of the reconstruction of the original Cu(111) surface, as seen in Fig. 2b. It should also be mentioned here that for completion of the reconstruction of Cu(111) surface at least 30 cycles in the potential range between –1.03 V and – 0.33 V must be applied to the electrode ($v = 100$ mV s⁻), meaning that the Cu(111) surface should be exposed to potentials more positive than – 0.53 V for at

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a   Analysis of the impedance measurements showed that the equivalent circuit predicted for diffusion controlled oxygen reduction cannot fit the experimentally obtained Z'-Z'' diagrams (to be published).

least 180 s in order to obtain a stable, but reconstructed Cu(111) surface. Hence, it is most likely that the surface reconstruction of Cu(111) in 0.1 M NaOH is a time consuming process involving the adsorption/desorption process of OH⁻ species. This is in agreement with the findings of Härtinger et al.,[16] while the statement of Maurice et al.[17] that the reconstruction of Cu(111) into its original state is very fast might be the cosequence of the use of non-deaerated solution, as well as the use of the *in situ* STM technique (some time is always needed for obtaining the corresponding image).

Contrary to the electrochemical behaviour of Cu(111) in 0.1 M NaOH solution, Cu(100) was found to be very stable, *i.e.*, the voltammogram shown in Fig. 1b was obtained after only a couple of cycles, it was insensitive to the initial potential value and the shape of the voltammogram did not change with the number of cycles at any anodic limit potential. Considering Fig. 1b, it is obvious that in the potential range between –1.13 V and – 0.83 V adsorption/desorption of OH⁻ species occurs, being characterized by a pair of well defined voltammetric peaks. As is shown in Fig. 4b, the charge *vs.* potential dependence is not characterized by the presence of a plateau at potentials more positive than – 0.85 V indicating continuation of the process of OH⁻ species adsorption at these potentials. Taking into account that the formation of ordered structures is usually accompanied by the presence of a sharp peak on the cyclic voltammogram, it seems reasonable to ascribe this process to the adsorption of randomly distributed OH⁻ species (most probably taking place at the steps and kinks present on the real surface), which can be expressed by the reaction

$$Cu + OH^- \rightleftharpoons Cu - OH_{ads} + e^- \tag{4}$$

It should be emphasized here that this is the first investigation of the electrochemical behavior of a Cu(100) face in 0.1 M NaOH solution, showing that adsorption/desorption of OH⁻ species takes place at potentials between –1.13 V and – 0.83 V.

Potentiostatic j–t transients

In the case of Cu(111), repetitive pulsing was found to be sensitive to the state of the electrode surface. On a freshly prepared, original surface pulses of duration from 20 ms to 10 s could be applied in the potential range from LPL = – 0.93 V to UPL = – 0.43 V and the current responses would be as the ones shown in Fig. 5. For MUPL = – 0.43 V (transient 1) the current density for both P and R pulses drops to zero after about 20 ms, while at UPL = – 0.67 V (transient 2) this time is shorter. In such a case the charge under the anodic (as well as under the cathodic) transients was found to depend on the potential in the way shown in Fig. 6 (curve Q_p). In the potential range from – 0.93 V to – 0.63 V a linear $Q_p - E$ dependence was recorded, while a significant adsorption of OH⁻ species is seen to start at potentials more positive than – 0.60 V accompanied by a sharp increase in charge. In the same Figure, the $Q_{CV} - E$ dependence, representing the charge obtained by integration of the area under the anodic peak presented in Fig. 1a and the $Q_{CV-1} - E$ dependence, representing the charge obtained by integration of the area under the anodic part of the voltammogram representing the first sweep on a non-reconstructed Cu(111) surface (Fig. 3a) are

shown. It is obvious that on a reconstructed Cu(111) surface (Q_{CV} – E curve), the adsorption of OH⁻ species commences at more negative potentials than on the non-reconstructed surface, while for a non-reconstructed surface the shape of the charge *vs.* potential dependence obtained by analyzing the *j*–*t* transients was almost identical to that obtained from the first cyclic voltammogram. This is in accordance with the statement that Cu(111) surface had not been reconstructed during repetitive pulsing when the duration of P and R pulses was no longer than 10 s.

Once this electrode had been exposed to a long time (more than 3 min) polarization at potentials more positive than – 0.40 V, or cycled for some time (about 30 cycles with 100 mV s⁻¹) in the potential range between –1.03 V and – 0.33 V the Cu(111) surface reconstructed and the *j*–*t* transients recorded during repetitive pulsing became sensitive to the duration of the R pulses for a short time P pulses. As can be seen in Fig. 7, if the P pulses are very short (20 ms) then a constant anodic current density of about 1.1 mA cm⁻² was maintained (transients 1) even during the R pulses. With increasing duration of both pulses, Fig. 7a, the anodic current density maintained during the R pulse became smaller and when duration of both pulses reached the value of 100 ms no anodic current was recorded during the R pulse. With increasing duration of the R pulse, with a P pulse duration of 20 ms, Fig. 7b, anodic current density maintained during the R pulse also became smaller and when duration of the R pulse reached a value of 140 ms, no anodic current was recorded during this pulse. Similar responses were recorded while pulsing the electrode between LPL = – 0.93 V and UPL = – 0.43 V although a shorter R pulse duration of 60 ms was needed for the anodic current recorded during this pulse to disappear, as can be seen in Fig. 8. It is interesting to note that the anodic current density maintained during the R pulse (j_a(c,end)) for a short duration of both the P and R pulses of 20 ms depends on the direction of repetitive pulsing. As can be seen in Fig. 9, if the repetitive pulsing was performed starting from MLPL = – 0.97 V and changing the UPL towards more positive values, j_a(c,end) maintained a constant value of about 1.1 mA cm⁻² up to a potential of about – 0.53 V with a linear decrease to about 0.95 mA cm⁻² at MUPL = – 0.33 V (curve 1). If the repetitive pulsing was performed starting from MUPL = – 0.33 V and changing the LPL towards more negative values, j_a(c,end) suddenly changed from about 0.32 mA cm⁻² to about 1.1 mA cm⁻² at a potential of about – 0.53 V (curve 2). It should be emphasized here that at the potential of about – 0.53 V, the cyclic voltammograms also started to change (Fig. 1a), indicating that there is a "critical potential" for surface reconstruction to take place. Considering the results presented in Fig. 10, it is obvious that there is also a "critical duration" of the R pulse needed for surface reconstrction into an "original state" (but not non-reconstructed state) to be completed (when Q_a(c) drops to zero and Q_a and Q_c become identical) and this time is about 140 ms for repetitive pulsing between LPL = – 0.93 V and UPL = – 0.83 V.

Considering results presented in Fig. 5, it is obvious that such effect cannot be detected on the Cu(111) surface which was not reconstructed. Hence, this effect is most likely the consequence of surface reconstruction involving process of adsorption/desorption of OH⁻ species, with the desorption of OH⁻ species being slower than the adsorption which

results in the surface reconstruction being a time consuming process. As suggested by Maurice *et al.,*[17] the adsorption of OH⁻ species is initiated preferentially at the step edges on the upper terrace side, decreasing the mobility of the Cu atoms along the step edges and inducing lateral growth of the terraces which results from the accumulation (at the step edges) of Cu atoms ejected from the adlayer superstructure due to reconstruction of the outermost Cu plane of the substrate. It was found that the same mechanism leads in the last stages of adsorption process to the formation of Cu adislands on the terraces. The reverse sequence is observed during the desorption process and it was found that surface modification (reconstruction) is instantaneous for large values of overpotential of adsorption or desorption. Hence, although the STM image, as well as the cyclic voltammogram, recorded after desorption are the same as the ones recorded before the adsorption of OH⁻ species, it seems (according to our results) that once reconstructed, Cu(111) surfaces never become the same as the original one, otherwise the pulses recorded on these two surfaces should be the same.

CONCLUSION

It was shown that Cu(111) undergoes an irreversible surface reconstruction in 0.1 M NaOH solution if the electrode is exposed to potentials more positive than – 0.53 V for some time. If this time is, in the case of repetitive pulse experiments, equal or lower than 10 s then reconstruction does not occur. Adsorption of OH⁻ species occurs in the potential range more negative than – 0.60 V only on reconstructed surfaces. For this process to take place onto non-reconstructed Cu(111) surface a higher overpotential is needed. The surface reconstruction was found to be a time consuming process depending on the upper potential limit (UPL) and involving the process of the adsorption/desorption of OH⁻ species.

The first investigation of the electrochemical behavior of the Cu(100) face in 0.1 M NaOH solution was performed in this work. It was shown that the adsorption/desorption of OH⁻ species occurs in the potential range between –1.13 V and – 0.73 V forming a low coverage adsorbate.

ИЗВОД

РЕКОНСТРУКЦИЈА ПОВРШИНЕ ПРИ АДСОРПЦИЈИ И ДЕСОРПЦИЈИ ОН⁻ ЈОНА НА МОНОКРИСТАЛИМА БАКРА ОРИЈЕНТАЦИЈА (111) И (100) ИЗ РАСТВОРА 0.1 M NaOH

В. Д. ЈОВИЋ и Б. М. ЈОВИЋ

Каӣедра за инжењерсӣво маӣеријала, Дрексел Универзиӣеӣ, Филаделфија, ПА 19104, САД

Процес адсорпције и десорпције ОН⁻ јона на монокристалима бакра оријентација (111) и (100) испитиван је методама цикличне волтаметрије и потенциостатског пулса из раствора 0,1 M NaOH. Показано је да се на Cu(100) адсорпција/десорпција ОН⁻ јона одвија у распону потенцијала од –1,13 V *vs.* SHE до – 0,83 V *vs.* SHE, да је окарактерисана са два струјна пика на волтамограму и да при процесу адсорпције долази до формирања адсорбата веома малог степена покривености површине. Показано је да у 0,1 M NaOH на Cu(111) долази до иреверзи-

билне реконструције површине при адсорпцији/десорпцији OH⁻ јона. Оригинална површина се не може повратити уколико се електрода изложи одређено време потенцијалима позитивнијим од – 0,53 V *vs.* SHE. Уколико је то време, у случају пулсних експеримената, једнако или краће од 10 s, реконструкције се не одиграва. Адсорпција OH⁻ јона на реконструисаној Cu(111) површини одвија се на потенцијалима негативнијим од – 0,60 V *vs.* SHE, док се овај процесс на оригиналној, нереконструисаној површини, одиграва на потенцијалима позитивнијим од – 0,60 V *vs.* SHE.

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