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Unusual anodic peak on negative potential scan for copper in alkaline media ^①

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[Abstract] The unusual anodic peak emerging on negative potential scan for copper in concentrated NaOH media was investigated by X-ray diffraction, X-ray photoelectron spectroscopy techniques, potentiodynamic scan, galvanostatic reduction and fast triangular voltage methods. The results show that CuO is formed on the electrode at potentials above this unusual peak $A_{2,3}$, but also produced at peak $A_{2,3}$ when copper has been beforehand anodized at high potentials. Longer pre-oxidation time and higher pre-oxidation potential are advantageous to the formation of CuO at peak $A_{2,3}$. It is presented that the pent-up growth of oxide layer in the high potential region occurs at the interface between metal and oxide by the field-assisted migration of O^{2-} ions to electrode, and when potential negatively shifts to the range of peak $A_{2,3}$, the O^{2-} (or cation vacancies) accumulated in the film could move towards the solution and combine with Cu^{2+} ions at the interface between oxide and solution.

[Key words] copper electrode; anodic film; ion transfer; capacitance

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1 INTRODUCTION

It is well known that anodic voltammetric peak usually emerges in the positive potential scan, but in some cases, anodic peak may extraordinarily rise during negative potential scan. Such behavior seems to be connected with the formation of adsorbed species^[1] or solid film^[2~4] on electrode surface. An example about the latter is that, a small anodic peak, which is related to the growth of the duplex layer on copper surface in alkaline media, can be recorded after the scan is reversed from high potential (as peak $A_{2,3}$ in Fig.1). Such feature was reported first by Burke^[2] et al, and was assigned to the chemical dissolution of the thin oxide film which allowed copper corrosion to occur in the region of peak $A_{2,3}$ ^[2,3]. The same behavior was reported for cobalt^[4] in alkaline media. So far, no more attention has been paid to the unusual anodic peak of metals in alkaline media.

Both soluble and insoluble products are involved in the anodic oxidation of Cu in alkaline solutions, and two main oxidation states of Cu(I) and Cu(II) may be produced to exhibit anodic current peaks A_1 and $A_{2,1}$ in voltammetric curves (see Fig.1)^[5~11]. Copper dissolution as Cu(II) species occurs at relatively fast rates in the ascending branch of $A_{2,1}$, and is quickly inhibited by the formation of solid Cu(II) layer on copper surface at more positive potentials. There is general agreement that the passive layer is a $Cu_2O/CuO \cdot Cu(OH)_2$ duplex film^[8~11]. The solid Cu(II) species in this film is only $Cu(OH)_2$ over the

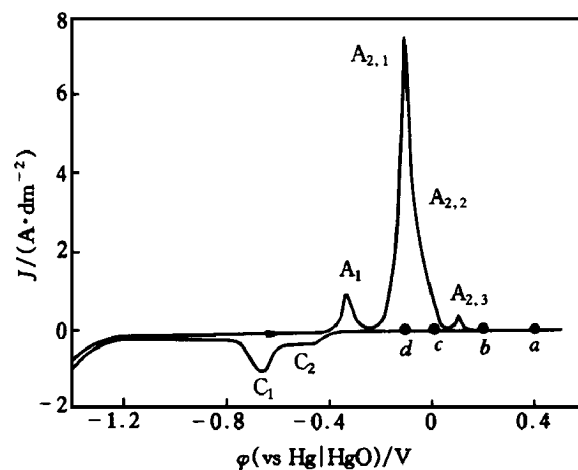


Fig.1 Cyclic voltammogram of Cu in 3.0 mol/L NaOH solution by scanning at 10 mV/s

range of the shoulder peak $A_{2,2}$ called partial passivation region (PP-range), and both CuO and $Cu(OH)_2$ are in the region above peak $A_{2,3}$ called final passivation region (FP-range)^[11]. The objective of this work is to explain the origin of peak $A_{2,3}$ by getting more information on composition, growth and transformation of the duplex films.

2 EXPERIMENTAL

Copper polycrystalline electrode (99.99% purity) was either a sheet of 1.0 cm² apparent area used for XRD and XPS analyses or a disc of 0.0145 cm² for

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electrochemical measurements. The counter electrode was a Pt sheet of 2.0 cm^2 . The electrolyte solutions were $2.5 \sim 6.0 \text{ mol/L}$ NaOH prepared from new-made twice-distilled water and carbonate-free NaOH. The reference electrode was a Hg/HgO electrode in the same solution. The electrochemical experiments were carried out using a JH2C potentiostat, a DCG-2 universal programmer, and an XFD-8 triangular wave generator. Solution was purged with purified nitrogen for 15 min and was maintained at 25°C before each run. The copper surface was gradually polished with emery paper down to particle size of $0.3 \mu\text{m}$, degreased with acetone, washed with twice distilled water, and precathodized at -1.4 V for 5 min to remove the air-formed oxides. XRD measurements were made with Rigaku Rotaflex max/rB X-ray diffractometer. XPS examinations were performed using a VG ESCALAB MK-II X-ray photoelectron spectrometer. The samples were introduced into the UHV-vessel immediately after the electrochemical treatment and after rinsed with twice distilled water and purged with purified N_2 . The $\text{Cl } 1\text{s}$ peak (bind energy 285.5 eV) was used for charge referencing and energy calibration. Spectra were recorded for the $\text{Cu } 2\text{p}_{3/2}$ band, Cu LMM Auger band and $\text{O } 1\text{s}$ band. The composite XPS bands were resolved by using Gauss curve fitting method to identify the composition of specimens against the standard XPS data^[12].

Interfacial capacity of copper was measured by superimposing a fast triangular voltage (span 25 mV , frequency $556 \sim 5000 \text{ Hz}$) upon a constant potential until the current response became nearly steady; the potential positively swept at 0.1 mV/s from one measuring site to the next.

3 RESULTS AND DISCUSSION

The cyclic voltammogram of metallic copper recorded in 3.0 mol/L NaOH (as shown in Fig.1) has well defined oxidation and reduction peaks. From previously reported investigations using different techniques^[5-11], peak A_1 represents the $\text{Cu}/\text{Cu(I)}$ transitions, A_2 (including $A_{2,1}$ and $A_{2,2}$) $\text{Cu}/\text{Cu(I)}$ and $\text{Cu}/\text{Cu(II)}$, $\text{C}_2\text{Cu(II)}/\text{Cu(I)}$, and C_1 $\text{Cu(I)}/\text{Cu}$. Note the anodic peak $A_{2,3}$ which emerges only on the reverse scan. Four potential sites selected for film formation are situated at point a : $\varphi_a = 0.40 \text{ V}$; b : $\varphi_a = 0.20 \text{ V}$; c : $\varphi_a = 0 \text{ V}$; and d : $\varphi_a = -0.12 \text{ V}$, respectively.

3.1 Nature of copper oxides

As can be seen from XRD patterns previously reported^[10] for copper after 3 min of oxidation at various potentials, a Cu_2O layer was detected for both FP-film and PP-film, and a thick and visible Cu(OH)_2 layer existed only in PP-film. The outer

cupric layer of FP-film was too thin to be detected by XRD, but was found to consist of Cu(OH)_2 and CuO and adsorbed H_2O ^[10]. The inner thin Cu_2O layer in these two kinds of films was not observed by analyzing $\text{Cu } 2\text{p}_{3/2}$, $\text{O } 1\text{s}$ and Cu LMM bands because of the limited escape depth of XPS electrons.

Figs. 2, 3 show the XRD patterns and XPS spectra of coppers after 30 min of oxidation at different potentials. For the film obtained at high anodic potential ($\varphi_a = 0.4 \text{ V}$, Fig. 2(a)), XRD peaks of CuO appear and those of Cu_2O intensify obviously as compared with XRD data for 3 min of oxidation^[10], but Cu_2O can not be observed yet from XPS bands (see Fig. 3(a)). This fact suggests that, under longer-time oxidation at high anodic potential, the growth of Cu_2O (and CuO also) has possibly occurred at the interface between film and metal. The XRD and XPS data of the films formed at more negative potentials of 0.20 V , 0 V and -0.12 V , exhibit no apparent change with the formation time t_a increasing from 3 min to 30 min (Fig. 2(b) and (c), Fig. 3(b) and (c)). However, when the film was formed when the potential was held at 0.20 V for 30 min and then shifted negatively to 0 V , both XRD and XPS examinations exhibit the presence of CuO (see Fig. 2(b'), Fig. 3(b')). Therefore, it can be seen that CuO has been formed at the interface of film and solution in the region of peak $A_{2,3}$ during the negative scan.

Fig. 2 XRD patterns of copper anodized at various potentials for 30 min in 4.0 mol/L NaOH

(a) — $\varphi_a = 0.40 \text{ V}$; (b) — $\varphi_a = 0.20 \text{ V}$;
(c) — $\varphi_a = 0 \text{ V}$; (b') — $\varphi_a = 0.20 \text{ V}$

3.2 Cathodically galvanostatic behaviors

The cathodic potential-time profiles recorded at 0.02 A/dm^2 for copper pre-anodized in FP-range show two distinct plateaus C_2 and C_1 (see Fig. 4)

Fig.3 XPS bands of copper anodized at various potentials for 30 min in 4.0 mol/L NaOH
(a) — $\varphi_a = 0.40$ V; (b) — $\varphi_a = 0.20$ V;
(c) — $\varphi_a = 0$ V; (b') — $\varphi_a = 0.20$ V

which can be attributed to the electroreduction of Cu(II) and of Cu(I) oxide species^[13], respectively. The earlier result^[14] showed that, as the applied constant current density increased from 0.02 A/dm² to 0.32 A/dm², both C₂ and C₁ shifted negatively and C₁ split apart into three small plateaus. These three

plateaus were attributed to the reduction of Cu₂O formed anodically on copper, Cu₂O and Cu₂O•H₂O formed by reduction of Cu(II) species, respectively. The fact that the total amount of cathodic charge was almost independent of constant current density for the same φ_a and t_a suggests that most of the soluble Cu species formed anodically could not be electroreduced because of their diffusion into solution under low-density galvanostatic conditions.

Therefore, the apparent thickness of the FP-film can be deduced from the cathodic charges, Q_{C_2} and Q_{C_1} of Fig.4. The thickness of Cu(II) layer (d_2) is given by Q_{C_2} whereas that of Cu(I) layer (d_1) is by the difference ($Q = Q_{C_1} - Q_{C_2}$). The result obtained for $\varphi_a = 0.4$ V shows that, d_2 and d_1 increase from 30 nm to 70 nm and from 140 nm to 280 nm with oxidation time increase, respectively. However, both d_2 and d_1 at lower potential ($\varphi_a = 0.2$ V) exhibit no appreciable change with increasing time; the mean values of 40 nm and 140 nm have been obtained for d_2 and d_1 , respectively. Apparently, the growth of FP-film, especially Cu₂O layer, can be promoted by strong interfacial electric field. It should particularly be pointed out that the plateau C₂ for $\varphi_a = 0.40$ V slowly lengthens with anodization time in a sloping form (see Fig.4(a)) that is obviously different from the normal behavior of galvanostatic reduction of solid species. Comparison of XRD and XPS examinations shows that such unusual behavior can be attributed to the reduction of the distorted CuO crystal formed at interface between oxide and copper. Any volume change accompanying such interface reactions may cause stresses and distortion in crystal lattice.

The same experiments have also been made for

Fig.4 Curves of galvanostatic reduction for oxidized copper electrode
(a) — $\varphi_a = 0.40$ V; (b) — $\varphi_a = 0.20$ V for different oxidation times ($J = 0.02$ A/dm² in 4.0 mol/L NaOH)

PP-film. When φ_a is set in the PP-range and reduction current is held at 0.02 A/dm^2 , the potential of plateau C_2 is always more negative only than $\varphi_{eq}(\text{Cu}(\text{OH})_2/\text{Cu}_2\text{O})$, indicating again that $\text{Cu}(\text{II})$ species in PP-film is only $\text{Cu}(\text{OH})_2$. Both C_2 and C_1 show no apparent changes in transition time and potential with anodization time. The mean values of d_2 and d_1 estimated from the plateau charges are 360 nm and 470 nm for φ_a set at 0 V, 540 nm and 470 nm for φ_a at -0.12 V , respectively. Since the thickness of the outer $\text{Cu}(\text{OH})_2$ layer in FP-film is nearly independent of formation time, an electrochemical reconstruction process of $\text{Cu}(\text{OH})_2$ layer should take place at the same time in equilibrium with the chemical dissolution of this thick $\text{Cu}(\text{OH})_2$ layer in basic media.

3.3 Negatively potentiodynamic behaviors

Fig. 5 shows the voltammograms recorded with scan rate of -3 mV/s for copper anodized at 0.40 V and 0.20 V in 4.0 mol/L NaOH . The cathodic peaks C_2 and C_1 severally represent the $\text{Cu}(\text{II})/\text{Cu}(\text{I})$ and $\text{Cu}(\text{I})/\text{Cu}$ transitions. Another complex peak emerges at more negative potentials ($-0.8 \sim -1.0 \text{ V}$) when φ_a is set positive and t_a is long enough (see Fig. 5(a)), so it may be assigned to the reduction of Cu_2O grown probably at the interface between oxide

and copper as discussed above.

The composite peak C_2 consists of three smaller peaks, $C_{2,1}$, $C_{2,2}$, and $C_{2,3}$. Only peak $C_{2,1}$ was recorded previously^[15] for $\varphi_a = -0.175 \text{ V}$ where no solid $\text{Cu}(\text{II})$ species was formed on copper, and disappeared under solution stirring during potential scan. When φ_a is set at 0.40 V where $\text{Cu}(\text{OH})_2$ and CuO can be produced, peak $C_{2,1}$ also disappears on the direct cathodic scan profile (see Fig. 6(c), the potential jumps over the anodic range prior to the negative scan). Accordingly, the peak $C_{2,1}$ can be assigned to the reduction of intermediate state $\text{Cu}(\text{II})$ ions, which have just been produced in the potential range of $A_{2,1}$, followed by a chemical transition to its stable state (CuO_2^{2-})^[13]. Most of the latter diffuses into solution under slow scan potentiodynamic conditions. Experiment showed that saturated CuO_2^{2-} ions in 4.0 mol/L NaOH can be electro-reduced at potential below -0.42 V .

Fig. 6 Curves of negatively potentiodynamic J vs φ of copper with scan rate of -0.5 mV/s in 4.0 mol/L NaOH after oxidation at 0.40 V for 3 min

Anodic switching potential: $a - 0.40 \text{ V}$;
 $b - 0 \text{ V}$; $c - -0.18 \text{ V}$

There are correspondingly three anodic peaks, $A_{2,1}$, $A_{2,2}$ and $A_{2,3}$, emerging in the PP-range associated with the formation of $\text{Cu}(\text{II})$ species. The peak currents of both $A_{2,3}$ and $C_{2,3}$ increase with the increasing anodization time t_a , and when φ_a is set more positive, the both peaks emerge earlier (shorter t_a required) and rise more slowly with increasing t_a (see Fig. 5(a)). Hence, peaks $A_{2,3}$ and $C_{2,3}$ seem certain to be a pair of oxidation-reduction peaks related to CuO , whereas $A_{2,2}/C_{2,2}$ couple can be attributed to $\text{Cu}(\text{OH})_2$. The decrease in current of peak $C_{2,2}$ with increasing t_a , which accords with the negative shift of plateau C_2 in Fig. 4(b), showing the dissolution of $\text{Cu}(\text{OH})_2$ on the surface of PP-film in basic solution. An interesting result is that the peak $A_{2,3}$ nev-

Fig. 5 Curves of negatively potentiodynamic J vs φ of copper with scan rate of -3.0 mV/s in 4.0 mol/L NaOH after oxidation for different times

(a) — $\varphi_a = 0.20 \text{ V}$; (b) — $\varphi_a = 0.40 \text{ V}$

er emerges in the positive potential scan. By all appearances, the peak $A_{2,3}$ is closely related to some effect of high anodic potential upon the thin FP-film.

The cathodic peak $C_{1,1}$ and the shoulder peak $C_{1,2}$ shown in Fig. 6 can be assigned to the reduction of Cu_2O formed anodically at 0.40 V and Cu_2O formed cathodically in the region of peak C_2 . The fact that the electric charge of peak $C_{1,1}$ keeps almost constant under the three potential perturbation programs indicates that the Cu_2O formed in the FP-range has not participate the anodic reactions occurring in the PP-range. The relationship between the thickness of Cu(I) layer and oxidation time obtained by galvanostatic reduction as stated above also suggests that Cu_2O can exist steadily on the electrode. Thus, various Cu(II) species all seems to be formed directly from the oxidation of metal copper.

The effect of high anodic potential on the thin FP-film is probably that the adsorbed OH^- (and H_2O) decomposed by strong interfacial field to H^+ and O^{2-} , the former moves towards the solution and the latter in the opposite direction and tends to combine with Cu^{2+} . Because of the high passivation of the FP-film, O^{2-} ions accumulates gradually in the film. Once the potential returns to the PP-range resulting in a small rise in electrode activity, the accumulated O^{2-} ions can combine with Cu^{2+} at relatively rapid rates to show an anodic current peak on negative sweep, as peak $A_{2,3}$. The same combination can also occur immediately when the potential is stepped from the FP-range to the PP-range (Fig. 6(b)); the steep current peak shown at 0 V in Fig. 6 actually corresponds to a potentiostatic current transient due to solid nucleation-growth processes. Apparently the high passivation of the FP-film can not exhibit independently of high anodic potential, and the less passivation of the PP-film is not due to its porosity.

3.4 Capacitance of interface

Measuring the capacitance of the electrode can follow the growth of oxide films on electrode. Fig. 7 shows the changes in capacitance with potential for copper in 4.0 mol/L NaOH under quasi-steady state condition. At potential slightly greater than the peak potential of $A_{2,1}$, the capacitance falls rapidly down to 0.094 F/m² resulting from the growing of a thick Cu(OH)_2 layer. As the potential increases, a high and broad capacitance peak C_p appears at the border between the PP-range and the FP-range. At each measurement site in the ascending branch of peak C_p , the amplitude (Δi) of the square-wave current response increases continuously (lasting for 0.5 ~ 2 h) until reaching a constant value, namely the capacitance increases with time. The contrary change in amplitude of current wave occurs at more positive potentials until a minimum capacitance of 0.99 F/m² at

0.25 V is reached. Apparently, the peak C_p is related to some slow time-dependent transition. Similar experiment made by changing the concentration of NaOH from 4.0 mol/L to 6.0 mol/L, shows that the peak potential of C_p shifts negatively by 0.05 V and that the peak value increases by nearly 100%. This suggests that the presence of hydroxide ion greatly enhance this time-dependent transition, which therefore is probably the dissolution of the thick Cu(OH)_2 layer in concentrated alkaline solutions. Because the electrochemical reconstruction process of Cu(OH)_2 layer restrained more and more with increasing potential over the PP-range (see Fig. 7, broken line), the net chemical dissolution occurs during the potential positive-going, resulting in a transformation from initially continuous film to porous film. The porosity caused by dissolution has been usually found to be $10^8 \sim 10^{12} \text{ cm}^{-2}$. Such a transformation may be reflected by the large rise in capacitance; the peak value of C_p indicates the maximum porosity. However, as the dissolution proceeds further with potential shifting positively, both porosity and capacitance decrease due to the loss of Cu(OH)_2 layer in large part. When the potential enters the FP-range, the film on copper is no longer visible to the naked eyes. Since the anodic current in PP-range does not increase with porosity, it can be known that the ion transfer through the pores is not the rate-determining step.

Fig. 7 Curves of capacitance vs potential (a) and voltammogram curve (b) under quasi-steady state condition for copper in 4.0 mol/L NaOH

For general cases, the space charge capacitance C_{sc} of a semiconductor electrode is very low compared with double layer capacitance C_{dl} ^[16]. However, in the FP-range, the capacitance gradually increases with potential and is limited to an order of magnitude about the same as is found for C_{dl} in the cathodic range (no oxide layer on electrode). Such behavior usually occurs when the density of surplus charge in the space-charge region is high enough to cause surface degeneracy^[17]. Accordingly, it is reasonable to

consider that a large quantity of O^{2-} are present by decomposition of OH^- (and H_2O) at high anodic potentials in the FP-range. As the oxidation of O^{2-} to O_2 occurs in the potential range above 0.65 V, the decrease in capacitance is simultaneous with the increase in the current of oxygen evolution. The similar change in capacitance happens in the region of peak $A_{2,3}$ on the reverse sweep because of the combination of O^{2-} with Cu^{2+} at the surface of the film.

It can be concluded that the growth of PP-film occurs at the $Cu(OH)_2/NaOH$ interface by the motion of Cu^{2+} ions through the film to solution, and that of FP-film take place at the Cu/Cu_2O interface by the field-assisted migration of O^{2-} ions in the reverse direction. The products formed in these two manners are naturally hydroxide and oxides, respectively. Furthermore, because the oxides formed at solid/solid interface are bound up with both the lattice structures and the size and shape of both crystals, the production of Cu_2O is reasonably preferable to that of CuO at Cu/Cu_2O interface (see Fig. 4(a)). The equilibrium opposing migration of Cu^{2+} ions and O^{2-} ions happens at the intermediate potentials resulting in the most complete passivation of copper. The cations and anions (or corresponding vacancies) meet each other within the film and have a tendency to combine, but their interaction is limited by crystal growth space, leading to the distortion in the crystal lattice and the very strong stresses; the ion-transfer and the film growth are therefore inhibited (see Fig. 4(b)). Once the potential is set more negative or more positive, either Cu^{2+} or O^{2-} migrates dominantly, reaches one interface and participate reactions. Because reaction can occur much more easily at solid/liquid interface than at solid/solid interface, the PP-film shows lower degree of passivation and may achieve a larger thickness than the FP-film.

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