

Photoresponse from oxide layers developed on copper electrode in Cu(II) solutions containing glycolic acid

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Potentiometric and voltammetric investigations of oxide layers spontaneously developed in a Cu|Cu(II) – glycolic acid system were carried out under chopped illumination conditions. The negative open-circuit photopotentials and the positive photocurrents detected at moderate cathodic polarizations are indicative of *n*-type conductivity of the surface oxides. The peculiarity of the system consists in occurrence of two well-defined voltammetric peaks. The first, observed at *ca.* –0.7 V (NHE), is attributed to Cu₂O reduction. An estimation of Cu₂O formation rate, based on the analysis of this peak, yields 2 nm min⁻¹ at pH 4.9 and a 6-fold larger quantity at pH 5.9. The second peak is supposed to be conditioned by electroreduction of oxygen-enriched surface layers involving Cu(II). An inversion of photocurrent sign resulting in *n* → *p* transition was found to occur at a certain E_{inv} depending on oxide layer thickness and solution pH.

Key words: copper – glycolic acid complexes, oxide layers, photoresponse

INTRODUCTION

Oxide layers developed on copper electrodes in systems containing Cu(II) complexes are interesting from various points of view. On the one hand, simultaneous formation of copper oxides belongs to the processes that often attend the electroreduction of Cu(II) and may affect not only the kinetics, but also the mechanism of charge transfer reaction. As a pronounced example, the reduction of Cu(II)–glycine complexes [1] may be referred to. The transfer of the first electron is known to be a rate-determining step for most of Cu(II)-containing solutions, and the glycine system is not an exception. However, it was found [1] that the transfer of the second electron to an intermediate product containing Cu(I) becomes a rate-determining step at a surface covered with cuprous oxide. Sufficiently thin oxide layers made it possible to characterize this process quantitatively by equations of formal electrochemical kinetics, but such a procedure failed when surface layers were considerably thicker, as, *e.g.*, in the case of Cu|Cu(II) – β -alanine system [2].

On the other hand, oxide layers developed in electrochemical systems are interesting by themselves, because their properties may be essentially different from those known for monocrystals or polycrystalline compacts. The latter are known as sub-

stances exhibiting *p*-type semiconductor properties and, therefore, sensitive to optical perturbation. However, quite often electrochemically formed Cu₂O layers display the so-called ‘anomalous’ *n*-type conductivity (see Refs. [3–6] and references cited therein). Besides, oxide layers were found to be liable to photocorrosion. Their instability under illumination conditions has been substantiated theoretically [7] and confirmed by pH probing [8] and EQCM data [6, 9].

An analysis of equilibrium characteristics of systems involving Cu(II) complexes made it possible to construct phase diagrams [10,] indicating, similarly to the Pourbaix ones, the regions where cuprous oxide is thermodynamically stable. According to [11, 12], the most favourable conditions for Cu₂O formation are conferred in the systems of low complexation degree. The irreversible reduction of oxide layers occurring at sufficiently high cathodic polarizations has been evidenced by voltammetric [11–13] and EQCM [14] data. This process manifests itself in the onset of well-defined current peaks linearly dependent on the potential sweep rate [11]. The latter result shows that the properties of cuprous oxide are more typical of adsorbed polylayers than of Cu₂O phase.

Due to moderately stable Cu(II)-glycolate complexes, the probability of Cu₂O formation in this

system is quite high as confirmed by the data given in [12]. At the same time, potentiometric and voltammetric investigations of acidic Cu(II) solutions ($\text{pH} < 4$) containing hydroxyacetic (glycolic) acid have shown [15] that well-defined current peaks observed at *ca.* -0.7 V (SHE) cannot be attributed to Cu_2O reduction due to their quite different kinetic characteristics. Similar in appearance current peaks have been also observed for acidic tartrate solutions [16]. According to [15], the electroreduction of hydronium ions proceeds in this case involving glycolic acid as labile donor of protons. Since the both above processes can occur within a similar range of potentials (-0.75 – -0.85 V) the revealing of their nature is among the problems to be solved generally. A response of the system to optical perturbation may serve for this purpose, as a very sensitive method for surface oxide detection.

The present paper deals with investigation of photoelectrochemical properties of the $\text{Cu}|\text{Cu(II)} - \text{glycolic acid}$ system in an effort to educe the formation conditions of copper oxides on the electrode surface.

EXPERIMENTAL

The study solutions contained 0.01 M CuSO_4 , 0.04 M glycolic acid and 0.3 M K_2SO_4 as a supporting electrolyte. Analytical-grade salts were purified by means of recrystallization. Required pH was adjusted by adding high purity H_2SO_4 or KOH. Thrice-distilled water was used for the preparation of solutions. A pure argon stream was passed through the solutions for 0.5 h before the experiments.

A Pt disc (1 cm² in area) fused into a glass holder served as the substrate for the working electrode. It was plated at a current density of 10 mA cm⁻² with a 5 – 7 μm thick copper layer in the solution containing (g dm⁻³): $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O} - 125$, H_2SO_4 ($d = 1.84$ g cm⁻³) – 50 . The working electrode was rinsed with water, immediately immersed into the deaerated solution and kept in it for the controlled exposure time τ .

A three-electrode cell with a quartz window was used in the experiments. Electrode potentials were measured with respect to $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat})$ reference electrode and were converted to the standard hydrogen scale. Cyclic voltammetric characteristics were recorded at a potential sweep rate of 10 mV s⁻¹ using a PI-50-1 potentiostat (Russia). All experiments were performed at 20 ± 1 °C.

A 150 W halogen lamp with chopped optical perturbation was used. To absorb the IR irradiation, a focused light beam was directed to the copper electrode through a 10 -cm thick water layer. The power density of polychromatic illumination was controlled

by an LM-2 device (Germany) and was estimated to equal ~ 100 mW cm⁻². Two types of measurements were employed: a) investigation of the dynamics of photopotential under open-circuit conditions; b) investigation of photocurrents under linear potential sweep conditions.

RESULTS AND DISCUSSION

The mechanism of Cu_2O formation in Cu(II)-containing solutions was discussed earlier [11–13]. According to it, the first step is the generation of intermediate Cu^+ ions due to the reaction:



Further, Cu^+ ions can act with OH^- or water molecules, yielding unstable CuOH , which in turn decomposes to Cu_2O and H_2O . The latter step is possible after a certain saturation of the solution at the electrode surface when the concentration of cuprous ions $[\text{Cu}^+]$ exceeds a definite value following from the Pourbaix diagrams [17]:

$$\log [\text{Cu}^+]_{\text{max}} = -0.84 - \text{pH} \quad (2)$$

An account for the constant $K = 6 \times 10^{-7}$ M characterizing the equilibrium (1) makes it possible to rearrange Eq. (2) and to obtain its modification:

$$\log [\text{Cu}^{2+}]_{\text{max}} = 4.54 - 2 \text{pH} \quad (3)$$

Judging from [13], the Cu_2O formation is quite a fast process the rate of which is eventually controlled by $[\text{Cu}^{2+}]$ and pH. Data on the stability constants of Cu(II)-glycollate complexes available in the literature [18] and obtained in [15] show that the complexation degree of this system may be classified as moderate. Using material balance equations, values of stability constants specified in [15] and Eq. (2) we found that Cu_2O phase layers become thermodynamically stable when pH exceeds 3.5 . Consequently, the probability of Cu_2O formation is sufficiently high even in an acidic medium. Data obtained under open-circuit conditions confirm this prediction: photopotentials of some hundred mV can be generated from Cu electrodes exposed to the solutions for a rather short time. A sharp E decrease induced by a light beam perturbation (Fig. 1) is indicative of n -type conductivity of developed surface layers. The observed phenomena are in agreement with potentiometric data reported in [12].

The formation of n - Cu_2O assumes positive photocurrents to be generated. This actually takes place at comparatively low cathodic polarizations. Be-

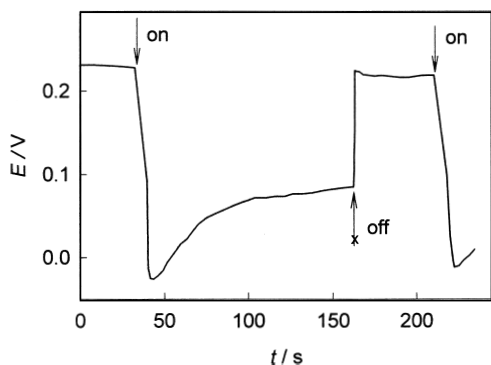


Fig. 1. Dynamics of open-circuit Cu electrode potential E obtained under chopped illumination conditions for solutions containing 0.01 M Cu(II) and 0.04 M glycolic acid at pH 5.9. Exposure time $\tau = 6$ min

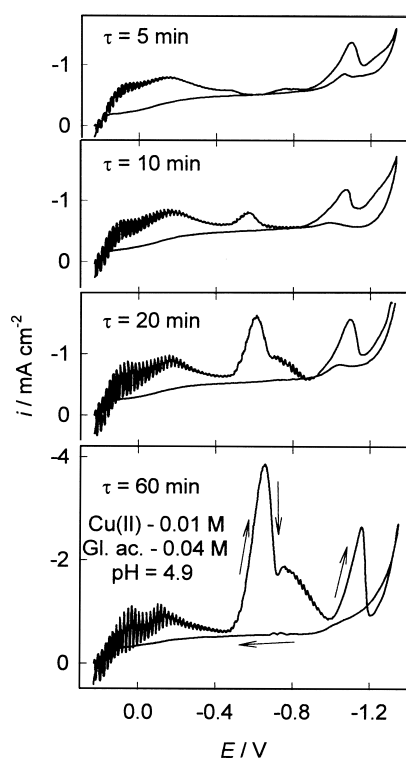


Fig. 2. Cyclic voltammograms obtained under chopped illumination conditions for solutions containing 0.01 M Cu(II) and 0.04 M glycolic acid at pH 4.9. Exposure time τ is indicated at the curves

sides, the highest level of photoresponse is characteristic at $E > -0.5$ V (Figs. 2 and 3).

The occurrence of two well-defined current peaks might be qualified as a peculiarity of the system. Essentially, this concerns the right maximum (i_{p2}), because the first current peak (i_{p1}) located at $E_p \approx -0.7$ V is not unique: similar peaks have been also observed in other systems [9, 11, 13, 14, 19, 20]. Specifically, the origin and properties of i_p arising in Cu|Cu(II), ethylenediamine system have been discussed in [11]. According to the cited papers, the

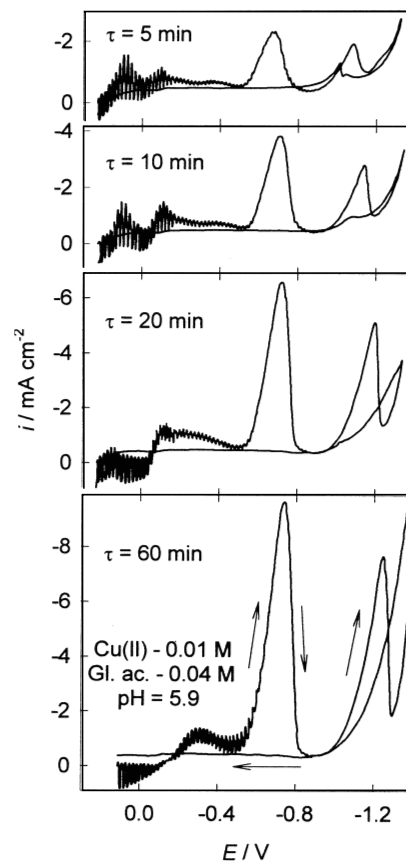


Fig. 3. The same as in Fig. 2 at pH 5.9

reduction of Cu_2O gives rise to a current peak in this potential region. A similar statement seems to be also acceptable in the case of the system under discussion. However, this should be done with some reservation, assuming that oxides of different nature are reduced at different i_p . It should be stated, firstly, that the well-defined current peaks observed at the direct potential sweep actually disappear when the reverse potential scan is applied (Figs. 2 and 3). This fact gives grounds to conclude that the electrode surface at $E < -1.2$ becomes considerably reduced and does not contain perceptible amounts of oxides. In accordance with this presumption, no photoresponse was detected on the reverse voltammogram. The second point that is worth mentioning lies in the fact that a weaker but quite detectable photoresponse can be observed at a direct scan between both current peaks. Thereby, only a certain part of the oxide layer is most probably reduced at i_{p1} . As judged from the position of this peak and specific features of photoresponse, Cu_2O could be the most likely substance for this process.

Some properties of both i_{p1} and i_{p2} are similar. Their heights increase with the exposure time τ ; besides, i_p are higher in less acidic solutions where conditions for oxide formation are more favourable. It can be seen from the data given in Fig. 4 that

variations of i_p with τ are actually linear within a rather large initial period of oxide formation. Slopes of these lines may serve as a measure for the rate of respective oxidation processes. For instance, it follows from the data in Fig. 4 that the formation rate of oxide (which is capable of reducing at i_{p1}) is ~ 6 times higher at pH 5.9 as compared with that at pH 4.9.

A sufficiently precise integration of the first voltammetric maximum was available and made it possible to estimate the charge Q_1 used in this potential region. The results show that Q_1 varies with τ in the same manner as i_{p1} . An average value of Q_1/τ established for the linear region is equal to 15 and 80 $\mu\text{C cm}^{-2} \text{s}^{-1}$ at pH 4.9 and 5.9, respectively. In the case of Cu_2O formed in an ethylenediamine system, this quantity is equal to 25 $\mu\text{C cm}^{-2} \text{s}^{-1}$ (pH 5.3) [11]. As one can see, all three charge values regularly vary with pH.

The nature of processes taking place at -1.2 V is not yet clear. The surface layers that are reduced in this region should have a composition different from that of cuprous oxide. XPS investigations have shown the deviations from Cu_2O stoichiometry, and oxygen content was found to diminish with the layer thickness [19, 20]. The layer enriched in oxygen, with the dominant p -type conductivity, is typical of the oxide|solution interface where the oxidation state of copper approaches 2 [19]. The properties of this interface should manifest themselves when oxide layers are thin enough. Such is indeed the case for low τ and pH values (see curve for $\tau = 5 \text{ min}$ in Fig. 2): the second current peak develops first, whereas i_{p1} is obscure.

Variations of photoresponse level with exposure time are also more prominent in such conditions. Increase in photocurrent with τ takes place at pH 4.9 up to $\tau = 20 \text{ min}$ (Fig. 2), but this is not the case for pH 5.9 (Fig. 3) when significantly thicker layers are formed. According to [21], the diffusion

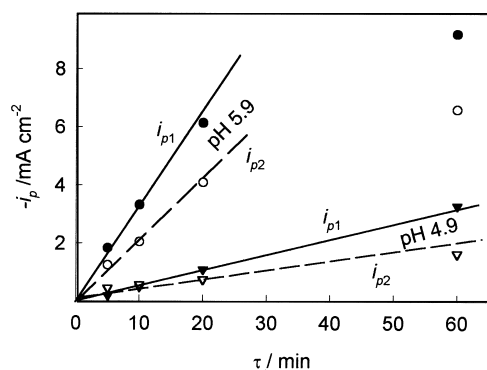


Fig. 4. Dependences of the first (i_{p1}) and the second (i_{p2}) peak currents on exposure time τ . Values of solutions pH are indicated at the curves

length of the minority charge carriers in the conduction band is in the range of 10–100 nm, and the estimated width of the charge separation at the Cu_2O |electrolyte interface is 20 nm. A rough estimation of Cu_2O layer thickness, based on Q_1/τ quantities given above, yields $\sim 40 \text{ nm}$ for pH 4.9 and $\tau = 20 \text{ min}$. Considering that the layers developed at pH 5.9 are 6-fold thicker, it is easy to establish conditions under which only part of the layers can be excited by light. The estimations performed are consistent with experimental observations.

Finally, the effects relating to the type of photoresponse and its changes need some discussion. In contrast to cuprous oxide, CuO formed in electrochemical systems is generally a p -type semiconductor. Therefore, $p \rightarrow n$ or $n \rightarrow p$ transitions are possible in electrochemical systems on somewhat different occasions. One of them is caused by the irregular composition of oxide layers with different conductivity at the metal|oxide and oxide|solution interfaces. The positive photopotential was observed at $\tau < 2 \text{ min}$ in the case of Cu(II) solutions containing glycolic acid followed by $p \rightarrow n$ transition [12]. Another case is the inversion of the photocurrent sign taking place at a certain potential E_{inv} . Since the photocurrent at this potential is equal to zero, E_{inv} is usually treated as a flat-band potential. Such $n \rightarrow p$ transition is also observed in the system under discussion (Fig. 5). E_{inv} was found to depend on solution pH and exposure time τ . A shift of E_{inv} to more negative values is observed in both cases. The first effect is typical of oxide or hydroxide layers that may be in chemical equilibrium with OH^- ions. The second one seems to arise from the mentioned above irregularities in the oxide layer, the predominant properties of which vary with its thickness.

In conclusion, it must be said that the occurrence of two voltammetric maxima can be to a certain extent related with the nature of a ligand that can-

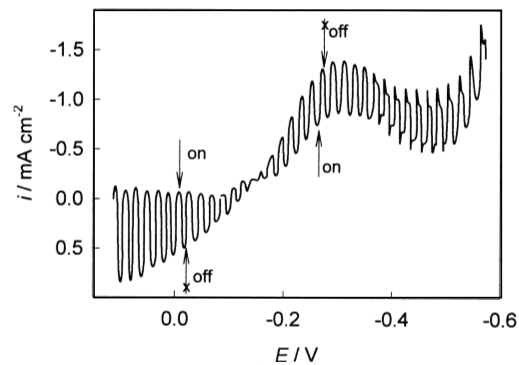


Fig. 5. The region of the voltammogram obtained at pH 5.9 and $\tau = 1 \text{ h}$ where photocurrent inversion is observed

not be classified as a reducing agent. Therefore Cu(II)-containing oxides can be rather stable. Conversely, no double peaks were observed in the case of such ligands as amino acids or ethylenediamine containing NH_2 -groups. Some aspects concerning the structure of oxide layers are intended to be improved by future investigations.

CONCLUSIONS

1. Oxide layers spontaneously developed in Cu|Cu(II) – glycolic acid system exhibit semiconductor properties and are sensitive to light beam perturbation. Negative photopotentials observed under open-circuit conditions and positive photocurrents detected at moderate cathodic polarizations are indicative of n -type conductivity of surface layers.

2. Two current peaks observed on voltammograms at ca. -0.7 and -1.1 V are attributed to the reduction of different substances, Cu_2O and unidentified copper oxide, respectively. The estimated rate of Cu_2O formation is 2 nm min^{-1} at pH 4.9 and 6-fold higher at pH 5.9.

3. An inversion of the photocurrent sign resulting in $n \rightarrow p$ transition was found to occur at a certain E_{inv} depending on oxide layer thickness and solution pH.

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Oksidiniø sluoksniø, susidarantiø ant vario elektrodo Cu(II) ir glikolio rūgšties tirpaluose, fotoatsakas

Santrauka

Oksidø sluoksniø, susidarantiø savaiminiø procesø metu sistemoje Cu|Cu(II), glikolio rūgšties, buvo tiriama pertraukiamo apdviavimo sąlygomis, taikant potenciometrinius bei voltamperimetrinius metodus. Tai, kad fotopotencialas, uþfiksuotas atviros grandinės sąlygomis, yra neigiamas, o fotosrovė, uþregistruota nedidelio katodiniø poliarizacijø srityje, yra teigiama, parodo, kad paviršiniai oksidai turi n tipo laidumą. Sistemos ypatybė reikia laikyti tą faktà, kad voltamperogramos turi dvi gerai iðreikðtas smailes. Pirmoji ið jø, esanti $-0,7$ V potencialo aplinkoje, priskirtina Cu_2O redukcijai. Ið ðios smailės analizės seka, kad Cu_2O susidarymo greitis yra apie 2 nm/min , kai $\text{pH} = 4,9$, ir 6 kartus didesnis, kai $\text{pH} = 5,9$. Manoma, kad antrąjã smailę sąlygoja paviršiniø Cu(II) sluoksniø, praturtintø deguonimi, redukcija. Tam tikro potencialo E_{inv} aplinkoje aptikta fotosrovės þenklo inversija, sąlygojanti $n \rightarrow p$ perėjimã. E_{inv} priklauso nuo oksidiniø sluoksniø storio ir tirpalo pH.