

Photoelectrochemical properties of oxide layers developed on copper electrode in Cu(II) solutions containing glycolic acid and small amounts of chloride

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The effect of small (micromolar) amounts of chloride on photoelectrochemical properties of oxide layers spontaneously developed in Cu|Cu(II) – glycolic acid system at pH 5.85 was investigated. Potentiometric data obtained under chopped illumination conditions show negative open-circuit photopotentials that are typical of *n*-type Cu₂O. The level of the photopotential was found to increase with the intensity and quantum energy of disturbing illumination. The estimated band gap of *n*-Cu₂O (~2.2 eV) actually coincides with that obtained for crystalline *p*-Cu₂O. Chlorides enhance formation of Cu₂O, increasing the height of a characteristic current peak. Positive photocurrents were detected at moderate cathodic polarizations. The inversion of the photocurrent sign resulting in *n*→*p* transition was found to occur at a certain potential that depends on oxide layer thickness.

Key words: copper, glycolic acid, chloride, complexes, oxide layers, photo-response

INTRODUCTION

Copper (I) oxide layers have been found to develop spontaneously in different electrochemical systems due to an interaction between Cu⁺ and OH⁻ ions. One case of Cu₂O formation is associated with the corrosion of copper in naturally aerated solutions [1-10], where Cu⁺ ions are produced as intermediate products of corrosion. However, the most pronounced conditions for Cu₂O formation arise in the systems containing Cu(II) complexes [11–15] which are stable in the wide pH region. In this case, the net reaction $\text{Cu} + \text{Cu}^{2+} + \text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$ occurs.

Primarily, oxide layers developed in electrochemical systems are interesting by themselves because they often display the properties that are not typical of common monocrystals or polycrystalline compacts. As an example, the so-called ‘anomalous’ *n*-type conductivity should be mentioned (see Refs. [16–20] and references cited therein). On the other hand, the formation of surface oxides is the phenomenon related to the reduction of Cu(II) complexes. Therefore, such layers 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 [11] may be referred to. This process may be described using equations of formal electrochemical kinetics, since sufficiently

thin oxide layers are formed in this case. However, such procedure failed when the surface layers were considerably thicker, as, e.g., in the case of the Cu|Cu(II), β-alanine system [12].

Irreversible reduction of oxide layers occurs at sufficiently high cathodic polarizations [13–15, 16, 21]. This process manifests itself in the onset of well-defined current peaks that linearly depend on the potential sweep rate [13]. The latter result shows that the properties of cuprous oxide are more typical of adsorbed polylayers than of Cu₂O phase. Besides, the oxide layers were found to be liable to photocorrosion [16, 20, 22, 23].

Analysis of equilibrium characteristics of the systems involving Cu(II) complexes has shown [14] that the most favorable conditions for Cu₂O formation can be conferred in solutions of a low complexation degree. 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 [14, 24]. The further investigations [16, 24] have shown that negative open-circuit photopotentials and positive photocurrents are detected at moderate cathodic polarizations, which is indicative of *n*-type conductivity of the surface oxides. The peculiarity of this system is the occurrence of two well-defined voltammetric peaks at sufficiently high cathodic polarizations. The first of them observed at ca -0.7 V (NHE) has been attributed [24] to Cu₂O reduction. The second peak has been supposed

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to be conditioned by electroreduction of oxygen-enriched surface layers involving Cu(II).

Among various ligands, halides are also known as surface-active ions capable of forming different Cu(I) complexes. It is evident that the state of the intermediate Cu^+ should play a significant role in the formation of oxide layers. The present paper deals with the further investigations of oxide layers developed in Cu(II)–glycolic acid solutions involving small amounts of chloride. Both mono- and polychromatic light perturbation is used to study the optical response of the system.

EXPERIMENTAL

The equipment used was similar to that described in Ref. [24]. The study solutions were prepared using tri-distilled water. They were deaerated with a pure argon stream passed through the solutions for 0.5 h. Analytical-grade KCl was added to the solutions containing 0.01 M CuSO_4 , 0.04 M glycolic acid and 0.3 M K_2SO_4 as a supporting electrolyte. The required pH (5.85 ± 0.05) was adjusted by adding KOH of high purity.

A Pt disc (1 cm^2 in area) was plated at current density of 10 mA cm^{-2} with 5–7 mm thick copper layer in the solution containing (g dm^{-3}): $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ – 125, H_2SO_4 ($d = 1.84 \text{ g cm}^{-3}$) – 50. The prepared working electrode was rinsed with water, immediately immersed into the deaerated solution and kept in it for the controlled exposure time τ of to 15 min.

Cyclic voltammetric characteristics were recorded at the potential sweep rate of 10 mV s^{-1} using a PI-50-1 potentiostat (Russia). 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. All experiments were performed at 20 ± 1 °C.

A chopped optical perturbation was directed from 150 W halogen lamp onto the electrode through a quartz window in a three-electrode cell. Therefore, the IR irradiation was absorbed in a 10-cm thick water layer. The power density of polychromatic illumination was controlled by an LM-2 device (Germany) and was estimated to be equal to $\sim 90 \text{ mW cm}^{-2}$. A monochromatic illumination with the wavelength λ was obtained using special light filters that lowered the power density by three orders of magnitude. The quantum energy $E = h\nu$ was calculated using the ratio of light rate in vacuum: $c = \nu\lambda$. Photopotentials under open-circuit conditions and photocurrents under linear potential sweep conditions were employed in the present research.

RESULTS AND DISCUSSION

The oxide layers formed in weakly acidic solutions (pH 5.85) show quite a high optical activity. This may be seen from the results of the experiments carried out under open-circuit conditions (Fig. 1) where an open-circuit potential (E_{oc}) is chosen as a datum-level. A

sharp and deep decrease in electrode potential, induced by a light beam perturbation, is indicative of n -type conductivity of the developed surface layers. This kind of conductivity is typical of most electrochemical systems and is in accordance with previously obtained data [14, 16, 24].

As may be seen in Fig. 1, the level of photoresponse depends on power density (N) of the perturbing light: ΔE increases gradually with N , approaching no limit. Such effect is possible in the range of sufficiently low light intensities when the saturation of semiconductor layer with generated charge carriers is not achieved.

More detailed information concerning the level of photoresponse may be gained from the data in Figs. 2 and 3. There the photopotential (E_{ph}) is defined as a limiting (maximum) ΔE value observed over a sufficiently long optical illumination. The increase in the absolute value of photopotential with N is observed at any wavelengths of the illumination, however, this

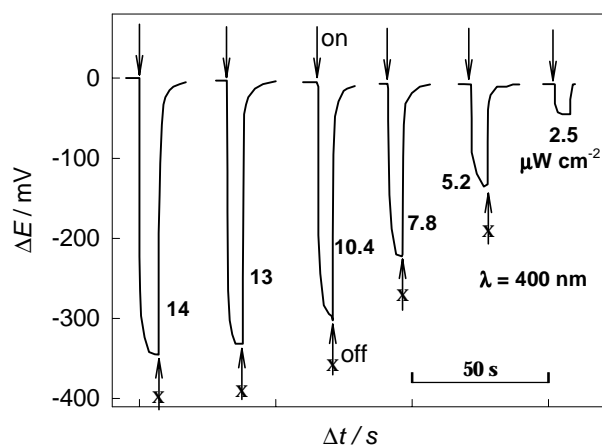


Fig. 1. Pulses of photoresponse obtained under open-circuit conditions at different power densities of perturbing light, as indicated by the curves. Corresponding arrows show the moments at which the light is switched on or switched off

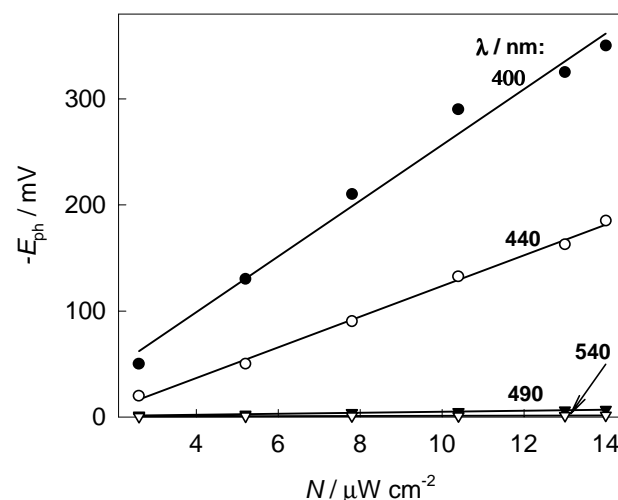


Fig. 2. Dependencies of photopotential on power density of applied illumination. Wavelengths of monochromatic light are indicated at the curves

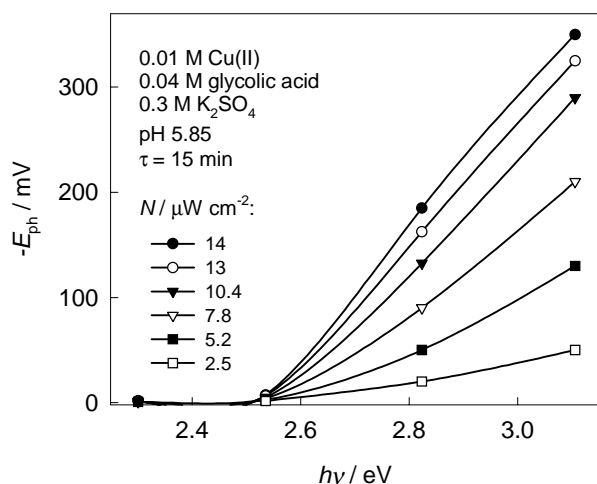


Fig. 3. Dependencies of photo-potential on quantum energy established at different power densities of applied illumination. Data obtained for Cu electrode exposed for 15 min in the solution of the indicated composition

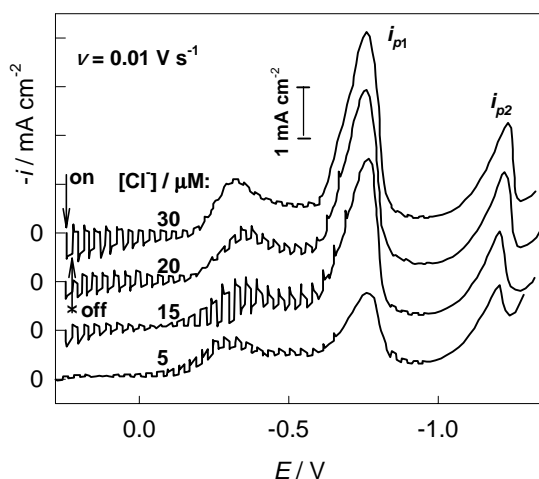


Fig. 4. Cathodic voltammograms recorded under chopped illumination conditions. Polychromatic light, $N \approx 90 W cm^{-2}$. The amounts of the added chlorides are given in respective curves

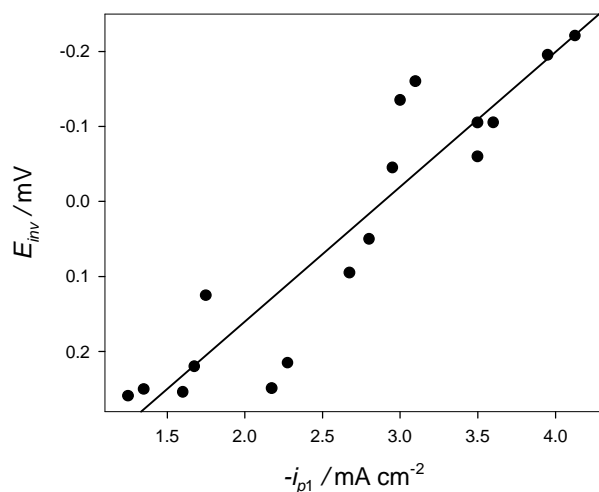


Fig. 5. Correlation between the inversion potential and height of the first peak current. Chloride concentration, varying from 5 to 165 mM, was used as a parameter. Polychromatic irradiation, $N \sim 90 mW cm^{-2}$

effect is most pronounced at short λ . It may be concluded from the data shown in Fig. 3 that the onset of the photoeffects under discussion takes place at a quantum energy of approximately 2.2 eV. Consequently, a band gap of $n-Cu_2O$ is characterized by the same value as that reported for 'normal' $p-Cu_2O$ [18].

It is common knowledge that the sign of the photocurrent (i_{ph}) should be opposite to that of photopotential. Indeed, we have observed positive (anodic) the photocurrents at comparatively low cathodic polarizations in halide-free solutions as well as in the solutions containing small quantities of chloride. Voltammograms recorded under chopped illumination conditions show (Fig. 4) that the photoresponse is most pronounced within quite a large region of cathodic potentials, viz. from E_{oc} up to $E \approx -0.7 V$ where the first current peak of Cu_2O reduction (i_{p1}) is located. The main part of the oxide layer is reduced at i_{p1} , but a certain quantity of the oxide remains on the electrode. This residual is able to produce a weaker but quite detectable photocurrent at the further scan of the potential, while the second current peak (i_{p2}) is reached. The origin of the latter maximum has been discussed in Ref. [24]; nevertheless, some problems remain to be solved.

The addition of small (micromolar) quantities of chloride results in the formation of the oxide layers that have somewhat different photoelectrochemical characteristics. Foremost, the height of i_{p1} grows with chloride concentration. Since i_{p1} may serve as a measure of Cu_2O amount, it must be concluded that chlorides accelerate Cu_2O formation. Secondly, the level of i_{ph} increases with $[Cl^-]$, but this regularity is valid only within a certain range of cathodic polarizations as long as positive i_{ph} is generated (Fig. 4). This takes place from E_{oc} up to the inversion potential E_{inv} where i_{ph} becomes negligible and later changes its sign. Such phenomenon is often observed in other systems. E_{inv} is usually treated as a flat-band potential; it depends on different factors including power density of the perturbing light, solution pH and thickness of the layers [14, 16, 19, 20, 22, 23]. According to the obtained data, the negative shift of E_{inv} from 0.125 to $-0.22 V$ is observed when $[Cl^-]$ increases from 5 to 30 μM . Thereby, chloride concentration should be also added into the list of the above named factors.

It should be noted that the regular changes of E_{inv} or i_{p1} with $[Cl^-]$ snarl up at higher $[Cl^-]$ ($> 30 \mu M$). According to Ref. [16], the equilibrium concentration of Cu^{2+} ions in the absence of chlorides is 2.7 mM. The maximum concentration of Cu^+ ions that could be generated by $Cu^{2+} + Cu \rightarrow 2 Cu^+$ cannot exceed $\sim 1\%$ of $[Cu^{2+}]$ amounting to 20–30 μM . Thus, irregularities of chloride action arise when $[Cl^-]$ becomes higher than $[Cu^+]$. However, this disadvantage does not prevent from making some correlations using $[Cl^-]$ as a parameter; one of them is shown in Fig. 5.

Since i_{p1} determine the amount of the reduced Cu_2O , the data in Fig. 5 could be treated as a correlation

between the inversion potential and the thickness of the oxide layer. Thus, thicker oxide layers are characterized by more negative potentials at which the $n \rightarrow p$ transition takes place. This effect seems to arise from the non-uniform structure of the oxide layer [16], the predominant properties of which varies with its thickness. Similar $n \rightarrow p$ transitions have also been observed in chloride-free solutions [24]: E_{inv} was found to depend on solution pH and exposure time τ . A shift of E_{inv} to more negative values was observed in both cases.

CONCLUSIONS

1. Negative photopotentials observed under the open-circuit conditions and positive photocurrents detected at moderate cathodic polarizations are indicative of n -type conductivity of the surface Cu_2O layers spontaneously developed in the $\text{Cu}|\text{Cu(II)}$ – glycolic acid system both in the absence and in the presence of chloride ions.

2. The level of the photopotential increases with the intensity and quantum energy of disturbing illumination. The estimated band gap of $n\text{-Cu}_2\text{O}$ (~2.2 eV) actually coincides with that obtained for crystalline $p\text{-Cu}_2\text{O}$.

3. Small (micromolar) amounts of chlorides enhance the formation of Cu_2O , increasing the height of the characteristic current peak and shifting the inversion potential to more negative values.

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References

- W. H. Smyrl, *Comprehensive Treatise of Electrochemistry*. J. O'M. Bockris and R.E. White (Eds.), Vol. 4, Ch. 2. Olenum Press, New York, 1981. P. 97.
- F. di Quarto, S. Piazza and C. Sunseri, *Electrochim. Acta*, **30**, 315 (1985).
- B. Millet, G. Fiaud, C. Hinner and E. M. M. Sutter, *Corr. Sci.*, **37**, 1903 (1995).
- Y. Feng, K.-S. Siow, W.-K. Teo, K.-L. Tan and A.-K. Hsieh, *Corrosion*, **53**, 389 (1997).
- A. G. Brolo, M.L.A. Temperini and S. M. L. Agostinho, *Electrochim. Acta*, **44**, 559 (1998).
- R. Babič, M. Metikoš-Hukovič and M. Lončar, *Electrochim. Acta*, **44**, 2413 (1999).
- J. O. Zerbino, *Electrochim. Acta*, **45**, 819 (1999).
- N. Bellakhal, K. Draou, A. Addou and J.L. Brisset, *J. Appl. Electrochem.*, **30**, 595 (2000).
- M. Metikoš-Hukovič, R. Babič, and I. Paič, *J. Appl. Electrochem.*, **30**, 617 (2000).
- P. Kalinauskas, I. Valsiūnas, A. Survila, and V. Jasulaitienė, *Materials Sci.*, **7**, 137 (2001).
- A. Survila and V. Uksienė, *Electrochim. Acta*, **37**, 745 (1992).
- A. Survila and V. Uksienė, *Sov. Electrochem.*, **29**, 202 (1993).
- A. Survila, S. Kanpeckaitė and A. Survilienė, *J. Electroanal. Chem.*, **501**, 151 (2001).
- A. Survila, P. Kalinauskas and I. Valsiūnas, *Russ. J. Electrochem.*, **38**, 1068 (2002).
- A. Survilienė and A. Survila, *Russ. J. Electrochem.*, **38**, 1216 (2002).
- A. Survila, A. Survilienė, S. Kanpeckaitė, J. Būdienė, P. Kalinauskas, G. Stalnionis and A. Sudavičius, *J. Electroanal. Chem.*, **582**, 221 (2005).
- B. Pointu, H. Braizaz, P. Poncet and J. Rousseau, *J. Electroanal. Chem.*, **122**, 111 (1981); **151**, 65 (1983).
- A. Aruchamy and A. Fujishima, *J. Electroanal. Chem.*, **266**, 397 (1989); **272**, 125 (1989).
- A. Survila, P. Kalinauskas and V. Uksienė, *Electrochim. Acta*, **38**, 2733 (1993).
- A. Survila, P. Kalinauskas, E. Ivaškevič and W. Kutner, *Electrochim. Acta*, **42**, 2935 (1997).
- A. Survila, A. Survilienė and G. Stalnionis, *Chemija*, **10**, 203 (1999).
- A. Survila, P. Kalinauskas and V. Uksienė, *Chemija*, **9**, 51 (1998).
- A. Survila, P. Kalinauskas and I. Valsiūnas, *Chemija*, **10**, 37 (1999).
- J. Būdienė, P. Kalinauskas and A. Survila, *Chemija*, **15**, 7 (2004).

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OKSIDINIŲ SLUOKSNIŲ, SUSIDARANČIŲ ANT VARIO ELEKTRODO Cu(II) IR GLIKOLIO RŪGŠTIES TIRPALUOSE SU MAŽAIS CHLORIDŲ KIEKIAIS, FOTOELEKTROCHEMINĖS SAVYBĖS

S a n t r a u k a

Taikant potenciometrinius bei voltamperometrinius metodus iš-tirta nedidelių (mikromoliarinių) chlorido kiekių įtaka fotoelektrocheminėms savybėms oksidinių sluoksnių, kurie susidaro savaiminių procesų metu sistemoje $\text{Cu}|\text{Cu(II)}$, glikolio rūgštis, kai pH 5,85. Potenciometriniai duomenys, gauti naudojant impulsinį apšvietimą, rodo, kad fotopotencialai, užfiksuoti atviros grandinės sąlygomis, yra neigiami; tai yra būdinga n -tipo Cu_2O . Aptikta, kad fotopotencialo lygis auga, didėjant žadinančios spinduliuotės intensyvumui ir kvanto energijai. Įvertintas $n\text{-Cu}_2\text{O}$ uždraustos zonos plotis (~2,2 eV) praktiškai sutampa su dydžiu, gautu $p\text{-Cu}_2\text{O}$ kristalams. Maži (mikromoliariniai) chloridų kiekiai skatina Cu_2O susidarymą, didindami būdingos srovės smailės aukštį. Fotosrovė, užregistruota nedidelių katodinių poliarizacijų srityje, yra teigiama. Tam tikro inversijos potencialo E_{inv} , kuris priklauso nuo oksidinio sluoksnio storio, aplinkoje aptikta fotosrovės ženklo inversija, sąlygojanti $n \rightarrow p$ perėjimą.