Effect of Mo(VI) and W(VI) on photoelectrochemical properties of oxide layers developed on copper electrode

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Photosensitive oxide layers were found to develop on a copper electrode exposed to a naturally aerated 0.3 M K_2SO_4 solution containing 0.01 M molybdate or tungstate. Slow and weak variations of the open-circuit potential arise under chopped illumination conditions in solutions containing either Mo(VI) or W(VI) at pH 5. These phenomena cannot be treated as photoelectrochemical effects and seem to be of thermal nature. Well-defined pulses of negative photopotential ranging up to –150 mV develop in Mo(VI)-containing solutions at pH 7. On the contrary, the onset of positive photopotential takes place in W(VI) solutions at the same pH. The oxide layers developed in alkaline (pH 10) medium exhibit *p*-type conductivity for both systems. The $n \rightarrow p$ transition occurs when the equilibrium potential of Mo(VI)|Mo(IV) or W(VI)|W(IV) couples is *ca* –0.6 V.

Key words: copper, corrosion, cuprous oxide, photoresponse, molybdate, tungstate

INTRODUCTION

Corrosion of copper in naturally aerated solutions results in the formation of surface layers involving copper oxides, which display the properties of semiconductors and are photosensitive. Cu_2O monocrystals and polycrystalline compacts are known as *p*-type semiconductors [1]. However, different cuprous oxides (*p*-Cu_2O or *n*-Cu_2O) may be formed depending on pH and anion nature [2–5]. The formation of a duplex oxide layer with two semiconducting components of different stoichiometries has been reported in [3, 5]. Besides, a $p \rightarrow n$ transition as a function of immersion time has been observed in sulphate solutions containing Cl^- [2]. The same effect was also discovered for oxide layers formed in sodium sulphate solutions [6].

This paper deals with a further investigation of the photoelectrochemical behaviour of copper oxides formed in electrochemical systems. Solutions containing Mo(VI) or W(VI) and K_2SO_4 are under discussion.

EXPERIMENTAL

A three-electrode electrochemical cell with a quartz window was used in the experiments. A platinum plate (1 cm^2 in area) fused into a glass holder served as the substrate for the working electrode. It was plated with a 5 μm thick copper layer in acid sulphate solution. A platinum plate of 5 cm^2 served as an auxiliary electrode and the saturated Ag|AgCl, KCl electrode was used as reference. All values of potentials are given with respect to the SHE.

Solutions were prepared using triply distilled water and K_2SO_4 of high purity. All experiments were carried out at 20 ± 1 °C with naturally aerated 0.3 M K_2SO_4 solutions containing 0.01 M K_2MoO_4 or K_2WO_4 at different pH which was adjusted by adding H_2SO_4 or KOH. Prior to the experiments, the working electrode was exposed to the solution for the controlled time τ.

A 150 W halogen lamp was used for optical perturbation. To absorb the IR irradiation, the focused light beam was directed to the copper electrode through a 6 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 *ca* 120 mW cm^{-2}.

The voltammograms were recorded at a 10 mV s^{-1} potential sweep rate after each photoelectrochemical experiment, using a PI-50–1.1 potentiostat and H-307–1 recorder (Russia).

RESULTS AND DISCUSSION

Photoeffects occurring in the Cu|K_2SO_4 system are rather wellpronounced. Their level depends both on
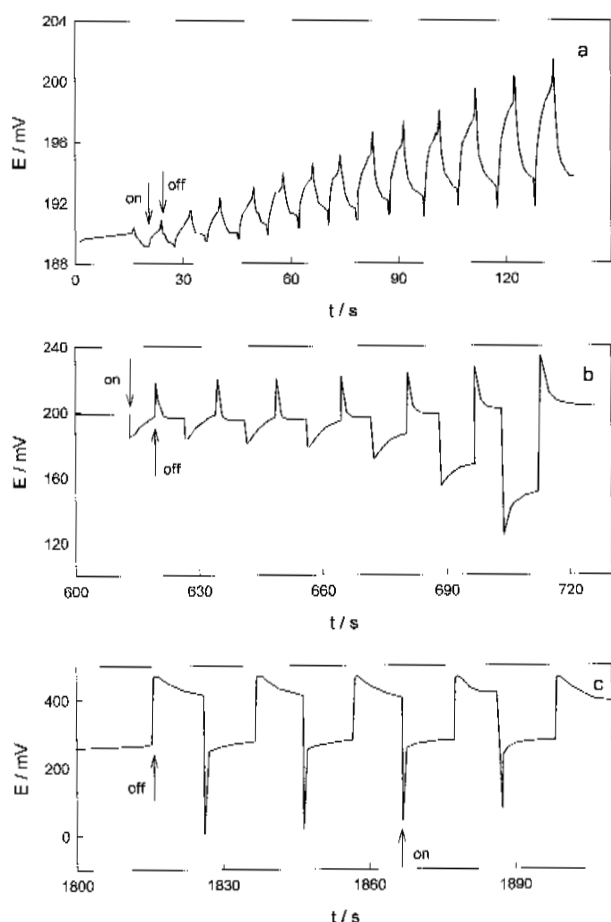
Fig. 1. Potential transients obtained under chopped illumination conditions in 0.3 M K_2SO_4 solutions at pH 5. Exposure time (min): *a* – 0, *b* – 10, *c* – 30

the solution pH and exposure time τ. The development of photoresponse may be seen from the data shown in Fig. 1. Potential pulses take the characteristic shape. An abrupt potential drop immediately follows light beam perturbation and is indicative of *n*-type conductivity. Then potential variations become slower and seem to arise from diffusion processes in the solution [6]. Similar changes of opposite direction are observed after switching off the illumination.

A comparatively intense development of oxide layers gives rise to a high (*ca* –200 mV) photopotential (E_{ph}), which is attained after 30 min of exposure (Fig. 1c). Similar data were also obtained in neutral media (pH 7) with weaker E_{ph} (*ca* –40 mV). In contrast, positive E_{ph} not exceeding 2 mV are typical of alkaline (pH 10) solutions. In general, the same effects have been found to occur in the Cu|Na_2SO_4 system (see [6] for details).

As is well known, molybdenum and tungsten can form substances with a rather great variety of oxidation states. Some data on standard potentials (E^0) available in literature [7] make it possible to estimate the equilibrium potentials (E_{eq}) of redox processes involving Mo(VI) or W(VI), which are commonly treated as oxidants. Results obtained on the basis of Nernst equation are listed in Table. As follows, open-circuit potentials (E_{oc}) of Cu electrodes in solutions under investigation take the values of *ca* 0.2 V. Since E_{eq} (Table) are significantly more negative, the anions involving Mo(VI) or W(VI) cannot be considered as species capable of enhancing the oxidation of copper. Moreover, some inhibition of this process might be expected, as compared with similar data shown in Fig. 1 or obtained for Cu|Na_2SO_4 system [6] where a pronounced photoresponse has been found at pH 5.

Actually, only slow and weak variations of E_{oc} arise under chopped illumination conditions in solutions containing either Mo(VI) (Fig. 2) or W(VI) at pH 5. It is hardly probable that these phenomena could be treated as photoelectrochemical effects; they are most likely to be of thermal nature.

A pronounced photoresponse develops in neutral solutions containing Mo(VI) (Fig. 3). A progressive increase in photopotential level is seen during exposure of the Cu electrode to the solution. A negative photopotential indicating the *n*-type conductivity ranges up to –150 mV at τ = 30 min. W(VI)-containing solutions show quite a different behaviour at the same pH. No photoeffects were detected for a long time (up to *ca* 15 min) except E_{oc} variations similar to those shown in Fig. 2. Weak pulses of

N	Redox process	E^0	E_{eq} at pH:		
			5	7	10
1	$MoO_4^{2-} + 4\ H^+ + 2\ e \rightarrow MoO_2 + 2\ H_2O$	0.606	–0.03	–0.27	–0.62
2	$MoO_4^{2-} + 8\ H^+ + 3\ e \rightarrow Mo^{3+} + 4\ H_2O$	0.32			
3	$MoO_4^{2-} + 8\ H^+ + 6\ e \rightarrow Mo + 4\ H_2O$	0.394	–0.01	–0.17	–0.40
4	$WO_4^{2-} + 4\ H^+ + 2\ e \rightarrow WO_2 + 2\ H_2O$	0.218	–0.42	–0.66	–1.00
5	$WO_4^{2-} + 6\ H^+ + 4\ e \rightarrow WO + 3\ H_2O$	0.07	–0.40	–0.57	–0.83
6	$WO_4^{2-} + 8\ H^+ + 6\ e \rightarrow W + 4\ H_2O$	0.033	–0.37	–0.53	–0.76

Table. **Equilibrium potentials (E_{eq}/V) of different redox processes estimated at $c_{Mo(VI)} = c_{W(VI)} = 0.01$ M**
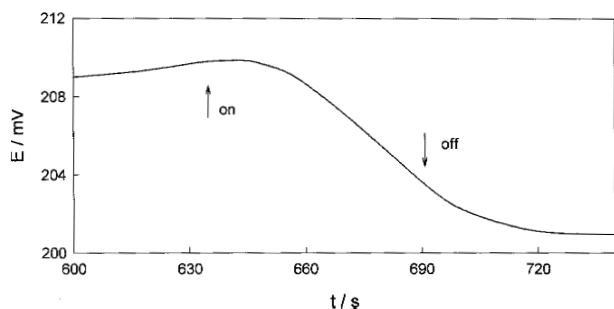
Fig. 2. Variations of electrode potential under light beam perturbation. 0.3 M K_2SO_4 solutions containing 0.01M K_2MoO_4 at pH 5.
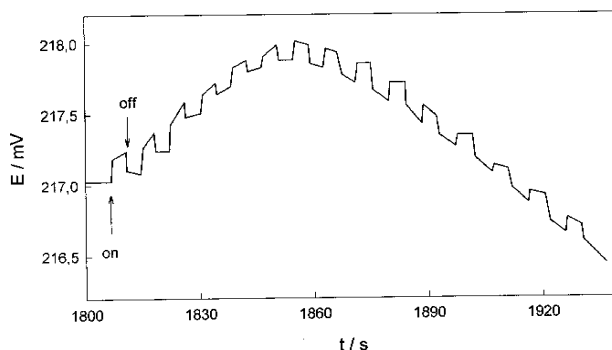

Fig. 4. Potential transients obtained under chopped illumination conditions in 0.3 M K_2SO_4 solutions containing 0.01M K_2WO_4 at pH 7
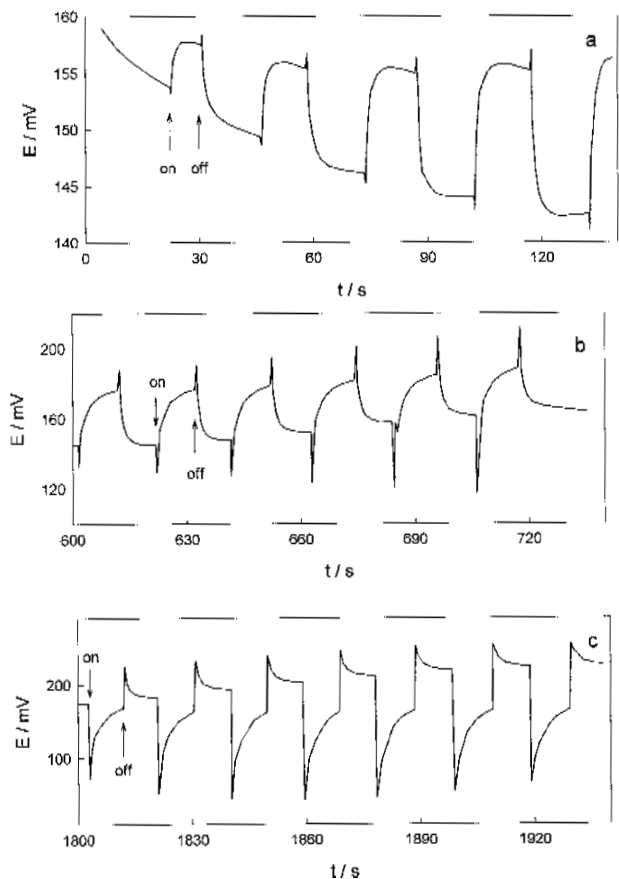

Fig. 3. Potential transients obtained under chopped illumination conditions in 0.3 M K_2SO_4 solutions containing 0.01M K_2MoO_4 at pH 7. Exposure time (min): *a* – 0, *b* – 10, *c* – 30

Fig. 5. Potential transients obtained under chopped illumination conditions in 0.3 M K_2SO_4 solutions containing 0.01M K_2MoO_4 at pH 10. Exposure time (min): *a* – 0, *b* – 10, *c* – 30.

positive photopotential accompanied by thermal effects developed latered on (Fig. 4).

A positive photoresponse is more pronounced in alkaline media, as shown in Fig. 5 for Mo(VI)-containing solution. Similar data were also obtained for W(VI) solutions, with the only difference that the level of photoresponse was half as high.

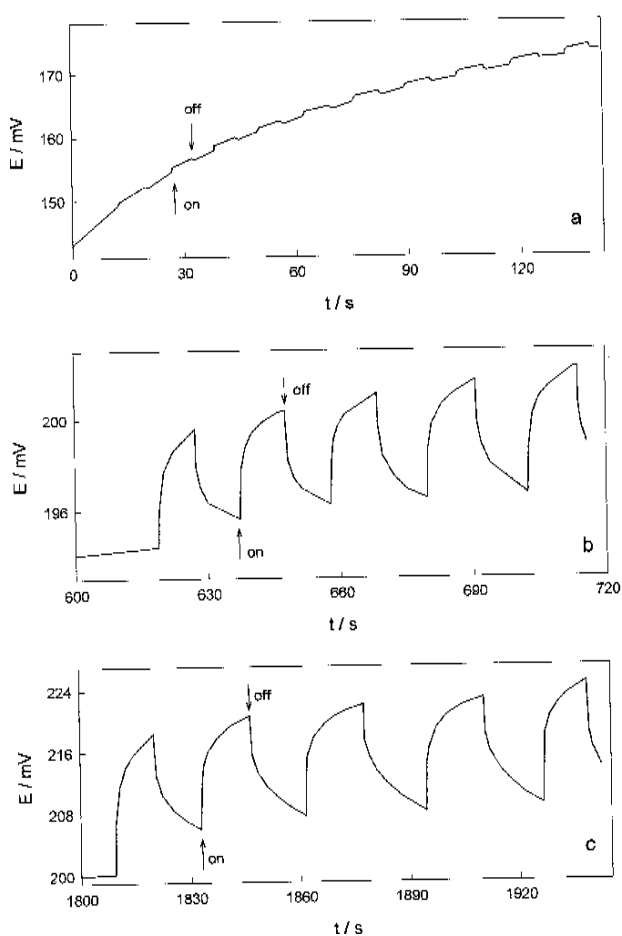Cathodic voltammograms show a certain correlation with the above data. It may be seen from a

typical example (Fig. 6) that certain maxima arise when the systems exhibit detectable photoeffects. Moreover, the height and position of the current peak depend on the photoresponse level and the type of conductivity, respectively. According to [8],
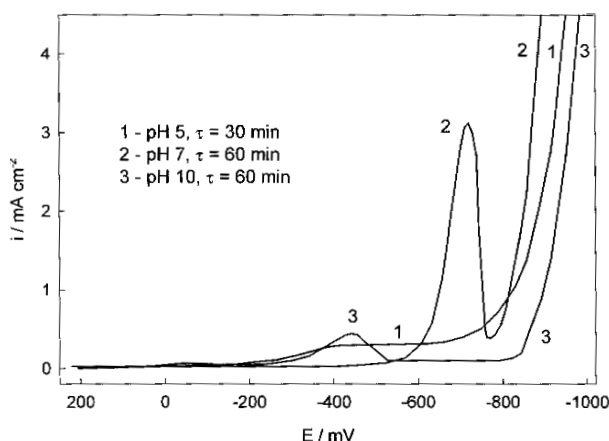
Fig. 6. Cathodic voltammograms obtained for 0.3 M K_2SO_4 solutions containing 0.01M K_2MoO_4 at indicated pH and exposure times

current maxima at –0.7 V (curve 2) are attributable to the reduction of thin Cu_2O layers. The peak at –0.45 V (curve 3) is typical of alkaline media and might be related to oxide layers with deviations from stoichiometry. This aspect has been discussed earlier [3, 4, 9].

Thus, oxide layers developed in the solutions under discussion may acquire *n*- or *p*-type conductivity depending on the solution composition. The effect of Mo(VI) or W(VI) may be somewhat revealed assuming that the processes N 1 and 4 (Table) are the most probable in the solutions as the simplest redox reactions. Their equilibrium potentials differ by *ca* 0.4 V that seems to be the most probable reason for the different behaviour of the two systems. A comparison of experimental data and those listed in Table 1 shows that the onset of *p*-type conductivity takes place at $E_{eq} \approx -0.6$ V. The physical sense of this value is not yet clear and needs further investigations.

CONCLUSIONS

1. Slow and weak variations of the open-circuit potential of Cu electrode were found to arise under chopped illumination conditions in solutions containing either Mo(VI) or W(VI) at pH 5. These phenomena seem to be of thermal nature and cannot be treated as photoelectrochemical effects.

2. Well-defined pulses of negative photopotential ranging up to –150 mV develop in Mo(VI)-containing solutions at pH 7. On the contrary, the onset of positive photopotential is observed in W(VI) solutions at the same pH.

3. Oxide layers developed in alkaline (pH 10) media exhibit *p*-type conductivity for both systems. The $n \rightarrow p$ transition was found to occur when the equilibrium potential of Mo(VI)|Mo(IV) or W(VI)|W(IV) couples was *ca* –0.6 V.

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MO(VI) IR W(VI) ĮTAKA OKSIDŲ, SUSIDARIUSIŲ ANT VARIO ELEKTRODO, FOTOELEKTROCHEMINĖMS SAVYBĖMS

S a n t r a u k a

Aptikta, kad eksponuojant vario elektrodą natūraliai aeruojamuose 0,3 M K_2SO_4 tirpaluose, turinčiuose 0,01 M molibdato ar volframato, susidaro šviesai jautrūs oksidų sluoksniai. Impulsinio apšvietimo metu Mo(VI) ar W(VI) tirpaluose, kurių pH 5, atsiranda lėti ir silpni atviros grandinės potencialo pokyčiai. Šie reiškiniai nepriskirtini fotoelektrocheminiams ir yra matyt šiluminės kilmės. Ryškūs neigiamo fotopotencialo impulsai (–150 mV) yra būdingi Mo(VI) tirpalams, kurių pH 7. To paties pH W(VI) tirpaluose, priešingai atsiranda teigiamas fotopotencialas. Oksidų sluoksniai, susidarę šarminėse terpėse (pH 10), rodo *p* tipo laidumą abiejų sistemų atveju. Perėjimas iš *n* į *p* tipo laidumą įvyksta tada, kai Mo(VI)|Mo(IV) ar W(VI)|W(IV) redoks potencialai yra lygūs apie –0,6 V.