

# COPPER AS A REPLACEMENT OF LEAD AS AN ANODIC MATERIAL OF GALVANIC OXYGEN SENSOR

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Attempts to improve the amperometric oxygen sensors of the galvanic type remain relevant because of their advantages: the ability to function without energy consumption, constant readiness for measurements, the ability to quickly go into working mode after overloads or complete shutdown from the measuring system. One of the drawbacks of such sensors in the Clark system is the presence of a consumable anode of toxic lead. For the first time, the possibility of replacing lead with a significantly less toxic material is shown. The choice of copper as a promising anode material for galvanic type oxygen sensors according to Pourbaix diagrams is theoretically justified. It has been experimentally confirmed that the kinetics of the oxidation of copper in the alkaline electrolyte of the Clarke cell allows it to become a full-fledged replacement of lead and its alloys in galvanic-type oxygen sensors.

## **1. Introduction**

Amperometric oxygen sensors are widely used due to the electrical nature of their current signal, the linear dependence of the signal on gas concentration, reliability, and the practical absence of cross-sensitivity to other oxidizing gases [1]. Today, two types of amperometric oxygen sensors are common: the first is a two-electrode sensor of the so-called galvanic type, the second is a four-electrode sensor [2], which is the result of the development of a three-electrode sensor in the direction of decreasing background currents. Galvanic type oxygen sensors were invented by Clark [3] for detecting oxygen in a water environment. Since then, their electrochemical system has remained unchanged: a platinum cathode, an aqueous solution of KOH as an electrolyte, a lead anode.

The Clark system has a number of disadvantages, to eliminate which went to the system with four platinum electrodes in acidic electrolyte. The presence of lead is the most obvious drawback for the modern consumer, since the toxicity of this heavy metal to most living organisms is well known. After the invention of the four-electrode system, attempts to improve the Clark element continued in the direction of eliminating carbonization of the electrolyte [4], however, non-toxic replacement of lead was not found. The relevance of improving two-electrode sensors can be justified by increased reliability and lack of energy consumption, which is important for portable gas analyzers. The lack of power consumption in the operation of the galvanic sensor is due to the fact that this sensor is essentially a solid fuel element. Fuel (lead) is spent on the development of a useful analytical signal - electric current. In this case, the sensor can always be ready to measure, regardless of the electrical power supply of the e-filling of the gas analyzer. This is very important primarily for portable devices, which should determine the suitability of air for human breathing before visiting enclosed spaces and volumes without special isolating breathing apparatus.

Objective: To show the first time the possibility of replacing highly toxic lead in galvanic oxygen sensors of the Clark element by less harmful metals.

## **2. Justification of the choice of copper**

An alternative material for the anode of the galvanic oxygen sensor should be a metal whose toxicity is significantly lower than the toxicity of lead, which is the first requirement.

The second requirement for the selected metal is sufficient corrosion resistance. The criterion of sufficient stability is its equilibrium potential, which must be higher than the potential of the hydrogen electrode calculated for the same environment. This will avoid the release of hydrogen on a platinum cathode, which the auxiliary electrode of the selected metal imposes its potential when the electrical circuit is locked. Fulfillment of this condition allows to eliminate 99% of the possible background current of the oxygen sensor. It is obvious that the equilibrium potential of the selected metal should also be significantly lower than the potential of the

oxygen electrode. Then, the second requirement for the anode material is formulated as follows:

$$E_{H_2} \leq E_M \leq E_{O_2} \quad (1)$$

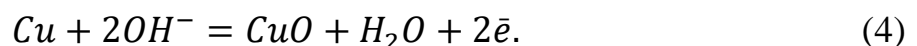
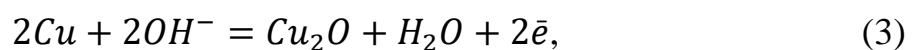
where  $E_{H_2}$ ,  $E_{O_2}$ ,  $E_M$  – the equilibrium potentials of the hydrogen and oxygen electrodes and the selected metal.

The third requirement for the material of the anode is the lack of a tendency to passivation, in which the anode is unable to support the generation of a current signal. For sensors unified series Igor Sikorsky Kyiv Polytechnic Institute [5] a planned current of oxygen sensors is 30 ... 50  $\mu A$ . The diameter of the working surface of the monolithic anode should be 18 mm, taking into account the design features of these sensors. That is, the anode has to allow the current density indicated below even in the passive state with short-term peak loads:

$$i_{max} = 50 \cdot 4 / (\pi \cdot 1.8^2) = 20 [\mu A / cm^2] \quad (2)$$

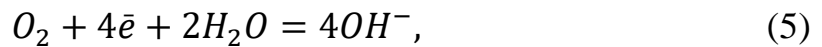
At peak loads, only the external surface of the porous anode often works, as if it is a monolithic one. Normal operation of the anode should be at a current density of at least two orders of magnitude lower, since the true surface area of the porous anode greatly exceeds its geometric surface.

The theoretical selection for the second requirement was carried out among the relatively non-toxic metals according to reference data. After analyzing the Pourbaix diagrams was found that among the relatively non-toxic and affordable metals, copper responds to the second requirement. The copper Pourbaix diagram shows that the potential of the copper electrode should be determined by the reactions, that are described by the lines (7) and (9) on fig. 1, whose equations are [6]:



The potentials of these reactions are approximately midway between the potentials of the hydrogen and oxygen electrodes.

The occurrence of copper oxidation reactions ensures the maintenance of the material balance of the electrolyte, since together with the cathodic process of oxygen reduction

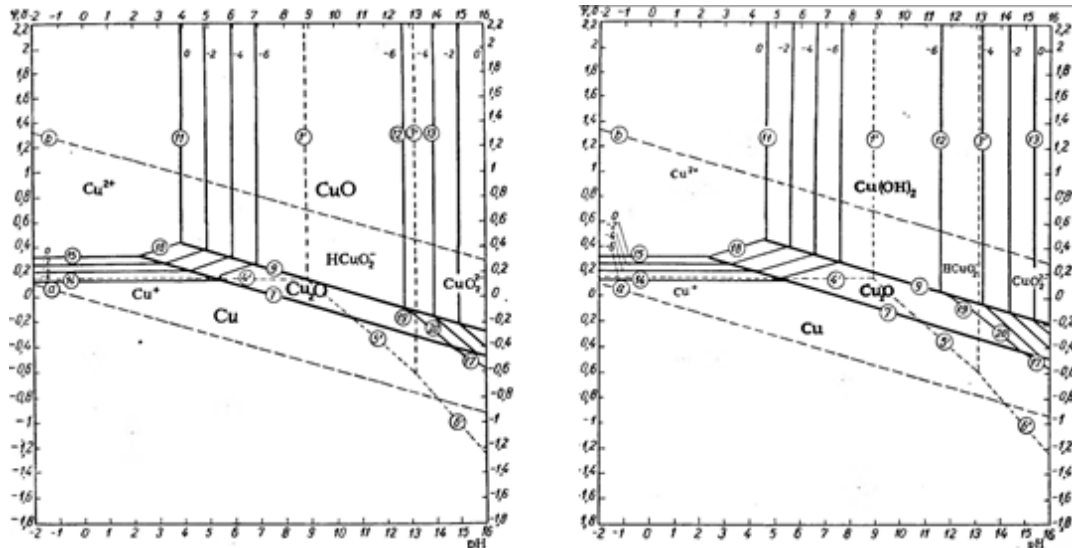


the total process in the electrochemical cell corresponds to the reactions:



As seen from the recent reactions, the functioning of the copper anode does not provide for quantitative and qualitative changes in alkaline and neutral electrolytes in a wide pH range from pH6 to pH13. A traditional electrolyte for galvanic oxygen sensors is an aqueous solution of 30% KOH, capable of storing homogeneity over a wide range of water activity (relative humidity).

For comparison, it is necessary to investigate the behavior of lead anodes and anodes of technical lead, which is doped with common additives to increase their strength.



**Fig. 1.** Diagram Pourbaix for copper-water system.

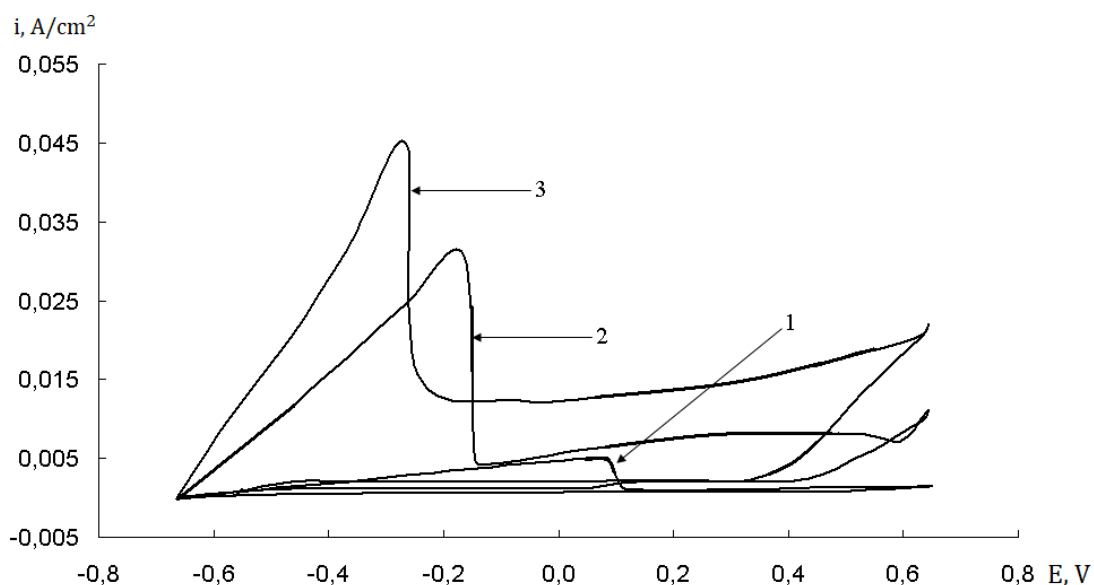
### 3. Method of experiment

Experiments were performed in a three-electrode cell from the potentiostat kit PI-50-1.1. The polarization for the working electrode was set with a complex of a PI-50-1.1 potentiostat and the programmer PR-8. Registration of the current dependency of

the potential were recorded using a two-coordinate potentiometer PDA 1-01. Working electrodes were made in the form of plates of copper, lead and lead, which is doped with antimony to increase strength and hardness. A platinum cathode and a mercury oxide reference electrode were used. All potentials are given in the scale of the hydrogen electrode.

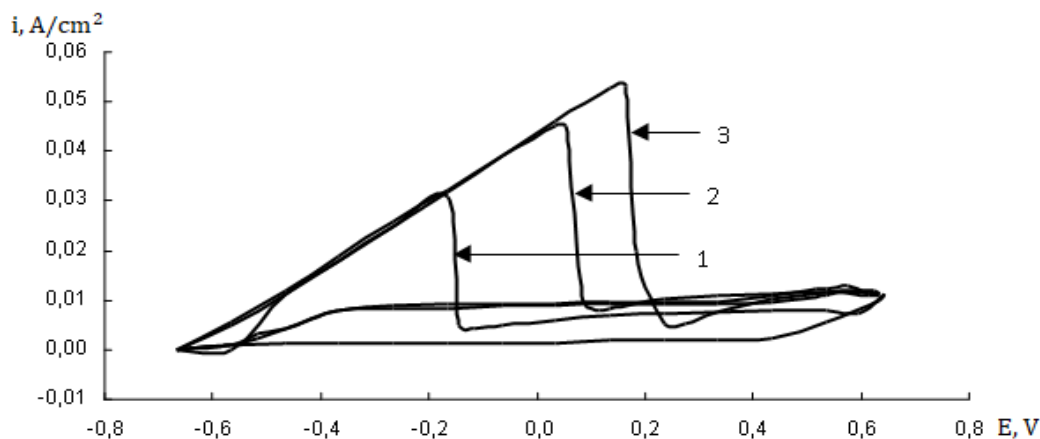
#### 4. The results of the experiment and their discussion

At the first stage of research, the behavior of lead anodes was studied. Cyclic voltammogram obtained with the potential change rate of 1 mV/s (Fig. 2) have a linear section of lead active oxidation with subsequent passivation. The slope of the active oxidation site can be conditionally represented as resistance, whose value increases from  $8.8 \Omega \cdot \text{cm}^2$  to  $15 \Omega \cdot \text{cm}^2$  and further to  $130 \Omega \cdot \text{cm}^2$ , with decreasing concentration of KOH solution from 7 M to 1 M and further to 0.1 M.



**Fig. 2.** Cyclic voltammograms obtained with scanning capacity 1 mV/s on lead in solutions KOH concentration, mol/l: 1 – 0,1; 2 – 1; 3 – 7.

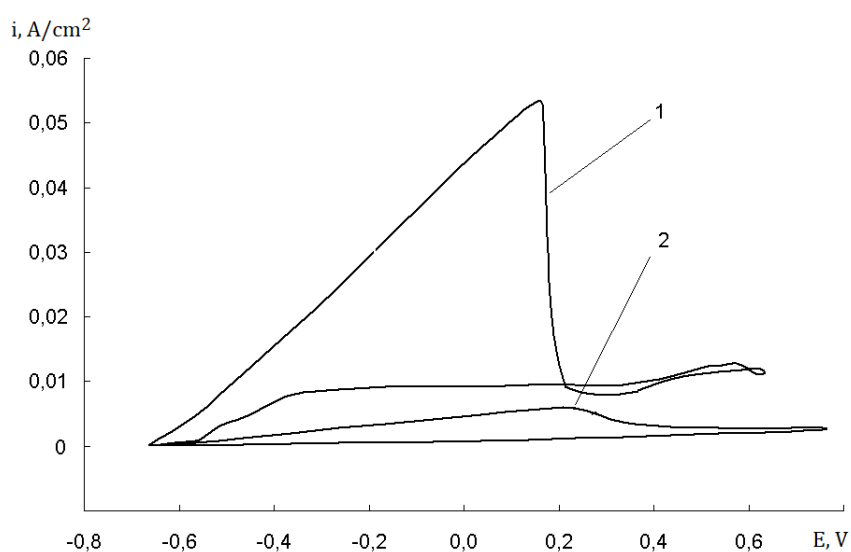
Ohmic nature of this resistance becomes evident when analyzing the results of changes in the row scan rate of 1, 5 and 10 mV/s (Fig. 3).



**Fig. 3.** Cyclic voltammograms obtained on lead in 1 M KOH solution at a rate of potential sweep, mV/s: 1 – 1; 2 – 5; 3 – 10.

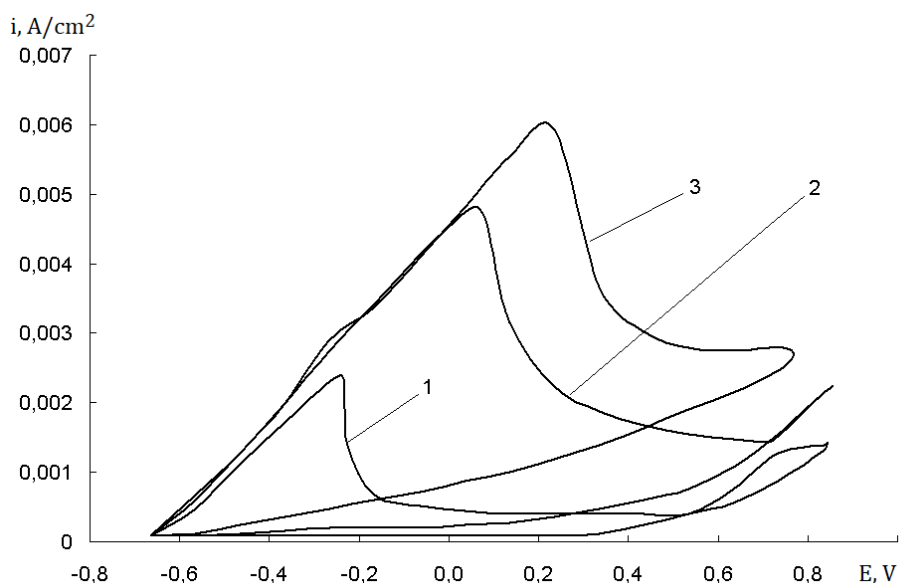
Fig. 3 clearly shows that the slope of the linear region of the active lead oxidation does not change due to a change the potential scan rate. Since the anode after polarization had a gray color, it indicates the formation and the gradual increase in white lead hydroxide particles (II), not yellow or red lead oxide (II). At the second stage, the behavior of the antimony lead alloy, which is common in the technique, was studied.

Comparison of the behavior of lead and lead-antimony anodes (Fig. 4) shows much higher anodic oxidation resistance due to the introduction of antimony in the alloy composition.



**Fig. 4.** Cyclic voltammograms obtained on lead 1 and antimony lead alloy 2 in 1 M KOH solution at a rate of potential sweep 10 mV/s.

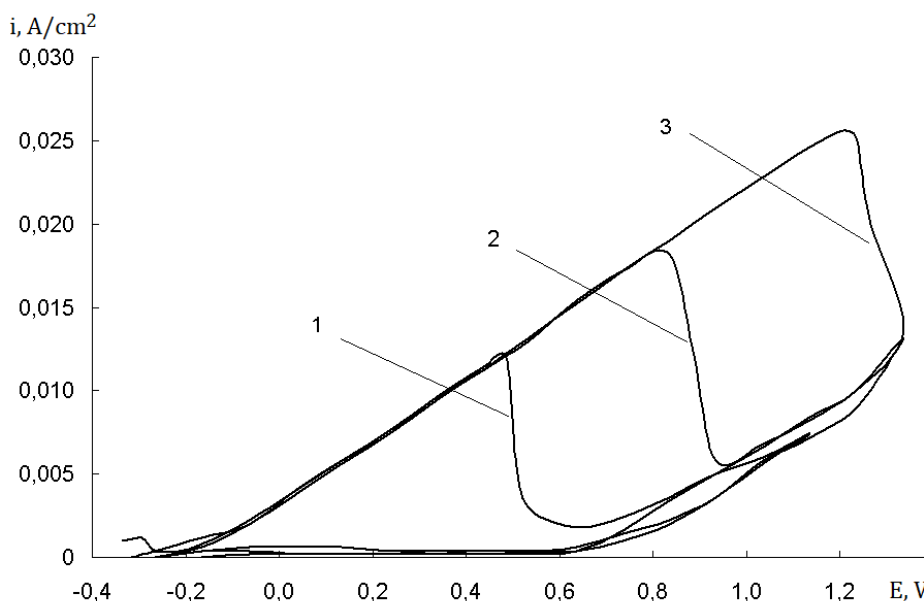
The ohmic nature of the resistance is confirmed by the practically unchanged value of this resistance when the potential sweep rate changes (Fig. 5).



**Fig. 5.** Cyclic voltammograms obtained on antimony lead alloy in 1 M KOH solution at a rate of potential sweep,  $\text{mV/s}$ : 1 – 1; 2 – 5; 3 – 10.

Some decrease in ohmic resistance and a blurring of the passivation zone of the cycloramas with an increase in the sweep rate from 1  $\text{mV/s}$  to 5  $\text{mV/s}$  can be attributed to the loosening of passive layers during the removal from the anode of the  $\text{SbO}_3^-$  ions. These ions are formed at pH 14 and at  $E > -0.6 \text{ V}$  according to Pourbaix diagrams for antimony [6]. Dissolution of antimony also explains the growth of ohmic polarization of the anode in active oxidation compared to pure lead 10 times, since the formation and removal of hydrated  $\text{SbO}_3^-$  anions through the pores in the layers of lead oxidation products should inhibit the delivery of  $\text{OH}^-$  ions to the electrode reaction zone.

At the final stage of the study, the behavior of the copper anode in a solution of 7 M KOH, which is close to the composition of a solution of galvanic type oxygen sensors, was studied. There are ohmic limitations similar to the results of testing lead and its alloy with antimony (Fig. 6).



**Fig. 6.** Cyclic voltammograms obtained on copper in 7 M KOH solution at a rate of potential sweep, mV/s: 1 – 1; 2 – 5; 3 – 10.

That is, the oxidation of copper in KOH is accompanied by the growth of individual crystals of the corresponding oxide, between which water is drained and hydroxide ions are delivered to the reaction zone with limitations that are close to ohmic. The ohmic resistance of the active site from Fig. 6 is  $52.6 \Omega \cdot \text{cm}^2$ . Since for lead the ratio of resistances in solutions of 1M and 7M KOH is 0.57, we can assume that for an alloy of lead and antimony, the resistance in a solution of 7M KOH should be about  $84 \Omega \cdot \text{cm}^2$ . The ohmic resistance of the active region is  $52.6 \Omega \cdot \text{cm}^2$ . The calculated value is even over than that determined for the copper anode. That is, copper can be a better anode for the oxygen sensor than lead alloy with antimony. At the same time, according to the experience of the development and use of oxygen sensors of a unified series Igor Sikorsky Kyiv Polytechnic Institute known about the successful use of lead alloy with antimony. Thus, it can be argued that the copper anode is suitable for replacing lead in the anodes of the oxygen sensor with a similar design (equal to the true surface area). Lead anodes were made by pressing from granules about 1.5 mm in size.



## 5. Conclusions

For the first time it was proposed to use copper as the anode material of amperometric galvanic type oxygen sensors to fully replace the much more toxic lead. Copper fully complies with theoretically reasonable requirements for the anode material of the oxygen sensor. The ability of copper to maintain the generation of the current signal of the sensor at least at the level of a common alloy of lead with antimony, the suitability of which was previously known, has been experimentally confirmed.

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