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Electrochemical Behavior of Copper in Aqueous Solutions Under Industrial-Frequency Alternating Current Polarization

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Abstract

The electrochemical behavior of copper under industrial-frequency (50 Hz) alternating current polarization was investigated in sulfate- and chloride-containing aqueous solutions using Cu-Cu and Cu-Ti electrode pairs. Copper–copper pairs showed practically no directional electrochemical processes, whereas replacing one electrode with titanium caused copper oxidation owing to a passive TiO_2 film that forms on the titanium surface during the anodic half-cycle and acts as a rectifier. By varying the electrolyte composition (H_2SO_4, Na_2SO_4, HCl, NaCl), current density (from 2×10^4 to 1.5×10^5 A·m^{-2}) and Cu^{2+} concentration (5–30 g·L^{-1}), different copper compounds could be synthesized selectively and with high current efficiency: copper(II) oxide (CuO) formed in Na_2SO_4 (current efficiency up to 89.2%), metallic copper powder formed in H_2SO_4 containing Cu^{2+} (up to 75.2%), copper(I) oxide (Cu_2O) formed in NaCl (99.1%), and copper(I) chloride (CuCl) formed in HCl with an apparent current efficiency exceeding 100% owing to concurrent processes.

Keywords: electrochemical synthesis; industrial-frequency alternating current; copper electrode; sulfate and chloride electrolytes; Cu(I) and Cu(II) compounds; current efficiency

1. Introduction

Copper compounds are characterized by considerable functional diversity, which underlies their use across a wide range of technological fields. Copper oxides (Cu_2O and CuO) are widely used in the production of glass, ceramics, paints and pigments, as well as catalysts and functional materials in electrochemical and photocatalytic systems [1–3]. Copper(I) chloride (CuCl) is of particular interest, being widely employed as a catalyst in organic synthesis, including oxidation, carbonylation and chlorination reactions of organic compounds [4–6]. In addition, CuCl-based systems are used for the selective absorption of gases, in particular carbon monoxide, which is applied in gas purification and analytical gas-analysis methods [7,8]. In this context, various methods for synthesizing copper compounds, including electrochemical approaches, are of considerable interest.

The literature describes chemical, thermal and electrochemical methods for obtaining copper(I) and copper(II) compounds [9].

Copper(I) oxide is obtained by partial oxidation of copper at temperatures above 200 °C with a limited amount of oxygen:

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$$4Cu + O_2 \xrightarrow{t>200} 2Cu_2O$$

With an excess of oxygen and under harsher conditions (350–500 °C), the product can be further oxidized to CuO:

$$2Cu_2O + O_2 \xrightarrow{t=300-500} 4CuO$$

Therefore, obtaining pure Cu_2O requires control of the temperature, time and partial pressure of oxygen. Copper(I) oxide can be obtained by the solid-state reaction of copper(II) oxide with metallic copper:

$$CuO + Cu = Cu_2O$$

To accelerate the solid-state reaction, the process is carried out at elevated temperatures, approximately 500–900 °C, preferably in an inert atmosphere or at a reduced partial pressure of oxygen. The specific temperature and degree of conversion are determined by the dispersity of the starting materials, the heating time and the oxygen potential of the medium.

This method is based on the redistribution of copper between the 0 and +2 oxidation states with the formation of Cu(I). Furnace reduction of a mixture of copper oxides with metallic copper is one of the industrial methods for producing Cu_2O [9].

Copper(I) oxide Cu_2O is also obtained by reducing copper(II) compounds in an alkaline medium with glucose or other reducing agents in the presence of sodium hydroxide upon heating:

$$2CuSO_4 + C_6H_{12}O_6 + 5NaOH = Cu_2O + 2Na_2SO_4 + C_6H_{11}O_7Na + 3H_2O$$

As can be seen from the above reactions and the conditions under which they proceed, copper(I) oxide is predominantly obtained at high temperatures, and this process is accompanied by the formation of by-products that require further processing.

Cu_2O can form during the electrolysis of weakly alkaline aqueous electrolytes with copper electrodes. Reference data list the electrolysis of an aqueous NaCl solution between copper electrodes among the industrial methods. The main drawback of this method is the passivation of the copper anodes even at low current densities [10].

Copper(II) oxide CuO is predominantly obtained by oxidation of metallic copper powder with oxygen at elevated temperatures, as well as by thermal decomposition of copper(II) hydroxide, carbonate or nitrate. Dehydration of $Cu(OH)_2$ yields CuO and water, whereas the decomposition of carbonate and nitrate compounds is accompanied by the release of gaseous products [9].

Copper(II) oxide can be obtained electrochemically using copper electrodes from a weakly alkaline sodium sulfate solution. In this case, copper(II) hydroxide $Cu(OH)_2$ first forms on the anode surface and, under the electrolysis conditions at the electrolyte temperature, can immediately undergo dehydration to form copper(II) oxide.

Electrochemical synthesis is conventionally carried out using direct current, whereby oxidation proceeds at the anode and reduction at the cathode, ensuring the directional electrochemical transformation of substances in solution. Nevertheless, studies conducted in recent years show that non-stationary currents, including pulsed and alternating currents, are also capable of initiating targeted electrochemical processes and of modifying reaction kinetics. For example, in a recent review, in a recent review [11], the authors discuss alternating current electro-organic synthesis as a promising direction for the electrochemical synthesis of organic compounds. Unlike conventional direct current, the periodic reversal of electrode polarity and the possibility of tuning the current frequency allow more precise control over the electrochemical and chemical stages of a reaction. Such an approach enables control of the concentration of reactive intermediates

and suppresses over-oxidation or over-reduction. Recent advances in AC electrolysis have been summarized, showing that this method can markedly enhance reaction selectivity and broaden the scope of electro-organic synthesis compared with conventional DC methods [11]. Other authors have shown that, in organic synthesis, alternating current electrolysis makes it possible to control the sequence of chemical steps and to achieve selectivities unattainable under conventional DC polarization, through the temporal modulation of the concentration of reactive intermediates and the periodic reversal of the current direction at the electrode during each polarization cycle [12].

A characteristic feature of electrochemical processes under industrial-frequency alternating current polarization is the periodic alternation of anodic and cathodic half-cycles, which substantially changes the conditions under which the electrode reactions proceed compared with conventional DC polarization.

Our previous studies [13] have shown that the use of industrial-frequency (50 Hz) alternating current makes it possible to realize electrochemical processes that are not characteristic of conventional anodic polarization. In particular, polarization of titanium and lead electrodes in sulfuric acid solutions led to their dissolution, with the formation of titanium(III) sulfate, $Ti_2(SO_4)_3$, and lead(II) sulfate, $PbSO_4$.

It should be noted that this behavior differs substantially from the electrochemical processes that occur under direct current. It is known that, under anodic polarization of titanium in aqueous solutions, a dense passivating TiO_2 film with pronounced valve (rectifying) properties forms almost instantaneously. This film effectively hinders further anodic dissolution of the metal, limiting electron transfer across the metal–electrolyte interface and providing titanium with high corrosion resistance even in acidic media [14]. Similarly, under anodic polarization of lead in sulfuric acid, a stable layer of lead dioxide, PbO_2, forms on the electrode surface, exhibiting high chemical stability and sufficient electrical conductivity to sustain the oxygen evolution reaction. Under these conditions, lead dissolution is practically absent, which is why lead electrodes are widely used as insoluble anodes in industrial electrochemical processes, for example in zinc electrowinning [15]. These earlier results indicate that alternating current polarization can fundamentally alter the electrochemical behavior even of metals that are conventionally regarded as passive under direct current. An analysis of the current literature shows that systematic studies of the electrochemical behavior of copper in aqueous sulfate and chloride electrolytes under industrial-frequency (50 Hz) alternating current are lacking.

Unlike established electrochemical synthesis methods based on controlling the potential or the density of a direct current, the present work proposes the use of industrial-frequency (50 Hz) alternating current as an independent tool for controlling electrochemical processes. A distinctive feature of the proposed approach is the possibility of selectively obtaining CuO, Cu_2O, CuCl or metallic copper, mainly by varying the nature of the electrolyte without changing the polarization regime; in addition, the use of industrial alternating current without rectifiers simplifies the instrumental configuration of the process.

2. Results and Discussion

2.1. Electrochemical Behavior of Copper Under 50 Hz Alternating Current Polarization in Sulfate-Containing Aqueous Solutions

The experiments were carried out using the setup shown in Figure 1; experimental details are given in Section 3. The electrochemical behavior of copper under industrial alternating current polarization was studied in sulfuric acid and sodium sulfate solutions using Cu-Cu and Cu-Ti electrode pairs. It was found that, in the copper–copper system, no appreciable electrochemical transformations occur in either electrolyte under the

conditions studied. In the copper–titanium system, by contrast, electrochemical reactions do take place, the nature of which is determined by the electrolyte composition.

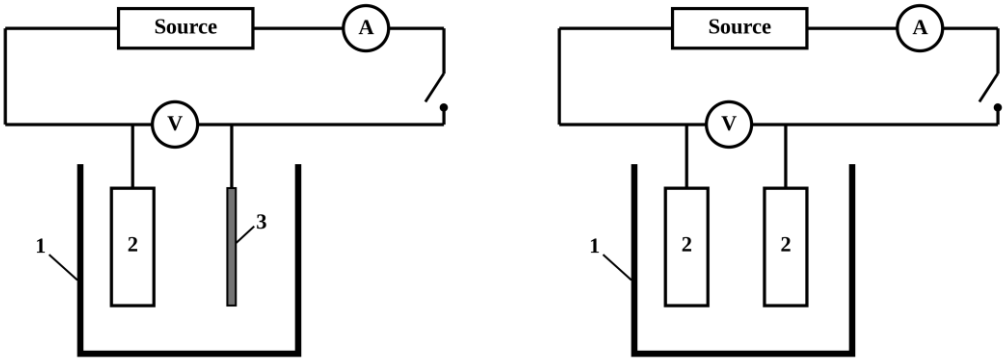


Figure 1. Schematic diagram of the setup for studying the electrochemical behavior of copper under industrial alternating current polarization: 1—glass electrochemical vessel; 2—copper plate electrodes; 3—titanium electrode.

Preliminary studies made it possible to select the electrode materials and dimensions and the electrolysis conditions in such a way that targeted electrochemical processes became possible under AC polarization. It was shown that the titanium electrode passivates under anodic polarization within a fraction of a second, and the current flow through the electrochemical circuit stops. This is because a TiO_2 oxide film with valve properties forms on the titanium surface. It was also established that, at very high current densities, passivation of the titanium anode, that is, the formation of a thin dense oxide film on its surface, occurs instantly, depending on the electrolyte composition. Therefore, when the Cu–Ti electrode pair is used in the electrochemical circuit, different current densities can be created at the titanium and copper electrodes at the same current strength by changing the ratio of the electrode surface areas. This ratio is achieved by using a titanium electrode in the form of a wire of relatively small diameter (1–2 mm) and a copper plate whose surface area is many times larger than that of the titanium electrode.

As shown previously [16], in sodium sulfate solution, polarization of the Cu-Ti pair is accompanied by anodic dissolution of the copper electrode with the formation of Cu^{2+} ions. These ions subsequently react with hydroxide ions to form a copper(II) oxide precipitate, which gradually accumulates at the bottom of the electrolyzer. One of the main factors governing the efficiency of the process is the current density at the titanium electrode. The effect of this parameter on the current efficiency (CE) of CuO formation, at a constant current density at the copper electrode, is shown in Figure 2.

The results obtained show that the use of industrial-frequency (50 Hz) alternating current provides stable CuO formation without the use of a DC source. The key role in this process is played not only by the electrolyte composition but also by the presence of the titanium electrode, whose surface becomes covered with a passive TiO_2 oxide film during the anodic half-cycle.

As is known [17], anodic polarization of titanium in aqueous solutions rapidly produces a dense TiO_2 film with pronounced semiconducting (valve) properties. Figure 3 shows the surface microstructure of the titanium electrode after anodic polarization. The electrode surface is seen to be completely covered with a continuous oxide layer exhibiting a well-developed granular morphology, typical of anodic titanium oxide films.

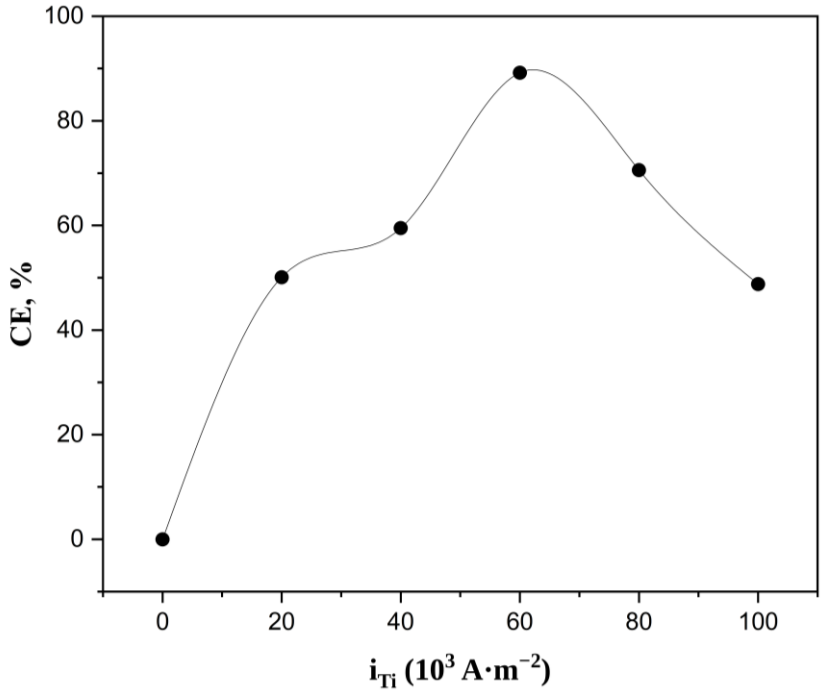
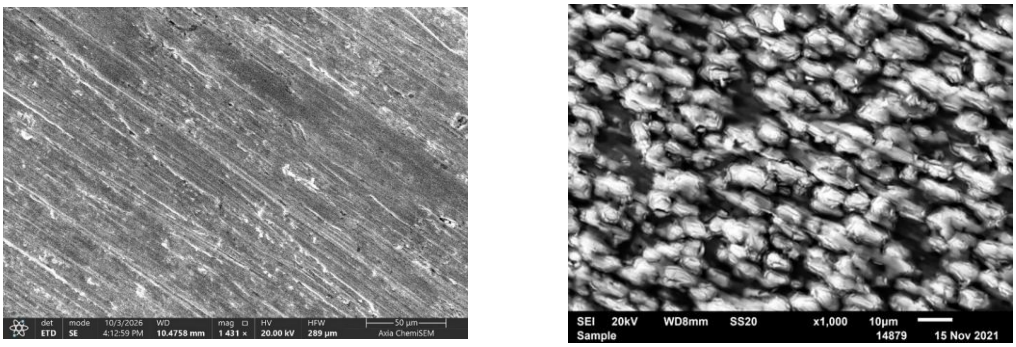


Figure 2. Effect of current density at the titanium electrode on the current efficiency of copper(II) oxide formation: Na_2SO_4—70 g·L^{-1}, i_{Cu}—400 A·m^{-2}, T = 25 °C, τ = 0.5 h.



(**a**) (**b**)

Figure 3. Micrographs of the titanium electrode surface: (**a**) initial electrode at ×1500 magnification; (**b**) anodically polarized electrode at ×1000 magnification.

In the initial state, the surface of the titanium electrode bears characteristic traces of mechanical preparation in the form of parallel scratches and grooves. After anodic polarization, the original relief is largely lost, and the surface becomes covered with a continuous granular-aggregated layer. The observed morphology indicates surface oxidation of titanium with the formation of an oxide film. The appearance of a granular-globular structure and the increase in microroughness indicate surface development, which may lead to an increase in the true electrode area and to a change in the conditions under which the electrochemical reactions proceed.

The formation and growth of the oxide layer on the titanium surface during anodic polarization may enhance its barrier and valve properties. An increase in the thickness and continuity of the oxide film, which consists predominantly of titanium dioxide, increases the resistance to charge transfer across the metal–oxide–electrolyte interface and promotes the valve behavior characteristic of titanium. Under AC polarization, a rectifying effect may therefore arise: during the anodic half-cycle, the oxide layer restricts electron transfer across the metal–electrolyte interface, whereas during the cathodic half-cycle its resistance decreases considerably, favoring the hydrogen evolution reaction.

Thus, it can be assumed that the formation of the passive TiO_2 film is the key factor determining the asymmetry of the electrochemical processes in the Cu-Ti system.

The formation of the oxide film is confirmed by elemental analysis (Table 1). After anodic polarization, the titanium content decreased from 98.47 to 60.77 at.%, while the oxygen content increased from 1.53 to 39.23 at.% (values normalized to 100%), indicating intensive oxidation of the titanium surface.

Table 1. Change in the elemental composition of the titanium electrode surface before and after anodic polarization.

Sample	Ti (at.%)	O (at.%)
Initial titanium electrode	98.47	1.53
Anodically polarized titanium electrode	60.77	39.23
Total	100.00	100.00

The Ti and O contents were normalized to 100 at.% excluding trace components.

The formation of copper(II) oxide during AC polarization of the Cu-Ti electrode pair can be explained as follows. When the titanium electrode is in the anodic half-cycle of the alternating current, an oxide film (TiO_2) with semiconducting (valve) properties forms instantaneously on its surface. In this direction, current flow through the electrochemical circuit is interrupted, so that no electrochemical reaction occurs at the other electrode, i.e., the copper electrode. In the next instant, when the titanium electrode is in the cathodic half-cycle, gaseous hydrogen evolves at its surface (reaction 1).

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \quad (1)$$

At this moment, the copper electrode is in the anodic half-cycle, and copper oxidation occurs (reaction 2).

$$Cu^o - 2e \rightarrow Cu^{2+} \quad (2)$$

The hydroxide ions formed in reaction (1) react in the bulk of the solution with copper(II) ions to give copper(II) hydroxide (reaction 3).

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \quad (3)$$

Depending on the experimental conditions, mainly with increasing solution temperature, copper(II) hydroxide undergoes dehydration to form copper(II) oxide (reaction 4).

$$Cu(OH)_2 \overset{t}{\rightarrow} CuO + H_2O \quad (4)$$

The increase in the current efficiency of copper(II) oxide with increasing current density at the titanium electrode is apparently associated with intensified formation of the semiconducting oxide film. As seen in Figure 2, at current densities above 6×10^4 $A \cdot m^{-2}$ the CE of copper(II) oxide formation decreases. According to the literature [18,19], the electrophysical properties of anodic TiO_2 films depend on their formation conditions and determine the charge-transfer kinetics. It is likely that changes in these properties affect the valve effect of the oxide film and, consequently, the current efficiency of CuO formation.

Varying the current density at the copper electrode up to 400 $A \cdot m^{-2}$ has practically no effect on the CE.

The results of X-ray phase analysis of copper(II) oxide synthesized under polarization of the Cu-Ti electrode pair with industrial alternating current in Na_2SO_4 solution are shown in Figure 4.

The X-ray diffraction pattern of the copper(II) oxide sample is characterized by intense reflections with interplanar spacings of approximately 2.75, 2.52, 2.32, 1.85 and 1.58 Å. The positions of the main diffraction maxima correspond to the crystalline phase of copper(II) oxide CuO with the tenorite structure, which belongs to the monoclinic crystal system.

The most intense reflections at d ≈ 2.52 and 2.32 Å are characteristic of CuO and correspond to the main crystallographic planes of the monoclinic tenorite structure. The additional maxima at d ≈ 2.75, 1.85–1.87 and 1.58 Å are also consistent with the diffraction lines of CuO. Reference data for tenorite list, in particular, interplanar spacings of about 2.752, 2.524–2.531, 2.311–2.323, 1.867 and 1.581 Å. The reflections obtained indicate the formation of the crystalline copper(II) oxide phase. The presence of pronounced and relatively narrow diffraction maxima indicates a fairly high degree of crystallinity of the product. The characteristic peak positions correspond to the monoclinic structure of CuO (tenorite), whose unit-cell parameters reported in the literature are approximately a = 4.68 Å, b = 3.42 Å, c = 5.13 Å and β ≈ 99.5°.

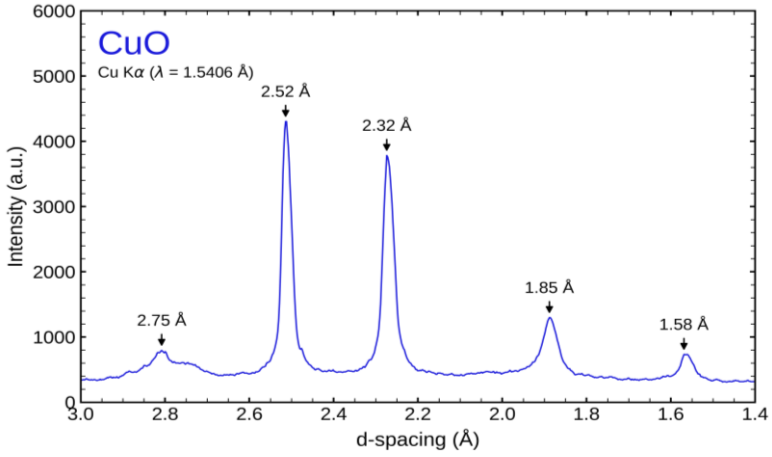
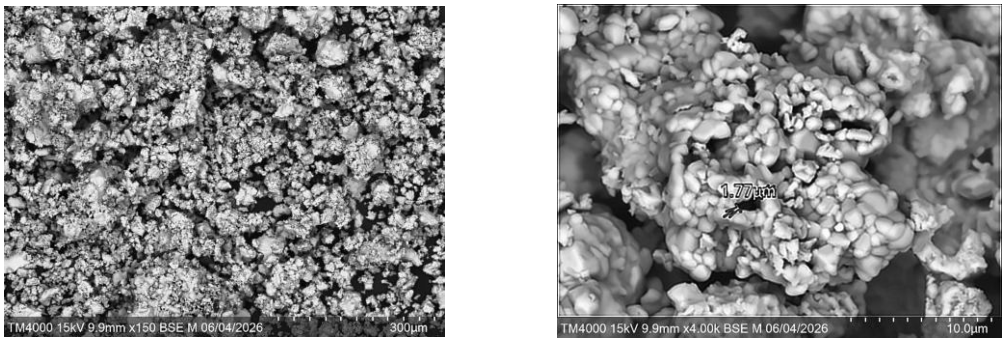


Figure 4. X-ray diffraction pattern of copper(II) oxide obtained by using Cu K_α radiation (λ = 1.5406 Å), plotted against the interplanar spacing *d*.

The low-magnification scanning electron microscopy (SEM) image (Figure 5a) shows that the CuO powder obtained is characterized by non-uniform particle size and pronounced particle agglomeration. The material consists of aggregates of various shapes and sizes, between which smaller particles are located. Such morphology indicates the tendency of the primary copper oxide particles to combine into larger secondary formations.



(**a**) (**b**)

Figure 5. SEM images of the copper(II) oxide (CuO) powder at different magnifications: (**a**) ×150; (**b**) ×4000.

At ×4000 magnification (Figure 5b), the developed surface of the agglomerates is clearly visible. They are formed from a large number of smaller particles of rounded and irregular shape. The particles are in close contact with each other and form porous aggregates with a non-uniform surface relief. According to the measurement marker on the micrograph, the local characteristic size of an individual structural element is about 1.77 μm.

Taken together, the SEM study shows that the CuO obtained is a polydisperse agglomerated powder with a developed microrelief surface.

It is appropriate to explain the mechanism of copper oxide formation upon polarization of the Cu–Ti electrode pair with 50 Hz alternating current. At the moment when the titanium electrode is in the anodic half-cycle, a TiO_2 oxide film forms instantly on its surface. This film has valve properties and does not pass current in this direction. When the titanium electrode is in the cathodic half-cycle of the alternating current, the reduction of hydrogen ions, that is, hydrogen evolution, takes place on it (on the titanium electrode) (reaction 5).

At this instant, the copper (second) electrode is in the anodic half-cycle and dissolves (reaction 6) to form copper ions, which subsequently form oxygen-containing copper compounds. The reactions are repeated cyclically. In this case, the titanium electrode serves both as an auxiliary electrode and as a rectifier.

$$2H^+ + 2e \rightarrow H_2 \quad (5)$$

$$Cu^{2+} + SO_4^{2-} \rightarrow CuSO_4 \quad (6)$$

The current efficiency of copper electrode dissolution depends mainly on the current density at the titanium electrode (Figure 6).

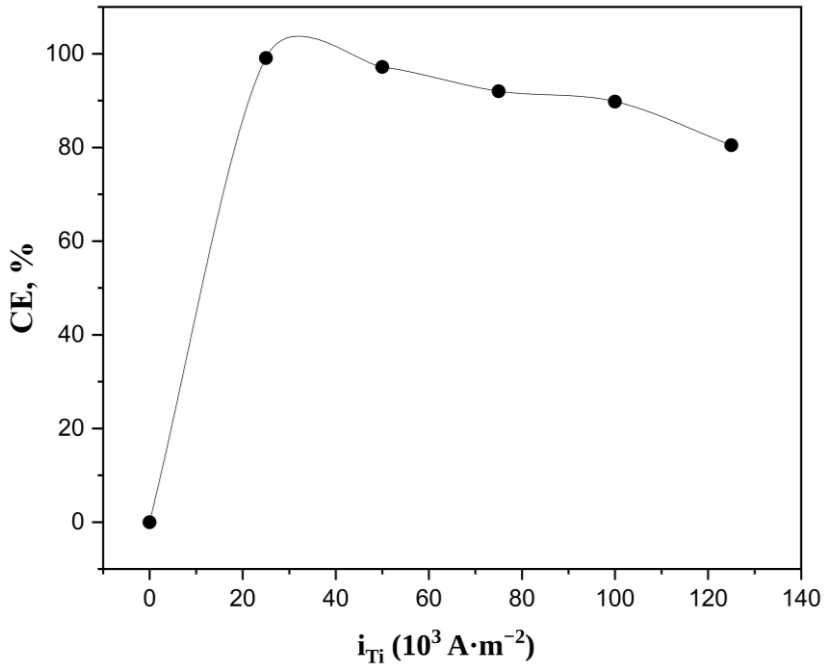


Figure 6. Effect of current density at the titanium electrode on the current efficiency of copper electrode dissolution with the formation of copper(II) ions: i_{Cu} = 200 A·m^{-2}, H_2SO_4—50 g·L^{-1}, τ = 0.5 h.

Figure 6 shows that, as the current density at the titanium electrode increases up to 1 × 10^5 A·m^{-2}, the current efficiency of copper dissolution increases, after which it begins to

decrease. This is associated with changes in the structure of the oxide film on the titanium surface in the sulfuric acid solution.

It should be noted that the formation of the valve properties of titanium dioxide, which forms under anodic polarization and in the anodic half-cycle of alternating current, depends on the current density at the titanium electrode and on the solution composition. It is assumed that, depending on the solution composition, at very high current densities looser oxide films of various compositions (Ti_xO_y) are formed, which weaken the valve properties; accordingly, the dissolution of the second (copper) electrode slows down, and therefore the current efficiency of copper oxide formation decreases.

The slight excess of the current efficiency above 100% is explained by the chemical dissolution of the copper electrode in air (reaction 7). The possibility of copper oxidation in the presence of oxygen is reported in well-known literature sources, for example, in [20].

$$Cu + 0.5\ O_2 + H_2SO_4 \rightarrow CuSO_4 + H_2O \quad (7)$$

It should be noted that, at the beginning of electrolysis, reaction (5), i.e., hydrogen evolution, proceeds at the titanium electrode during the cathodic half-cycle. With time, copper(II) ions accumulate in solution, and a reduction reaction leading to the formation of metallic copper powder is observed at the titanium electrode:

$$Cu^{2+} + 2e \rightarrow Cu^o \quad (8)$$

It can therefore be concluded that, in the presence of copper(II) ions in the sulfuric acid solution, it becomes possible to obtain copper powders by polarization with industrial alternating current.

Known methods for producing copper powders [21,22] involve electrolysis under direct current at high cathodic current densities, in which oxide formation is governed by the applied potential, current density and solution pH. In this connection, the observed reactions were used to obtain copper powder. Electrolysis was carried out using a copper plate electrode paired with a titanium electrode in a copper(II) sulfate solution. The effect of the current density at the titanium wire electrode (i_{Ti}) was studied at a constant current density at the copper electrode (1000 A·m^{-2}). The results are shown in Figure 7.

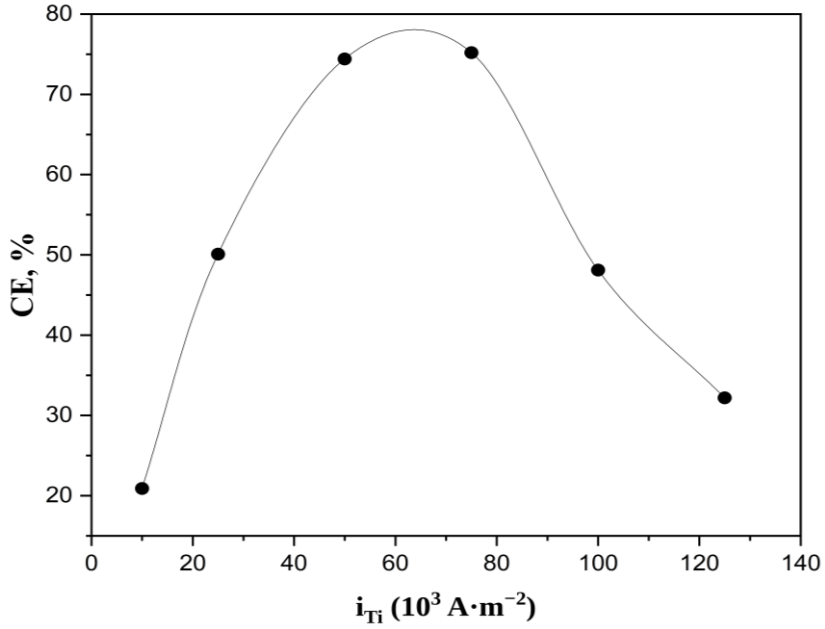


Figure 7. Effect of current density at the titanium electrode on the current efficiency of copper powder formation under alternating current polarization: H_2SO_4—100 g·L^{-1}, Cu(II)—15 g·L^{-1}, i_{Cu} = 1000 A·m^{-2}, τ = 1 h.

The results of studying the effect of the current density at the titanium wire (i_{Ti}) at a constant current density at the copper electrode (i_{Cu} = 1000 A·m^{-2}) show (Figure 7) that the current efficiency of copper powder formation increases with increasing current density at the titanium electrode up to 7.5 × 10^4 A·m^{-2}. The subsequent decrease in current efficiency is apparently associated with an increased contribution of the side reaction of hydrogen evolution (reaction 5), as well as with changes in the structure of the oxide film on the titanium surface, leading to a reduction in the rectifying effect. It should be noted that the current efficiency was calculated for the cathodic half-cycle of the alternating current.

2.2. Electrochemical Behavior of Copper Under Alternating Current Polarization in Acidic and Neutral Chloride-Containing Solutions

Under AC polarization of the copper–titanium pair in sodium chloride solution, the copper electrode is oxidized during the anodic half-cycle to form Cu^+, with the subsequent formation of copper(I) oxide (Cu_2O). It is noted that Cu^{2+} ions are stable in sulfate solution, whereas Cu^+ ions are stable in chloride medium. In chloride medium, copper is oxidized stepwise:

$$Cu + Cl^- - e \rightleftarrows CuCl \qquad E^0 = +0.137\ \text{V} \tag{9}$$

$$CuCl - e \rightleftarrows Cu^{2+} + Cl^- \quad E^0 = +0.538\ \text{V} \tag{10}$$

When the titanium electrode is in the cathodic half-cycle of the alternating current, the reduction of hydrogen ions (reaction 1) takes place at its surface. At the same moment, the copper electrode is in the anodic half-cycle and dissolves to form Cu^+. Because the reversal of current direction under AC polarization occurs rapidly, almost instantaneously, it is assumed that only the first stage of copper oxidation has time to proceed during the anodic half-cycle.

Copper(I) chloride reacts with hydroxide ions to form copper(I) hydroxide:

$$CuCl + OH^- \rightarrow CuOH + Cl^- \tag{11}$$

The latter undergoes dehydration, which is enhanced with increasing temperature:

$$CuOH \overset{t}{\rightarrow} Cu_2O + H_2O \tag{12}$$

The formation of a dark-red, finely dispersed copper(I) oxide powder is observed visually. It was found that the current efficiency of copper(I) oxide decreases with increasing current density at the titanium electrode (Figure 8).

The copper(I) oxide powder obtained was separated from the solution by filtration, washed, dried, and identified by X-ray phase (Figure 9) and elemental analyses.

The results of X-ray phase analysis of the synthesized sample (Figure 9) showed that the powder obtained corresponds to the crystalline phase of copper(I) oxide (Cu_2O). Intense reflections are observed in the diffraction pattern at d = 3.00, 2.46, 2.13, 1.51 and 1.28 Å, corresponding to the cubic cuprite-type structure. The positions and intensities of the main diffraction maxima are in good agreement with the standard PDF (ICDD) data for Cu_2O. No additional peaks characteristic of copper(II) oxide or metallic copper were observed, indicating the high phase purity of the synthesized product.

To confirm the elemental composition of the powder obtained, energy-dispersive X-ray spectroscopy (EDS) was performed. According to the data obtained (Table 2), the average oxygen content was 11.22 wt.%, and the copper content was 88.78 wt.%. These values are very close to the theoretical stoichiometric composition of Cu_2O (O—11.18 wt.%, Cu—88.82 wt.%). Taken together, the results of X-ray phase and elemental EDS analyses confirm the formation of high-purity crystalline copper(I) oxide.

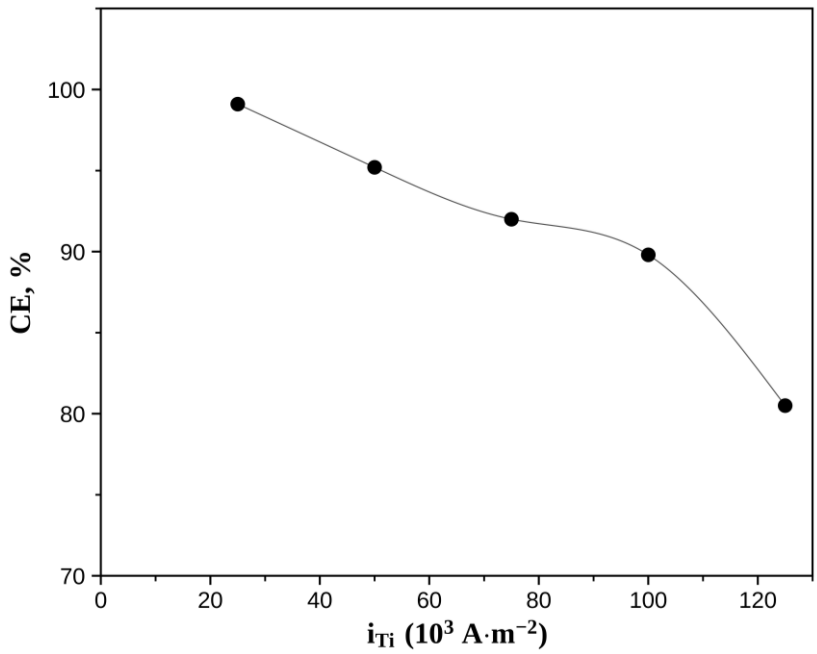


Figure 8. Effect of current density at the titanium electrode on the current efficiency of copper(I) oxide under alternating current polarization: i_{Cu} = 300 A·m^{-2}, C(NaCl) = 50 g·L^{-1}, τ = 0.5 h.

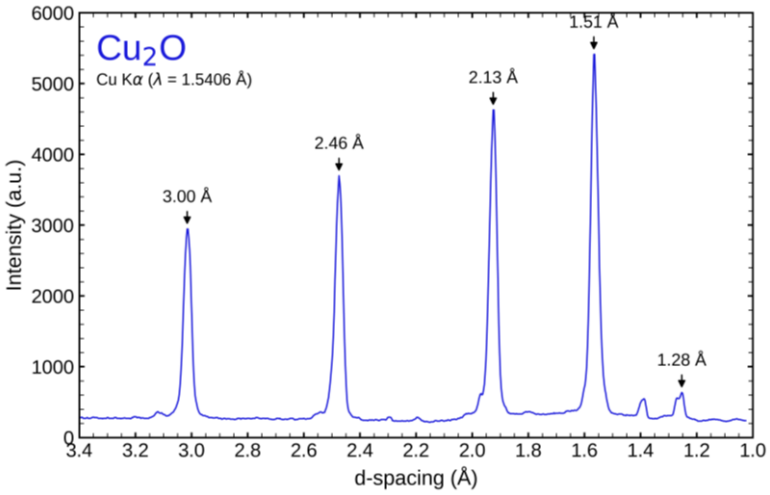


Figure 9. X-ray diffraction pattern of copper(I) oxide obtained using Cu Kα radiation (λ = 1.5406 Å), plotted as a function of interplanar spacing, *d*.

Table 2. Elemental composition of copper(I) oxide according to EDS analysis (wt.%).

Spectrum	O (wt.%)	Cu (wt.%)	Σ (%)
1	11.22	88.78	100
2	11.24	88.76	100
3	11.20	88.80	100
Average	11.22	88.78	100

It was established experimentally that, upon polarization of a pair of copper electrodes with industrial-frequency (50 Hz) alternating current in hydrochloric acid solution, they dissolve to form copper(I) chloride. Unlike sulfate electrolytes, in chloride medium the processes of copper oxidation and copper(II) ion reduction proceed predominantly with the formation of copper compounds in a single (monovalent) oxidation state. This is attributable to the stabilization of Cu(I) ions by chloride ions

through the formation of stable Cu(I)–Cl complex species, which prevent their further oxidation to Cu(II) and their disproportionation in solution [23,24].

In this connection, upon polarization of copper electrodes with industrial alternating current, mainly the first stages of the electrochemical reactions proceed in both the anodic and the cathodic half-cycles, leading to the formation of copper(I) chloride.

To evaluate the effect of copper(II) ions on the CuCl synthesis process, similar experiments were carried out in a solution containing Cu^{2+}. It was found that the introduction of copper(II) ions intensifies the dissolution of both copper electrodes, with the observed current efficiency exceeding 100% (Figure 10). This increase is due to the concurrent occurrence of chemical dissolution of copper alongside the electrochemical reactions. During the anodic half-cycle, metallic copper is oxidized to Cu^{+}, whereas during the cathodic half-cycle Cu^{2+} ions are reduced to Cu^{+}. Simultaneously, a comproportionation reaction between metallic copper and Cu^{2+} ions takes place in solution:

$$Cu + Cu^{2+} \rightarrow 2Cu^{+} \quad (13)$$

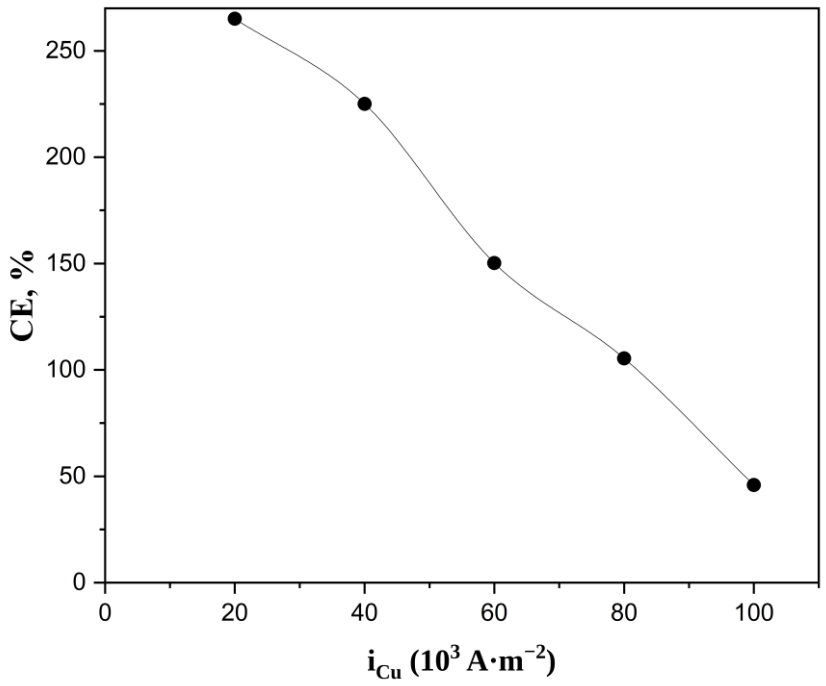


Figure 10. Dependence of the current efficiency of copper(I) chloride formation on the current density at the copper electrodes: Cu(II)—20 g·L^{-1}, 2 M HCl.

As a result, Cu^{+} ions are formed by both electrochemical and chemical pathways, which accounts for the current efficiency exceeding the theoretical value. As the current density increases, the current efficiency gradually decreases, which is probably related to a change in the ratio of the rates of the electrochemical and chemical stages of the process, as well as to the intensification of side reactions.

Thus, the presence of Cu^{2+} ions in the chloride electrolyte promotes the intensification of Cu(I) formation, ensuring the efficient synthesis of copper(I) chloride. To confirm the phase composition and chemical purity of the product obtained, after completion of electrolysis the solution was evaporated, and the resulting precipitate was separated by filtration, dried, and examined by X-ray phase analysis (Figure 11) and energy-dispersive X-ray spectroscopy (EDS).

The X-ray diffraction pattern of the sample studied contains pronounced diffraction maxima at interplanar spacings of approximately 3.31, 1.91 and 1.63 Å. This set of reflections corresponds to the crystalline phase of copper(I) chloride CuCl.

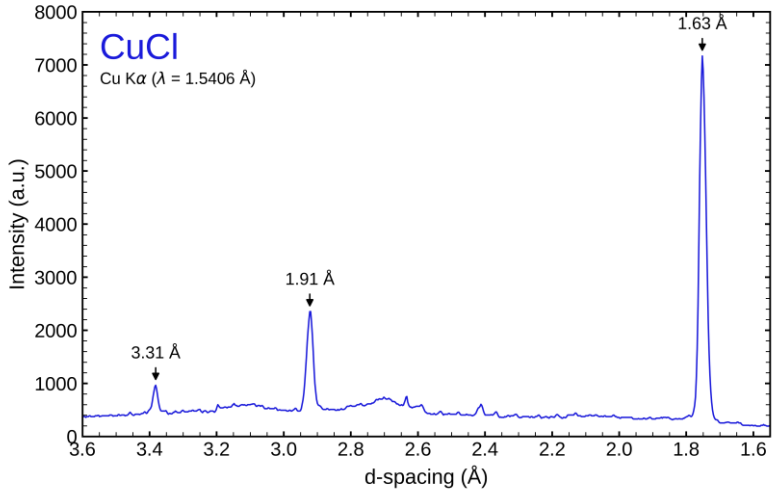


Figure 11. X-ray diffraction pattern of copper(I) chloride CuCl (Cu K_α radiation, $\lambda = 1.5406$ Å; plotted against the interplanar spacing d).

The most intense maximum is observed at d ≈ 1.63 Å, whereas the reflections at d ≈ 3.31 and 1.91 Å are less intense. The presence of well-defined and relatively narrow diffraction maxima indicates the crystalline nature of the product.

The set of interplanar spacings obtained indicates the formation of crystalline CuCl. In the absence of additional intense reflections attributable to other copper compounds, the data obtained can be regarded as confirming the predominant presence of copper(I) chloride in the sample.

Thus, the results of X-ray phase analysis confirm the formation of the crystalline copper(I) chloride phase CuCl.

These results are also consistent with the elemental analysis data, which confirm the composition of CuCl (Table 3).

Table 3. Elemental composition of copper(I) chloride according to EDS analysis (wt.%).

Spectrum	Cl (wt.%)	Cu (wt.%)	Σ (%)
1	35.52	64.48	100
2	35.19	64.81	100
3	35.37	64.63	100

According to the EDS data, copper and chlorine are the main elements in all three spectra studied. The normalized chlorine content is 35.19–35.52 wt.%, and the copper content is 64.48–64.81 wt.%. The slight scatter of values between individual spectra indicates a fairly uniform elemental composition of the synthesized compound.

The experimental values obtained are in good agreement with the theoretical composition of copper(I) chloride CuCl. For stoichiometric CuCl, the calculated content is approximately 64.2 wt.% Cu and 35.8 wt.% Cl. The closeness of the experimental and calculated values confirms that the elemental composition of the synthesized compound corresponds to the formula CuCl.

Thus, the results of EDS analysis confirm the predominant formation of copper(I) chloride, and the similar Cu and Cl contents in the different areas studied indicate the relative chemical homogeneity of the product obtained.

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3. Materials and Methods

Experiments were carried out in a thermostatically controlled 100 mL glass electrolyzer at 25 ± 1 °C. A schematic diagram of the experimental setup is shown in Figure 1. Two electrode pairs were used: copper–copper and copper–titanium. The copper electrode was a plate of M1-grade copper with a working surface area of 0.001 m^2. A VT1-0 grade titanium wire, 0.1 mm in diameter, was used as the second electrode. Before each experiment, the electrode surfaces were mechanically abraded with abrasive paper, rinsed with distilled water, degreased with ethanol, and dried in a ShS-80-01 SPU drying oven (Smolenskoye SKTB SPU, Smolensk, Russia).

Aqueous solutions of H_2SO_4, Na_2SO_4, HCl, NaCl and $CuSO_4$, prepared from analytical-grade reagents in distilled water, were used as electrolytes. Component concentrations corresponded to the conditions specified for each individual experiment.

Electrode polarization was carried out with industrial-frequency (50 Hz) alternating current supplied by an ASR-721000 power source (GW Instek, New Taipei City, Taiwan). The AC and voltage were monitored with a TsMA8500-6 ammeter (MNPP Elektropribor LLC, Vitebsk, Belarus) and a V7-78/2 voltmeter (AKIP, Moscow, Russia), respectively. Current efficiency (CE) was calculated for each half-cycle of the alternating current, taking into account the direction of the electrochemical reactions. All current-efficiency experiments were carried out three times under identical conditions, and the results presented are mean values of three independent measurements (n = 3). For each data point, the sample standard deviation (SD), relative standard deviation (RSD), and two-sided 95% confidence interval (CI) were calculated. The 95% CI was determined using Student's t-distribution (df = 2). Across all non-zero current-efficiency data points presented in Figures 2, 6–8 and 10, the RSD ranged from 0.36% to 3.14%, with a median RSD of 1.05%, while the corresponding 95% CI half-widths ranged from 0.861 to 7.653 percentage points. All RSD values were below 5%, indicating good experimental reproducibility.

The phase composition of the synthesized products was determined by X-ray diffraction on a DRON-4-07 diffractometer (Burevestnik, St. Petersburg, Russia). Surface morphology and elemental composition were examined by scanning electron microscopy (SEM) at several randomly selected areas of the surface, with subsequent averaging of the results, using a TM4000Plus microscope (Hitachi, Tokyo, Japan) equipped with a Quantax 75 energy-dispersive X-ray spectrometer (Bruker, Berlin-Adlershof, Germany).

The copper compounds obtained by our methods form on the surface of the copper electrode and subsequently precipitate as insoluble powders. The powders were separated from the solution by filtration using an ISOLAB Laborgeräte vacuum pump (ISOLAB Laborgeräte GmbH, Eschau, Germany), washed several times with distilled water, dried and identified by physicochemical methods of analysis. The resulting compounds are practically free of impurities, since cathode copper (99.99%) was used for the copper electrodes and sodium chloride of chemically pure grade was used. Regarding the titanium electrode covered with a stable oxide film, it should be noted, first, that the titanium electrode is insoluble. Under anodic polarization, or under AC polarization during the anodic half-cycle, a stable TiO_2 oxide film with valve properties forms on the surface of the titanium electrode [14]; the thickness of this oxide film does not exceed 100 nm, but it is sufficiently stable, and therefore titanium does not dissolve in aqueous solutions. Consequently, the possibility of impurities from the titanium electrode (present in its composition in trace amounts) entering the obtained powders can be practically ruled out.

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4. Conclusions

It was established that the electrochemical behavior of copper under polarization with industrial-frequency (50 Hz) alternating current is determined by the electrolyte composition and by the nature of the second electrode. The use of titanium promotes the directional course of the processes owing to the formation on its surface of a passive oxide film with valve properties.

It was shown that, in the Cu–Ti system, CuO, Cu_2O, CuCl and copper powder can be obtained depending on the electrolyte composition. The maximum current efficiency of CuO formation in Na_2SO_4 solution was 89.2%, and that of Cu_2O formation in NaCl solution was 99.1%, calculated per the corresponding half-cycle of the alternating current. It was established that, in the Cu–Cu electrode system in hydrochloric acid solution, copper(I) chloride is formed with a high apparent current efficiency exceeding 100%.

Prospects for further research are associated with establishing the mechanism of the processes in individual half-cycles of the alternating current; studying the effect of frequency, current density, waveform and electrolyte composition on the selectivity and yield of the products; investigating the structure and functional properties of the materials obtained; and evaluating the energy and technological efficiency of the process.

The results obtained allow polarization with industrial-frequency alternating current in the "Cu–Ti" and "Me–Me" electrode systems to be regarded as a promising basis for the development of controllable electrochemical methods for producing Cu_2O, CuO, CuCl and copper powder. Of particular interest are the processes of selective formation of metal ions in lower oxidation states and the possibility of extending this approach to other metals, including refractory metals.

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