

Laws of Dissolution of Copper Electrodes Polarized by the Alternating Current in Solution of Potassium Iodide

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Electrochemical behavior of copper in solution of potassium chloride under polarization with industrial alternating current is investigated. It is shown, that at polarization of copper-titanium electrode pair by an alternating current with frequency of 50 Hz in the solution of potassium iodide the copper electrode is dissolved, forming compound of copper (I) iodide. It is also shown, that current efficiency of formation of copper (I) iodide is influenced by (i) the density of alternating current, (ii) concentration of potassium iodide and hydrochloric acid in solution. On the basis of the research the optimum conditions of obtaining of copper (I) iodide have been determined. At the optimum conditions the current efficiency of formation of copper (I) iodide was more than 100.0%. The advantages of the electrochemical method are the economical efficiency, simplicity of process, purity of the obtained product, electrolysis at room temperature, improvement of the working conditions.

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1. Introduction

The remarkable property of the alternating current is that it is possible to transform, increase or decrease, its voltage in a very wide range. When a high voltage is available, it is not difficult to decrease the voltage, with help of a transformer, for the optimum operation condition of traction motors and machines [1, 2].

In recent years, more attention is paid to the use of alternating currents of different forms, including industrial alternating current with frequency of 50 Hz [3, 4]. The use of non-stationary electrolysis mode extends the possibility of studying of electrode processes and opens up entirely new possibilities for solution of a number of problems of applied electrochemistry.

The possibility of a targeted processes under the influence of symmetrical alternating current with frequency of 50 Hz has been doubtful for a long time. It was supposed that the processes of deposition or dissolution of the metal should not progress, as with frequent changes of the direction of current the amount of metal deposited at cathode during one half-period must be compensated by metal passing into the solution in the form of ions at the anodic half-cycle.

Our investigation conducted over the last 15–20 years shows that under certain conditions it is possible to carry out the electrolysis under the action of alternating current due to possibility of rectification during one of the half-periods.

Decrease of the current in one half-period of the alternating current can cause the formation of oxide, salt or other films, diffusion of ions to the electrode surfaces,

the discharge and recharge of the complex anions or cations, crystallization of the metal etc. Altogether this contributes to the fact that for symmetrical alternating current in the forward and backward directions, unequal conditions are created, contributing to preferential behavior of one of the process (oxidation or reduction).

It is now known that the use of different forms of AC allows speeding up the processes of anodic dissolution and destruction of the passivation of the electrode.

The feature of unsteady electrolysis, is the possibility of obtaining pure metals or their compounds, reduction of reagent consumption and absence of waste [5–7].

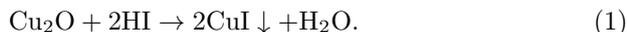
The copper iodide particle has hydrophobic properties. It is used as conventional catalyst in organic synthesis and to create super ionic conductors [8]. In [9] a useful catalytic application of copper (I) iodide for one pot odor-free generation of unsymmetrical aryl alkyl thioethers was proposed. The process proceeds by the reaction of phenolic esters such as acetates, triflates, tosylates and phosphonates with benzyl, n-octyl, cyclohexyl, cyclopentyl, n-hexyl and n-butyl iodides, bromides, chlorides and tosylates in wet polyethylene glycol (PEG 200), by using thiourea as the sulfur source under homogeneous conditions.

Copper (I) iodide, in conjunction with 1.10-phenanthroline as ligand, accelerates the reaction rate and enhances reaction yields by $\sim 30\%$ [10].

Since Ag^+ and Cu^+ are known to have approximately same size and polarizability, as well as the tendency to form similar compounds, the use of CuI , as a possible dopant in silver salt matrices for realization of cost-effective fast ionic glasses, was also found to be feasible and meaningful [11–14].

Production of copper (I) iodide is carried out by the chemical method through reaction of copper (I) oxide with the dissolved ionic acid:

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Also it is possible to obtain copper (I) iodide, by heating up, through reaction of copper (I) oxide with aluminum iodide:



There are also some disadvantages of this method: at room temperature the formation of copper (I) iodide proceeds very slowly, therefore to increase the rate of reaction it is carried out at high temperature. Additionally, copper (I) iodide obtained with the help of reaction (2) is polluted by aluminum [15].

2. Experimental section

The preliminary research has shown that at polarization by an alternating current with frequency of 50 Hz of electrode pair copper-titanium in a solution of potassium iodide the copper electrode had dissolved, forming the compound of copper (I) iodide. In this respect, in order to liquidate the above specified disadvantages, copper (I) iodide production by the electrochemical method through polarization by industrial alternating current has been found beneficial.

Advantages of an electrochemical method are: the economical efficiency, simplicity of process, purity of the obtained product, electrolysis at room temperature and improvement of working conditions.

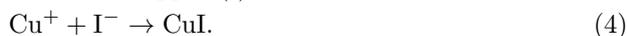
Experiments for research of the electrochemical properties of dissolution of a copper electrode in the potassium iodide solution were carried out in the glass electrolytic cell with the thermostat, with a capacity of 100 ml.

The electrode space was non-arranged, as electrodes the titanium wires (the area $3 \times 10^{-6} \text{ m}^2$) and the rectangular copper plates (with size of $13.68 \times 10^{-4} \text{ m}^2$) were used. By polarization of the electrode pair of copper-titanium in a solution of potassium iodide with the industrial alternating current with with frequency of 50 Hz, it is possible to observe dissolution of the copper electrode with formation of copper (I) iodide deposit.

It is possible to explain the formation of this compound as follows. During anode half-cycle, copper is oxidized, having formed the ions:



The obtained ions of copper, interact with iodide ions and form the copper (I) iodides:



Formation of this compound is possible to explain by the low value of CuI solubility, equal to $E_k = 1 \times 10^{-12}$.

3. Results and discussion

The influence of current density on the titanium electrode on the current efficiency of formation of copper (I) iodide on the copper electrode, polarized with the industrial alternating current in solution of potassium iodide, was investigated. In Fig. 1 the results of research are

shown. It is seen that with the increase of current density the current efficiency of formation of copper (I) iodide decreases. The decrease of current efficiency of copper (I) iodide formation is observed in the current density interval of 100–250 kA/m^2 .

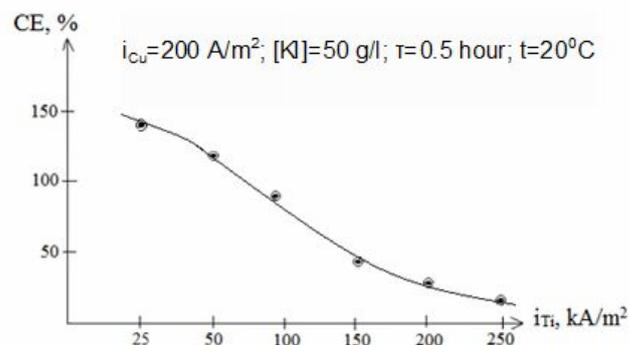


Fig. 1. Influence of density of current on the titanium electrode on current efficiency of formation of copper (I) iodide in a solution of potassium iodide on a copper electrode, polarized by industrial alternating current.

The influence of electrolyte concentration (KI), in the interval 25–125 g/l, on the current efficiency of formation of copper (I) iodide in solution of potassium iodide on a copper electrode polarized with industrial alternating current was investigated (Fig. 2). With the increase in concentration of potassium iodide in the solution the current efficiency of formation of copper (I) iodide reaches a maximum. In the interval of potassium iodide concentrations of 25–50 g/l, the current efficiency of formation of copper (I) iodide reached 83.2%, and in the interval of concentrations 50–125 g/l, the current efficiency of formation of copper (I) iodide had decreased. With the increase of concentration of electrolyte the formation of copper iodide deposit became slower.

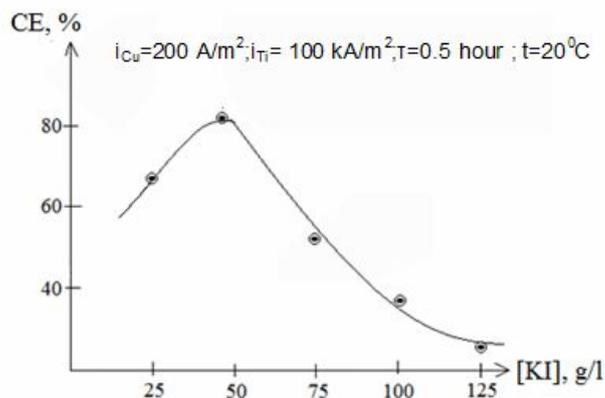


Fig. 2. Influence of electrolyte concentration on current efficiency of formation of copper (I) iodide in solution of potassium iodide, with the copper electrode polarized by the industrial alternating current.

TABLE

Influence of concentration of sulfuric acid on current efficiency of formation of copper (I) iodide ($i_{Cu} = 200 \text{ A/m}^2$; $i_{Ti} = 100 \text{ kA/m}^2$; $[KI] = 50 \text{ g/l}$; $\tau = 0.5 \text{ hours}$; $t = 20 \text{ }^\circ\text{C}$)

H ₂ SO ₄ , [g/l]	25	50	100	125	150
CE, %	82.3	72.5	63.3	50.0	45.0

After the electrolysis in a solution of potassium iodide the electrolyte was evaporated, filtered, dried up, separated in the form of a deposit of copper (I) iodide. The X-ray diffraction diagram of copper (I) iodide salt formed during electrolysis is shown in Fig. 3.



Fig. 3. X-ray diffraction diagram of CuI (ASTM 6-344).

4. Conclusions

On the basis of the research the deposition of copper (I) iodide using electrode pair of copper-titanium in the solution of potassium iodide polarized by an alternating current has been achieved for the first time. The influence of the (i) density of alternating current, (ii) concentration of potassium iodide and sulfuric acid in the solution and (iii) the optimum conditions of process, on the current efficiency of obtaining of this compound was studied. Under the effective conditions the current efficiency of formation of copper (I) iodide reached 100.0% and more.

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