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THE ELABORATION OF COPPER BROMIDE SYNTHESIS BY ELECTROCHEMICAL METHOD

Abstract. The electrochemical behaviour of copper electrode was studied by anodic polarization in potassium bromide aqueous solution for the first time. To investigate the processes specificity occurring at anodic polarized copper electrode, anodic polarization curves were carried out in the potassium bromide solution. The influences of current density of copper ($i_{Cu}=100-600$ A/m²) and titanium ($i_{Ti}=20-120$ kA/m²) electrodes, electrolyte concentration ([KBr]=1-5 M), solution temperature ($t=20-70^{\circ}C$) and electrolysis duration ($\tau=0.5-1.5$ h) on the anodic current polarized copper electrode dissolution were investigated and optimal electrolysis conditions of copper (I) bromide formation were determined. The current efficiency of copper (I) bromide formation reached 72.1% at 200A/m² anodic current density in the copper electrode; this value decreased by 60% when the current density was further increased. The effect of the electrolyte concentration on copper (I) bromide formation was found to be significant. At 2 M potassium bromide solution, the current efficiency increased (~ 70%) and reached a maximal value. As a result of the further increase of the solution concentration, the current efficiency declined sharply. The research result on defining the electrolyte temperature effect on copper (I) bromide formation process during anodic polarization has shown that the current efficiency decreases due to an increase in the temperature. This can be explained by the excessive voltages reduction of oxygen gas evolution in the anode due to the increased temperature, by the increase in its proportion or by the dissolution of copper (I) bromide compounds.

Keywords: copper electrode, anodic polarization, potassium bromide, electrolyte, current efficiency.

Currently, electrochemical methods are widely used in obtaining valuable inorganic substances used in many fields of science and technology, chemical industry. A distinctive feature of this method is that it allows to obtain the valuable substances in pure form without additives and is characterized by a low flow rate of reagents. The advantages of the electrochemical method are the process simplicity, purity of the obtained products, no emission of toxic gases, electrolysis occurring at room temperature and the improvement of working conditions [1, 2].

Nowadays, various inorganic copper compounds are in high demand due to their wide usage in the modern scientific and technical spheres. For example, copper halides are a powerful oxidizer used in chemical production, especially in the synthesis of organic substances and used as a catalyst in many organic reactions [3-6].

The data provided in works [7-10] show that the copper bromide forms complex coordinate compounds with organic compounds.

Copper (I) bromide is thermally resistant light-green tetrahedron crystals. It is rapidly oxidized in the moist air, molds in the light, insoluble in cool water, ethanol and ether and decomposes in hot water. It dissolves in HCl, HBr, ammonium, ammonium salts, pyridine, concentrated chloride solutions, alkaline metals bromides and thiosulfates by forming coordinate compounds [11].

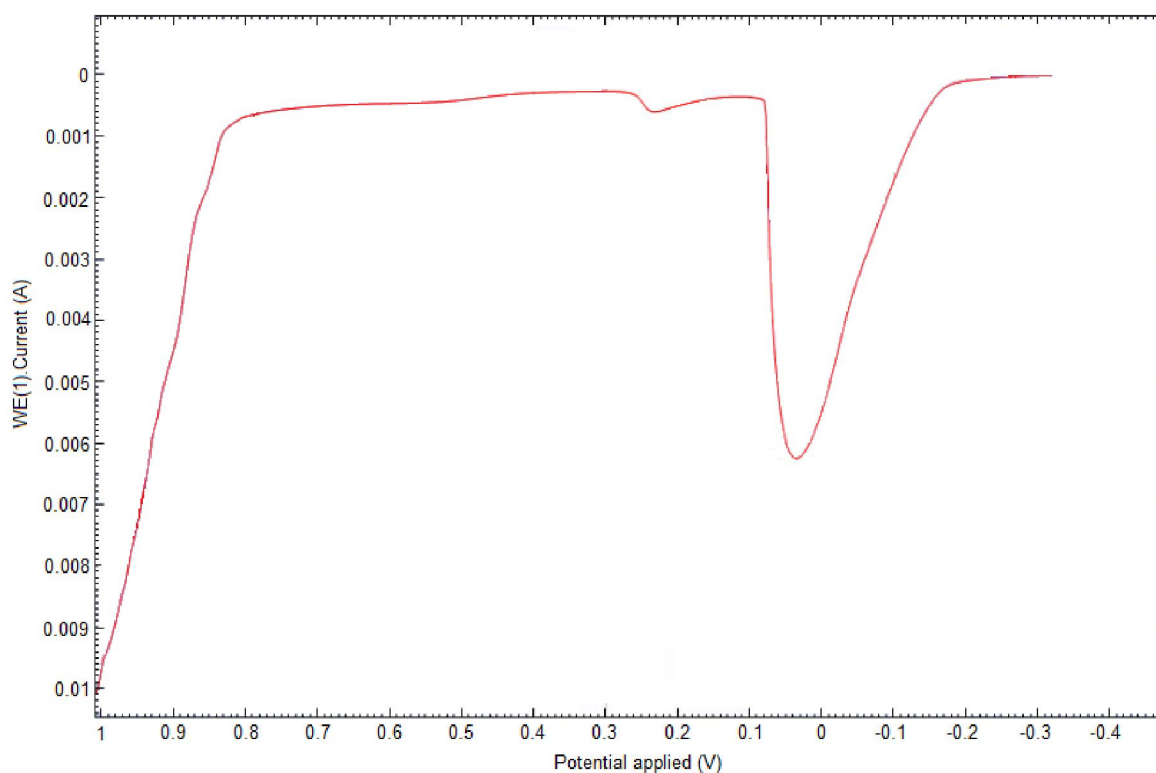
In previous studies, the electrochemical properties of copper in sulphate, chloride, iodide and acidic media were studied and the ways to obtain copper chloride, sulphate, iodide and oxide were offered and their novelty was protected by patents [12-16].

The authors [17] investigated copper dissolution in bromide medium in the absence and presence of HMTA by using Spectroelectrochemical techniques. In this work a passivant Cu/HMTA/Br⁻ film was observed in the presence of the inhibitor. The nature of the passivant film was confirmed by in situ surface-enhanced Raman scattering (SERS) and SEM/EDX measurements. However, in this work the method of copper (I) bromide obtaining is not suggested.

There are known chemical methods of obtaining copper (I) bromide by a chemical way. According to this method, the corresponding amount of pure copper sulfate and potassium bromide is heated slowly in boiling distilled water for 2 hours and then a strong flow of SO₂ gas is passed until the solution is completely cooled. At this point, the copper bromide is precipitated as sediment in the form of thin white-yellow crystals. The sediment is filtered by preserving from daylight, rinsed with boiled water containing SO₂ for 5-7 times and then filtered again. Subsequently, the sediment is washed with absolute alcohol containing SO₂ and then with absolute ether with SO₂. The obtained salt can be dried in hydrogen atmosphere over H₂SO₄ and potassium hydroxide for 3 days and then can be dried in vacuum. Obtaining copper bromide in a chemical way takes long time, has multistage steps and consists from complex mechanism [18].

In the presented work electrochemical dissolution of copper electrode was investigated by taking anodic potentiodynamic polarization curves in 2M potassium bromide solution. The measurements were performed in a three-electrode thermostatic cell with potentiostat "Autolab". Silver chloride (E = +0,203 V) served as the relative electrode, the platinum as an auxiliary electrode, while the teflon covered copper wire edge was used as a working electrode.

In the works of A.K.Bayeshova and others, the electrochemical properties of copper were investigated in 1M potassium bromide aqueous solution by taking cyclic anode-cathodic and cathode-anodic potentiodynamic polarization curves. The effects of the rate of potential change and electrolyte temperature on the copper electrolyte oxidation process were considered. It was assumed that in this process the electrode reactions would be accompanied by a very complex mechanism and that copper (I) bromide could be formed on the electrode surface.



V = 100 mV/s, t = 25°C, [KBr] = 2M

Figure 1 – The anode polarization curve of copper electrode in the potassium bromide solution

Two anodic maximum corresponding to the oxidation of copper Cu^+ and Cu^{2+} copper in the "plus" 0,03V and "plus" 0,28V potentials on an anode polarization curve of the copper electrode in the potassium bromide solution can be observed. Since the solubility of copper (I) bromide is considerably lower, formed copper (I) ions form CuBr by reacting with the Br^- anions in the solution volume and its stability increase [19].

Mainly, investigation on electrolytic formation of copper (I) bromide were performed in thermostatic glass cell. The electrolysis was conducted in a galvanostatic mode using the copper electrode as anode and the titanium wire as cathode. After the electrolysis, copper (I) bromide was filtered off and washed with distilled water and absolute alcohol, dried and weighted by the weight method. The electrolyte solutions were prepared from reagent grade KBr and distilled water.

The influence of anodic current density on current efficiency (CE) of copper (I) bromide formation was investigated in potassium bromide aqueous solution during anodic polarization (figure 2). There was observed, that the current efficiency of copper (I) bromide formation reached just over 72% at the current density in the copper anode 200 A/m^2 ; this value decreased by 60% when the current density was further increased up to 600 A/m^2 . This can be explained by the additional reaction of the oxygen gas evolution in the anode or a gradual passivation of the electrode covered with the copper bromide. The scientist of work [17] also established that CuBr precipitates on the electrode surface as the anodic current density becomes large enough.

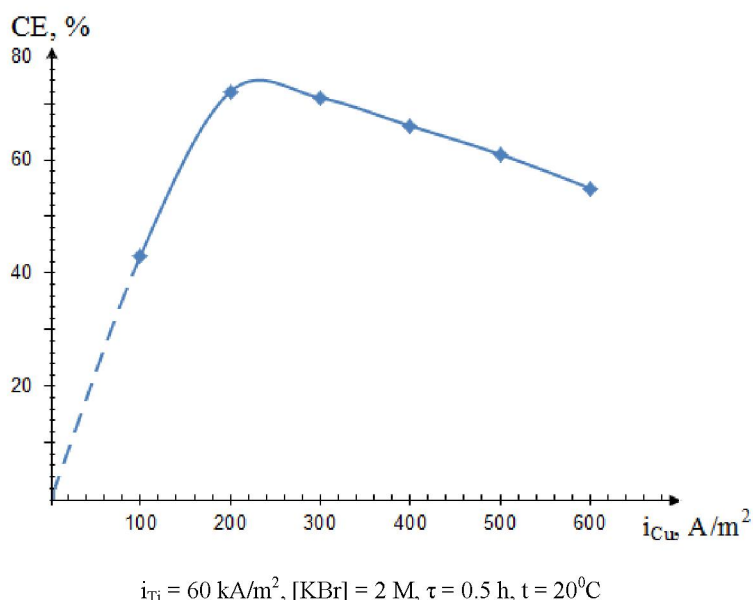
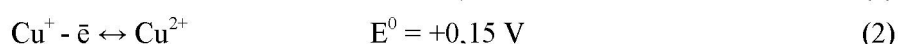
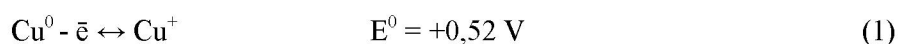


Figure 2 – Effect of the anodic current density in copper electrode on the current efficiency of copper (I) bromide formation

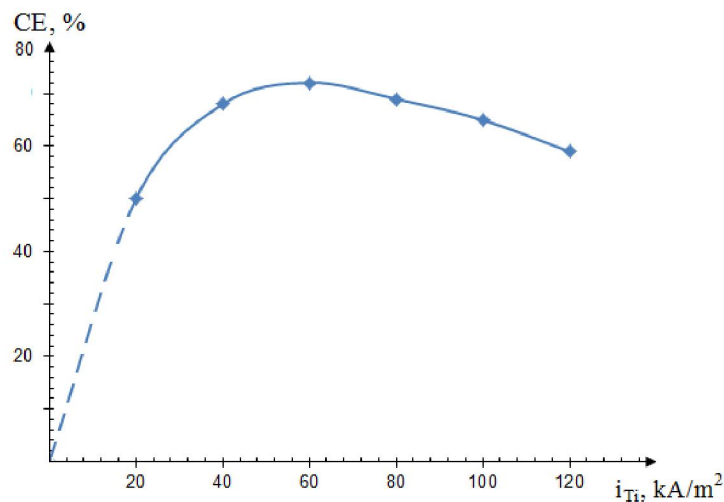
The impact of the current density in the additional titanium electrode on the current efficiency of the copper electrode was studied. According to figure 3, as a result of increasing the current density in the titanium electrode, the current efficiency initially increases until 60 kA/m^2 and then followed by gradually decrease; the maximum CE accounted more than 70%.

During the anodic polarization of copper electrode, the following electrochemical reactions can be occurred:



The solubility of copper (I) bromide is low ($\text{SP} = 5,25 \cdot 10^{-9}$) [20], so that formed Cu (I) ions react with Br^- ions and form copper (I) bromide. It can be observed by the formation of orange sediment formed at the bottom of the solution:





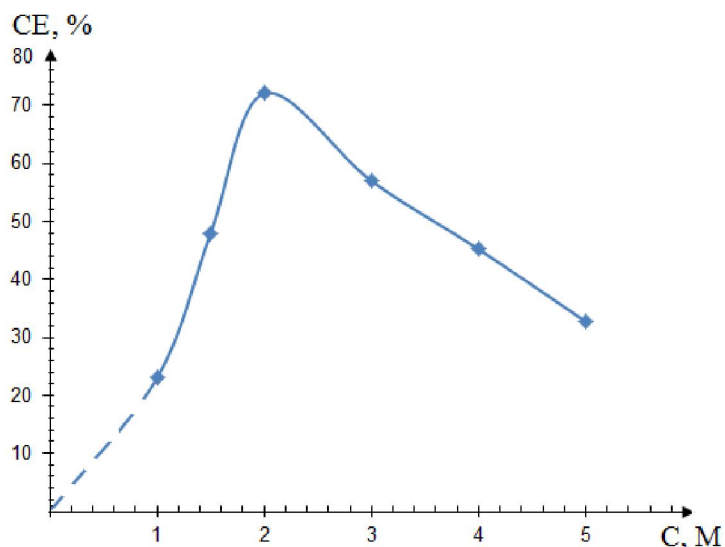
$$i_{Cu} = 200 \text{ A/m}^2, [\text{KBr}] = 2 \text{ M}, \tau = 0.5 \text{ h}, t = 20^\circ\text{C}$$

Figure 3 – Effect of the current density in additional titanium electrode on the CE copper (I) bromide formation during anodic polarization of copper electrode

In work [21], the solubility of cuprous bromide in aqueous KBr and aqueous KBr-KNO₃ mixtures was measured at 24.8⁰C. Based on the results of the analysis, the equilibrium constants for formation of neutral and negative charged CuBr complexes were given and the ways to calculate the activity coefficients for the complexes were determined.

The effect of potassium bromide concentration on the current efficiency rate of the CuBr formation at the anodic polarization of the copper electrode is presented in figure 4. With increasing the concentration of potassium bromide from 1.0 M to 5.0 M there was observed a sharp growth of the current efficiency of the copper (I) bromide formation until 2.0 M, while decrease-trend in the current efficiency observed in higher concentrations.

Initially, the interaction of Br⁻ anions with Cu⁺ ions in the solution increases with the rise of the solution concentration. In high concentrations of the bromide ion, the copper electrode is covered with its bromide film and becomes passivated.



$$i_{Cu} = 200 \text{ A/m}^2, i_{Ti} = 60 \text{ kA/m}^2, \tau = 0.5 \text{ h}, t = 20^\circ\text{C}$$

Figure 4 – Effect of potassium bromide concentration in the solution on the current efficiency of copper (I) bromide formation

The influence of the solution temperature on the current efficiency of the copper electrode dissolution anodic polarized in the potassium bromide solution was investigated (figure 5). The electrolysis was performed in temperature intervals 20-70°C. There was continuous decrease of current efficiency of copper bromide formation through the electrolyte temperature increased. This phenomenon can be explained by the excessive voltages reduction of oxygen gas evolution in the anode due to the increased temperature, by the growth its proportion or by the dissolution of copper (I) bromide compounds.

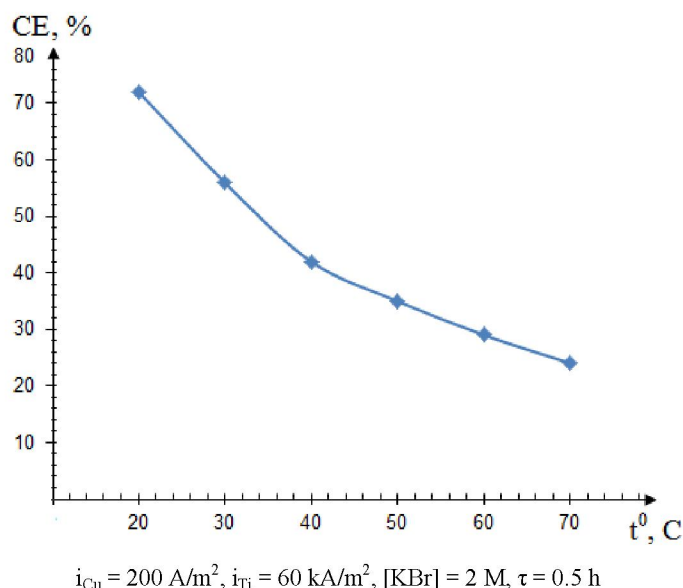


Figure 5 – Effect of the solution temperature on the current efficiency of copper (I) bromide formation

The effect of the electrolysis duration on the current efficiency on dissolution of anodic current polarized copper electrode was studied between 0.5-1.5 hours (figure 6). Gradual failing trends of current efficiency of copper (I) bromide formation was observed as a result of increasing the duration of electrolysis. This can be explained by the increase in the number of additional reactions as time goes by, the decrease of the concentration in the bromide ions solution and the passivation of electrode with electrolysis products.

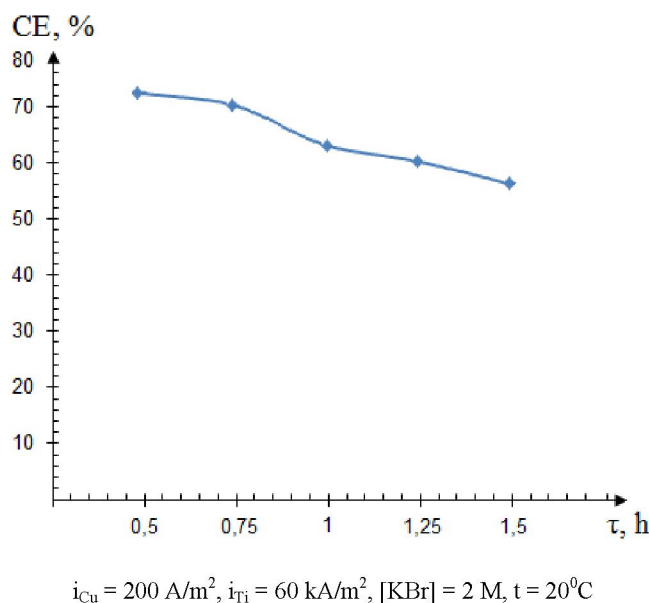


Figure 6 – Effect of the electrolysis duration on the current efficiency of copper (I) bromide formation

In conclusion, the formation of copper (I) bromide compound was detected during anodic polarization of the copper electrode in the potassium bromide solution. The obtained product was analyzed by the X-ray phase analysis method and the formed product was proved to be CuBr based on these analyses (figure 7).

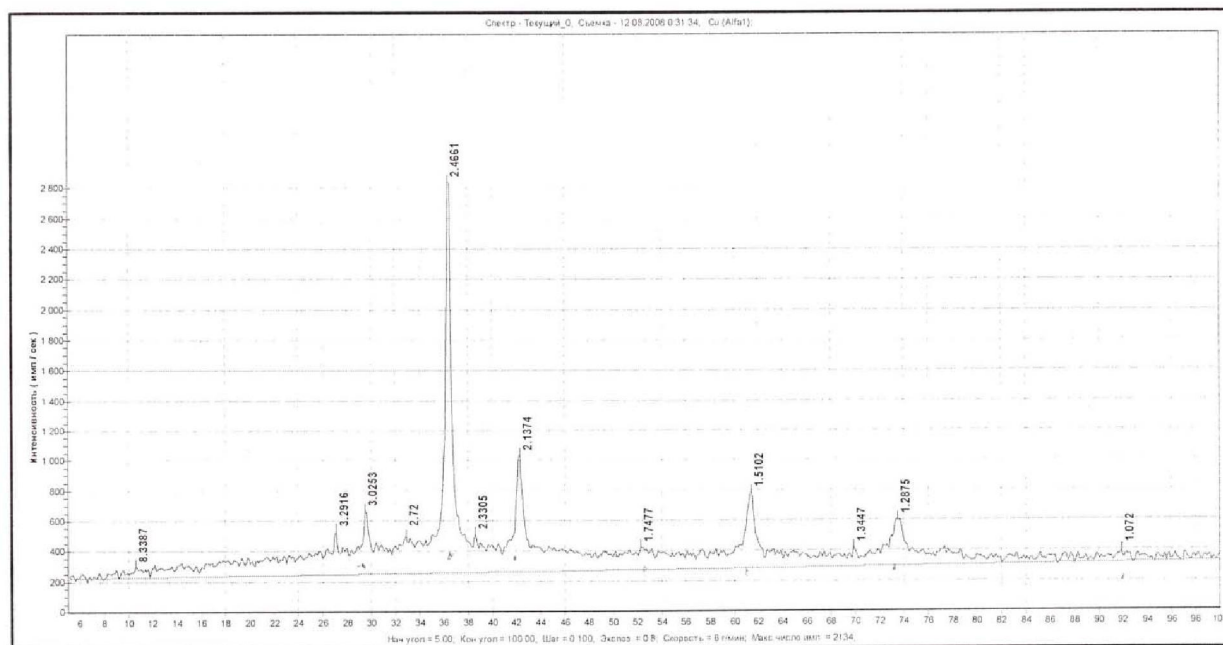


Figure 7 – Rentgenogram of copper (I) bromide formed during the electrolysis

Thus, the effect of basic electrochemical parameters (current density of copper and titanium electrode, potassium bromide concentration, electrolyte temperature, electrolysis duration) on copper (I) bromide formation during anodic polarization of copper electrode in potassium bromide aqueous solution was investigated. On the basic experimental data, the optimal conditions for the formation of copper (I) bromide compound were established: $i_{Cu}=200 \text{ A/m}^2$, $[\text{KBr}]=2\text{M}$, $t=20^\circ\text{C}$. The current efficiency of copper (I) bromide formation by copper dissolution reached 72.1%.

REFERENCES

- [1] James Evans, Lutgard De Jonghe (2017) The Production and Processing of Inorganic Materials. Springer Nature, TMS. ISBN: 3319485660.
- [2] Nurdillayeva R N. (2014) Electrochemical methods of synthesis of copper and zinc compounds [Mys zhane myrlystyn beyorganikalyk kosylstaryn sintezdeudin elektrokhimiyalyk tasilderi]. Monograph, Shymkent. ISBN 978-9965-20-479-7.
- [3] Grishin ID, Kurochkina DYu, Grishin DF (2017) The Influence of the Activating Agent on the Controlled Synthesis of Polyacrylonitrile Using Systems Based on Copper (I) Bromide and Tris(2-pyridylmethyl)amine. DOI: 10.1134/S1560090417030071. (In Eng)
- [4] Mohammad T I, Yuvaraj H, Van H N, Muhammad N I, Choon S R, Jae-Jin S. (2014) Controlled radical polymerization of vinyl acetate in supercritical CO_2 catalyzed by CuBr/terpyridine. DOI: 10.1007/s11814-014-0031-5. (In Eng)
- [5] Zhang Hongyu, Huang Jing, Yang Shangdong (2015) Copper (I) Bromide-Catalyzed for the Synthesis of Sulfoxonium Ylides. DOI: 10.6023/cjoc201504005. (In Chinese)
- [6] Jiang Yunbing, Wang Yanlong, Han Qian, Zhu Rongjun, Xiong Xingquan (2014) Highly Efficient Synthesis of 1,2,3-Triazoles Catalyzed by Silane Coupled Chitosan-CuBr Catalyst. DOI: 10.6023/cjoc201404024. (In Chinese)
- [7] Muhammad M, Anvarhusein A I, Tobias R, Heinrich L, Saeed A, Najma A, Abdul W. (2011) Synthesis, characterization, and antibacterial activities of copper (I) bromide complexes of thioureas: X-ray structure of $[\text{Cu}(\text{Metu})_4]\text{Br}$. DOI: 10.1007/s11243-011-9496-9. (In Eng)
- [8] Davydov V V, Sokol V I, Rychagina N V, Linko R V, Ryabov M A, Shklyayev Yu V, Sergienko V S. (2009) Synthesis, Crystal Structure, and Spectra of 9(E)-Phenanthrene-9,10-dione [(1Z)-3,3-Dimethyl-3,4-Dihydroisoquinolin-1(2H)-ylidene] hydrate and its Cation-Anion Complex with Copper (I) Bromide. DOI: 10.1134/s0036023609060126. (In Eng)

- [9] Berezin S A, Nadolinny VA, Lavrenova L.G. (2015) Synthesis, Structure, and Properties of a Copper Bromide Coordination Compound with 3-Amino-4 EthoxyCarbonylPyrazole. Nature of the Nonresonant and Ferromagnetic Absorption Observed by EPR. DOI 10.1007/s10948-014-2720-z. (In Eng)
- [10] Gurjaspreet Singh, Jasbhinder Singh, Gurpreet Kaur, Jandeep Singh (2017) Fabrication of silicon embedded isomeric chalcone linkers using $[CuBr(PPh_3)_3]$. DOI: 10.1016/j.poly.2016.10.001. (InEng)
- [11] Lidin R A, Molochko V A, Andreyeva L L.(2007)Inorganic chemistry in reactions [Neorganicheskaya khimiya v reaktsiyakh] Handbook. Moscow. ISBN 978-5-358-01303-2
- [12] Bayeshov A B, Kadirbayeva A S, Bayeshova A K, Zhurinov M Zh. (2014) Syntesis of chloride (I) and copper sulfate (II) for industrial polarization acidic environment [Ondiristik aynymalı tokpen polyarizatsiyalau arkyly mys (II) sul'fatyn zhane khloridin alu]. News of NAS RK, Chemistry, 4: 20-24. (In Kazakh)
- [13] Bayeshov A B, Kadirbayeva A S, Bayeshova A K. (2015) Method for the production of copper (I) iodide [Sposob polucheniya iodida medi (I)]. Preliminary Patent of the Republic of Kazakhstan [Predvaritelnyy patent Respubliki Kazakhstan]. (In Russian)
- [14] Dospayev M M. (2008) Preparation of copper powder from copper (I) oxide by electrolysis [Polucheniye mednogo poroshka iz oksida medi (I) elektrolizom]. Science news of Kazakhstan. (In Russian)
- [15] Kadirbayeva A S, Nurdillayeva R N. (2011) Syntesis of copper (I) chloride with alternating current polarization in hydrochloric acid solution [Tuz kyshkyly eritindisinde aynymalı tokpen polyarizatsiyalau arkyly mys (I) khloridin alu.] Herald of the IKTU, Chemistry and Technology, 3 (75): 104-108. (In Kazakh)
- [16] Kreizer IV, Tutukina ID, Zartsyn ID, Marshakov IK. (2002) The Dissolution of a Copper Cathode in Acidic Chloride Solutions. DOI: 10.1134/S1560090417030071. (In Eng)
- [17] Brolo A G et al. (1998) Copper dissolution in bromide medium in the absence and presence of hexamethylenetetramine (HMTA). PII: S 0013-4686(98)00179-0
- [18] Under the editorship of Brauer G M. (1985) Manual on preparative inorganic chemistry [Rukovodstvo po preparativnoy neorganicheskoy khimii]. Moscow.
- [19] Bayeshova A K, Bayeshov A B, Adaybekova A A. (2015) Electrochemical behavior of copper in aqueous solutions of potassium bromide [Mystyn suly kaliy bromidi eritindisindegi elektrokhimiyalyk kasiyeti]. News of NAS RK, Chemistry, 6: 46-52. (In Kazakh)
- [12] Sokolovsky A E, Radion E V. (2005) Analytical chemistry. Reference materials [Analiticheskaya khimiya. Spravochnyye materialy]. Minsk. ISBN 985-434-463-0
- [21] James J. Fritz and Eddie Luzik (1987) Solubility of Copper (I) Bromide in Aqueous Solutions of Potassium Bromide. (In Eng)

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МЫС БРОМИДІН АЛУДЫҢ ЭЛЕКТРОХИМИЯЛЫҚ ТӘСІЛІН ЖАСАУ

Аннотация. Ұсынылып отырған жұмыста алғаш рет мыс электродының электрохимиялық қасиеті калий бромиді сулы ерітіндісінде анодты поляризациялау арқылы зерттелді. Анодты токпен поляризацияланған мыс электродында жүретін үрдістердің ерекшелігін зерттеу үшін калий бромиді ерітіндісінде анодты поляризациялық қисықтар түсірілді. Анодты токпен поляризацияланған мыс электродының еруіне мыс ($i_{Cu}=100-600 \text{ A/m}^2$) және титан ($i_{Ti}=20-120 \text{ A/m}^2$) электродтарындағы ток тығыздықтарының, электролит концентрациясының ($[KBr]=1-5 \text{ M}$), ерітінді температурасының ($t=20-70^\circ \text{C}$) және электролиз ұзақтығының ($\tau=0,5-1,5 \text{ сағ.}$) әсерлері қарастырылып, мыс (I) бромидінің түзілуінің тиімді жағдайлары анықталды. Мыс анодындағы ток тығыздығы 200 A/m^2 -ге тең болғанда мыс (I) бромидінің түзілуінің ток бойынша шығымы $72,1\%$ құрады, ал ток тығыздығы одан ары жоғарылатқанда ТШ мәні төмендеп 60% көрсетті. Мыс (I) бромиді түзілу процесіне электролит табиғатының әсері мардымды екені анықталды. 2 M калий бромиді ерітіндісінде ток бойынша шығым жоғарылап ($\sim 70\%$), максималды мәнді көрсетті. Ерітінді концентрациясын одан ары жоғарылату нәтижесінде ток бойынша шығым күрт төмендеді. Анодты ток қатысында мыс (I) бромидінің түзілу процесіне ерітінді температурасының әсерін зерттеу нәтижесі температураның жоғарылауынан ток бойынша шығымның төмендейтіндігін көрсетті. Мұны температура артуымен анодта оттегі газының бөлінуінің аса кернеулігінің төмендеп, оның үлесінің көбеюімен немесе мыс (I) бромиді қосылысының қайта еруімен түсіндіруге болады.

Түйін сөздер: мыс электроды, анодты поляризация, калий бромиді, электролит, ток бойынша шығым.

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РАЗРАБОТКА ЭЛЕКТРОХИМИЧЕСКОГО МЕТОДА ПОЛУЧЕНИЯ БРОМИДА МЕДИ

Аннотация. В предложенной работе впервые исследовано электрохимическое свойство медного электрода при анодной поляризации в водном растворе бромида калия. С целью изучения специфичности процессов, протекающих на медном электроде при анодной поляризации, сняты анодные поляризационные кривые в растворе бромида калия. Рассмотрено влияние плотности тока на медном ($i_{Cu}=100-600 \text{ A/м}^2$) и титановом ($i_{Ti}=20-120 \text{ кA/м}^2$) электродах, концентрации электролита ($[KBr]=1-5 \text{ M}$), температуры раствора ($20-70^\circ\text{C}$) и продолжительности электролиза ($\tau=0,5-1,5 \text{ ч.}$) на растворение меди при анодной поляризации и были определены оптимальные условия образования бромида меди (I). Выход по току образования бромида меди (I) при анодной плотности на медном электроде 200 A/м^2 составляла 72,1%, а дальнейшее увеличение плотности тока привело к уменьшению значения ВТ на 60%. Установлено, что природа электролита оказывает существенное влияние на процесс образования бромида меди (I). При 2 М концентрации раствора бромида калия выход по току возрастает, и величина ВТ достигает максимального значения (~70%). В результате дальнейшего увеличения концентрации раствора выход по току резко снижается. Изучение влияния температуры раствора на процесс образования бромида меди (I) при анодной поляризации тока показало, что с повышением температуры выход по току снижается. Это связано с тем, что с увеличением температуры в аноде снижается перенапряжение выделения газообразного кислорода и увеличивается его доля, или можно объяснить растворением бромида меди (I).

Ключевые слова: медный электрод, анодная поляризация, бромид калия, электролит, выход тока.