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## ELECTROCHEMICAL PROPERTIES OF THALLIUM IN SOLUTIONS CONTAINING NITRATE IONS

**Abstract.** The electrochemical behavior of the thallium electrode in solutions of sodium nitrate and nitric acid has been studied by the method of removing potentiodynamic polarization curves and by electrolysis. Preliminary studies have shown that thallium electrode does not dissolve in sodium nitrate solution, but it dissolves well in nitric acid. The laws of electrochemical dissolution of a thallium electrode for polarization with an alternating current at a frequency of 50 Hz in solutions of nitric acid was first studied. The influence of a number of electrochemical parameters on the current yield of the product of electrolysis - thallium nitrate (I) is considered. It is shown that the formation of thallium ions (I) with high current efficiency (95-97%). Electrolysis results show that the concentration and temperature of the electrolyte have a significant effect on the current efficiency of Tl (I) ions. It is shown that as the potential of the electrode is increased, the metal is passivated by the formation of thallium hydroxide, an insoluble protective layer, on the electrode surface. As a result of the studies, an effective method for the synthesis of Tl (I) salts has been developed. Carried out an elemental analyzes of the crystals and microphotographic thallium nitrate Tl (I). Due to the fact that thallium salts have low solubility in aqueous solutions, it has been shown that metallic thallium dissolves only in acid solutions under the action of alternating current.

**Key words:** thallium, micro photography, electrolysis, electrochemistry, electrode, crystal, alternating current, nitric acid, thallium (I) nitrate.

Though thallium and its compounds are poisonous, they are widely used in technics, medicine and other fields. 75% of thallium is used in electronics, electronics and infrared radiation, 7% in agriculture, 3% in medicine, and 15% in other industries.

The chemical and electrochemical properties of thallium have not yet been studied and are significantly different from those characteristic to metals of Group III (Al, In, Ga). Since thallium is dispersed in the environment, its chemical and electrochemical properties are poorly studied. The detection and separation of thallium from the composition of natural minerals and synthesizing its compounds cause difficulties due to its low concentration. The tendency of metal surface to passivity due to oxide shells formation during the electrochemical deposition determines the specificity of electrochemical properties of thallium. As shown by the results of studies dedicated to investigate electrical oxidation and electrical deoxidation processes of thallium, several authors [1-4] show that the kinetics and mechanisms of these processes depend on a number of factors and have significant features.

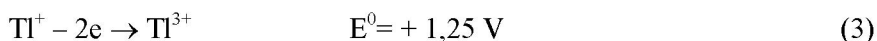
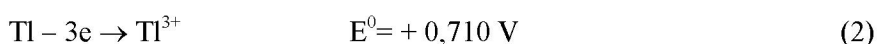
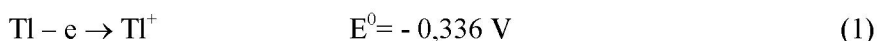
The authors of work [5-7] have found that passivation of thallium electrode in the anode polarization of HCl or NaCl solutions are carried out in two stages. According to them, thallium ions are formed in the first phase of passivation and in the second phase they become thallium salts. However, the passivation process in the solution of HClO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> is carried out in a single phase. In general, the literature review on electrochemical properties of thallium in aqueous solutions indicates that they had been conducted in the field of stationary current and requires replenishment of theoretical data. Moreover, all the known inorganic salts of thallium are obtained by the chemical exchange reaction.

The first study of thallium anode properties began with the release of thallium batteries [6]. Therefore, this work focuses on the oxidation reduction system  $Tl/Tl_2O_3$ . According to the results of the study, the potential of  $Tl/Tl^+$  is that the anode current decreases in the alkaline environment than acids. In [6], it is established that the thallium oxidative ion is in the stationary electrodes with the threshold of tension at the threshold of the polarization hole "b" - 60 mV. It has been pointed out that there is a point of concentration polarization.

In [8], information is given on the electrochemical properties of thallium in the solution of hydrochloric acid and its solubility forming a monovalent compound.

The purpose of this research is to develop effective methods for the synthesis of Tl (I) salts by studying the dependence on various parameters of electrochemical oxidation of thallium electrodes in the presence of alternating current in nitric acid and its salts in solutions of sodium nitrate.

Thallium shows I and III valence in chemical compounds. Its standard electrode potential in aqueous solution has the following value at 25 °C:



Further, studies on the electrochemical dissolution laws of the thallium electrode were continued by shooting cathodic, anode and cyclic potentiodynamic curves in neutral nitrate acid solution and electrolyzing in the neutral nitrate ion solution.

Potentiostat "Autolab" was used for shooting potentiodynamic polarization curves. The experiments were carried out in three electrode cells with separated electrode spaces. As a working electrode, the surface part of thallium wire in 2 mm diameter was used. The second additional electrode was platinum wire. All potential values were compared to silver chlorine electrode immersed in the saturated solution of potassium chloride for "an exclusive clean" analysis (+0,203 V).

When the thallium electrode was immersed in the solution of 100 g/l of sodium nitrate, the potential value "minus" was found to be 0.7 V. The metallic oxidation current is detected on the maximum polarogram when the potential value of thallium is shifted to the anode direction (figure 1). The dissolution rate of thallium does not continue to grow when the potential value "minus" is 0.45 V, from which the metal surface is covered by a thallium nitrate film and remains in the passivation state.

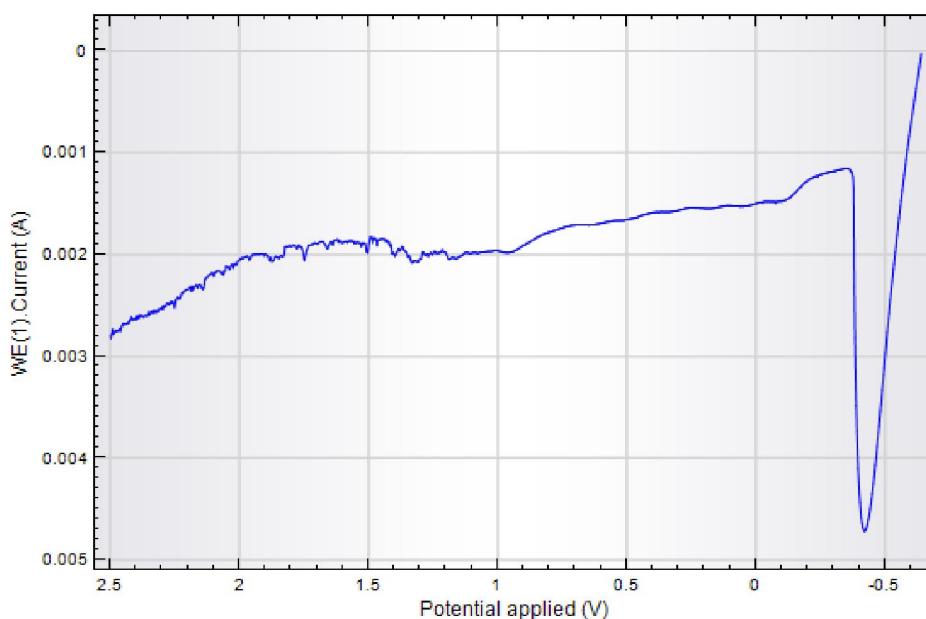


Figure 1 – Anode potentiodynamic polarization curve of the thallium electrode in the sodium nitrate solution:  
 $[NaNO_3] = 100 \text{ g/l}$ ;  $v = 50 \text{ mB/s}$ ;  $t = 25^\circ\text{C}$

Figure 2 shows the cathode polarization curves of the thallium electrode in a solution of sodium nitrate. When the potential of the thallium electrode is shifted to the cathode direction and the minus approximates the potential of 0.6-0.50 V, the oxidation current is detected in the polarogram.

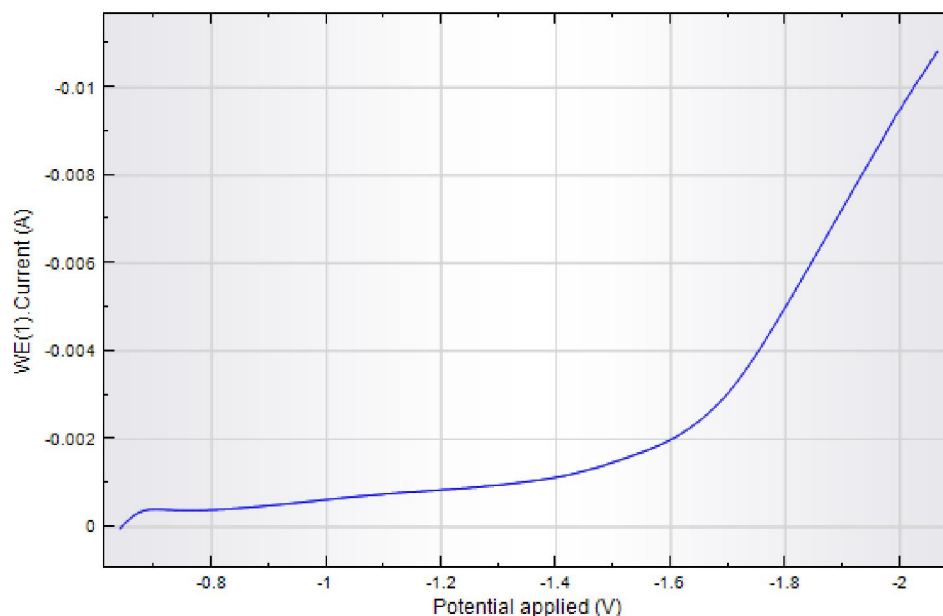


Figure 2 – Cathode potentiodynamic polarization curve of the thallium electrode in the sodium nitrate solution:  
[NaNO<sub>3</sub>] = 100 g/l; v = 50 mV/s; t = 25 °C

Figure 3 shows the anode-cathode cycle polarization curve of the thallium electrode in the solution of sodium nitrate. When moving the electrode potential towards the positive potential zone, the anode oxidation maximum of the thallium is detected at minus 0.5-0.45 V. It can be argued that the observed maximum occurs due to the oxidation of the thallium (I) nitrate on reaction (1). When the potential of thallium is shifted to the negative values, the maximum oxidation of thallium (I) nitrate formed on its surface is detected and the reduction reaction of the water molecules ions in the potential of "minus" 1,7 V is realized.

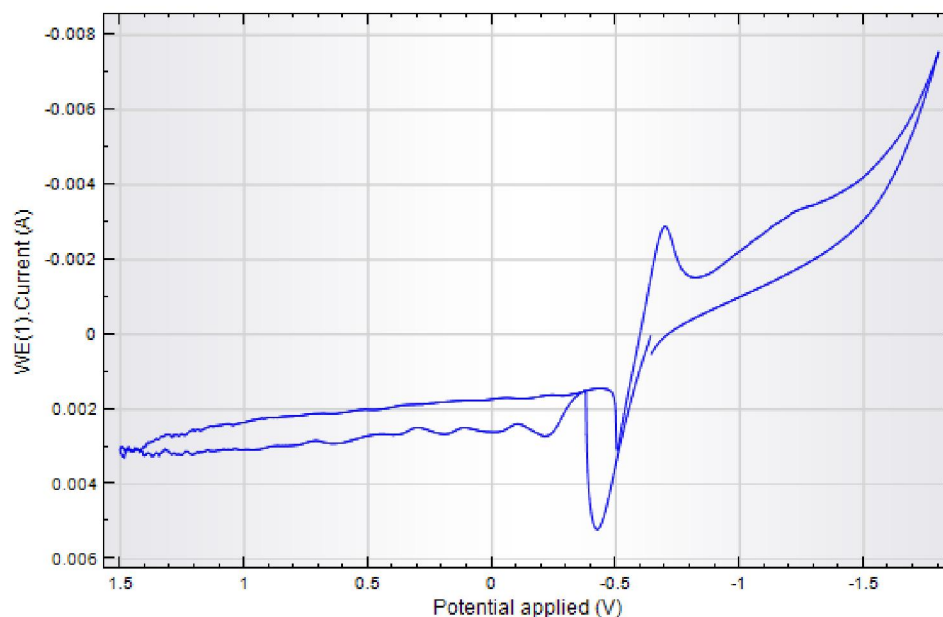


Figure 3 – Cathode-anode potentiodynamic polarization curve of the thallium electrode in the sodium nitrate solution:  
[NaNO<sub>3</sub>] = 100 g/l; v = 50 mV/s; t = 25 °C

Preliminary studies revealed the insolubility of the thallium electrode in a solution of sodium nitrate. The work on the study of electrochemical melting laws of thallium electrode continued with further electrolysis in the nitrogenic acid solution.

Thallium can simultaneously form compounds that are present in two different oxidation states, although its one valence compounds are more stable in the aqueous solution. The ways to obtain inorganic salts of thallium were determined by polarizing its electrochemical properties in the presence of alternating current with frequency of 50 Hz in the HNO<sub>3</sub> solution for the first time and its dissolution through forming one valence compounds was defined.

Preliminary studies revealed the insolubility of the thallium electrode in a solution of sodium nitrate. In the liquefied HNO<sub>3</sub> solution under the alternating current, Tl (I) nitrates are formed in the form of white sediment (figure 4). The formed TlNO<sub>3</sub> salt is poorly soluble in water at room temperature (0.3 g/100g water) and in liquefied acids, and its solubility in hot water increases (100 °C - 1.97 g/100g). The maximum current efficiency of thallium (I) nitrate is 76% for  $i=6000\text{A/m}^2$ .

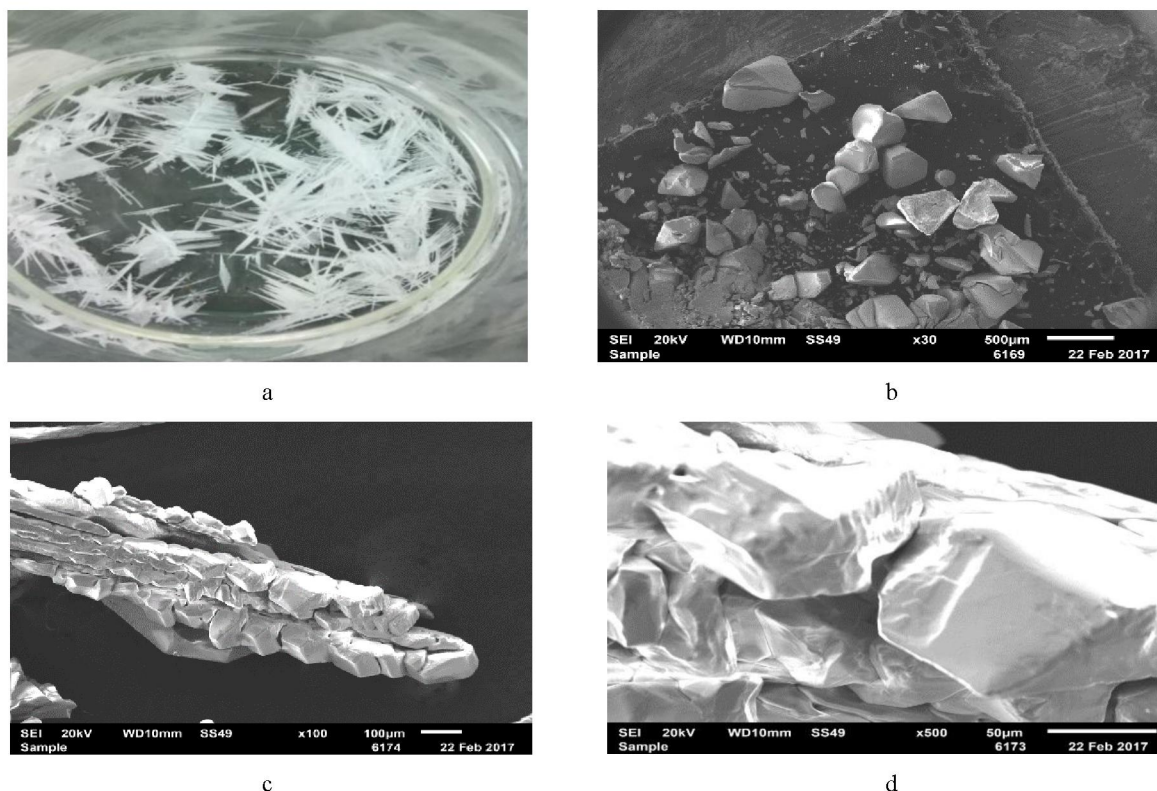
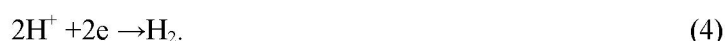


Figure 4 – Photos Crystals of Thallium nitrate:  
a – formed TlNO<sub>3</sub> crystals; b – 30 times enlarged; c – 100 times enlarged; d – 500 times enlarged

TlNO<sub>3</sub> crystals are formed in HNO<sub>3</sub> solution (1.0-4.0 n) by polarizing thallium electrodes with industrial alternating current of 50 Hz frequency (figure 4,a). The maximum current efficiency of thallium (I) nitrate is 91.6% for  $i=8000\text{ A/m}^2$ . The influence of HNO<sub>3</sub> concentration on the current efficiency of thallium electrodes in the acidic solutions by forming Tl (I) was investigated. At each phase, thallium electrode (I) is able to dissolve in the anodic half period of the alternating current by forming its ions according to the reaction. At the cathodic half period of the alternating current, hydrogen ions are oxidized on the surface of thallium electrodes:



In conclusion, the results of the research show that, in an optimal condition, the reaction of forming one valence ions basically occurs in the anodic half period on the surface of thallium electrodes, while in the cathodic half period, the reaction of hydrogen gas formation takes place [9].

The effect of the concentration of electrolyte on the current efficiency of thallium (I) ions, which are formed by polarizing thallium (I) electrodes in nitric acid with the help of alternating current is shown in figure 5.

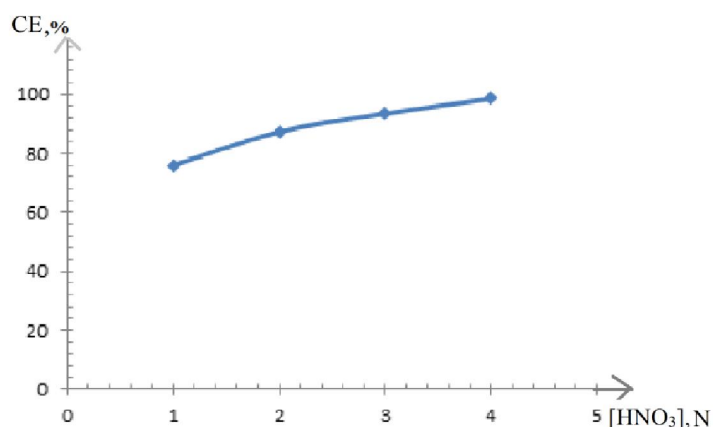


Figure 5 – The electrolyte concentration effect on current formation efficiency of thallium (I) ions:  
 $i = 6000 \text{ A/m}^2$ ,  $\tau = 0,5 \text{ h}$ ;  $t = 20 \text{ }^\circ\text{C}$

The initial concentration of nitric acid has a significant effect on the formation of thallium (I) nitrate during the polarization by alternating current. The concentration of the nitric acid solution is obtained within 1.0-4.0 N. Minimal current efficiency of  $\text{Tl}^+$  ions is  $\sim 76\%$  in 1.0 N.  $\text{HNO}_3$  solution. The maximum current efficiency is  $\sim 99\%$  in 4.0 N.  $\text{HNO}_3$  solutions. The increase of the current efficiency in high concentrations of the nitric acid can be explained by the electrochemical and chemical dissolution processes of the metal. When the concentration of the solution is increased, the recrystallization process takes place as a result of the over-saturation process. The  $\text{HNO}_3$  solution prevents the formation of an oxide layer on the surface of the electrode in the anode half-period of alternating current, which ultimately increases the current efficiency of the thallium nitrate formation.

The electrolyte temperature effect on thallium electrodes dissolution processes was investigated between 20-80°C by providing thallium electrodes with the current density of  $6000 \text{ A/m}^2$  when polarizing them with alternating current (figure 6). As the electrolyte temperature increases, the current efficiency increases dramatically from 37% to 100%. The loss of electrolyte temperature has a beneficial effect on the electrode processes that occur on the surface of thallium electrodes. This is due to the solubility of Tl (I) nitrate at high temperature.

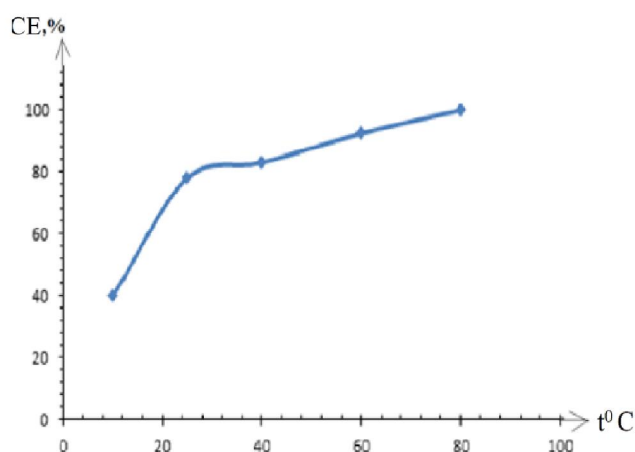


Figure 6 – Influence of temperature on thallium (I) ion current flow rate:  
 $C_{\text{HNO}_3} = 1\text{n}$ ;  $\tau = 0.5 \text{ h}$ ;  $i = 6000 \text{ A/m}^2$

The results of the spectral elemental analysis carried on the thallium nitrate composition that has been obtained by the electrochemical way are shown in table.

The result of the analysis on the elemental composition of sediment (TlNO<sub>3</sub>) obtained after electrolysis

Spectrum	N	O	Tl	Total
1	8,42	16,45	75,13	100,00
2	8,03	16,03	75,94	100,00
3	8,27	16,30	75,43	100,00
Average	8,24	16,26	75,5	100,00

It is worth noting, the electrochemical property of the thallium in the aqueous solution has not been comprehensively studied yet [10, 11]. Currently, electrochemical study of the properties of rare heavy metals is of great importance [12-21]. The acquisition of new data on the electrochemical properties of the thallium polarized by industrial alternating current highlights the theoretical and practical value of the work. The obtained results contribute to the electrosynthesis field that allows obtaining analytically clean metal compounds.

Electrochemical properties of thallium electrode and its salt were comprehensively investigated in the nitric acid and the sodium nitrate solutions by the method of electrolysis and by shooting potentiodynamic polarization curves.

The results of experiments conducted to investigate the nature of electrode processes in electrochemical oxidation of thallium and the analytical properties of the formed compounds will allow to detect thallium compounds in the field of metal waste and raw materials, as well as to create new ways of obtaining its required compounds.

#### REFERENCES

- [1] Twidwell L.K., William-Bim S., Williams-Beam C. [Potential technology to remove mine from the mine and process water. Shortened annotation of the literature.] *European Journal of Processing of Mineral Resources and Environmental Protection*. 2002. Vol. 2, N 1. P. 3-10.
- [2] Songina O.A. [Reddy Metal, Metallurgy]. Moscow, 1964. 568 p.
- [3] [Chemistry of Red and Spatial Elements] Sub. red. Bolshackova K.A. M.: Wyssh. school, 1965. 348 p. ISBN 2224-5286
- [4] Chemistry and technology of inferior and diffused elements. Subd. K. A. Bolshakova, Uchebnoye posobie dlya vuzov. Part I. M.: Wyssh. school, 1976. 368 p.
- [5] Pourbaix Marcel. [Atlas of Electrochemical Equilibria in Aqueous Solutions]. Cebelcor, Brussels: Pergaman Press, 1966. 645 p.
- [6] Jonas L. [Electrochemical behavior of thallium] *Z. Electrochem.* 1903. Bd 9. 523 p.
- [7] Muller-Mulhaisen W.J. [Electrochemical behavior of thallium in aqueous solutions] *Z. Electrochem.* 1909. Bd 15. 696 p.
- [8] Sarbayeva G.T., Bayeshov A.B., Matenova M.M., Tuleshova E.Zh. [Ondiristik aynymaly tokpen polyarizassialangan tallii electrodynyn tuz khyshkyly eritindisindegi erui]. *Izvestia NAN RK*. 2017. N 2. P. 73-78. ISSN 2224-5286.
- [9] Matenova M., Sarbayeva G. Aynymaly tokpen polyarizacialangan tallii electrodtarynyn tuz khyshkyly eritindisindegi electroximialyk khasieti. *Khalykharalyk gylymi-tajiribelik konferensia materialdary [Bilim, gylym zhane ondiristi integracialau koncepciasy-2]*. Shymkent, 2016. P. 251-253. (In Kaz.)
- [10] Sinyakova M.A., Semenova E.A., Gamuletskaya O.A. Published in *Ekologicheskaya Khimiya*. 2013. Vol. 22, N 4. P. 234-238. DOI:10.1134/S1070363214130040 (In Eng.)
- [11] Usipbekova E.Zh. [Electrochemical conveying of talliol in different electrolytes] *Vestnik KazNU Series chem.* 2014. Vol. 74, N 2. P. 47-52. (In Kaz.)
- [12] Usipbekova E.Zh. [Electrochemical refining of the thallium in the neutral medium] *Proceedings of NAN RK. Series of chemistry and technology*. 2014. Vol. 408, N 5. P. 64-69.
- [13] Seylxanova G.A. [Voltammetry of thallium in various electrolyteselectroacross] Conference, FCT-UNL, September 11-12. Portugal, 2014. International conference on international conferences. 2014. Vol. 1, N 1. P. 51-52.
- [14] Ivanov A.V., Bredyuk O.A., Gerasimenko A.V., Lutsenko I.A., Antzutkin O.N., Forsling W. Published in *Koordinatsionnaya Khimiya*. 2006. Vol. 32, N 5. P. 354-364. DOI:10.1134/S107032840605006X (In Eng.)
- [15] Baeshov A., Abiyjanova D. Dzhurinov M.Zh. [Electrochemical adhesion in India to dissolve sodium chloride in polarization with non-stationary current]. Report NAN RK. 2009. N 1. P. 13-16.
- [16] Babanly L.F. Mashadieva M.B. Babanly, 2017, Published in *Neorganicheskie Materialy*. 2017. Vol. 53, N 5. P. 524-529. DOI:10.1134/S002016851705003X (In Eng.)
- [17] Seylxanova G.A., Kurbatov A.P., Berezovsky A.V., Usipbekova E.Zh., Nauryzbaev M.K. Electrochemical deposition and dissolution of oxide tall (III). *Izvestia NAN RK*. 2016. N 5. P. 200-205. ISSN 2224-5286.
- [18] Lidin R.A. et al. [Chemical properties of neuronic phenomena], *Ucheb.posobyie dlya vuzov. 3-e izd., ispr. M.: Chemistry*, 2000. 480 p. ISBN 5-7245-1163-0.
- [19] Levitsky C.A., Aldamzharova S.H., Zebreva A.I. [Electrochemical conveying of the tallow on the porous and gallium electrodes]. *Izvestia AN KazSSR. The series is chemically*. 1983. N 36. P. 26-287.

[20] V.A. Popkov, S.A. Puzakov. General Chemistry. M.: Publishing house [GOETTAR-MEDIA], 2014, 374-382.

[21] Kunkely H., Vogler A. Monatshefte für Chemie (2004) 135. DOI: 10.1007/s00706-003-0103-4. Online ISSN:1434-4475.

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### **ТАЛЛИЙДІҢ НИТРАТ ИОНДАРЫ БАР ЕРІТІНДІЛЕРДЕГІ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІ**

**Аннотация.** Таллий электродының натрий нитраты және азот қышқылы ерітінділеріндегі электрохимиялық қасиеті потенциодинамикалық поляризациялық қисықтар түсіру арқылы және электролиз жүргізу арқылы зерттелді. Алдын ала жүргізілген зерттеулер таллий электродының натрий нитраты ерітіндісінде ерімейтіндігін, ал азот қышқылы ерітіндісінде жақсы еритіндігін көрсетті. Алғаш рет таллий электродының азот қышқылы ерітіндісіндегі электрохимиялық еру заңдылықтары жиілігі 50 Гц өндірістік айнымалы ток қатысында зерттелді. Электролиз өнімі - таллий (I) нитратының түзілуінің ток бойынша шығымына бірқатар электрохимиялық параметрлердің әсері қарастырылды. Азот қышқылы ерітіндісінде таллий (I) иондарының жоғары ток бойынша шығыммен (95-97%) түзілетіндігі көрсетілді. Электролиз нәтижелері Тl (I) иондарының түзілуінің ток бойынша шығымына - электролит концентрациясы мен температурасының елеулі әсері бар екендігін көрсетті. Электрод потенциалының өсуі, электрод бетінде ерімейтін қорғаныштық қабат - таллий қосылысының түзілуіне байланысты металды пассивті күйге түсіретіндігі көрсетілді. Жүргізілген зерттеулердің нәтижесінде Тl (I) тұздарын синтездеудің тиімді әдісі жасалды. Түзілген таллий (I) нитраты кристалдарының құрамына элементтік анализ және микрофотографиялық сараптамалар жасалды. Таллий (I) тұздарының судағы ерігіштігі төмен болғандықтан, таллий тек қышқылды ерітінділерде айнымалы ток әсерімен еритіндігі көрсетілді.

**Түйін сөздер:** таллий, микрофотография, электролиз, электрохимия, электрод, кристалл, айнымалы ток, азот қышқылы, таллий (I) нитраты.

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### **ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ ТАЛЛИЯ В РАСТВОРАХ, СОДЕРЖАЩИХ НИТРАТ-ИОНЫ**

**Аннотация.** Методом снятия потенциодинамических поляризационных кривых и методом электролиза изучено электрохимическое поведение таллиевого электрода в растворах нитрата натрия и азотной кислоты. Предварительные исследования показали, что таллиевый электрд не растворяется в растворе нитрата натрия, но хорошо растворяется в азотной кислоте. Впервые исследованы закономерности электрохимического растворения таллиевого электрода при поляризации переменным током с частотой 50 Гц в азотнокислых растворах. Рассмотрено влияние ряда электрохимических параметров на выход по току продукта электролиза - нитрата таллия (I). Показано, что происходит образование ионов таллия (I) с высокими выходами по току (95-97%). Результаты электролиза показывают, что концентрация и температура электролита оказывают значительное влияние на выход по току образования ионов Тl (I). Показано, что при увеличении потенциала электрода металл пассивируется вследствие образования на поверхности электрода нерастворимого защитного слоя - соединения таллия. В результате проведенных исследований разработан эффективный способ синтеза солей Тl (I). Проведены элементный и микрофотографический анализы кристаллов нитрата таллия Тl (I). В связи с тем, что соли таллия имеют низкую растворимость в водных растворах, было показано, что металлический таллий растворяется только в растворах кислот под действием переменного тока.

**Ключевые слова:** таллий, микрофотография, электролиз, электрохимия, кристалл, переменный ток, азотная кислота, нитрат (I) таллия.