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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 $HClO_4$ and Na_2SO_4 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 $T1/Tl^{+}$ 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 ^{0}C:

$$Tl - e \rightarrow Tl^{+} \qquad E^{0} = -0{,}336\ V \qquad (1)$$

$$Tl - 3e \rightarrow Tl^{3+} \qquad E^{0} = +0{,}710\ V \qquad (2)$$

$$Tl^{+} - 2e \rightarrow Tl^{3+} \qquad E^{0} = +1{,}25\ V \qquad (3)$$

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.

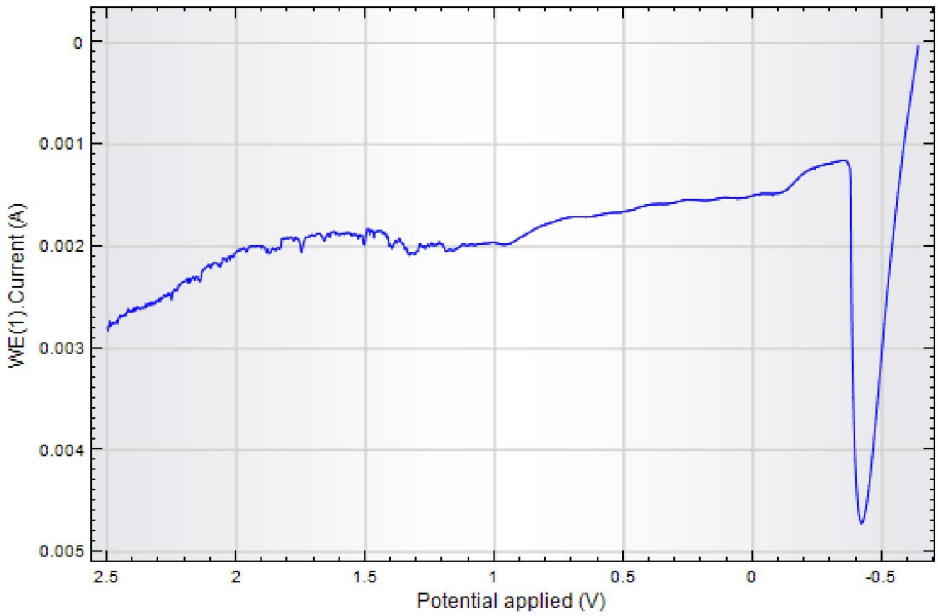

Figure 1 – Anode potentiodynamic polarization curve of the thallium electrode in the sodium nitrate solution: $[NaNO_3]$ = 100g/l; v = 50 mB/s; t = 25^{0}C

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.

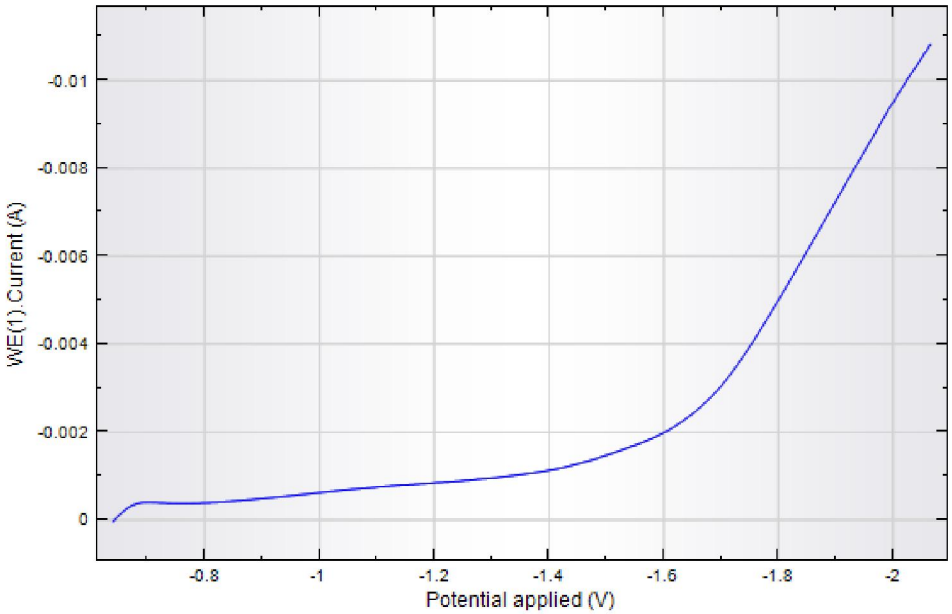

Figure 2 – Cathode potentiodynamic polarization curve of the thallium electrode in the sodium nitrate solution: $[NaNO_3]$ = 100 g/l; v= 50 mV/s; t = 25 ^{0}C

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.

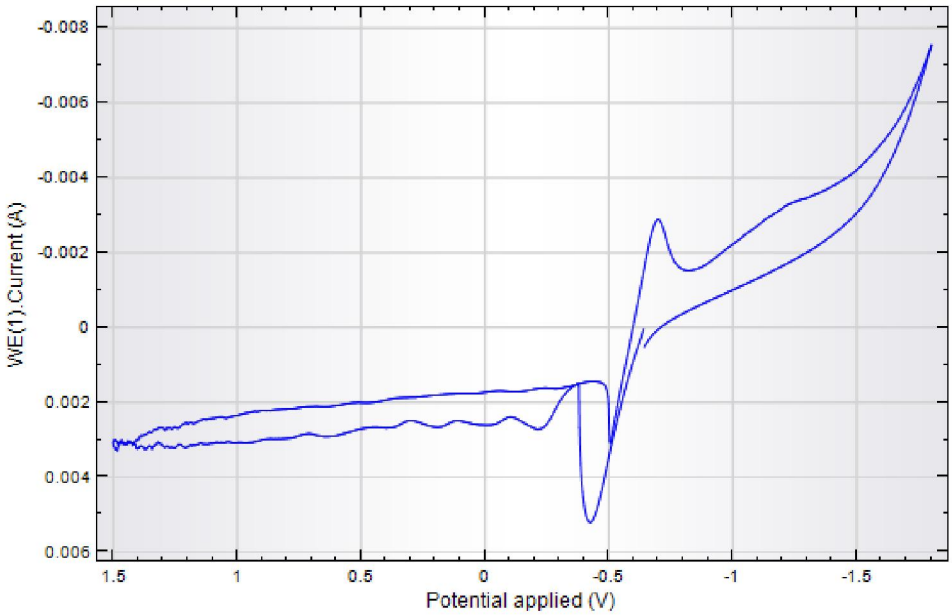

Figure 3 – Cathode-anode potentiodynamic polarization curve of the thallium electrode in the sodium nitrate solution: $[NaNO_3]$ = 100 g/l; v = 50 mV/s; t = 25 ^{0}C