ELECTROCHEMICAL DEPOSITION AND DISSOLUTION OF THALLIUM OXIDE (III)

Graphs 7 and 8 show that a linear increase of the speed of the cathode and anode processes occurs with the increase of temperature up to 60°C. Further, the speed maintains the same level and does not change. Therefore, it means that $\omega = 500 \text{ rev/min}$ and T = 60° C can be considered as optimal conditions for the precipitation and dissolution of thallium oxide. In Table 2, the activation energies for the cathode and anode process were calculated with and without stirring the electrolyte.

Process	W, rev/min	Number of	Correlation	E _a , kJ/mole
		points	coefficient	
cathode	0	5	0,90	11,7±0,13
anode	0	5	0,97	33,4±0,35
cathode	500	5	0,99	6,5±0,08
anode	500	5	0,97	11,8±0,13

Table 2. The value of activation energy of cathode and anode processes

The values of the activation energies lead to the following conclusions: the anode process of thallium oxide precipitation is limited by the rate of supply of the TI^+ ion to the electrode surface. It is also evident that with stirring, the activation energy increases, indicating the transition to the internal-diffusion region of the precipitation process. It means that the process is limited by the rate of charge transfer through the film formed by TI_2O_3 .

The anode process, even without stirring the electrolyte, is characterized by a high activation energy. At electrolyte mixing rates equal to 500 rpm, the activation energy significantly reduces. This can be explained by the fact that without mixing, the process of dissolution of TI_2O_3 is limited by mixed-diffusion kinetics: the thallium transfer process through the oxide film and the TI^+ withdrawal process from the electrode surface to the solution volume. When the solution is stirred, the cathode process is limited by the rate of charge transfer through the oxide film.

It is also found that with the increase of temperature, the formation of trivalent thallium intensifies, which can lead to acceleration of the formation of thallium oxide in the anode's space:

 $2TI^{+}+3H_{2}O=TI_{2}O_{3}+6H^{+}+4e^{-}$