

FIGURE 1: Cyclic voltammogram of Tl^+ ($c = 10^{-3} \text{ mol L}^{-1}$) recorded with a glassy carbon electrode in the absence of oxygen (electrolyte $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, $\text{pH} = 7$, $v = 20 \text{ mV/s}$).

mercury electrodes are presented in [11]. Generally, the electrochemical deposition and dissolution of thallium have been insufficiently studied so far, possibly because of the toxicity of this element. The present investigation was undertaken with the goal to widen the knowledge about possible ways to refine thallium, and for this, the deposition-dissolution behavior has been studied on glassy carbon electrodes.

2. Experimental Part

The electrochemical behavior of thallium was studied in sulfuric acid solutions on glassy carbon electrodes. The auxiliary electrode was a platinum electrode, a silver chloride electrode (Ag/AgCl (3 M KCl)) served as reference electrode ($E = -0.222 \text{ V}$ versus SHE). The electrochemical measurements were carried out with a computer interfaced AUTOLAB-30 (Metrohm) potentiostat-galvanostat. The thallium(I) sulfate standard solution was prepared according to the procedure described in [12]. Cyclic polarization curves were measured at various scan rates using thallium(I) concentration of $10^{-3} \text{ mol L}^{-1}$, at different concentrations of electrolyte ($1 \cdot 10^{-3}$, $1 \cdot 10^{-4}$, $1 \cdot 10^{-5} \text{ mol L}^{-1}$) and in the temperature range of $25\text{--}65^\circ\text{C}$. The electrolyte contained 0.5 mol L^{-1} sodium sulfate. Each experiment was carried out in 5–10 replicates. The obtained data was processed by mathematical statistics method [13].

For scanning electron microscopy (SEM) the instrument Quanta 3D 200i Dual System FEI (USA) equipped with an EDX detection system was used.

3. Results and Discussion

Figure 1 depicts a cyclic voltammogram of a 10^{-3} mol/L Tl^+ solution in the absence of oxygen. The peak at -0.85 V corresponds to the cathodic reduction of Tl^+ to thallium metal, and the anodic peak at -0.67 V to the anodic dissolution of the plated metal.

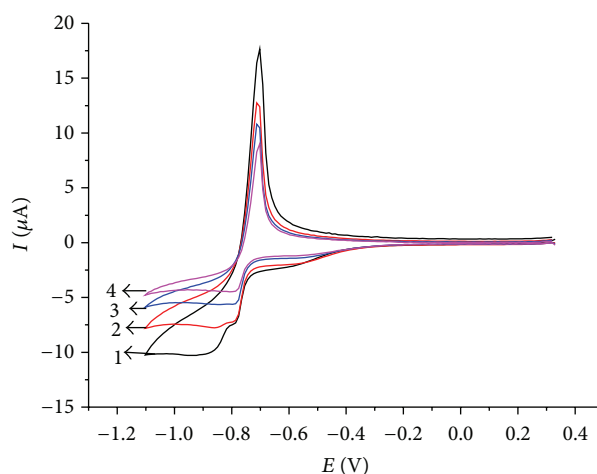


FIGURE 2: Cyclic polarization curves of Tl^+ ($c = 10^{-3} \text{ mol L}^{-1}$) on glassy carbon electrode at different scan rates in the presence of oxygen (air saturated solutions). The electrolyte was $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$, $\text{pH} = 7$. (1) 50 mV/s ; (2) 20 mV/s ; (3) 10 mV/s ; (4) 5 mV/s .

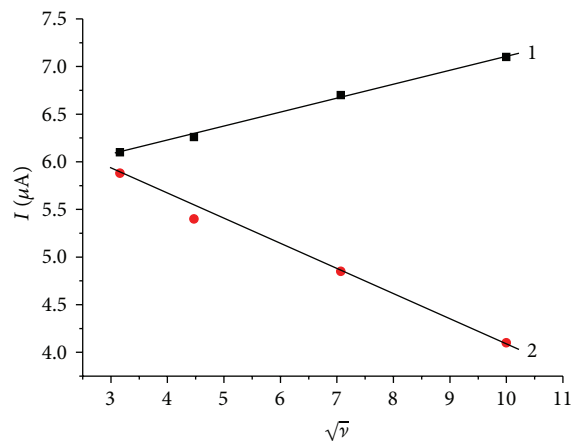


FIGURE 3: The dependence of peak currents on square root of scan rate. All experimental conditions as in Figure 2. (1) Reduction peak currents, (2) oxidation peak currents.

In order to characterize the electrochemical behavior of thallium in sodium sulfate solutions, the following parameters were varied: scan rate, temperature, and concentration of thallium sulfate.

Unfortunately, the midpeak potential of the thallium system in the CV shown in Figure 1 is -0.74 V , which is rather negative and in the range where oxygen is reduced. If one is interested in performing an electrochemical deposition of thallium under technical conditions, the presence of oxygen should be tolerated, as any kind of deaeration is unrealistic. Therefore, it was interesting to study the electrochemical behavior in the presence of oxygen at concentrations corresponding to the partial pressure of oxygen in ambient air. Figure 2 shows the results of experiments using different scan rates (v) in the presence of oxygen. The peak currents increase with increasing scan rate, exactly with the square root of scan rate (Figure 3), as it is typical for a processes