

INVESTIGATION OF ANODE DEPOSITS FORMED IN THE ELECTROLYSIS OF SOLUTIONS OF CERTAIN THALLIUM SALTS. III

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The study of the properties of thallium and its compounds is now an important problem of chemical science. This element is finding ever-increasing practical application. Thallium is an accessory element in lead-zinc ores. In the present method of electrolytic separation of zinc at the cathode the possibility of formation of thallium oxides at the anode, in the form of anode deposits, should be taken into account; such deposition of thallium oxides on the anode may take place in the electrolytic preparation of thallium.

The possibility of obtaining anode deposits from solutions of thallium salts (nitrate and sulfate) has repeatedly been pointed out by various authors. However, neither the conditions for obtaining anode deposits nor the composition of the latter was definitely established in earlier works. It was assumed that anode deposits consists of higher oxides of thallium, but the oxidation states were not precisely specified. Some authors consider the deposits to be composed of oxides of trivalent thallium [1-7]; others consider them to consist of a mixture of the oxides of 3- and 4-valent thallium [4, 5] or a peroxide of thallium [8], similar to the peroxides of potassium, rubidium, and other metals. The addition of various organic substances such as alcohol, oxalic or benzoic acid, acetone, etc., was considered a necessary condition for carrying out electrolysis.

The purpose of the present work is to answer the following questions: 1) under what conditions of electrolysis of thallium-salt solution the anode deposits are best formed; 2) what the composition of these deposits is; i.e., whether they are oxides of thallium in one valence state or another or have a more complicated composition; 3) whether complex formation affects the composition of the deposit or the conditions of its production.

EXPERIMENTAL

For investigation of the anode deposits obtained on electrolysis of thallium-salt solutions we chose the following soluble thallous salts: the nitrate, fluoride, sulfate, and carbonate and the complex salts of silver nitrate with thallium nitrate and of ammonium nitrate with thallium nitrate, having the compositions $\text{Ag}[\text{Tl}(\text{NO}_3)_2]$ and $\text{NH}_4[\text{Tl}(\text{NO}_3)_2]$; of these, four salts were investigated for the first time.

Saturated solutions were electrolyzed in electrolyzers of 100-300 ml capacity, at relatively low current densities from 12 to 20 ma/cm^2 and an electrode potential of 2-2.5 v. Platinum plates, 1 cm^2 in area, served as electrodes.

When the stated conditions are met, finely crystalline, black deposits with a metallic luster are produced in the form of a close-fitting film on the anode, from electrolytes without organic admixtures. The highest possible concentration of solutions and low current strength are essential. Otherwise, gas bubbles begin to appear at the anode together with the deposit, and the latter is obtained in an extremely fine, brownish form and does not adhere to the electrode.

We carefully washed the electrolyte from the shiny, black deposit obtained at the anode and dried the deposit to constant weight at 110-120°. It was very stable to washing with water and drying up to 170°. Concentrated sulfuric acid did not dissolve the deposit, and on heating, evolution of oxygen, which would have occurred in the case of peroxide formation at the anode, was not observed. The deposit was readily soluble

at room temperature in concentrated and dilute hydrochloric acid without evolution of chlorine, and the precipitate described by Gallo and Cenni [9] was not formed at all.

The anode deposits were subjected to a detailed analytical determination of their content of thallium, total oxygen, and higher oxides, as well as any possible additional components.

Thallium was determined by two methods - precipitation as $Tl(OH)_3$ and precipitation as TlI . The total amount of oxygen contained in the anode deposit was determined by the method of reducing it with hydrogen and collecting the water formed. We determined the amount of oxygen in higher oxides, easily detached in the presence of any reducing agent, firstly by the usual method of reducing the oxides with oxalic acid and subsequently precipitating the excess acid as calcium oxalate monohydrate, and secondly by measuring the volume of oxygen evolved from the deposits on heating the latter at $700-750^\circ$ in a current of carbon dioxide (used for removal of oxygen). The acid ions contained in the deposit were determined in each case by means of the appropriate reagents. The fluorine found in the deposit was quantitatively determined by the volumetric method through the reaction



The standard solutions of sodium fluoride and aluminum chloride were prepared by the method developed by I. M. Tananaev.

Average Results of Analyses of Deposits Obtained on Electrolysis of Thallium Salts

Element determined	Found (in %) in anode deposit from:						Calculated (in %) for	
	$TlNO_3$	$Ag[Tl(NO_3)_2]$	$NH_4[Tl(NO_3)_2]$	TlF	Tl_2SO_4	Tl_2CO_3	Tl_2O_3	$Tl_2O_3 \cdot HF$
Thallium								
a) determination as Tl_2O_3	89.24	89.26	89.33	85.79	87.34	89.10	89.49	85.78
b) determination as TlI	—	—	—	—	87.59	89.30	—	—
Oxygen								
a) total quantity	10.42	10.49	10.51	10.14	—	10.54	10.51	10.07
b) evolved on heating	—	—	—	—	6.99	6.57	7.00	—
c) participating in the oxidation of oxalic acid	6.98	6.89	6.90	—	7.15	6.99	7.00	—
Fluorine	—	—	—	3.94	—	—	—	3.99
Sulfate ion	—	—	—	—	1.78	—	—	—
Tl_a/Tl_c ratio	0.502	0.503	0.504	0.50	0.49	0.50	0.50	0.50

The analytical results are given in the summary table. From the data obtained it follows that anode deposits from the nitrate, the carbonate, and the complex salts consist only of thallium trioxide. The anode deposit from thallium fluoride contains fluorine. On the basis of analysis the formula $Tl_2O_3 \cdot HF$ should be assigned to it; this is in accord with cited data [10].

Analysis of the anode deposit from thallium sulfate showed the presence of sulfate ion in the amount of 1.78% on the average. The anode deposit obtained from thallic sulfate solutions apparently consists of thallium trioxide with an admixture of sulfate ion in some undetermined form.

For the purpose of a more accurate determination of the composition of the anode deposits obtained on electrolysis of thallic-salt solutions, X-ray analyses of all the anode deposits, as well as a parallel analysis of pure, chemically prepared thallic oxide, were conducted in the Laboratory of Dielectric Physics of the Physical Institute of the USSR Academy of Sciences. The purity of the original salts was checked by spectral

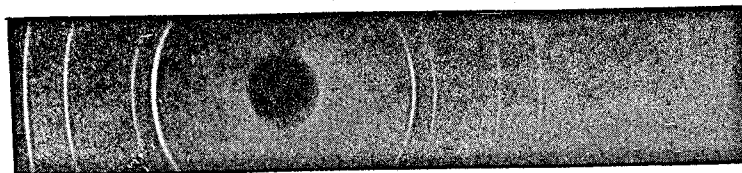


Fig. 1. X-ray diffraction pattern of chemically-prepared Tl_2O_3 .

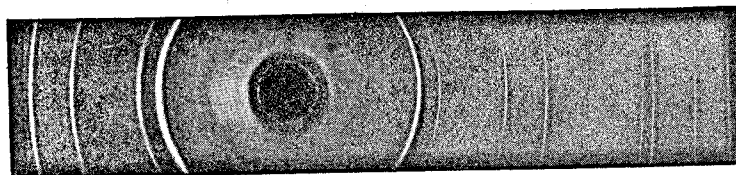


Fig. 2. X-ray diffraction pattern of anode deposit from TlNO_3 .

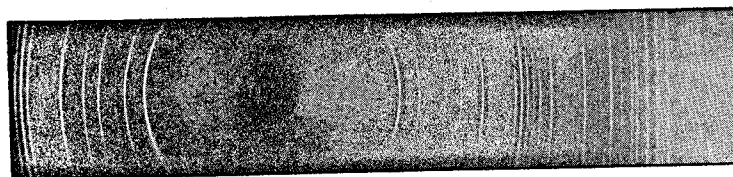


Fig. 3. X-ray diffraction pattern of anode deposit from TlF .

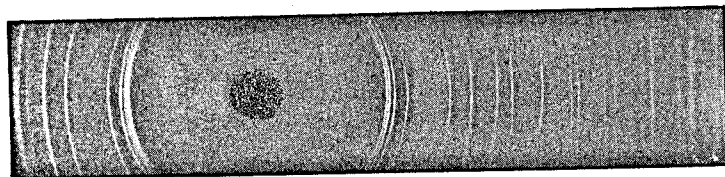


Fig. 4. X-ray diffraction pattern of anode deposit from Tl_2SO_4 .

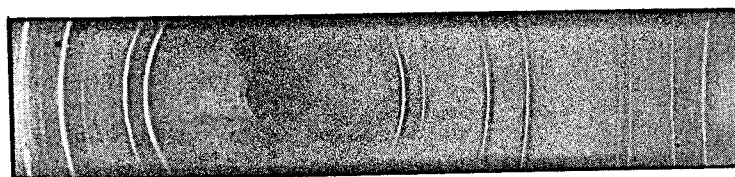


Fig. 5. X-ray diffraction pattern of anode deposit from Tl_2CO_3 .

analysis, which revealed only unweighable traces of Pb and Zn in the nitrate prepared by us from metallic thallium.

X-ray diffraction patterns of the anode deposits obtained on electrolysis of thallium nitrate and carbonate solutions and the X-ray pattern of chemically prepared thallium trioxide have identical lines, which exactly coincided when superposed.

X-ray diffraction patterns of the anode deposits from solutions of thallium fluoride and sulfate and X-ray patterns of thallic oxide chemically prepared from the salt have common lines corresponding to Tl_2O_3 ; besides, the X-ray patterns of these anode deposits contain many additional lines, which evidently belong to the fluoride and sulfate ions present in the deposits.

X-ray diffraction patterns of anode deposits are shown in Figures 1-5.

In order to confirm the composition of the deposits obtained on the anode we used not only analytical and X-ray methods, but also a method proposed earlier [11], which consists in determining the ratio of the quantity of thallium in the anode deposit (Tl_a) to the quantity of thallium which separated out at the cathode (Tl_c) during the same time. If a deposit containing two trivalent thallium atoms is formed on the anode as a result of the anodic oxidation of thallium from the univalent state to the trivalent, the total number of electrons lost by the thallium in oxidation at the anode is equal to four: $2Tl^+ - 4e^- = 2Tl^{+++}$. At the cathode, then, four univalent thallium atoms may be reduced during the same time: $4Tl^+ + 4e^- = 4Tl$. Therefore the ratio of the quantity of thallium deposited on the anode to the quantity of thallium deposited on the cathode, Tl_a/Tl_c , must be equal to 0.5. In a great number of experiments on the electrolysis of thallium salts we were able to confirm this ratio in all cases (see summary table).

SUMMARY

1. It has been shown that in the electrolysis of solutions of thallous salts - the nitrate, fluoride, sulfate, and carbonate and complex salts of the compositions $Ag[Tl(NO_3)_2]$ and $NH_4[Tl(NO_3)_2]$ - black, extremely stable, finely-crystalline deposits, which have a metallic luster and closely fit the electrode, are obtained at the platinum anode. In the literature the electrolysis of solutions of thallium nitrate and sulfate, only, is described. Solutions of the other four salts were electrolyzed for the first time.

2. It has been shown that the anode deposit is thallium trioxide, Tl_2O_3 . The deposit obtained from thallium sulfate solution contains an admixture of sulfate ion in the amount of 1.78%; the anode deposit from the fluoride solution has the composition $Tl_2O_3 \cdot HF$.

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