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Anomalous features of thallium oxide electrodeposited layers and room temperature HTSC electrosynthesis*

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The results of gravimetric, chemical and X-ray diffractometric analysis of anodic deposits formed in alkaline $TlNO_3$ and Tl_2SO_4 solutions are presented and discussed in connection with the kinetics of Tl^+ electrooxidation on copper and platinum anodes. In addition to Tl_2O_3 as the main product other phases were also discovered, for example TlCuO(OH). This new phase is of great interest as a HTSC precursor. The incorporation of Tl^+ into the deposits on both substrates has been confirmed by their excess weight amounting to 30%. Also the influence of the current density on the excess weight has been revealed. The excess weight was a result of co-crystallization of Tl^+ and Tl^{3+} in the form of a mixed-valence oxide.

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1. Introduction

Oxide layers on electrode surfaces, in particular non-stoichiometric ones, play a prominent role in electrochemical and corrosion interfacial phenomena and have been thoroughly investigated [1, 2]. As interesting examples of preparation of oxide layers of various stoichiometry with special features the results of investigations by Conway may be mentioned [3–7]. In this communication the example of anodic oxide electrodeposition combining crystallization from the solution and in the oxide layer itself is demonstrated. The processes taking place in aqueous basic solutions of Tl^+ are discussed.

The electrode reaction of Tl^+ oxidation giving insoluble Tl_2O_3 layers on the substrate surface was thoroughly studied at the turn of the century in connection with its synthetic and analytical applications [8–12]; some additional information has been obtained during the last thirty years [13–17]. A new application has been recently found for this reaction [18]: Tl^+ oxidation on copper in the presence of Ba^{2+}-ions in alkaline media at room temperature produced Tl–Ba–Cu-oxide HTSC-film. Without heating, a critical temperature of $T_C \sim 45\,K$ can be obtained for the superconducting transition. Drying at comparatively low temperatures ($\sim 100°\,C$) enhances T_C up to about 80 K, i.e. to the highest value for Tl–Ba–Cu-system known so far. HTSC properties of this material were confirmed by magnetic and resistivity measurements [18]. The possibility to reduce synthesis temperatures by several hundred degrees in comparison with conventional chemical techniques was based on unique properties of electrocrystallization.

The HTSC-films mentioned above are always inhomogeneous, containing both Tl_2O_3 and thallium cuprate which was previously unknown. Structural and chemical analysis of the black crystals of the substance separated from the deposit leads to the formula TlCuO(OH) [18]. A more hydrated light-blue form was also found, which has been transformed into the black one at 100° C. HTSC was localized in thallium cuprate surface layers with barium incorporated into thallium vacancies.

According to X-ray data, TlCuO(OH) contains Tl in the monovalent state, which is difficult to understand bearing in mind a long anodic oxidation during the preparation process.

Incorporation of monovalent thallium into galvanostatically electrodeposited Tl_2O_3 films on platinum was discovered long ago [11] by gravimetry (the value of current density i was not pointed out in [11]). The excess deposit weight was about 1% compared with the calculated weight of Tl_2O_3. In our preliminary experiments on copper the excess was substantially higher, while the theoretical weight may be lower if a part of the charge is associated with copper oxidation and dissolution.

In order to find the correlations between Tl^+ incorporation effects and anodization conditions several sets of preparative experiments were conducted on platinum and copper substrates and the results were compared with polarization data for the same systems.

2. Experimental details

Platinum and electrolytic copper foils 0.1–0.2 mm thick were used as substrates. Before the deposition the foils were polished in a conc. H_3PO_4, HNO_3 and CH_3COOH mixture, washed with distilled water, dried at room temperature and weighed.

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* This paper is dedicated to Professor Brian E. Conway on the occasion of his 65th birthday, and in recognition of his outstanding contribution to electrochemistry.

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For preparation of solutions Tl_2SO_4, $TlNO_3$, $Ba(NO_3)_2$, NaOH and distilled water were used. By putting foils between two large parallel platinum auxillary electrodes the homogeneous distribution of the current in the cell was achieved. The volume of the cell was large, and the decrease in Tl^+ concentration during polarization was negligible.

Galvanostatic electrolysis was carried out for $t = (1–35) \times 10^3$ s with i varying from 0.1 to 4 mA cm^{-2} (geometric surface area). The corresponding charge Q was about 20–200 C giving deposits of about 20–200 mg (Table 1).

Anodized electrodes were washed with ethanol and dried to constant weight. The quantity of deposit (M_d) was calculated as the difference between the weights of the initial and the anodized substrate. The theoretical weight of Tl_2O_3 (M_{th}) was estimated from Q, and the ratio M_d/M_{th} was calculated.

After the treatment described above the oxide layer was mechanically separated, dispersed and mixed with GeO_2 powder and petroleum jelly, and the resulting suspension was used for X-ray diffractometry (Genie technique). The later was performed using an Enraf–Nonius diffractometer with CuK_α-irradiation. In several specially selected experiments, powder diffractometry was also used.

Polarization measurements were performed in a standard three-electrode cell with divided compartments. All values of potential (E) are given with respect to SCE.

3. Results and discussion

Anomalous values of $M_d/M_{th} > 1$ were found in most experiments. These values were strongly influenced by the pH: for example, in 0.24 M NaOH solutions values up to 1.2–1.3 were determined, but when the NaOH concentration was increased up to 0.5 M only M_d/M_{th} about 1.05 were observed (Table 1). This difference occurred with both copper and platinum electrodes and cannot be related only to the increase in the charge associated with copper dissolution in an alkaline medium.

The influence of other experimental conditions was analysed for solutions with a lower NaOH concentration, where the effect is more pronounced. Variations of anionic and cationic composition gave no systematic effects (accuracy of M_d/M_{th} determination depended on the deposit weight, 0.01–0.04, as indicated in brackets for each sample in Table 1).

The influence of i on M_d/M_{th} is illustrated by Fig. 1 (data for the solutions of different composition with constant NaOH concentration were used). M_d/M_{th} decreases with i. The points showing $M_d/M_{th} < 1$ result from partial loss of deposit while washing and drying.

In order to determine the degree of hydration of synthesized deposits, a set of thermogravimetric experiments was performed. No decrease of weight was registrated after heating to 200–700° C; on the contrary, a slight increase was found. The same effect was ascribed earlier [12] to the formation of thallium salts by interaction with atmospheric CO_2 and SO_2. Hence, it may be concluded that excess deposit weights are not a result of hydration.

Diffractograms of separated oxide coatings have shown the presence of Tl_2O_3 as the main phase, its crystallographic parameters being in good agreement with literature values [19]. At the same time, there were several lines of another nature and anomalously high intensities of some Tl_2O_3 lines were also noticed. No other phases could be detected because of their low concentrations in the deposits. But some general conclusions and assumptions will be presented here.

First, at least one additional phase in the investigated systems contains no copper, because $M_d/M_{th} > 1$ were found not only for copper, but also for platinum substrates. Hence, the possible elemental composition of this additional phase may include thallium, sodium, barium, hydrogen and oxygen. Barium and sodium could be present only in salts, but there are no experimental lines characteristic for diffractometrically studied salts MTlO, M_5TlO_4, etc. (M = Na, Ba) [19]. In principle, the presence of some metastable salt-type structures cannot be dismissed.

As for individual oxides and hydroxides of monovalent thallium, their characteristic lines were found in the samples with $M_d/M_{th} \sim 1$ synthesized at high i values ($i > 1.5$ mA cm^{-2}) on both substrates. The simplest explanation for the incorporation of Tl_2O and TlOH into the deposits is the intercalation of solution portions into rapidly growing deposits.

For all samples with $M_d/M_{th} > 1$ the presence of polyvalent oxide Tl_4O_3 could be inferred from the appearance in the diffractograms of 3–5 lines of highest intensity firmly established for this phase [19]. However, the quality of the spectrum was not sufficient to allow further conclusions. The presence of Tl_4O_3 may be assumed based on the differential coulometric analysis data giving up to 5 at % of Tl^+ in the samples under investigation.

Thallium cuprate lines [18] were observed in the samples synthesized on copper in 0.5 M NaOH solution at low i values.

Some lines in the diffractograms could be interpreted in terms of thallium sulphides (Tl_2S, TlS and TlS_2). In the case of the deposits on copper, sulphides could be formed from sulphur traces in the substrate prepared by deposition from sulphate electrolyte, but the same lines were observed for deposits on platinum, so the suggestion about sulphides appears unrealistic.

There were several samples with diffraction behaviour which could not be explained by the presence of the phases mentioned above. Some of these with relatively high interatomic distances may be due to binary oxides or hydroxides with unknown structure, for example, other new thallium cuprates.

In considering the polarization behaviour of the Tl(1+)/Tl(3+) system in alkaline media, the impossibility in principle of obtaining correct steady state data because of the progressive potential-dependent

Table 1. Experimental results on excess weight and phase composition of deposits prepared on copper and platinum substrates

NaOH M	Cationic composition	i/mA cm^{-2}	Q/C	t/S	M_d/M_{th} (accuracy of last sign)	Suggestions concerning phase composition
1	*2*	*3*	*4*	*5*	*6*	*7*
0.24	94 mM $TlNO_3$ + 3 mM $Ba(NO_3)_2$	3.21	84.0	7200	0.99(2)	*g*
		1.39	78.0	7800	1.07(2)	*a, b, c*
		1.19	91.5	18 300	1.07(2)	*g*
		0.26	49.8	24 900	1.21(2)	*a, e*
0.24	47 mM Tl_2SO_4	2.25*	198	13 200	0.76(1)	*a*
		2.19*	110	10 980	1.01(1)	*a*
		1.72*	102	10 200	1.01(2)	*a*
		0.87*	225	22 500	1.12(1)	*a, c*
		0.94	183	18 300	1.11(1)	*a, c*
0.24	94 mM $TlNO_3$ + 53 mM $Ba(NO_3)_2$	6.38	72.0	3600	1.01(2)	*a, e*
		1.24	129	12 900	0.53(2)	*g*
		0.86	126	25 200	1.12(1)	*a, e*
		0.42	32.4	32 400	1.21(3)	*a, e*
0.24	94 mM $TlNO_3$ + 105 mM $Ba(NO_3)_2$	1.48	48.0	4800	1.07(3)	*a*
		0.71	81.6	16 320	1.16(2)	*a, c*
		0.34	42.1	21 060	1.33(3)	*a, c*
		0.15	32.8	32 760	1.01(4)	*a, c*
		0.19	30.0	30 000	1.11(4)	*a, c*
		0.15*	36.6	36 600	1.27(3)	*a, c*
0.24	24 mM $TlNO_3$ + 0.8 mM $Ba(NO_3)_2$	3.16	18.0	900	1.00(3)	*a, b*
		2.59	18.0	1200	0.97(3)	*a, b, f*
		0.62	37.5	7500	0.96(2)	*a, c*
		0.29	99.4	33 120	0.99(2)	*a*
		0.26	53.4	26 700	0.83(3)	*a*
		0.30	51.6	34 380	1.17(3)	*a, c*
		0.12	33.8	33 840	1.17(3)	*a, c*
0.24	12 mM Tl_2SO_4	2.56	66.0	3300	partial loss	*g*
		2.84	89.1	5940	partial loss	*g*
		0.91	99.0	19 800	0.98(2)	*a*
		0.79*	105	21 000	1.05(1)	*a, c*
		0.48	58.7	29 340	1.11(2)	*a, c*
		0.16	28.7	28 740	1.38(3)	*g*
0.24	50 mM $TlNO_3$ + 30 mM $Ba(NO_3)_2$	2.11	85.5	5700	0.93(2)	*a, f*
		0.95	134	26 700	1.02(1)	*a, c*
		0.52	86.3	34 500	1.03(2)	*a, c, e*
		0.20	32.7	32 700	1.04(3)	*a, g, e*
0.48	24 mM Tl_2SO_4	3.54	132	6600	0.97(1)	*a*
		2.04	144	9600	0.99(1)	*a*
		0.83	135	27 000	0.98(1)	*a, g*
		0.79	122	24 420	0.92(1)	*c, d*
		0.83*	134	26 800	0.98(1)	*a, c*
		0.48	81.9	27 300	0.92(1)	*a*
		0.43	92.7	30 900	0.92(1)	*a*
		0.16	32.4	32 400	1.06(2)	*a, c, d*
0.48	47 mM $TlNO_3$ + 27 mM $Ba(NO_3)_2$	3.57	142	7800	1.02(1)	*a, c, d*
		2.68	170	11 340	1.00(1)	*d, f*
		0.77	129	25 800	1.04(1)	*a, c, d*
		0.16	35.5	35 460	1.26(4)	*g*
0.48	25 mM $TlNO_3$ + 15 mM $Ba(NO_3)_2$	2.40	86.4	4320	0.87(2)	*g*
		2.07	133	8880	0.83(3)	*g*
		0.85	107	21 300	1.02(2)	*g*
		0.77*	130	25 920	1.09(1)	*g*
		0.66	91.4	30 480	1.00(2)	*g*
		0.72	32.7	32 700	1.02(3)	*g*
0.48	47 mM $TlNO_3$ + 15 mM $Ba(NO_3)_2$	2.19	96.0	4800	0.96(2)	*g*
		2.20	133	8800	0.94(1)	*g*
		0.91	120	24 120	0.86(1)	*g*
		0.15	27.3	27 300	0.98(4)	*g*

* Data for platinum.

(*a*) Tl_2O_3; (*b*) features of Tl_2O or TlOH; (*c*) features of Tl_4O_3; (*d*) TlCuO(OH); (*e*) phases with high interatomic distances, not identified; (*f*) other phases, not identified; (*g*) diffractometric analysis was not done.

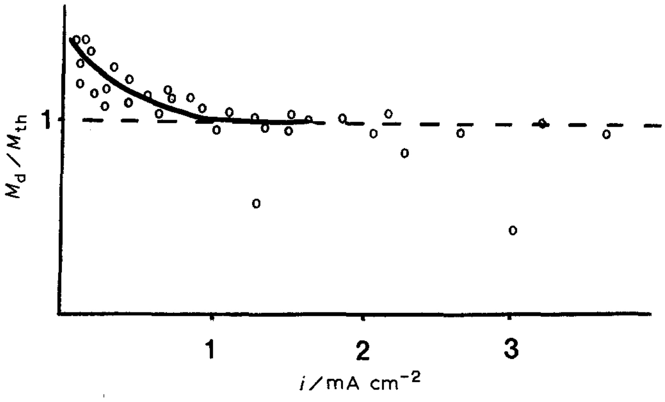

Fig. 1. Excess mass of deposits formed in the presence of 0.24 M NaOH as a function of i.

roughening of the surface during the deposit growth must be considered. For this reason a quasistationary technique was used. Long potentiostatic pretreatment at a selected E_p value initially gave a 6–8 fold increase in i. After this the rate of growth of i became negligible. The resulting rough deposit-covered black surfaces permit the observation of Tafel regions while measuring quasisteady state i values at constant E after 3–5 min polarization. These i values were independent of the direction of E shift, and no change in i was observed excluding the first few seconds after each shift.

Data obtained in the manner described above (Fig. 2) illustrate the deposition of Tl_2O_3 on Tl_2O_3-substrate. Experimental values for $dE/d[Tl^+]$ and the Tafel coefficient, b, about 100 mV are in good agreement with similar quasisteady state data [16] for solutions with pH $\sim$ 12. At the same time, $dE/d\,pH$ in the present experiments was about 60 mV, i.e. lower than the value obtained in [16] for $8 < pH < 12$. The reason for this disagreement may lie in the different nature of the discharging particles; Tl^+ at lower pH and TlOH at higher values (the critical pH value is about 13, 5 [20]).

The most essential result of the measurements presented on Fig. 2 is the high overpotential for the Tl_2O_3 electrocrystallization process on platinum, amounting to 0.3 V or even higher. Beginning the measurements at $E_i < 0$–0.05 V has failed to initiate crystal growth.

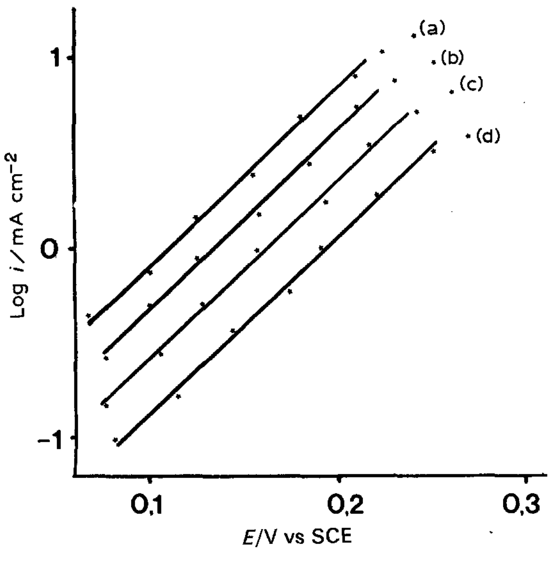

Fig. 2. Quasi steady state polarization curves measured on platinum in 0.5 M NaOH solutions with additions of 0.071 (a), 0.048 (b), 0.024 (c) and 0.012 (d) M Tl_2SO_4.

For the copper substrate in the region of active dissolution, the steady state data shown in Fig. 3 were obtained. A drastic difference of copper behaviour in the presence or absence of Tl^+ was found at the beginning of the passive region. Unlike the latter case, a sharp increase in i took place in the former case, with quasisteady i values being the higher for the higher $[Tl^+]$. Crystallization of a solid black film on copper was clearly visible at $E > -0.2$ V, demonstrating a pronounced decrease in the electrocrystallization overpotential in comparison with a platinum substrate.

At lower pH, when no active dissolution of copper occurs and the copper surface is covered by an oxide over a wide range of E, the beginning of crystallization was observed only at $E > 0$–0.05 V (Fig. 4),

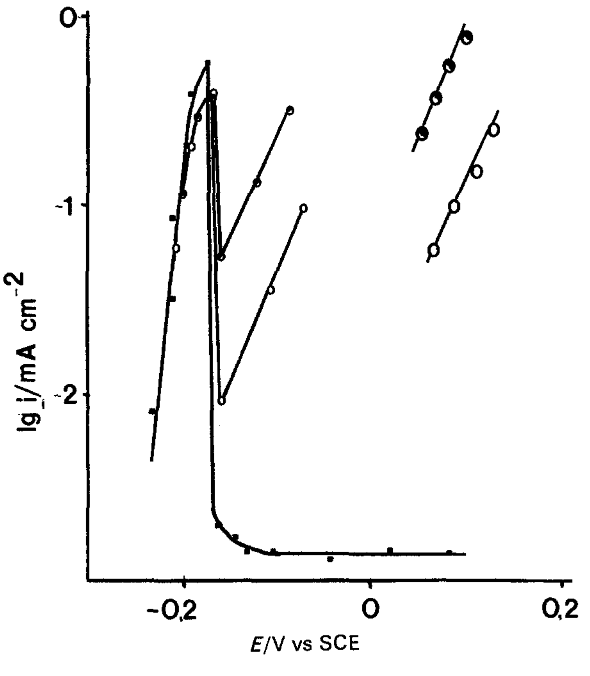

Fig. 3. Steady state copper dissolution and quasisteady polarization behaviour of copper in pure 0.5 M NaOH solution (■) and in the presence of 0.071 (◑) and 0.012 (○) M Tl_2SO_4. Curves obtained on platinum in the same solutions (◑ and ○, respectively) are presented for comparison.

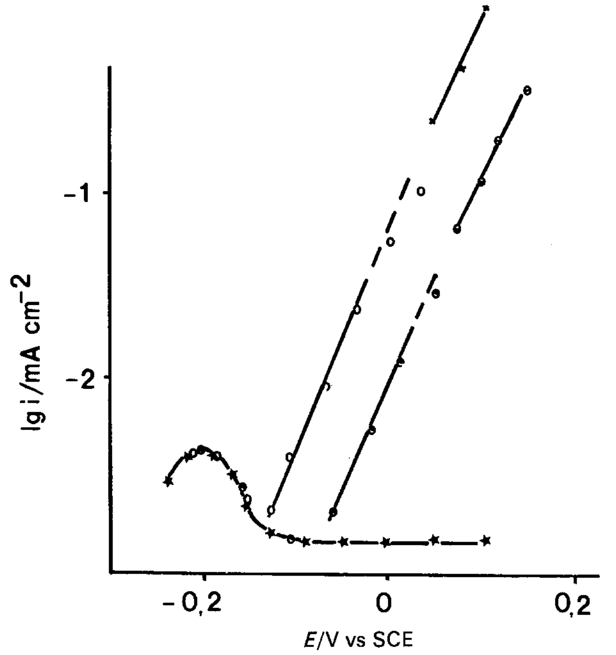

Fig. 4. Steady state copper oxidation and quasisteady polarization behaviour of copper in pure 0.1 M NaOH solution (∗) and in the presence of 0.71 (○) and 0.12 (●) M Tl_2SO_4. Curves obtained on platinum in the same solutions (★ and ●, respectively) are presented for comparison.

i.e. the overpotential was as high as on platinum.

In analysing these polarization data and the results of preparative electrolysis experiments, we conclude that the difference in the behaviour of platinum and copper is connected with different crystalline nuclei (Tl_2O_3 or TlCuO(OH)). Conversely, even on platinum, the nucleation is complicated by the formation of crystals of another type, assumed to be Tl_4O_3, and other mixed-valence compounds cannot be excluded. The schematic representation of the phase composition of deposits at different *i* is given in Fig. 5. It must be stressed, that the value ~ 0.2 mA cm^{-2} (found earlier as the empirical maximum *i* at which the superconductive films may be formed [18]) is in good agreement with the *i* value corresponding to the simultaneous copper dissolution and Tl^+ oxidation processes (Fig. 3). This implies that the main condition of precursor thallium cuprate formation is a simultaneous rapid copper dissolution and a relatively slow thallium electrode process. If the initial *i* value is higher, passivation of copper takes place, hence the conditions of nucleation become the same as on oxidized copper at lower pH and no HTSC-precursor is formed.

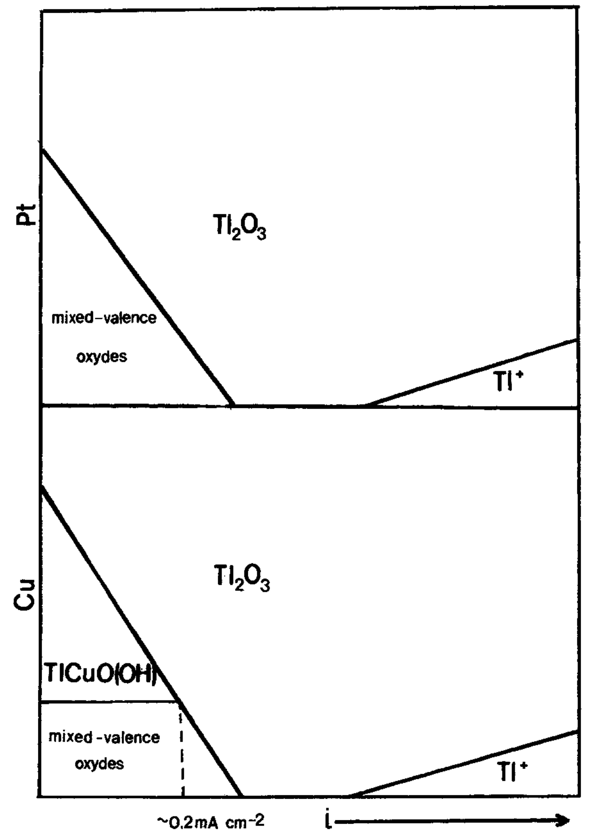

Fig. 5. Schematic representation of the phase composition of anodic deposits on platinum and copper at different *i* values.

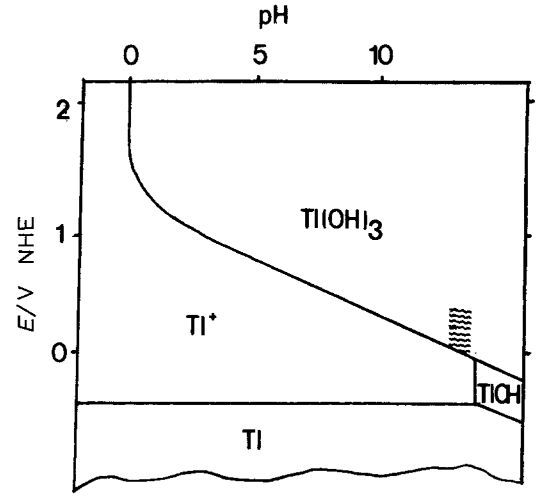

Fig. 6. Pourbaix diagram for thallium according to [20]. Region investigated in this work is shaded.

The results presented here are of interest, not only in connection with anodic HTSC electrosynthesis, but with the electrochemistry of thallium itself. Figure 6 presents a Pourbaix diagram where the region investigated in the present work is shaded. It is evident, that monovalent thallium is presented in Tl_2O_3 deposits at pH and potential values characteristic for thallium (3+) only. There are no kinetic limitations for Tl(1+) oxidation in the deposits, because the diffusion coefficients for oxygen ions in oxide layers at room temperature are no less than 10^{-10} cm^2 s^{-1}, giving characteristic times of 10–1000 s for the oxidation processes in micrometre-thick layers, and the duration of our experiments was much higher. It seems useful to draw some additional lines on the thallium Pourbaix diagram considering the new redox-system: mixed-valence oxide/Tl_2O_3, but this task needs accurate identification of the mixed oxide and determination of its thermodynamic characteristics.

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