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ORIGINAL PAPER

Adsorption of thallium cations on RuO_2–TiO_2 electrodes

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Abstract The electrochemical ion-exchange properties of RuO_2–TiO_2 film electrodes with different composition have been studied in acidic and alkaline media. Thallium-cation uptake has been observed only from the latter and its extent was found to be a function of electrode potential and composition. At potentials near 0.0 V (RHE), the amount of adsorbed Tl^+ exhibited a maximum, and decreased with increasing potential, reaching a broad minimum in the range 0.4–0.8 V. A further increase in the electrode potential, above about 1.0 V, led to an increase of adsorbed thallium species, essentially due to deposition of a few layers of Tl(III) hydroxide. In fact, the release of the latter species was found to be much slower than that of thallium ions adsorbed at 0.0 V. For the latter, in turn, the double injection/ejection mechanism, currently accepted to explain the charge-storage in oxide electrodes, seems to be confirmed. The high Γ values attained at 0.0 V indicate that the large ionic radius of Tl^+ does not prevent its diffusion through the thinner pore texture of the oxide coatings, possibly because of its poor hydration, related with lower charge density at the ion surfaces.

Keywords Thallium ion · Adsorption · Ruthenium oxide · Titanium oxide · Coatings

1 Introduction

Electrodes based on ruthenium and titanium oxides (DSA) have found wide application in industry since the end of the 60's, particularly in electrochemical production of chlorine and caustic soda [1–4]. Their revolutionary impact in industrial electrochemistry has prompted, in turn, a considerable number of fundamental investigations on the physicochemical properties of oxide-based film-electrodes and their correlations with electrochemical properties like charge-storage-capacity (e.g. [5, 6] and literature therein) and catalytic activity toward chlorine and oxygen evolution reaction (e.g. [7–9] and literature therein).

In fact, both of the above properties are strictly related with solid-state redox equilibria of the type:

$$MO_x(OH)_y \rightleftharpoons MO_{x+1}(OH)_{y-1} + H^+ + e \quad (\text{with } M = Ru, Rh, Pd, Os, Ir, Pt) \tag{1}$$

which, to different extents, are typical of group VIII noble-metal oxides (e.g. [5–7]). In the specific case of RuO_2-based electrodes, three oxidation-state changes of the type represented by (1) occur in the potential range between h.e.r. and o.e.r. [6, 7]. The broad shape of voltammetric peaks associated with these electrode reactions causes an extended convolution of signals, leading to an optimal behaviour of the material in question as electrochemical supercapacitor. Likewise, the higher oxidation state(s), preceding the o.e.r. are responsible for the good catalytic activity toward anodic processes, like the chlorine evolution reaction.

However, in spite of the interesting results reported in the literature, many questions remain open, essentially because of the complexity of the precursor path leading to the film electrocatalysts and the many factors that can

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influence properties like composition, microstructure and morphology [10–13]. This makes the reproducibility of their preparation, and of their performance, extremely poor. This consideration applies in particular to the structure of the oxide-solution interface and related adsorption phenomena. The pH of zero charge of RuO_2, for instance, is affected by the preparative conditions and, although to a minor extent, the same also holds for TiO_2 [14]. With this in view, a series of studies on the adsorption properties of RuO_2–TiO_2 electrodes was carried out by combined radiochemical and electrochemical methods [15–24]. The obtained results were generalized and analyzed in a review [25] in which, in particular, an interpretation of the main features of anion adsorption at RuO_2–TiO_2 electrodes has been attempted, and the influence of various physicochemical parameters on anion adsorption was established. This has led to a better understanding of the kinetics of chlorine and oxygen evolution at such electrode materials. On the other hand, the behaviour of cations at oxide electrodes was scarcely considered in [15–25], the only information being that Na^+ adsorption takes place at pH > 8–9. Accordingly, in consideration of the exiguity of experimental results and of the important role played by cations in the mechanism of the charge-storage capacity of metal-conducting oxides (see equilibrium 1), it was thought of interest to carry out a study on the adsorption of Tl^+ ions. The RuO_2–TiO_2 mixture was chosen as a model oxide-electrode, because of its importance in the chlor-alkali process and in related fields of application. Different coating compositions have been investigated, in order to rationalize the correlations between coating properties and RuO_2 concentration. Tl^+ has been chosen as a probe ion, because of its relatively large radius (1.64 Å) and, consequently, low primary hydration number. Also, the closest-approach parameter a, for the case of aqueous solutions of thallous hydroxide, is 1.23 Å while the sum of crystallographic radii is 2.93 Å, which has been explained assuming that the Tl^+–OH^- bond is at least partially covalent [26]. This evidence supports the expectation for a strongly favoured adsorption of Tl^+ at hydroxylated surfaces. The study of the properties of TlOH solutions also indicates that only a fraction of free Tl^+ is present in 0.1 M NaOH [26], but its amount is sufficient to sustain cation exchange processes at the oxide electrodes.

2 Experimental

The radiotracer technique proposed in [27] was used. Tl^+ adsorption was studied from 10^{-3} M aqueous Tl_2SO_4 solutions labelled with Tl^{204}. 0.1 M H_2SO_4 and 0.1 M NaOH were used as supporting electrolytes and measurements were performed at 22 ± 2 °C. All electrode potentials were referred to a reversible hydrogen electrode, in the same solution.

Results by Burke and co-workers [28, 29] and of Trasatti and co-workers [30, 31] on the electrochemical properties of RuO_2 and by Burke and co-workers on the electrochemical properties of RuO_2–TiO_2 mixed-oxide coatings [32] have proved the satisfactory stability of these materials in alkaline media.

The oxide electrodes were prepared using the procedure described in [33]; this procedure is specific in that solutions of ruthenium and titanium chlorides in isopropanol were used, rather than their aqueous solutions; the investigated RuO_2–TiO_2 electrode-coating compositions were 10, 20, 30, 40, 50, 60 and 100% RuO_2. The adsorption of thallium cations was measured as follows: at the potential of 0.0 V, the adsorbate was introduced into the supporting electrolyte solution (0.1 M NaOH) and the change with time in the amount of thallium cations adsorbed on the electrode was measured. When adsorption reached steady-state values, the potential was stepwise shifted by 0.1 V in the anodic direction, up to 1.6 V. Subsequently, in the same manner, the potential was shifted in the cathodic direction down to $E = 0.0$ V.

Since the oxide electrodes used in the present study were prepared by a procedure differing from that described elsewhere [15–25], it was necessary to find whether this change led to modifications of the basic adsorption properties of the electrodes. This preliminary investigation was carried out making use of sulphate anion, labelled with S^{35} as probe species, by measuring its adsorption from 10^{-3} M H_2SO_4 + 0.1 M HCl as a function of pH. In the explored range, from 0.0 to 1.0 V, the extent of anion adsorption was found to be practically independent of electrode potential. The dependence of the adsorption extent on the oxide-coating composition, at constant potential and pH, was similar to that found in [17, 22]. It was also shown that, with increasing solution pH, the adsorption of sulphate anions decreases, becoming lower than the experimental error at pH ≥ 9. Thus, taking into consideration the data in [15–25], there are no fundamental differences in the adsorption behaviour of electrodes prepared by the techniques in [15–25] and in [33].

3 Results

The adsorption of Tl^+ was studied in the potential range 0.0 to 1.6 V (vs. RHE), carrying out measurements in solutions of composition 10^{-3} M Tl_2SO_4 + 0.1 M H_2SO_4 or 10^{-3} M Tl_2SO_4 + 0.1 M NaOH. In the latter case, formation of TlOH ion pairs is expected, in equilibrium with Tl^+ [26]. The composition of the oxide electrodes has been specified in the previous section.

Following the procedure outlined in the experimental part, it was shown that, in acidic thallium sulphate solutions, no adsorption of thallium ions occurs at the electrodes investigated here. In alkaline solutions, on the contrary, adsorption was observed in all experiments, reaching steady-state values in about 30–40 min. The kinetics of adsorption of thallium cations was, however, not studied in detail.

Part of the data are shown in Fig. 1, for one coating composition; for the other compositions, Γ vs. *E* plots were, on the whole, similar to the data in Fig. 1. In all cases, three potential ranges can be distinguished on the curves: in the range from 0.0 to 0.4 V, the amount of adsorbed Tl^+ decreases with increasing electrode potential; it reaches a minimum between 0.4 and 0.9 V, increasing again between 0.9 and 1.6 V. When the electrode potential is varied from 1.6 to 0.0 V, the shape of the Γ vs. *E* curves remains qualitatively the same, but the potential limits of the adsorption regions shift somewhat (curves 2 and 2′, in Fig. 1). Some quantitative changes are observed when the oxide coating composition is changed: Fig. 2 shows the extent of adsorption of thallium cations, as a function of coating composition, at $V = 0.0$, 0.6 and 1.4, respectively. The noble-metal concentration in the films affects the Γ values at different extents, depending on the electrode potential.

The dependence of the adsorption of thallium cations on time was measured at $E = 0.0$ V. When the adsorption reached a steady-state value, the electrode potential was shifted, in the shortest time possible, from 0.0 to 1.5 V, and the electrode was kept at this potential until the adsorption reached the new steady-state value; the data obtained with these measurements are shown in Fig. 3 (empty circles). The full circles in Fig. 3 relate to data of the experiment in which the electrode was at first exposed at 1.5 V and then at 0.0 V. It is clear from Fig. 3 that, in the two cases, the abrupt potential change leads to a sharp decrease of the amount of Tl^+ species on the electrode, followed by an increase. These experiments were replicated with electrodes of different composition and results were similar to those reported in Fig. 3. Thus, data in Fig. 3 suggest that, independently of the specific electrode composition, the thallium species accumulated on the electrode at 0.0 V differ from those accumulated at 1.5 V.

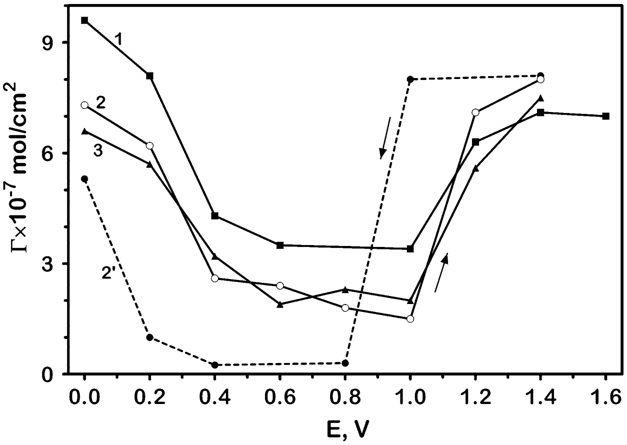

Fig. 1 Dependences of the extent of adsorption of thallium cations on the potential of RuO_2–TiO_2 electrodes of different composition: 1–20% RuO_2 + 80% TiO_2; 2,2′–50% RuO_2 + 50% TiO_2; 3–100% RuO_2. Measurements were performed in solution of composition 10^{-3} M Tl_2SO_4 + 0.1 M NaOH. Arrows show the direction of the change of electrode potential

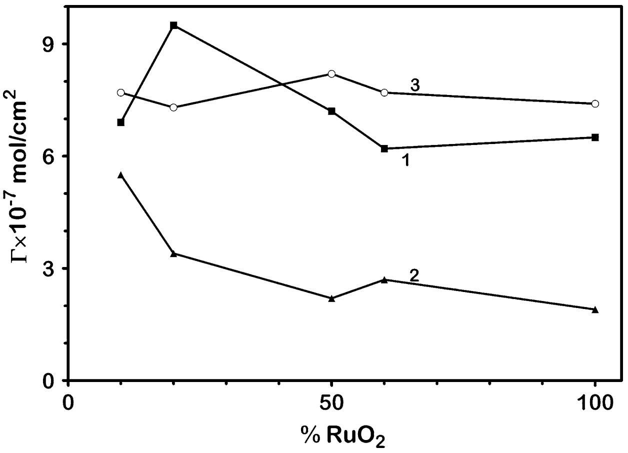

Fig. 2 Dependences of the extent of adsorption of thallium cations on oxide coating composition, measured at potentials: (1) 0.0 V; (2) 0.6 V and (3) 1.4 V. Solution composition as in Fig. 1

More experimental evidence on this aspect was obtained by studying the desorption processes of Tl^+ ions in the supporting electrolyte. When their adsorption reached the steady-state value, at a constant potential (0.0 or 1.5 V), the adsorbate solution was replaced by 0.1 M NaOH,

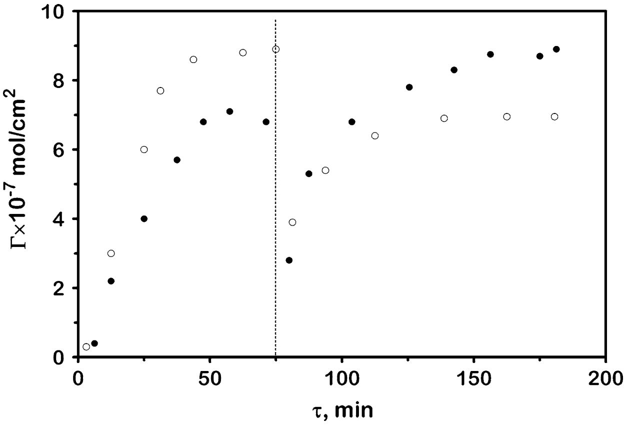

Fig. 3 Dependences of the extent of adsorption of thallium cations on adsorption time, at potentials: 0.0 and 1.5 V (empty circles), or 1.5 and 0.0 V (full circles). The sharp decrease in Γ is related to the abrupt potential change, as described in the text. Solution composition as in Fig. 1

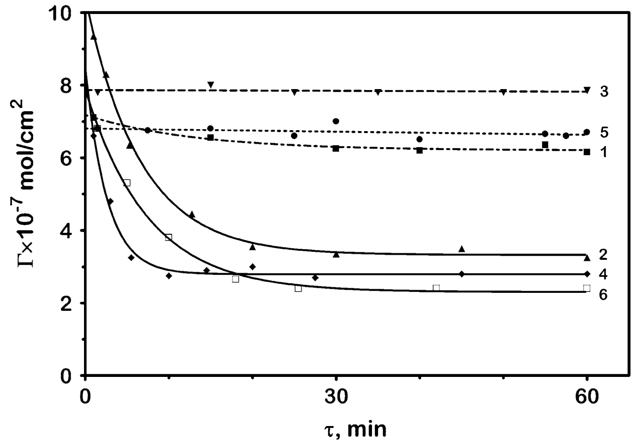

Fig. 4 Desorption kinetics in 0.1 M NaOH of thallium cations accumulated, at 1.5 V (curves 1, 3 and 5) or at 0.0 V (curves 2, 4 and 6), on oxide coatings of composition: 1,2–20% RuO_2 + 80% TiO_2; 3,4–50% RuO_2 + 50% TiO_2; 5,6–100% RuO_2 (explanation in text)

where the electrode was kept for 60 min. Experiments were carried out on electrodes with coatings of different composition; Fig. 4 shows the data obtained by measuring the amount of adsorbed thallium cations on the electrode surface at a given time upon exposure in 0.1 M NaOH. It should be noted that the replacement of the original adsorbate solution with 0.1 M NaOH inevitably causes the removal of a certain amount of the adsorbate itself, whose extent was estimated to be no more than 10–15% of the total amount of adsorbed cations.

As can be seen from Fig. 4, Tl^+ ions adsorbed at 1.5 V are practically not desorbed during electrode exposure in 0.1 M NaOH (curves 1, 3 and 5), unlike the cations adsorbed at 0.0 V (curves 2, 4 and 6). The results of measurements on electrodes of other compositions are in agreement with the data in Fig. 4. Further studies on the desorption kinetics of thallium cations at open circuit in bi-distilled water and 0.1 M H_2SO_4 were carried out. In this case, the desorption of thallium cations takes place irrespective of the potential at which adsorption took place. However, the desorption rate is lower for Tl^+ adsorbed at 1.0 V than in the case of adsorption at 0.4 V. For instance, in the case of exposure in 0.1 M H_2SO_4, Tl^+ ions are completely desorbed in 30 min, from an oxide electrode with 20 mol% of RuO_2, if they were adsorbed at 0.4 V. In contrast, only ~50% of adsorbed thallium cations are desorbed, under the same conditions, if adsorption took place at $E \geq 1.0$ V.

4 Discussion of results and conclusions

As shown by the above results, adsorption of Tl^+ ions on the different RuO_2–TiO_2 electrodes is observed only for pH > 8. In previous literature [10, 13], this range was defined as a possible region for cation adsorption. In our work [25] this was experimentally confirmed for the case of the adsorption of sodium cations. On the other hand, the point of zero charge of surface hydroxyls at RuO_2 surfaces is between 5 and 6, and that of hydroxyls bound to Ti is in the same range [14]. Their weak acidic character suggests poor interaction with larger cationic species, like Tl^+; only upon complete dissociation, can the latter species adsorb. On a hypothetical lyophilicity scale, the adsorption of much smaller cations, with higher charge density, would be favoured. The experimental data of Fig. 1 show that, at variance with adsorption of anions, the adsorption of thallium cations reaches quite large values and depends on the oxide electrode potential. On the other hand, it is well known that charging of metal-conducting oxides takes place via double-injection/double-ejection of one electron and one proton (see equilibrium 1). Experiments carried out by McIntyre and co-workers on anodic iridium oxide (AIROF), basing on nuclear methods for surface analysis, indicated that cations (H^+, D^+, Li^+) are taken up during reductive potential scans and ejected during oxidative scans [34]. Anion (F^-) participation, although possible on a mere electrostatic basis, could not be confirmed by experiments. The data of the present work allow an extension of these considerations to different cationic species, like Tl^+, whose insertion into the porous texture of the oxide film is most probably favoured by the partially covalent interaction with ionized hydroxyl groups on its outer and inner surface. The Γ vs. E dependences obtained in the 0.0–0.5 V range can be explained in terms of cation ejection while E is increased. Γ values around 0.0 V are high, due to Tl^+ accumulation at this initial potential value. The potential increase toward 0.6 V is accompanied by an increase in the oxidation state of Ru ions in the oxide surface (inner, outer) and consequently by Tl^+ ejection. The ejection process is, however, not accomplished during the anodic scan, possibly due to the slow release of the adsorbed cations from the inner surface and narrower porosity. A similar behaviour was observed at oxidized Au surfaces [35]. This process is not necessarily stopped in correspondence with the Γ increase at potentials more positive than 1.0 V, but most probably superimposed on other changes. As indicated by the experimental evidence (Fig. 1), the increase in thallium uptake, observed for $E > 1.0$ V, cannot be understood in terms of a conductive-oxide charging mechanism. Considering that Tl^+ itself undergoes further oxidation to Tl(III) in the same potential range (e.g. [36]):

$$Tl_2O_3 + 3H_2O + 4e \rightleftharpoons 2Tl^+ + 6OH^-;$$
$$E^0 = 1.252\,V \quad (\text{vs. SHE})$$

under the experimental conditions chosen for our experiments (0.1 M NaOH and 10^{-3} M Tl_2SO_4), the increase in the Tl amount on the electrode surface above about 1.0 V (RHE) can be satisfactorily explained by the formation of insoluble Tl(III), rather than assuming a mere adsorption phenomenon. The data in Figs. 3 and 4 are in favour of the above concepts. If thallium cations are accumulated on the oxide surface at $E \geq 1.0$ V, and the potential is subsequently shifted to ~ 0.0 V, Tl(III) species are first converted into Tl^+ and re-dissolved. With further decrease in electrode potential, Tl^+ ions are again adsorbed from the solution onto the surface. Considering that, at 0.0 V, trivalent thallium cations are known to change to univalent thallium cations, we can assume that, already at $E = 0.0$ V, only univalent thallium cations are adsorbed on the oxide. In principle, the possibility of a transition from Tl(III) to Tl(I) without desorption from the oxide surface cannot be ruled out either.

According to the data in Fig. 4, the cations accumulated on the surface at $E > 1.0$ V are more strongly bound to the oxide surface than those accumulated at more cathodic potentials. Consequently, we have reason to believe that univalent thallium cations, in the potential range from 0.0 to 0.8 V, and trivalent thallium cations, at $E > 1.0$ V, are accumulated on the oxide surfaces. The same situation also exists at the other investigated coating compositions. Taking into consideration the non-linear nature of the change in the acid–base properties of oxides, while changing oxide coating composition [10, 13, 37–39], and the absence of simple additivity in the adsorption properties of RuO_2–TiO_2 electrodes [25], we think that an exhaustive analysis of the experimental data shown in Fig. 2 may be difficult. In a more general frame, coatings based on different types of binary oxide mixtures exhibit maxima in effective surface area and in cation uptake properties, for low-intermediate noble-metal concentrations, in agreement with Fig. 2 [37–39]. On the other hand, considering other details of Fig. 2, when different coating compositions are polarized at the highest positive potential (Tl(III) stability region), no effect of injection/ejection can be observed, because the amount of Tl(III) uptake is due to a precipitation process, which can hardly follow the porosity of the film, but rather reflects the extension of the external, or "apparent" component of surface area. As a consequence, it cannot adequately respond to changes in coating composition. At 0.6 V, ejection of Tl^+ should take place and, again, the effect of the coating composition of residually adsorbed Tl^+ may be less important. Following the above approach, the data obtained at coatings polarized at 0.6 V should better reflect the "electrochemical porosity" (the micro component, in particular) of the films and the interpretation of curve 2 in Fig. 2 would follow the same lines discussed in [37] for the case of D^+ exchange at IrO_2–TiO_2 oxide electrodes. It is also meaningful that the Tl species taken up at the coating with the lowest RuO_2 concentration is less affected by electrode potential, as the electronically-conducting component is too dilute, in the film, to play a significant role. In conclusion, present data show that, in the case of oxides as well, there exist systems in which the adsorbability of solution ions is determined, not only by solution pH, but also by electrode potential. This, in turn, supports the assumption that the potential drop distribution at the oxide/solution interface may depend on solution composition.

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