Combined radiometric and electrochemical study of the behaviour of Tc (VII) ions at gold and platinized surfaces in acidic media*

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The sorption and deposition of technetium species formed from TcO_4^- at gold and platinized surfaces was followed by a coupled *in situ* radiometric and electrochemical technique. It was found: (i) that a layer of TcO_2 species is formed preceding the massive deposition of technetium species, and (ii) that the deposition process is not connected with hydrogen evolution or reaction with adsorbed hydrogen as has been assumed in the literature. An important new finding, the electrocatalytic reduction of ClO_4^- ions at surfaces covered by technetium species, was demonstrated on the basis of a comparative study of the phenomena observed in H_2SO_4 and $HClO_4$ supporting electrolytes.

1. Introduction

^{99}Tc, mostly in the form of pertechnetates, is obtained as a byproduct in the nuclear industry. It is produced in significant quantity by separation from nuclear fission products. Technetium, being the first artificially synthesized element and available in large quantities, has been the subject of many electrochemical studies [1–6].

However, some controversial data and observations have been published in the literature concerning the electrochemical behaviour of technetium and the corresponding ions formed from it. The main problem is the simultaneous occurrence of various valency states in the course of most electrochemical studies.

For instance, there is no unambiguous picture in the literature about the reduction and the electrochemical behaviour of TcO_4^- ions at solid (noble) metal electrodes, although several studies have been devoted to the electrodeposition of technetium from pertechnetate solutions [5].

According to the literature, the deposition of technetium at a platinum electrode occurs at potentials where simultaneous hydrogen evolution takes place [5]. It is assumed [2] that the reduction of technetate (VII) ion can be described by its direct reaction with adsorbed hydrogen atoms corresponding to the following overall reaction:

$$TcO_4^- + 3H_{ads} + H^+ \longrightarrow TcO_2 + 2H_2O$$
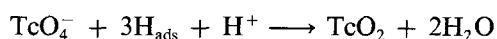
Unfortunately, no information is available concerning the reduction processes occurring at potentials where, for instance, underpotential deposition of technetium containing species is expected. In order to fill this gap a coupled radiometric and electrochemical study of

the sorption phenomena occurring with the TcO_4^- ion and its reduction products at gold and platinum surfaces over a wide potential range is needed. Considering the fact that Tc-99 emits soft β-radiation ($E = 0.292$ MeV) the use of a method [7] applied in the *in situ* study of sorption phenomena of ions labelled with isotopes emitting β-radiation can be used.

The aim of this paper is to report some new information on the electrosorption of technetium at gold and platinum surfaces in acidic media at potentials preceeding massive electrodeposition.

2. Experimental details

The experimental procedure and technique used previously for electrosorption studies [7] were applied without any change.

The main electrode, a vacuum plated thin gold layer or platinized gold (on a thin plastic foil) formed the base of the cell. The radiation detector was placed under the main electrode. $KTcO_4$ was used (Amersham) for the preparation of the solutions, mostly in 1 M H_2SO_4 and $HClO_4$ supporting electrolytes. All potentials quoted in this paper are given relative to the standard hydrogen electrode.

3. Results and discussion

3.1. *Electrosorption phenomena on a smooth gold surface*

Experiments were carried out in 1 M H_2SO_4 supporting electrolyte at about 5×10^{-4} M TcO_4^- concentration. Figure 1 shows the count rate against time curves obtained at various potentials in the potential range 0 to 1000 mV.
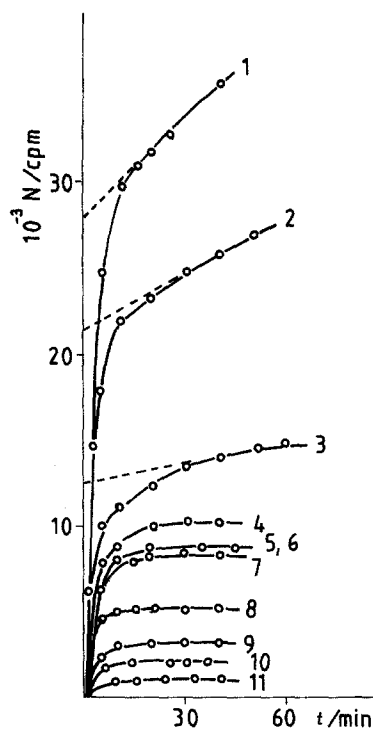

Fig. 1. Count rate against time curves at different potentials obtained in the presence of 5×10^{-4} M $KTcO_4$ in 1 M H_2SO_4 supporting electrolyte. (1) 0, (2) 100, (3) 200, (4) 300, (5) 400, (6) 500, (7) 600, (8) 700, (9) 800, (10) 900, and (11) 1000 mV.

It may be seen from this Figure that at potentials above 200 mV a steady state (or equilibrium) coverage is attained in 20–30 min. At lower potentials, but under the hydrogen equilibrium potential, a continuous increase in the count rate occurs indicating a continuous deposition of technetium containing species. Figure 2 shows the Γ against E curve calculated from data presented in Fig. 1. The curve is indicated by the solid line in the potential range where reliable Γ values could be attained. The dotted line is for values obtained from extrapolation of the linear sections of curves 1, 2 and 3 in Fig. 1 as indicated.

The experimental results reflected by Figs 1 and 2 contradict the assumption that the deposition of technetium containing species is connected with simultaneous discharge of H^+ ions and that the reduction
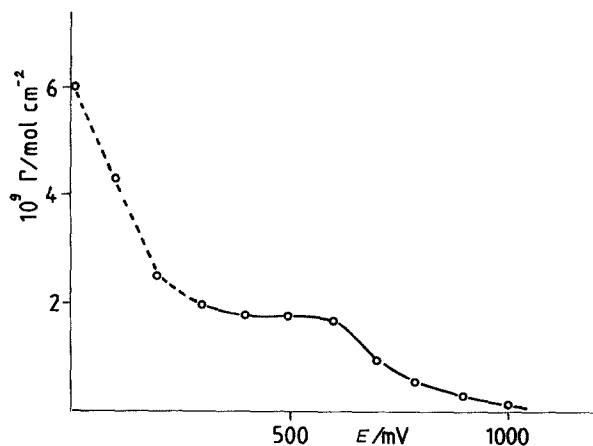

Fig. 2. Γ against E curve obtained from data presented in Fig. 1. (Dotted section represents the values obtained by the extrapolation of the linear sections of curves 1, 2 and 3 in Fig. 1 to $t = 0$.)
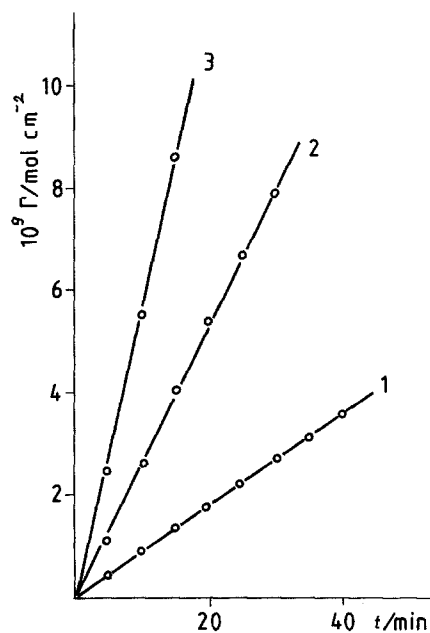

Fig. 3. The continuous increase in the depositon of technetium at different potentials ($TcO_4^- = 8 \times 10^{-4}$ M in 1 M H_2SO_4). (1) 50, (2) -50, and (3) -100 mV.

occurs via a step involving adsorbed H atoms. It is well known that the presence of adsorbed H atoms on gold surfaces at potentials above 0 mV can be discounted.

Figure 3 shows that the deposition rate of technetium species, at low potentials where continuous deposition occurs, depends on the potential and a constant rate can be observed at each potential for a long period. The transients during the first 3–5 min were not taken into consideration. It is quite evident that at $E = 50$ mV (curve 1, Fig. 3) no hydrogen evolution occurs, thus only the processes connected with the reduction of TcO_4^- take place.

An interesting question is whether the nature of the anion present in the system exerts an influence on the deposition of the technetium species or not. Therefore
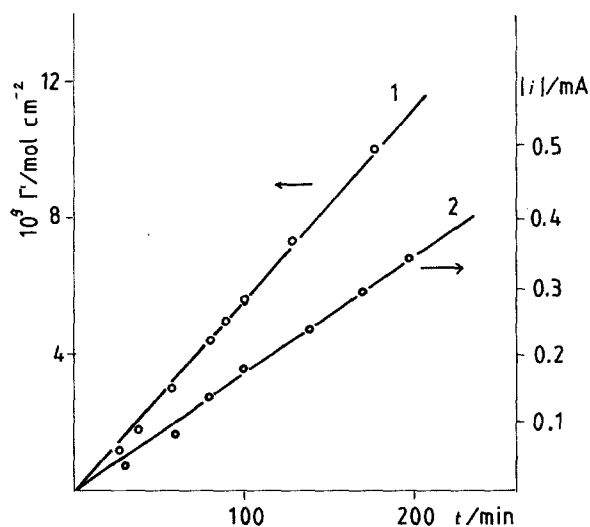

Fig. 4. Γ against time (curve 1) (absolute value) and current against time (curve 2) obtained in the course of a simultaneous radiometric and electrochemical measurement of the deposition of technetium species ($c_{TcO_4^-} = 8 \times 10^{-4}$ M) from a 1 M $HClO_4$ supporting electrolyte at $E = 50$ mV.
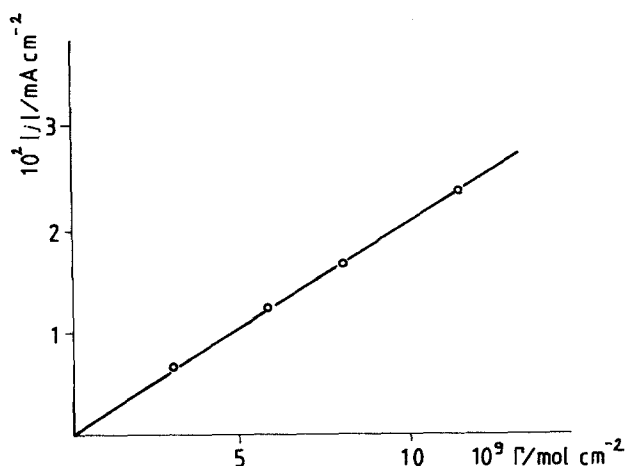
Fig. 5. The $|j|$ (current density) against Γ relationship obtained from data presented in Fig. 4.

Fig. 7. Amount of sorbed technetium species (referred to the real surface area) against time curve at a platinized surface (5×10^{-4} M TcO_4^- in 1 M H_2SO_4) in the case of consecutive potential switches. (1) 600, (2) 500, and (3) 400 mV.

some experiments were carried out in the presence of 1 M $HClO_4$ supporting electrolyte. No significant differences were observed between the Γ against E curves in H_2SO_4 and $HClO_4$; however, at low potential values ($E < 100$ mV) an anomalous increase in the (negative) current was observed with increasing amounts of technetium species (Fig. 4).

In order to clarify this problem the Γ against time and current against time curves were recorded simultaneously at a potential where no hydrogen evolution occurs but where the deposition rate of technetium species is significant.

The results obtained are shown in Figs 4 and 5. It follows that the slow deposition of technetium species at $E = 50$ mV is accompanied by a slow increase in the reduction rate that may be ascribed to the reduction of perchlorate ions. In order to eliminate any doubt about the validity of this assumption a simple experiment was carried out. The cell was washed out continuously with 1 M $HClO_4$ solution at 50 mV without disconnection of the electric circuit and dissolution of the deposited technetium layer. (The latter was controlled by continuous measurement of the radiation intensity). Thus TcO_4^- and other technetium
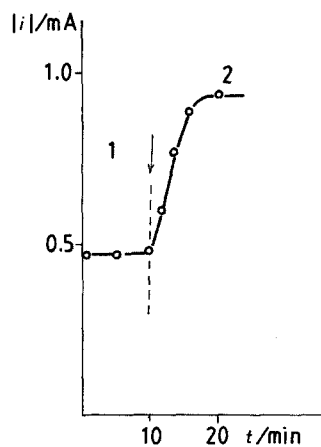
species in the solution were eliminated and the negative current measured may be completely ascribed to the reduction of ClO_4^- ions.

A doubling of the concentration of $HClO_4$ by addition of concentrated $HClO_4$ to the solution phase in the main compartment of the cell resulted in a significant increase, almost a doubling, in the current. This is shown by Fig. 6.

All these results clearly demonstrate that the deposited technetium layer behaves as an electrocatalyst in the reduction of ClO_4^- ions in acid medium. Similar behaviour was found for platinum [8,9], rhodium [10] and some other metals. Thus it can be assumed that the reduction of ClO_4^- ions at metal surfaces is a more general phenomenon than was believed earlier.

3.2. Behaviour of TcO_4^- ions at a platinized surface

In a second series of experiment the gold surface was slightly platinized in order to attain roughness factor values of about 70–80.

By this means there was a possibility of increasing the sensitivity of the radiometric method when studying the behaviour of a platinum surface.

A continuous increase in the count rate occurs at potentials under 600 mV as shown by Fig. 7. This means that a Γ against E curve may be determined

Fig. 6. Effect of doubling of $HClO_4$ concentration on the reduction current of ClO_4^- ions at 50 mV on a layer of technetium species deposited on gold at the same potential. Initial concentration: 1 M $HClO_4$. The concentration of $HClO_4$ was increased at the moment indicated by the arrow.
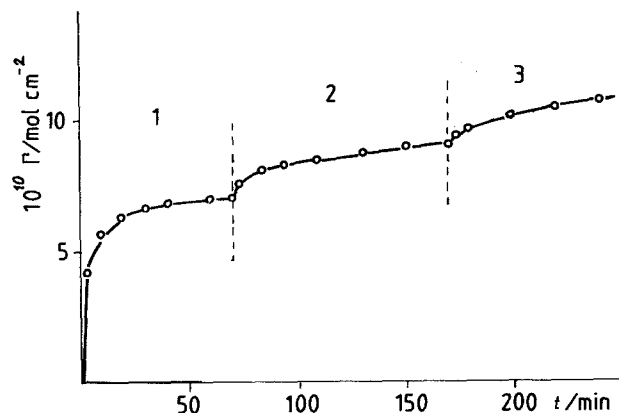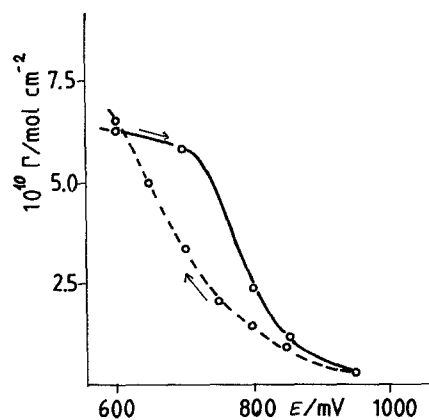

Fig. 8. Potential dependence of the sorption of technetium species. (5×10^{-4} M TcO_4^- in 1 M H_2SO_4).
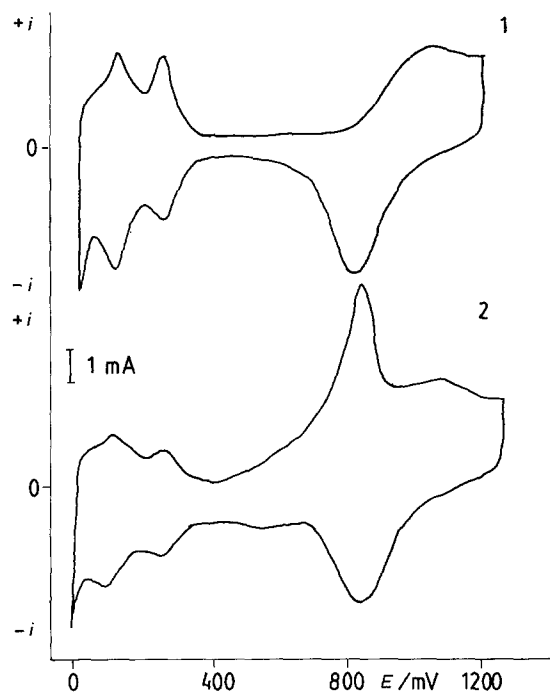
Fig. 9. Cyclic voltammetric curves obtained in the absence (1) and presence (2) of TcO_4^- (5 × 10^{-4} M) in 1 M H_2SO_4 supporting electrolyte. Sweep rate 2.5 mV s^{-1}.

Fig. 11. Desorption of technetium species from the electrode surface at 800 mV following a potential switch from 100 mV. (1) Amount of technetium; (2) current.

only above 600 mV. The results of this study are shown in Fig. 8.

In the potential range from 1000 to 600 mV a hysteresis can be observed between the curves obtained with increasing and decreasing potentials. This phenomenon can presumably be ascribed to the well known irreversibility of the formation of surface oxides at platinum. In all these experiments H_2SO_4 supporting electrolyte was used in order to avoid the complications caused by the reduction of ClO_4^- ions. The behaviour of ClO_4^- ions will be discussed later.

The simultaneous cyclic voltammetric and voltradiometric studies furnish interesting information about the state of the surface in the course of potential sweeps. This is shown in Figs 9 and 10. The sorption of technetium species results in a decrease in the
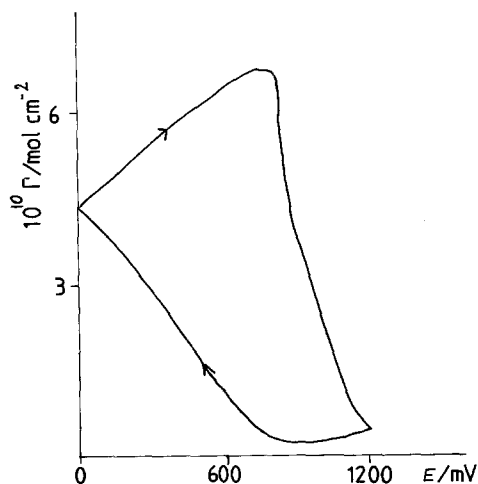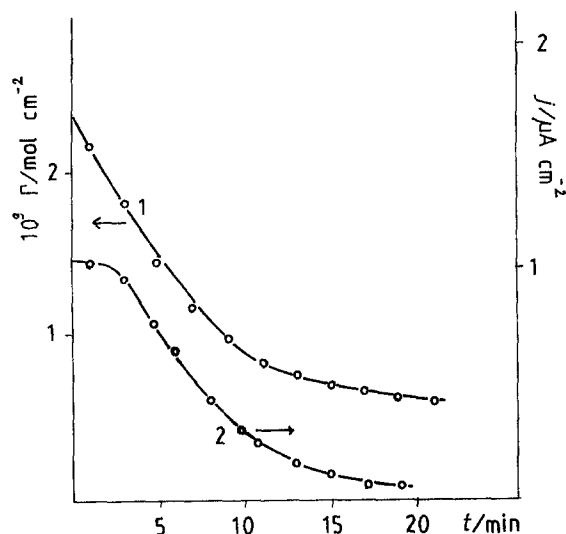
hydrogen adsorption. In accordance with the steady state measurements the elimination of sorbed technetium species occurs above 750 mV and there is a coincidence of this process with oxygen adsorption.

Owing to the slowness of the diffusion and adsorption processes of technetium species, the curves presented in Figs 9 and 10 cannot be considered as 'absolute' ones representing equilibrium or steady state. This is the reason why the curves in Fig. 10 differ from those reported in Fig. 8. The latter curves were obtained by a steady state potentiometric measurement.

A similar consideration refers to the position of the anodic peak on curve 2 in Fig. 9. (Fig. 11 demonstrates the slowness of the desorption.)

Owing to the possibility of simultaneous measurement of the amount of technetium on the surface and
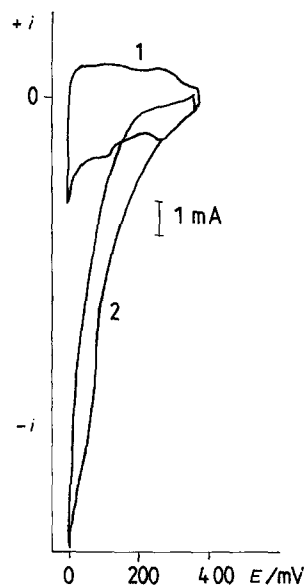

Fig. 10. Cyclic voltradiometric curve reflecting the changes in the amount of deposited technetium species in the course of a voltammetric sweep reported in Fig. 9.

Fig. 12. Cyclic voltammetric curves registered at a platinized surface covered by technetium species (Γ = 2 × 10^{-8} mol cm^{-2}). (1) in 1 M H_2SO_4, and (2) in 3 M $HClO_4$. Sweep rate 2.5 mV s^{-1}.
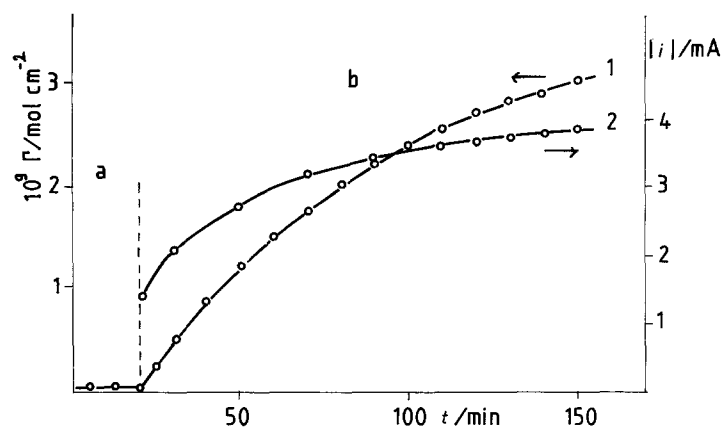
Fig. 13. The simultaneous increase of the amount of deposited technetium species and ClO_4^- reduction rate following a potential switch from (a) 1200 mV to (b) 50 mV. ($c_{TcO_4^-}$ = 4 × 10^{-4} M in 1 $HClO_4$).

the current in the course of the desorption of technetium species at positive potentials (as shown by Fig. 11) the number of electrons involved in the oxidation process leading to the desorption of one molecule of the adsorbed species can be calculated.

Values of about 3.3 were found, indicating that the

$$TcO_2 + 2H_2O \longrightarrow TcO_4^- + 4H^+ + 3e^-$$
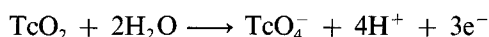
transformation is the main process, characterizing the dissolution of the sorbed technetium species.

The results of experiments carried out in $HClO_4$ supporting electrolyte again demonstrate the occurrence of ClO_4^- reduction at technetium films deposited on a metal support. For platinized surfaces a more pronounced effect was found, as in the case of gold, owing to the higher real surface area. In Fig.12 the cyclic voltammetric curves obtained at a technetium-covered platinized surface are shown. It may be seen from this Figure that in the presence of $HClO_4$ high negative current values are obtained on both cathodic and anodic going sweeps. A correlation between the amount of technetium deposited on the surface and the reduction rate can be found by the procedure applied in the case of the gold support. Fig. 13 shows the two curves obtained following a potential switch from 1200 mV (section *a*) to 50 mV (section *b*). The curve given in Fig. 14 reflects the relationship between
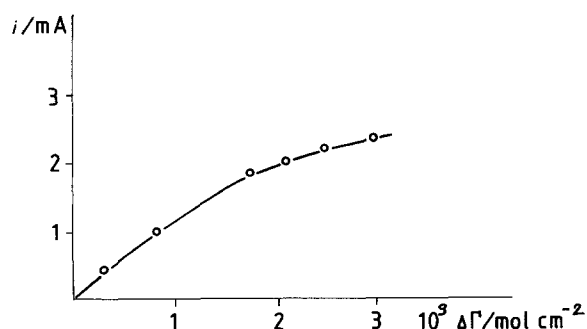
the amount deposited and the current, which is proportional to the reduction rate of ClO_4^- ions. Curve 1 of Fig. 13 clearly demonstrates that at 50 mV there is a continuous increase in the amount of deposited technetium species attaining values corresponding to several monolayers. It is, however, very interesting that complete blocking of hydrogen adsorption cannot be attained during this procedure (see, Fig. 12) indicating that, despite the high average value of coverage, some platinum sites remain available for hydrogen adsorption.

4. Conclusions

The experimental results highlight some new aspects of the electrochemistry of technetium. First of all it is important to emphasize that a more or less reversible formation of a monolayer of technetium species on gold and platinum surface can be observed in the potential range from 1000 to 600 mV. Considering the fact that the standard potential (E_0) of the redox system

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2 + 2H_2O$$
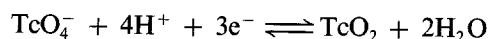
is 0.74 V it can be assumed that a layer of TcO_2 is formed on the surface that behaves like any other layer obtained by underpotential deposition. According to [2] the formation of Tc_2O_3 should play a role at lower potentials.

This may be the reason why a value higher than three was found for the number of electrons involved in the oxidation of the deposited technetium species (Fig. 11).

Another important conclusion that the deposition of technetium species should not involve participation of adsorbed hydrogen, no significant hydrogen adsorption occurs on gold above 200–300 mV and on platinum above 500 mV. Platinum and gold are equally convenient supports for technetium film formation.

Fig. 14. Δi against $\Delta \Gamma$ relationship obtained from the data of Fig. 13.

Finally, the occurrence of the electrocatalytic reduction of ClO_4^- ions,

$$ClO_4^- + 8H^+ + 8e^- \longrightarrow Cl^- + 4H_2O$$
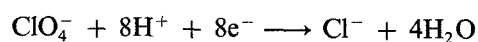
at surfaces covered by technetium species is an important finding. This means that there is another member of the family of metals acting as electrocatalyst for this reaction. It is not yet clear what kind of surface species take part in this process (Tc, Tc_2O_3 or TcO_2). This question and the role of the metal support in the reduction of ClO_4^- require further study.

Acknowledgement

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