Combined radiometric and electrochemical study of the behavior 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 $\text{TcO}_4^-$ at gold and platinized surfaces was followed by a coupled in situ radiometric and electrochemical technique. It was found: (i) that a layer of $\text{TcO}_2$ 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 $\text{ClO}_4^-$ ions at surfaces covered by technetium species, was demonstrated on the basis of a comparative study of the phenomena observed in $\text{H}_2\text{SO}_4$ and $\text{HClO}_4$ supporting electrolytes.

1. Introduction

$^{99}\text{Tc}$, 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 $\text{TcO}_2^{+}$ 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:

$$\text{TeO}_4^{-} + 3\text{H}_{\text{ads}} + \text{H}^+ \rightarrow \text{TeO}_2^{-} + 2\text{H}_2\text{O}$$

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 $\text{TeO}_4^{-}$ ion and its reduction products at gold and platinum surfaces over a wide potential range is needed. Considering the fact that $\text{Tc-99}$ emits soft $\beta$-radiation ($E = 0.292 \text{ MeV}$) the use of a method [7] applied in the in situ study of sorption phenomena of ions labelled with isotopes emitting $\beta$-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 preceding 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. $\text{KTeO}_2$ was used (Amersham) for the preparation of the solutions, mostly in $1 \text{ M H}_2\text{SO}_4$ and $\text{HClO}_4$ 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 $1 \text{ M H}_2\text{SO}_4$ supporting electrolyte at about $5 \times 10^{-4} \text{ M TeO}_4^-$ concentration. Figure 1 shows the count rate against time curves obtained at various potentials in the potential range 0 to 1000 mV.

* 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.
Fig. 1. Count rate against time curves at different potentials obtained in the presence of $5 \times 10^{-4}$M $\text{KTeO}_4$ in 1M $\text{H}_2\text{SO}_4$ supporting electrolyte. (1) 0, (2) 100, (3) 200, (4) 300, (5) 400, (6) 500, (7) 600, (8) 700, (9) 800, (10) 900, and (11) 1000mV.

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 $\Gamma$ against $E$ curve calculated from data presented in Fig. 1. The curve is indicated by the solid line in the potential range where reliable $\Gamma$ 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 $\text{H}^+$ ions and that the reduction occurs via a step involving adsorbed $\text{H}$ atoms. It is well known that the presence of adsorbed $\text{H}$ 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 $\text{TeO}_4^{2-}$ 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