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Corrosion of oxide-coated titanium (DSA) anodes in organic solvents (especially methanol)

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In certain organic solvents, notably alcohols (and in particular methanol), DSA-type anodes deteriorate rapidly under anodic conditions. The active RuO_2-based layer is itself quite resistant to corrosion; however, rapid dissolution of the titanium support through pores and cracks in the active oxide coating, eventually results in detachment of the surface layer. A survey of the titanium dissolution reaction in methanol, and (to a lesser extent) other common solvents, is reported first. Reaction was quite rapid in methanolic solutions at low pH, almost negligible in solutions of high pH, and inhibited in the former case on addition of increasing quantities of water or sulphuric acid. In similar experiments with oxide-coated titanium, the rate of metal dissolution in acidified methanol was reduced by addition to TiO_2 to the RuO_2 layer, increasing the active oxide loading, increasing the water or acid content of the solvent, use of low oxide annealing temperature, and operating at low current density. If this type of anode is operated in anhydrous alcohol systems, the use of a noble metal, or noble metal clad titanium, support would be worth considering. Of the other non-alcoholic solvents investigated, acetonitrile and propylene carbonate appeared to be more resistant to oxidation than dimethyl formamide or dimethyl sulphoxide – no trace of titanium dissolution was observed with any of these solvents.

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1. Introduction

The use of oxide-coated titanium (DSA) anodes is of increasing interest in organic electrooxidation processes [1]. The oxide film generally contains appreciable quantities (usually about 30 mol %) of RuO_2 and is produced as a microporous film [2–4] by thermal decomposition of a mixture of suitable salts such as $RuCl_3$ and $TiCl_3$. Evidence was obtained recently [5] that these highly active anodes corrode readily in acidified methanol solution. The oxide film itself appears to be relatively stable, the attack occurring at those points where pores or flaws in the film permit direct access of methanol to the titanium substrate. Corrosion of uncoated titanium in acidified methanol under anodic conditions is well established [6–11], the reaction having been investigated with regard to the coulometric generation of specific titanium cations [12].

Most studies to date on the corrosion of titanium have been carried out with hydrochloric acid as the electrolyte. Since this is not very suitable in the present case (as the main product with oxide-coated anodes would be chlorine gas), a survey of the behaviour of the uncoated metal in the presence of other electrolytes, especially sulphuric acid, was an essential part of the present investigation. While most of the work was carried out using methanol as solvent (this being the most active medium with regard to the corrosion reaction), some work was also carried out both with higher alcohols and a range of other common organic solvents of interest to electrochemists, e.g., dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), propylene carbonate (PC) and acetonitrile (AN).

2. Experimental procedure

Titanium was used in the form of wire, 99.9% pure, 1 mm diameter, 1.0 cm^2 exposed geometric area, sealed directly into glass. Before use the electrodes were abraded with silicon carbide paper (grit size 600) to remove any gross oxide. The solvents used were of Analar grade and their water

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contents, estimated (in some cases after drying) by the Karl Fischer technique, were generally less than 0.1 wt.vol.$^{-1}$%. Solutions were made up as recommended by Lueck [12], i.e., the concentrated acid was added slowly to the vigorously stirred solvent cooled to 0° C and the mixture was generally allowed to age at room temperature for a period of 24 h (see later) before use. Analysis for dissolved titanium after electrolysis involved reaction with excess hydrogen peroxide, the amount of peroxide complex produced being determined either photometrically using the original cell solution as a blank [13] or by addition of excess EDTA and back titrating with standard zinc nitrate solution using Eriochrome Black T indicator [12]. Standard titanium solutions were made up using potassium titanyl oxalate and calibration graphs were prepared for the range of water-methanol and sulphuric acid concentrations described in this work. Solutions were frequently checked after electrolysis for traces of dissolved ruthenium by atomic adsorption spectroscopy using Li_2SO_4 as a releasing agent. The absence of any positive response confirmed the high stability of the noble metal thermal oxide layer under anodic conditions. In experiments with oxide-coated electrodes each corrosion point involved the use of a fresh electrode, and at least two runs were carried out in every case to check the reproducibility of the data.

The dimensionally stable electrodes were prepared in the usual way [4] by painting etched titanium wires, sealed directly into glass, with a suspension of $RuCl_3xH_2O$ (or a mixture of $RuCl_3xH_2O$ and $TiCl_3xH_2O$) in isopropanol, drying at 50° C and firing in air for 10 min, usually at 420° C. Four coatings were normally applied in this manner and the final annealing was carried out for a period of 4 h.

A three-compartment glass cell was used with a sintered-glass disc separating the working and counter electrode compartments. Potentials were measured, and are quoted, with respect to a hydrogen reference electrode in the same solution. A Luggin capillary was used to minimize errors due to potential drop within the electrolyte. Currents were suppled by a potentiostat (Wenking, Model 68TS3) and potentials were measured using a Bryans Southern Instruments (type 28 000) potentiometric chart recorder. The solution in the working compartment of the cell was stirred with a vigorous flow of nitrogen gas.

3. Results

3.1. *Uncoated titanium*

Although steady state anodic dissolution of titanium was quite marked in solutions of high methanol concentration, there were indications of inhibition in the early stages of polarization. This was demonstrated for example by the appearance of a peak, Fig. 1a, in potential–time curves recorded under galvanostatic conditions. The process involved here is probably removal of a surface film; the potential required for this purpose, i.e., the peak maximum in Fig. 1a, increased rapidly with increasing applied current density and in some cases exceeded 20 V. Since this transition from passive to active state was not always readily achieved under potentiostatic conditions, the current–potential behaviour was generally investigated using a constant current technique. In most cases activation was completed in periods less than 1 min and potential values were recorded after an electrolysis time of 5 min at each current density.

An unusual feature of the anodic behaviour of titanium, noted also by Lueck [12], is the influence of both the preparation procedure and the age of the cell solution on the electrochemical behaviour of the metal. The initial activation phenomena were less marked, and the steady state potential at a given corrosion rate was appreciably lower, with a fresh cell solution prepared by adding the sulphuric acid slowly to vigorously stirred methanol at 0° C. The corrosion potential rose on ageing of the cell solution; for example, the polarization curve for 1.0 mol dm^{-3} H_2SO_4 in methanol (Fig. 2) was shifted anodically by about 130 mV on allowing the cell solution to stand for 24 h before use. A similar anodic shift in corrosion potential was observed on adding dimethyl sulphate to the cell solution (Fig. 3). As these time-dependent changes in potential appeared to be unavoidable in the case of the methanol–sulphuric acid system, a standard ageing period of 24 h was selected; longer ageing times had little further effect on corrosion potentials observed under current flow conditions.

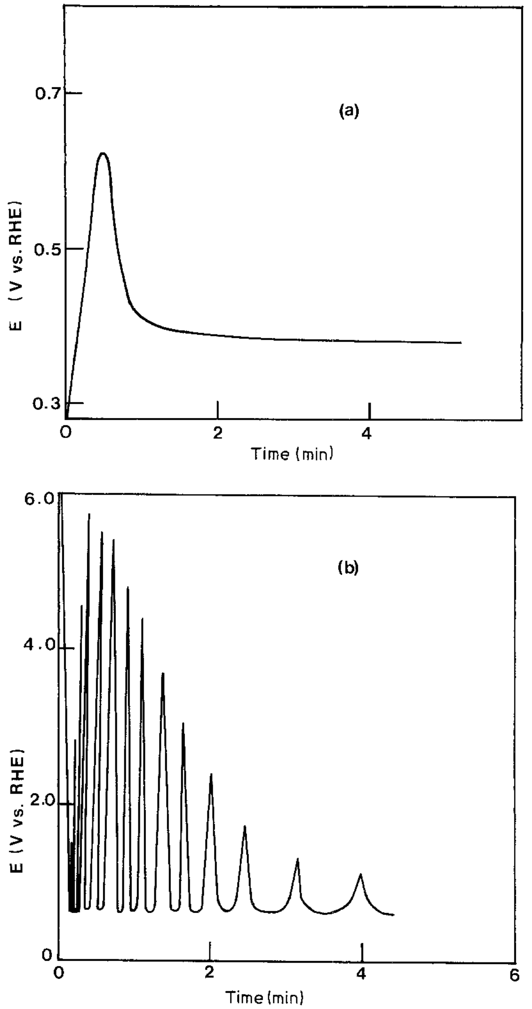

Fig. 1. (a) Initial variation of potential with time for an uncoated titanium anode in a methanol solution containing 1 wt.vol.$^{-1}$% water and 1.0 mol dm^{-3} H_2SO_4 (solution aged for 24 h); $i = 1.0 \times 10^{-4}$ A cm^{-2}, $T = 25°$ C. (b) Initial variation of potential with time in the case of an uncoated titanium anode in methanol containing 5 wt.vol.$^{-1}$% water and 1.0 mol dm^{-3} H_2SO_4 (aged for 24 h); $i = 1.0 \times 10^{-3}$ A cm^{-2}, $T = 25°$ C.

A further indication of inhibition of the anodic dissolution reaction with uncoated titanium was the occurrence of potential oscillations, Fig. 1b, which were more pronounced with aged solutions containing either appreciable quantities of water (about 3 wt.vol.$^{-1}$%) or high concentrations of acid (about 3.0 mol dm^{-3} H_2SO_4). The corrosion in methanol solution was also accompanied by the formation of a black surface layer which, according to Menzies and Averill [6], is the hydride, $TiH_{1.9}$.

Steady-state polarization curves for titanium in acid solution at various low water/methanol ratios are shown in Fig. 2. Corrosion occurred readily at low water content, the potential variation with current density (i.e., the Tafel slope) being surprisingly low in the active dissolution region. The limiting dissolution current densities, distinguished by the sharp increase in potential at higher values, decreased rapidly with increasing water content and reached negligibly low values in the case of methanol containing 10% water. The effect of acid concentration on the dissolution of titanium in methanol solution is shown in Fig. 4. Apart from the relatively high Tafel slope in the case of the most dilute acid solution, and a general increase in corrosion potential with increasing acid concentration, the overall behaviour was not greatly altered on increasing the acid content to values in the region of 3.0 mol dm^{-3}. It can also be seen from the diagram that the limiting current density for active dissolution was almost independent of acid concentration up to, and including, this value. However, at higher concentration, e.g., 5.0 mol dm^{-3}, the dissolution process was severely curtailed. Experiments carried out in sodium hydroxide saturated methanol (~ 1.0 mol dm^{-3} NaOH) indicated that passivation occurred at quite low current densities (~ 1 mA cm^{-2}) in this solution. Chemical analysis combined with coulometric data confirmed the report [12] that the major product (~ 98%) of the anodic dissolution of titanium in acidified methanol is the +4 oxidation state of the cation.

Results for titanium dissolution behaviour in acid media for a range of different solvents are shown in Fig. 5. In the case of the n-alkyl alcohols in Fig. 5a there was a significant increase in corrosion potential over the region where the latter was almost invariant with respect to current density, and a noticeable drop in the limiting current density for active dissolution, with increasing carbon content of these solvents. These changes were even more dramatic when the primary (n-propyl) alcohol was replaced by the secondary (iso-propyl) alcohol. Replacing the alcohol by one of the four other common aprotic solvents resulted in almost total inhibition of the corrosion reaction. As illustrated in Fig. 5b, reaction was somewhat more marked in DSMO and DMF as compared with PC and AN. With the

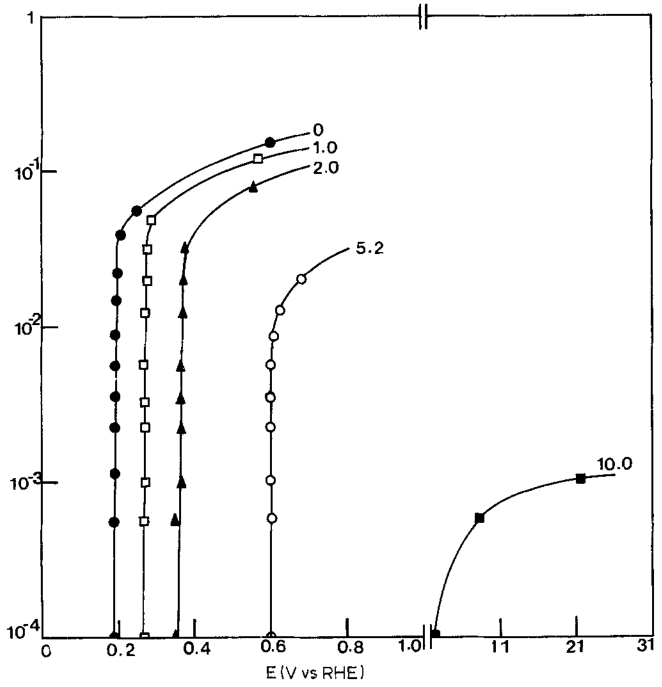

Fig. 2. Effect of the water content of the solvent on the current–potential behaviour of titanium under corrosion conditions in methanol-based solutions containing 1.0 mol dm^{-3} H_2SO_4 (solutions aged for 24 h); $T = 25°$ C. The numbers in the diagram give the volume of water (in cm^3) present in 100 cm^3 of the solvent mixture.

former solvents a grey film was produced on the titanium surface under anodic conditions; no trace of dissolved titanium was detectable in solution after the polarization experiments outlined in Fig. 5b.

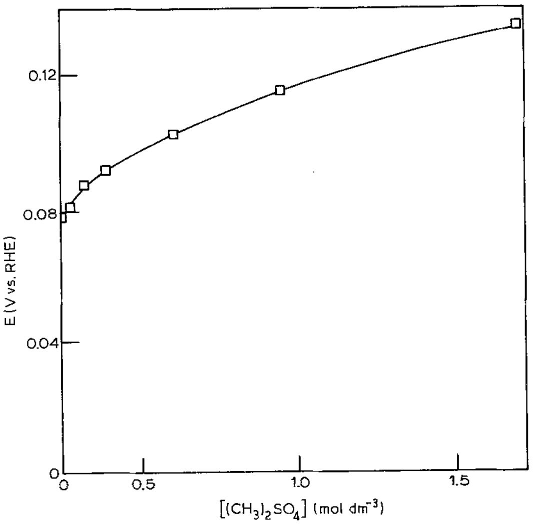

Fig. 3. Effect of addition of dimethyl sulphate on the corrosion potential of titanium under galvanostatic conditions ($i = 78.4$ mA cm^{-2}) in freshly prepared 1.0 mol dm^{-3} H_2SO_4 in methanol at 25° C; potential values were recorded in each case after 10 min of current flow.

3.2. *Oxide-coated titanium*

Current efficiencies with regard to titanium corrosion in acidified methanol were generally quite low, typically not more than 2%, with oxide-coated anodes; the main reaction being alcohol oxidation. Potential values were considerably higher also in this case, ranging from 0.98 V at 1 mA cm^{-2} to 1.30 V at 100 mA cm^{-2}, and the observed Tafel slope, 160 mV decade^{-1}, was identical to that quoted previously [5] for RuO_2-coated platinum in the case of the methanol–acid mixture. The extent of dissolution, estimated after electrolysis by spectrophotometric techniques, was found to be highly dependent on the composition of the oxide film (Fig. 6). For a given oxide loading, the mixed oxides, especially those containing less than about 80 mol% RuO_2, inhibited the corrosion of the substrate to a much greater extent than either pure RuO_2 or mixtures containing a very high content of the latter. In general, rates of corrosion increased with time (Fig. 7) and large increases, accompanied by detachment of flakes of oxide film from the anode surface, were frequently observed with electrodes having a low oxide loading. This oxide detachment appeared to occur in a random manner, thus restricting the reproducibility of the

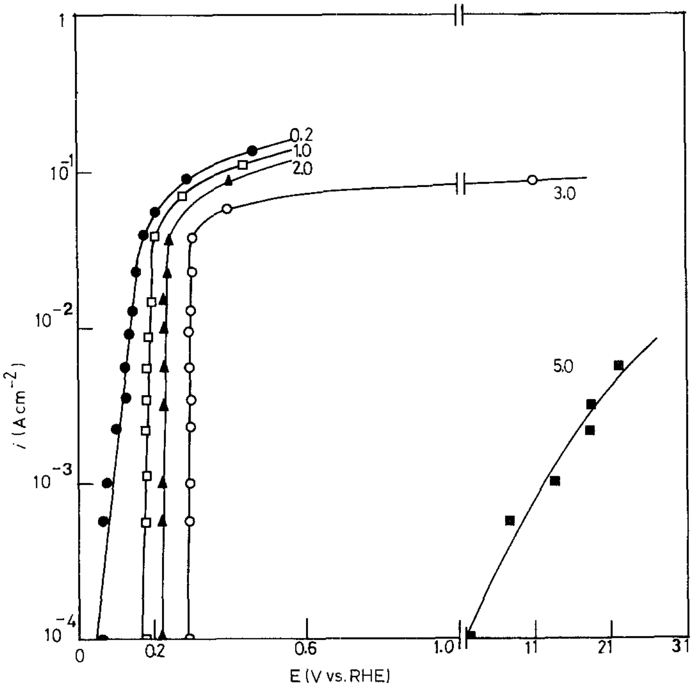

Fig. 4. Effect of sulphuric acid concentration on the current–potential behaviour of titanium under anodic conditions in methanol solution (aged for 24 h) at 25° C. The numbers in the diagram give the acid concentration (mol dm^{-3}).

results obtained under severe corrosion conditions or after prolonged periods of electrolysis.

Considerable care was required in handling the electrodes as any contact with the surface layer, e.g., in inserting the electrode in the cell, adjusting the position of the Luggin capillary, etc., removed some of the layer, resulting in very severe localized corrosion, usually with the creation of a broad semispherical pit and eventual detachment of the lower portion of the wire.

The corrosion of the oxide-coated electrodes was highly dependent on the composition of the

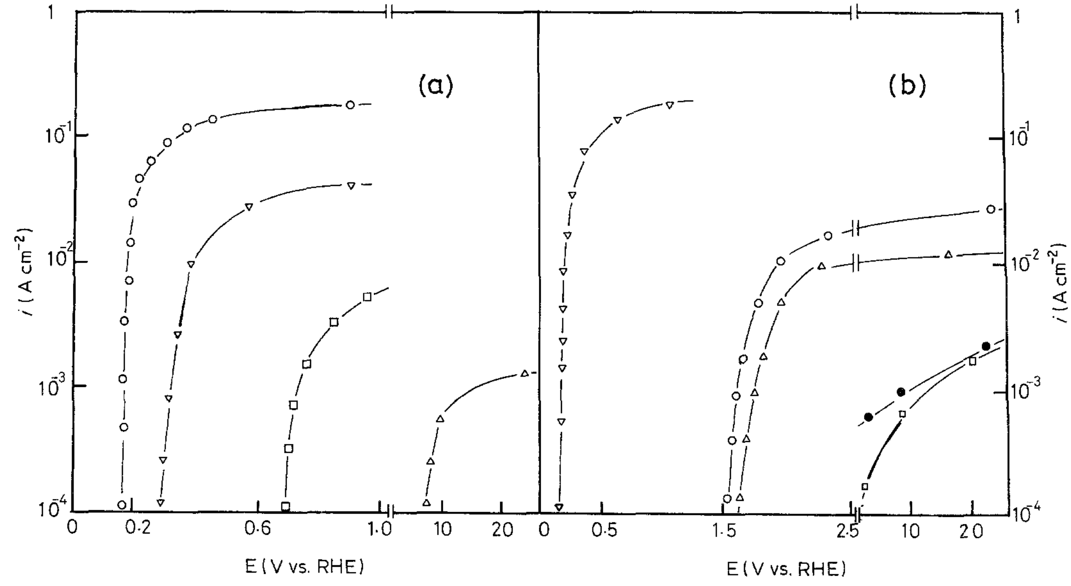

Fig. 5. Current–potential behaviour of a titanium anode in aged (24 h) solutions of 1.0 mol dm^{-3} H_2SO_4 in various solvents, $T = 25°$ C. (a) ○, methanol; ▽, ethanol; □, n-propanol; △, iso-propanol. (b) ▽, methanol; ○, DMSO; △, DMF; ●, PC; □, AN.

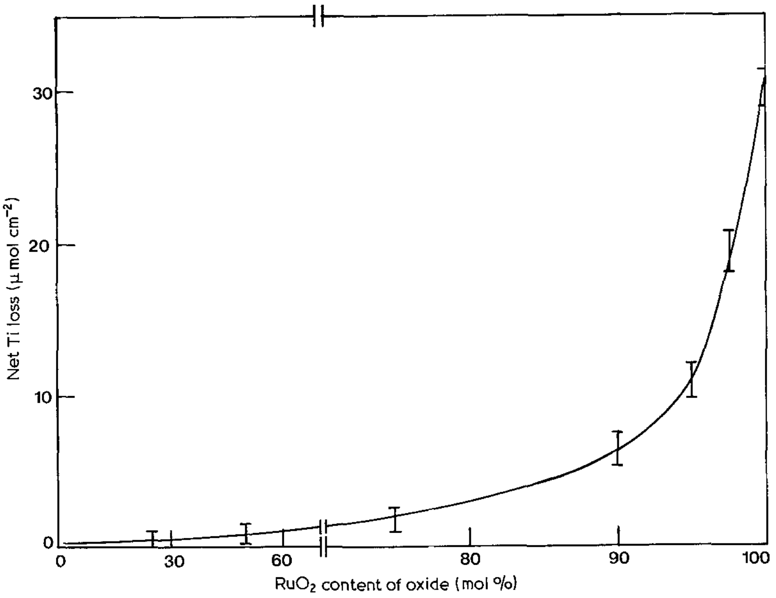

Fig. 6. Effect of composition of the oxide coating on the extent of anodic dissolution of titanium in methanol containing 1.0 mol dm^{-3} H_2SO_4 (solution aged for 24 h) after electrolysis at 0.20 A cm^{-2} for 3 h, $T = 25°$ C. The oxide film was annealed at 420° C and the loading was maintained approximately constant at 3.0 mg cm^{-2} in all cases.

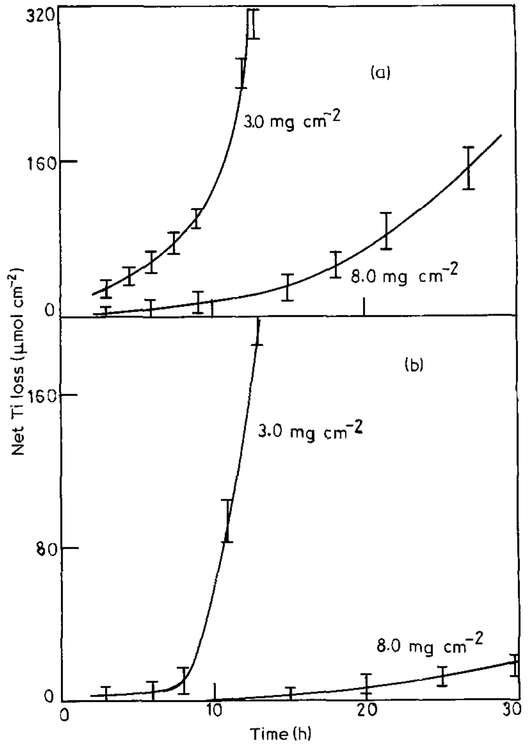

Fig. 7. Variation of the extent of titanium dissolution with time in the case of (a) pure RuO_2-coated anodes, and (b) 25 mol% RuO_2 (remainder TiO_2)-coated anodes, in methanol containing 1.0 mol dm^{-3} H_2SO_4 (solution aged for 24 h), $T = 25°$ C. Two different oxide loadings (see figures in diagram) were used in each case, the oxide annealing temperature was 420° C, and dissolution was measured after electrolysis for the specified times at a current density of 0.20 A cm^{-2}.

cell solution. Thus, the presence of as little as 1% water in the methanol (Fig. 8) almost totally suppressed the corrosion reaction. Increasing the sulphuric acid concentration to values above about 2.5 mol dm^{-3} also suppressed the dissolution process in the case of oxide-coated electrodes (Fig. 9). The difference in corrosion inhibition properties between the pure RuO_2 and a mixed oxide film is again demonstrated in Fig. 10; a major increase in corrosion rate was observed in the former case as the annealing temperature of the pure oxide was raised above 500° C. Finally, with methanol as solvent the rate of titanium dissolution showed an unusual variation with net current density. As illustrated in Fig. 11, a large increase in corrosion occurred when the net current was increased from 0.10 to 0.20 A cm^{-2}.

With regard to the four other solvents, i.e., the non-alcohols, there was little evidence of breakdown of oxide-coated titanium anodes in solutions containing 1.0 mol dm^{-3} H_2SO_4. It was demonstrated that several easily oxidized species, e.g., $[Fe(CN)_6]^{4-}$, oxidized in these acidified organic solvent systems at the same potential on RuO_2-coated titanium as on smooth platinum anodes. Studies of various electroorganic oxidation reactions at these oxide–solvent interfaces will be described later.

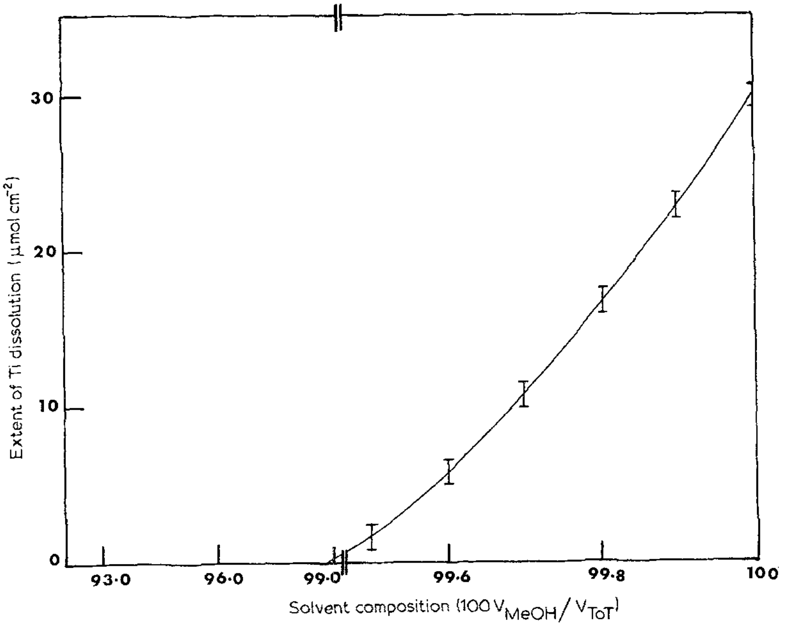

Fig. 8. Influence of solvent composition on the extent of anodic dissolution of titanium in the case of RuO_2-coated electrodes (3.0 mg RuO_2 cm^{-2}, annealed at 420° C) after 3 h at a current density of 0.20 A cm^{-2}, $T = 25°$ C. The methanol-water mixtures contained 1.0 mol dm^{-3} H_2SO_4 and the solutions were aged for 24 h.

4. Discussion

The fact that titanium is a highly reactive substance is demonstrated in the present investigation not only by its high rate of dissolution in acidified methanol but also by the spontaneous formation of the black hydride film. The apparently high stability of the metal in aqueous media is due to the rapid formation of a strongly adherent surface oxide layer which effectively eliminates electrochemical contact between the metal and its aqueous environment. The formation of such a highly passivating film may well be related to the fact that titanium readily forms oxygen-bridged polymers in aqueous media [14]. The formation of such coherent impermeable oxide layers is obviously not possible by reaction with anhydrous organic solvents. Corrosion inhibition at the initial stages of polarization (Fig. 1a) may be explained in terms of oxide formation either prior to immersion or by slow reaction with traces of water in the electrolyte (this water could come either from the H_2SO_4 – a very hydroscopic substance – or from the methanol). The passi-

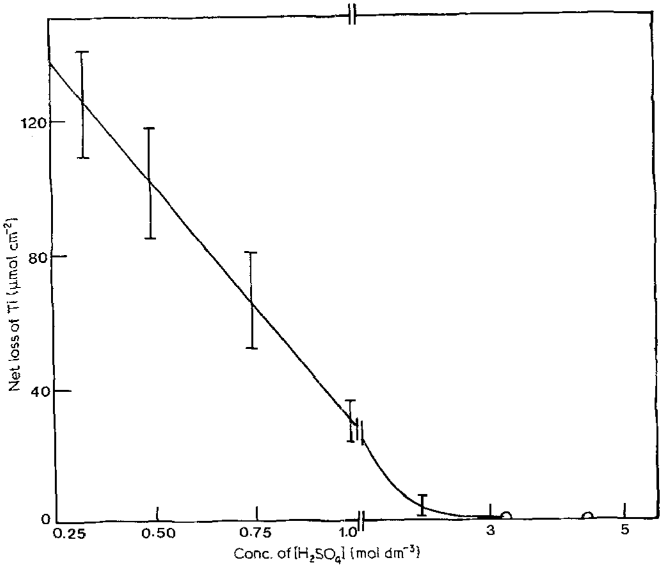

Fig. 9. Effect of acid concentration on the extent of anodic dissolution of titanium in the case of RuO_2-coated electrodes (3.0 mg RuO_2 cm^{-2}, annealed at 420° C) after 3 h at a current density of 0.20 A cm^{-2}, $T = 25°$ C. Solutions of 1.0 mol dm^{-3} H_2SO_4 were aged for 24 h.

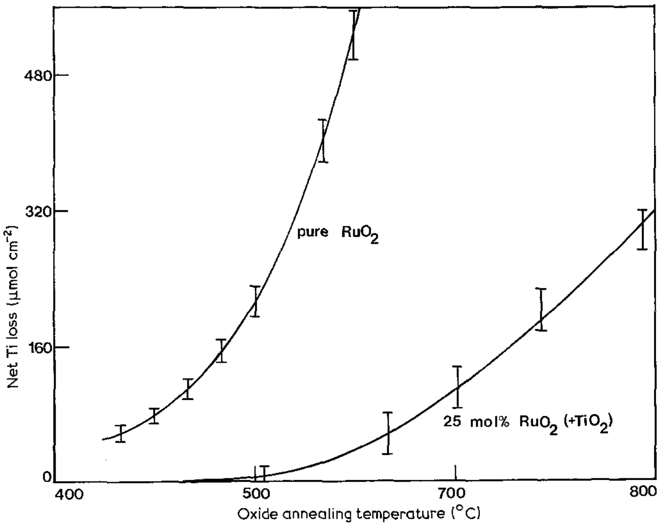

Fig. 10. Effect of oxide annealing temperature on the extent of anodic dissolution of titanium in the case of both pure RuO_2 and 25 mol% RuO_2 (remainder TiO_2) coated electrodes (3.0 mg oxide cm^{-2}, annealed at 420° C) after 3 h at a current density of 0.20 A cm^{-2}, $T = 25°$ C. Solution was 1.0 mol dm^{-3} H_2SO_4 in methanol, aged for 24 h.

vating layer may also include substantial amounts of anions other than oxide, and in sulphuric acid solutions the ratio of oxide to sulphate in this film probably varies with the ratio of water/acid activities in the solution.

The oscillatory behaviour outlined in Fig. 1b is characteristic of electrode systems undergoing passivation – activation transitions. Such oscillations, as in the case of iron which has been described by Vetter [15], usually occur with little diminution with time. The fact that they decay rather rapidly in the present case, the metal eventually remaining indefinitely in the active state under current flow conditions, shows that passivation is relatively slow compared with activation. Possibly the inhibition is determined by the presence of an impurity (for example, traces of water) whose transfer to the metal–solution interface is quite slow, such an impurity could accumulate at (and, therefore, passivate) the surface under open-circuit conditions.

The possibility of a further type of inhibition is suggested by the effect of the ageing of the methanol–sulphuric acid system. It seems likely, from the results shown in Fig. 3, that the source of this inhibition is related to the formation of dimethyl sulphate in the electrolyte.

$$H_2SO_4 + 2CH_3OH = (CH_3)_2SO_4 + 2H_2O \qquad (1)$$

The actual inhibiting species at the electrode surface in the presence of this ester may be some type of adsorbed methyl or methoxy compound.

The unusually low variation of potential with current density for titanium dissolution within the active region (Figs. 2 and 4) suggests that all reactions, including, the electron transfer processes, at the interface are quite rapid, i.e., the titanium ions in solution are essentially in equilibrium with the titanium atoms at the metal surface. As to the magnitude of the potential values, and in particular their variation with either the water content of the methanol (Fig. 2) or the nature of the organic solvent (Fig. 5), little can be deduced at present since, as is clear from the overall reaction to which these potential values refer, i.e.,

$$Ti + 4H^+ = Ti^{+4} + 2H_2 \qquad (2)$$

there may well be a significant (and variable) contribution here due to ion solvation effects. It is clear, however, that limiting titanium dissolution rates (denoted by the rise in potential at current densities at the end of the plateau region) are decreased by increasing the water concentration (Fig. 2). In this case oxide film passivation is assumed to be enhanced. In strong acid (5.0 mol dm^{-3} H_2SO_4, Fig. 4) either $Ti(SO_4)_2$ or $(CH_3)_2SO_4$ may be inhibiting at higher current densities.

In the case of the alcohols (Fig, 5a), the lower limiting dissolution rates, and the higher potential values over the active dissolution region, with increasing hydrocarbon content of the solvent probably reflect a decreasing energy of solvation of Ti^{+4} cations. In the case of the non-alcoholic solvents in Fig. 5 the potential values are significantly more anodic that with methanol. The absence of a titanium dissolution product in solution after such experiments suggests that the current–voltage behaviour here is determined by solvent oxidation. It is generally accepted [16] that DMF and DMSO are inferior solvents for anodic reactions compared with AN and PC; the latter have a much higher resistance to oxidation, an observation evidently borne out here by the data in Fig. 5b. The grey film formed on the titanium surface on anodization in acidified DSMO and DMF is possibly due to formation of a polymeric product on oxidation of these solvents. The absence of significant active dissolution in methanol solutions containing a base is understandable; the OH^- anions in this case obviously provide the oxygen required to form the passive film.

One of the most interesting observations in the work carried out with the oxide-coated metal anodes is the influence of the oxide composition on the rate of substrate dissolution (Figs. 6 and 7). While the origin of this effect is not quite clear at present, the validity of the result is borne out by an observed increase in the service life of RuO_2-based anodes used for oxygen gas evolution in aqueous media on addition of some TiO_2 to the surface layer [17]. Both pure RuO_2 and RuO_2/TiO_2 deposits are highly porous films with large surface areas [18], however, with samples prepared under identical conditions, the surface of the mixed oxide appear to be smoother. Possibly it is simply a difference in texture, with better adhesion between the microporous oxide particles, and between the particles and the metal surface, that is responsible for the reduced rate of titanium corrosion with the mixed oxide coatings.

The rate of dissolution of titanium is assumed to occur initially at cracks and weak spots in the active oxide coating. Lateral attack at these points is assumed to be responsible for detachment of particles or flakes of the surface layer. This may be the reason why raising the current density from 0.1–0.2 A cm^{-2} (Fig. 11) had such a surprisingly large effect on the titanium dissolution rate. The breakdown of weak spots, or nucleation of dissolution centres, may be greatly enhanced at higher current densities. With thicker coatings the higher surface area (largely internal surface) results, for the same apparent current density, in a lower true current density. This, together with the inhibition of the transfer of products away from the metal surface (through the porous oxide) and the decreased tendency for oxide particle detachment, is assumed to be responsible for the lower rates of titanium dissolution at higher oxide loadings (Fig. 7).

Increasing the oxide annealing temperature

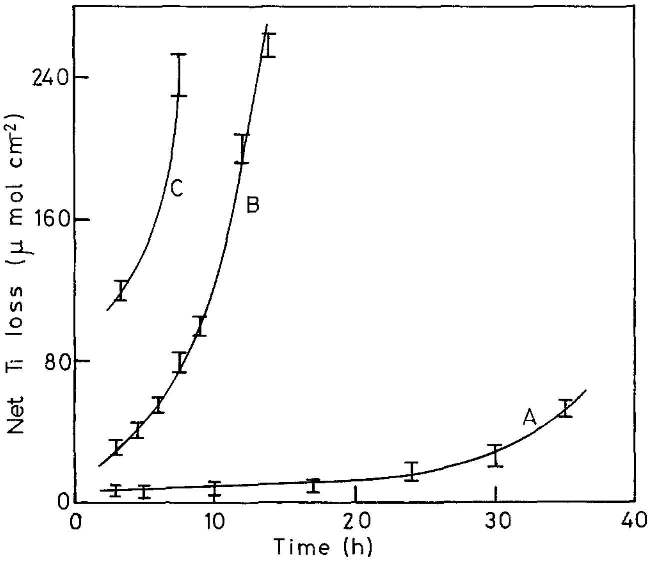

Fig. 11. Effect of current density on the extent of anodic dissolution of titanium in the case of RuO_2-coated electrodes (3.0 mg RuO_2 cm^{-2}, annealed at 420° C) $T = 25°$ C. Solution was 1.0 mol dm^{-3} H_2SO_4 in methanol, aged for 24 h. Current density values (A cm^{-2}): A, 0.10; B, 0.20; C, 0.30.

generally results in sintering of the surface layer [4]; cracks and weak spots are assumed to arise between the growing particles in the oxide coating which, as shown in Fig. 10, leaves the underlying metal more prone to dissolution. The inhibiting effects of water and acid on the titanium dissolution reaction become more marked in the case of the oxide-coated (Fig. 8 and 9), as compared with the oxide-free (Figs. 2 and 4), substrate. Apart from the fact that the potential values are much larger in the former case, the methanol in the active layer region is consumed in the electrolysis reaction. Thus, the water and sulphate concentration at the oxide–metal interface may be significantly larger than in bulk solution. This effect, along with the fact that the area of titanium in contact with the solution in the case of oxide-coated samples is quite small, would explain the more effective action of the passivating agents in the case of the RuO_2-coated anodes.

In summary, therefore, the present results demonstrate that with certain anhydrous organic solvents, e.g., alcohols (especially methanol), DSA-type anodes deteriorate rather severely due to dissolution of the underlying metal. One solution to this problem is to use DMSO or AN as the solvent. Alternatively, the titanium substrate could either be replaced by (or coated with) a noble metal such as platinum or gold. The applications of these anodes in the field of electroorganic chemistry are currently being explored.

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