Electron Transfer Reactions of Titanium(III)/(IV) on Passive Titanium

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The electron transfer reactions of titanium(III)/(IV) at passive titanium electrodes have been studied by transient polarization measurements at various values of the passive film thickness and of the concentration of the redox couple. The Tafel curves for the redox reactions are complex. The anodic curve exhibits two linear regions, and the cathodic curve is non-linear below −0.2 V (sce). Near the reversible Ti(III)/Ti(IV) potential, however, the Tafel curves are linear with $\alpha_- \approx 1$ and $\alpha_+ \approx 0$, and they extrapolate to a common value of the exchange current at the reversible Ti(III)/Ti(IV) potential. In this overvoltage region, the electron transfer is nearly independent of the film thickness. At higher anodic overvoltages, both j_+ and α_+ decrease with increasing film thickness. The polarization data indicate electron exchange with the conduction band of the passive film. The oxidation of Ti(III) appears to have the $TiOH^{2+}$ ion as the main electroactive species under stationary conditions. The rate of electron transfer is found to be first order in reactant dependence and to be independent of the product concentration, but to depend strongly on the nature of the supporting electrolyte.

The kinetics of electron-transfer reactions at passive electrodes has been the subject of numerous investigations, most of which are well reviewed.[1,2] From these investigations a rather uniform pattern of behaviour emerges: For thin films (a few nm), the exchange current decreases exponentially and the current-potential curves become more asymmetrical with increasing film thickness. For thick films, both the exchange current and the transfer coefficients are independent of film thickness. Such electrodes often exhibit pronounced asymmetrical current-potential curves. On the valve metals, anodic ETR is in fact almost blocked.

A fairly large number of photoelectrochemical and capacitance-voltage measurements on passive titanium have been reported in previous literature.[3–9] Such measurements give *in situ* information about optical and electronic properties of the passive film. It appears that the passive film consists of amorphous n-type TiO_2 with a mobility gap of approximately 3 eV. The density of donor states (i.e. oxygen vacancies) is high ($10^{19}-10^{20}$ cm^{-3}) and increases with decreasing film thickness. On the other hand, the kinetics of redox reactions at passive titanium in the absence of light has been the subject of few investigations.[10–15] It appears that anodic ETR is impeded on passive titanium and that cathodic ETR often has Tafel slopes from −60 to −100 mV decade^{-1}. As to the Ti(III)/Ti(IV) redox couple, previous papers[11–13] mostly discuss the influence of Ti(III) on the active and passive dissolution of titanium, and the capability of Ti(IV) to passivate titanium. However, Kelly[13] has made a thorough study of the oxidation of Ti(III: at passive titanium. This study shows that the rate of oxidation of

Ti(III) increases linearly with increasing Ti(III)concentration, but is independent of stirring. It further shows that the rate of dissolution of passive titanium is independent of the presence of Ti(III). Kelly moreover suggests that the hydrolyzed species $TiOH^{2+}$ is the electrochemically active one, since the rate of oxidation of Ti(III) increases strongly with increasing pH. In the previous literature[10–13] it has also been reported that the oxidation of Ti(III) is essentially potential independent under steady conditions.

Previous contributions from our laboratory concern the corrosion and passive behaviour of titanium under quasi-stationary and transient conditions,[16,17] and studies of the redox kinetics of the couples $VO^{2+}/V(OH)_4^+$ and $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ on passive titanium.[14,15] In the present work, the intention was to investigate further the oxidation of Ti(III) and the reduction of Ti(IV) at passive titanium. The reactions have been studied by stationary and transient polarization measurements. From these measurements, characteristics such as the exchange current density and the two transfer coefficients are determined. The dependence of these characteristics on the film thickness may reveal the nature of the main mechanism of electron exchange. For comparison, some polarization measurements on platinum electrodes have been included.

Experimental

The experiments were performed with pure (99.6 %, Goodfellow) titanium sheet electrodes (4.5 cm^2) in a thermostatted Pyrex cell. The platinum auxiliary electrode was kept in a separate vessel in order to avoid contamination of

the solution surrounding the titanium electrode. The reference electrode was a saturated calomel electrode (U^0 = 0.24 V (she)) thermostatted at 25 °C. The cell was shielded from light and stray fields by a surrounding aluminium foil. Instruments used were primarily a Tacussel-BIPAD potentio stat/galvanostat, a PAR-175 universal programmer and a BBC Goerz Metrawatt SE 120 recorder.

All test solutions were prepared from twice-distilled water and A. R. quality chemicals. A 15 % titanium(III) chloride solution (in HCl, about 10 %) was purchased from Merck. Stock solutions of Ti(IV) in 1.0 M HCl were prepared as follows. The requisite quantity of Ti(III) solution, except for a small volume, was transferred to a volumetric flask using a burette. The Ti(III) solution was then oxidized with hydrogen peroxide until the solution became faint yellow, after which the small remaining volume of Ti(III) solution was added [the excess of Ti(III) was considered to be negligible]. The solution was then diluted with H_2O and HCl to the mark. Solution compositions were 1.0 M HCl + x M Ti(III) + y M Ti(IV), with x and y = 0 to 0.1. The solutions were deoxygenated in the cell and kept under nitrogen atmosphere during the measurements.

The procedure for a measuring series generally was as follows: The titanium electrode was mechanically polished, cleaned in acetone, etched for 1 min in aqueous 1 M HF solution and rinsed with twice-distilled water. The electrode was then immediately immersed in 1.0 M HCl and brought potentiodynamically (sweep rate 10 mV s^{-1}) to the chosen stabilization potential. The current was then recorded over a stabilization period of 20 h for stationary behaviour to be approached. In order to determine the net rates of the electron-transfer reactions, current transients from potentiostatic pulses of 5–25 s duration were recorded first in the supporting electrolyte and then after addition of the redox system. The difference in current at any electrode potential was considered to be due to the redox system. After a pulse, a delay of 1–10 min was allowed for the pre-pulse state to be regained before a new pulse was applied.

Results

During the measurements of the redox kinetics, the thickness and composition of the passive film must be maintained constant. In order to meet these requirements, it is necessary first to establish a steady state of the passive titanium electrode, and then carry out fast polarization measurements – either fast potentiodynamic sweeps or fast square potentiostatic single-pulse measurements. In the present work the latter method was preferred since it gives the lowest detection limit for the redox current. In order to determine the net rate of the redox reaction, it was necessary to carry out measurements both in the presence and in the absence of the redox system.

The passive behaviour of titanium in acidic solutions has been discussed in a previous paper.[16] It emerges that titanium approaches the active—passive transition at low po-
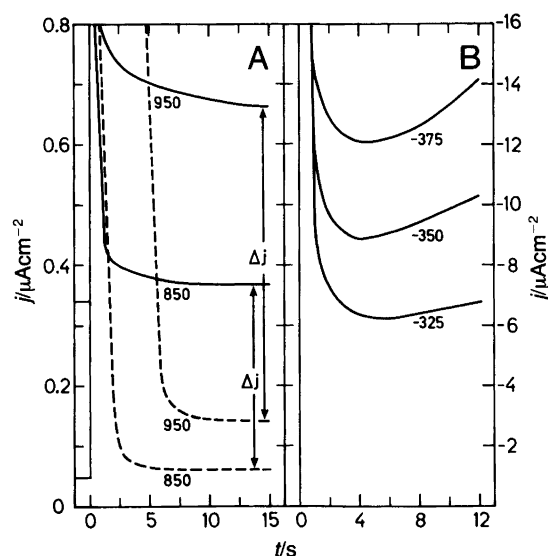

Fig. 1. Anodic (A) and cathodic (B) potentiostatic transients for titanium electrode stabilized (20 h) at 800 mV(sce) (A) and at 0 mV(sce) (B) in 1.0 M HCl at 25 °C. The numbers at the curves are the potentials [in mV(sce)] to which it is stepped. The anodic transients were measured in 1.0 M HCl (dotted curves) and in 1.0 M HCl + 0.01 M Ti(III) + 0.01 M Ti(IV) (fully drawn curves). The cathodic transients were measured in 1.0 M HCl + 0.01 M Ti(III) + 0.1 M Ti(IV).
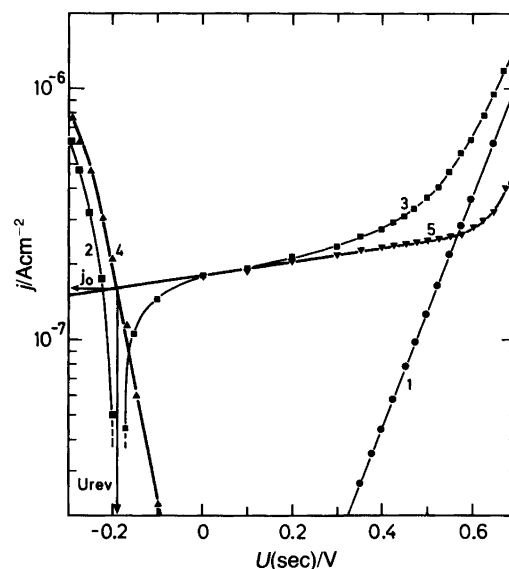

Fig. 2. Initial polarization data for titanium electrode stabilized (20 h) at 0.4 V(sce) in 1.0 M HCl at 25 °C. The curve 1, and the curves 2 and 3 represent measurements in 1.0 M HCl and in 1.0 M HCl + 0.01 M Ti(III) + 0.01 M Ti(IV), respectively. The curves 4 and 5 represent the net rate of reduction of Ti(IV) and oxidation of Ti(III), respectively.

tentials [about 0 V(sce)], regular passive behaviour over an intermediate potential range, and electron extraction from water and chloride ions at higher potentials [> 1.7 V(sce)]. The transients obey the Tafel law, with slope depending on the steady state from which it is stepped:

$$b/decade^{-1} = 0.14(U' - U_b)$$
$$U_b(sce)/V = -1.3 - 0.06pH \tag{1}$$

Fig. 1 gives examples of anodic (A) and cathodic (B) potentiostatic transient obtained in the presence and in the absence of the redox system. Generally, the net rate of oxidation of Ti(III) was determined by the difference in current at the end of the transients in the presence and in the absence of the redox system. However, the correction was found to be negligible with regard to the cathodic transients (for which the base current is approximately equal to zero).

Fig. 2 gives an example of a determination of the polarization curves for oxidation of Ti(III) and for reduction of Ti(IV). Curve 1 shows the initial polarization measured in the supporting electrolyte, and the curves 2 and 3 show the initial polarization in the presence of the redox system. Near the reversible titanium(III)/(IV) potential it was necessary to correct the measurements (Wagner-Traud correction). The curves 4 and 5 show the net rate of Ti(IV) reduction and Ti(III) oxidation, respectively. As shown by these curves, both the oxidation of Ti(III) and the reduction of Ti(IV) passive titanium yield straight Tafel lines near the reversible titanium (III)/(IV) potential. These lines meet at the reversible titanium (III)/(IV) potential (which was measured by a platinum electrode), thus yielding the exchange current of the redox reaction on the titanium electrode. No effect of stirring was observed on any of the polarization curves.

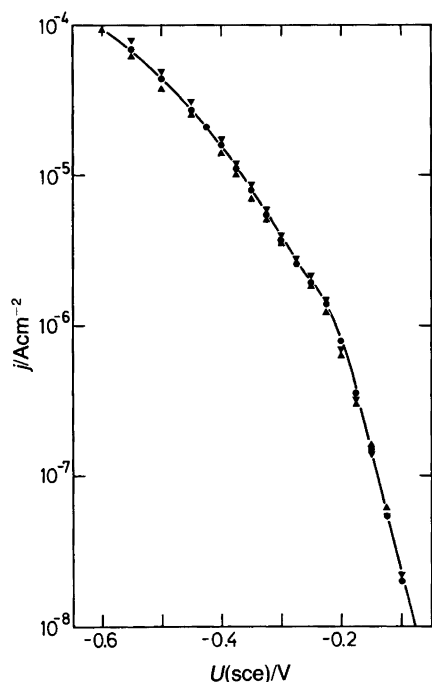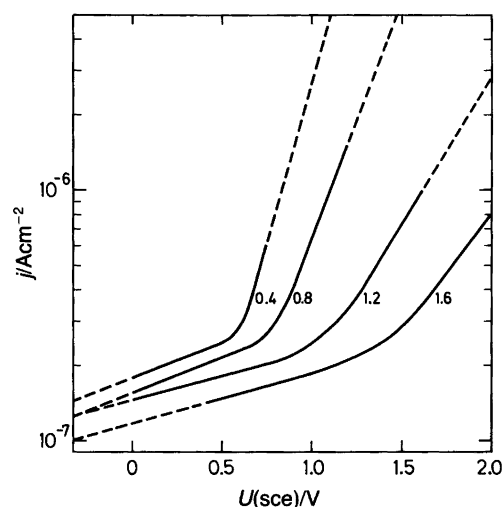The thickness of the passive film on titanium shows a

Fig. 4. Net rate of oxidation of Ti(III) at titanium electrodes stabilized (20 h) at various stabilization potentials in 1.0 M HCl. Values of the stabilization potential in V(sce) are given at the curves. The measurements were made in 1.0 M HCl + 0.01 M Ti(III) + 0.01 M Ti(IV) at 25 °C.

linear increase (about 2.5 nm V^{-1}) with increasing formation potential.[18,19] In order to investigate the influence of the film thickness on the rates of the redox reactions, the titanium electrode was prepolarized (20 h) in 1.0 M HCl at various formation potentials [$0 \leq U' \geq 1.7$ V(sce)] before the redox system was added. Fig. 3 shows the initial polarization curve for reduction of Ti(IV) on pre-passivated [0–0.8 V(sce)] titanium electrodes. This shows that the rate of reduction of Ti(IV) on passive titanium is independent of the oxide film thickness. At potentials higher than about -0.2 V(sce), this reduction gives a straight Tafel line with slope – 60 mV decade^{-1}, which yields $\alpha_- = 1$ for the cathodic transfer coefficient. At lower potentials [< -0.2 V(sce)], the reduction of Ti(IV) gives non-linear Tafel curves for which α_- decreases with decreasing potential. Fig. 4 shows initial polarization curves for oxidation of Ti(III) on pre-passivated [20 h at 0.4–1.6 V(sce)] titanium electrodes. These Tafel curves exhibit two linear regions. The low overvoltage curves exhibit extremely high Tafel slopes ($b_+ > 5500$ mV decade^{-1} or $\alpha_+ < 0.01$) and they show only a slight dependence on the film thickness. The high overvoltage curves show lower Tafel slopes ($b_+ = 490$–1100 mV decade^{-1} or $\alpha_+ = 0.05$–0.15) which increase with increasing film thickness. The potential of transition from the low to the high overvoltage region increases with increasing film thickness.

The influence of the concentration of Ti(III) and Ti(IV) on the anodic and cathodic polarization curves has been investigated. It appears that the rate of the redox reactions [i.e. the rate of oxidation of Ti(III) (j_+) and the rate of reduction of Ti(IV) (j_-)] increases linearly with increasing reactant concentration but is independent of the product concentration:

Fig. 3. Net rate of reduction of Ti(IV) at titanium electrodes stabilized (20 h) at ▼ 0, ● 0.4 and ▲ 0.8 V(sce) in 1.0 M HCl. The measurements were made in 1.0 M HCl + 0.01 M Ti(III) + 0.1 M Ti(IV) at 25 °C.

$$j_+ = Fk_+[Ti(III)]^1[Ti(IV)]^0 \qquad (2a)$$

$$|j_-| = Fk_-[Ti(III)]^0[Ti(IV)]^1 \qquad (2b)$$

where k_+ and k_- are potential-dependent constants. These constants also depend on the composition of the supporting electrolyte–i.e. its pH and the presence of complexing species as HSO_4^- and H_3PO_4. Eqn. (2a) agrees well with previous literature[13] as to the first-order dependence of j_+ on [Ti(III)]. On the other hand, the previous literature lacks data both for j_- and for any influence of Ti(IV) on j_+ at passive titanium.

The rate of oxidation of Ti(III) at passive titanium has previously been found to be about ten times higher in 0.5 M H_2SO_4 than in 1.0 M HCl[13]. Unfortunately, these two solutions have different pH (about 0 and 0.35 in 1.0 M HCl and 0.5 M H_2SO_4, respectively). Therefore, the increase in the rate of Ti(III) oxidation can be ascribed both to the presence of HSO_4^- ions and to the increase of pH. In order to determine the predominant effect, the present work includes initial polarization measurements in 1.0 M HCl + x M $NaHSO_4$ (x = 0–1). Fig. 5 shows examples of initial polarization data for oxidation of Ti(III) at passive titanium in the absence and in the presence of HSO_4^- ions. The effect of HSO_4^- ions on the rate of Ti(III) oxidation at passive titanium is shown in Fig. 6. In this figure the difference in current in the presence and in the absence of HSO_4^- ions (Δj) is log-log plotted against the HSO_4^- concentration to which it applies. As can be seen from the curve, $\log\Delta j$ shows a linear increase with increasing $\log[HSO_4^-]$, with slope equal to $\frac{2}{3}$ for $[HSO_4^-] < 0.2$ M. For higher $[HSO_4^-]$, the rate of Ti(III) oxidation is approximately independent of the HSO_4^- ion concentration. Fig. 6 also shows the effect of HSO_4^- ions on the rate of Ti(IV) reduction at passive titanium. As can be seen from the curve, $\log|\Delta j|$ shows a

Fig. 6. The influence of the HSO_4^- concentration on the rate of Ti(III) oxidation (●) and on the rate of Ti(IV) reduction (○) at passive titanium. The titanium electrode was stabilized (20 h) in 1.0 M HCl at 0.6 V(sce) or at 0 V(sce) prior to the anodic (●) and cathodic (○) transient polarization measurements, respectively. The anodic and cathodic transient polarization measurements were performed in 1.0 M HCl + 0.1 M Ti(III) + x M $NaHSO_4$ and in 1.0 M HCl + 0.1 M Ti(IV) + x M $NaHSO_4$, respectively. Δj is the difference of current at 0.6 V(sce) (●) and at −0.175 V(sce) (○) in the presence and in the absence of HSO_4^-.

creasing $\log[HSO_4^-]$–with slope equal to $\frac{2}{3}$. Altogether, the results of the present work fit with the following tentatively written rate equations:

$$j_+ = F(k_+[HSO_4^-]^{\frac{2}{3}})[Ti(III)]^1[Ti(IV)]^0 \qquad (3a)$$

$$|j_-| = F(k_-[HSO_4^-]^{\frac{2}{3}})[Ti(III)]^0[Ti(IV)]^1 \qquad (3b)$$

Some preliminary studies of the influence of H_3PO_4 on the rate of Ti(III) oxidation have also been performed. It appears that the Ti(III) oxidation current (j_+) never attains a constant value after addition of H_3PO_4–i.e. j_+ shows an initially strong increase and then a slow, continuous decrease. At the same time, the titanium electrode becomes coloured (the colour changes with the passage of time).

Although the main object of the present work was to study ETR at passive titanium electrodes, it has been found useful to perform some comparative measurements on platinum electrodes. It emerges that the rate of electron-transfer reactions are much higher on platinum electrodes than on passive titanium electrodes. The measurements also show that neither the cathodic nor the anodic polarization curves depend on the concentration of HSO_4^- ions.
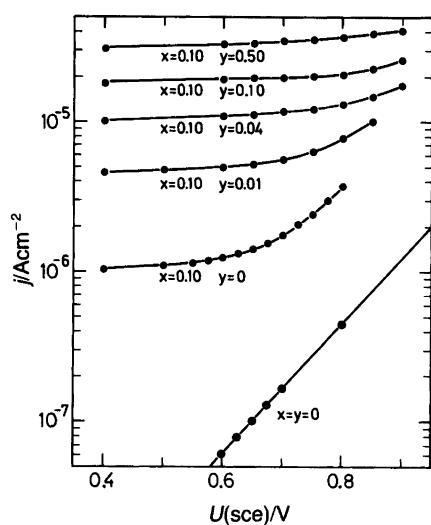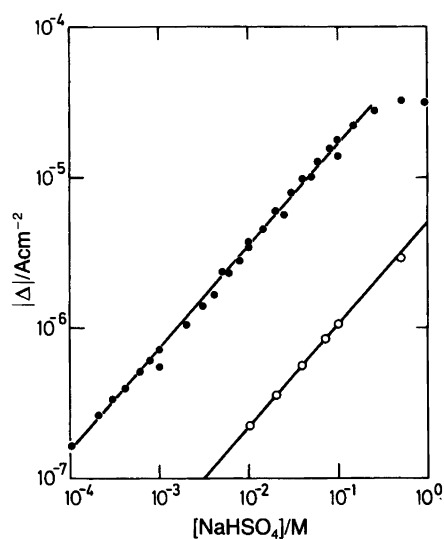

Fig. 5. The influence of the HSO_4^- concentration on the rate of Ti(III) oxidation at a titanium electrode stabilized (20 h) at 0.6 V(sce) in 1.0 M HCl at 25 °C. The initial polarization measurements were performed in 1.0 M HCl + x M Ti(III) + y M $NaHSO_4$. Values of x and y are given at the curves.

Discussion

The curves 4 and 5 in Fig. 2 have been assumed to represent reduction of Ti(IV) and oxidation of Ti(III) at constant film thickness, respectively. The validity of this assumption depends on the film thickness and the semicon-

ductor properties remaining unchanged during the measurements, and on there being no mutual influence of the ionic and electronic partial current densities. The latter requirement has previously been found to be fulfilled for passive titanium electrodes.[13] The other two requirements also seem to be fulfilled, since:

1. The titanium passive current is very low ($\approx$ 5×10^{-8} Acm^{-2}). Therefore, the film growth during the measurements (1–2 h) must be negligible.
2. When the same potentiostatic pulse is recorded twice (in the beginning and at the end of a measurement series), it gives the same current transient—thus indicating constant film thickness and semiconductor properties during the measurements.

The electron exchange at a passive electrode can be with the underlying metal or with the oxide layer. In the latter case, electrons can be exchanged with the conduction band (CB) or with the valence band (VB). The present measurements clearly show that the electron exchange must be with the conduction band, since:

1. The exchange current (j_o) has been found to be approximately independent of the film thickness, thus indicating electron exchange with the passive film.
2. The highly asymmetrical polarization curves (for which $\alpha_+ \approx 0$ and $\alpha_- \approx 1$) indicate electron exchange with the conduction band.

In addition, it is also foreseeable that the electron exchange must be with the conduction band, because the present films are too thick to give a reasonable probability of tunneling with the underlying metal, and because the redox level of the Ti(III)/Ti(IV) couple is much nearer the bottom of the conduction band than the top of the valence band.
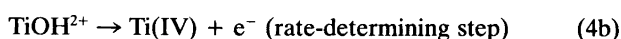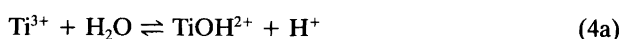
In order to explain the strange anodic polarization curves presently obtained (Fig. 6), one may assume:

1. Ti(III) exists in two different form – Ti(III)† and Ti(III)‡.
2. E_{red} is higher for Ti(III)‡ than for Ti(III)†. E_{red} for Ti(III)‡ is near E_{cs} (E_{red} is the energy level on the reducing agent in lowest free energy configuration and E_{cs} is the energy of the conduction band edge at the oxide surface).
3. [Ti(III)†] $\gg$ [Ti(III)‡].

These assumptions will be more thoroughly justified below. The influence of the tunneling barrier on α_+ has previously been investigated through model calculations.[2] It appears that α_+ should decrease with decreasing height of the tunneling barrier and, ultimately, approach zero as the energy of the tunneling electron approaches E_{cs}. Therefore, the present initial polarization measurements indicate that the Ti(III)‡ ion is the main electroactive one in the low over-voltage part of the anodic polarization curves (where α_+ <0.01). For the "steep" part of the anodic polarization curve, both forms of Ti(III) seem to be electroactive. However, the anodic current mostly represents oxidation of Ti(III)†, since [Ti(III)†] $\gg$ Ti(III)‡]. Both the increase in α_+ (to about 0.15) and the huge influence of the film thickness on j_+ indicate that E_{red} for Ti(III)† is below E_{cs}.[2]

Kelly[13] found that the rate of Ti(III) oxidation at passive titanium increases with increasing pH and that the reaction finally passes from activation to mass transport control. These observations were found consistent with the following mechanism:[13]

$$Ti^{3+} + H_2O \rightleftharpoons TiOH^{2+} + H^+ \qquad (4a)$$

$$TiOH^{2+} \rightarrow Ti(IV) + e^- \text{ (rate-determining step)} \qquad (4b)$$

This mechanism supports the assumptions made above, i.e. that Ti(III) actually exists in two different forms. Ti(III)† and Ti(III)‡ may represent Ti^{3+} and $TiOH^{2+}$, respectively. Using the value 6.3×10^{-3} for the equilibrium constant of reaction (4a)[20] one obtains [$TiOH^{2+}$]/[Ti^{3+}] = 6.3×10^{-3} in 1.0 M HCl. Therefore, the assumption [Ti(III)$\ddagger$] $\ll$ [Ti(III)†] seems acceptable. A simple analysis of the shift in energy level due to complex formation yields:[1]

$$E_{redox}^{complex} - E_{redox}^{aquo} = -(\Delta G_{ox}^L - \Delta G_{red}^L) \qquad (5)$$

where ΔG_{ox}^L and ΔG_{red}^L are the free energy change when the complex involving the oxidized and reduced species are formed, respectively. For the Ti(III)/Ti(IV) redox couple, $E_{redox}^{complex}$ should be higher than E_{redox}^{aquo} since the attraction to OH^- is higher for Ti(IV) than for Ti(III). Therefore, the assumption E_{red}(Ti(III)‡) ions E_{red}(Ti(III)‡) $> E_{red}$(Ti(III)$^{+}$) seems reasonable.

The presently observed independence of the cathodic current on the film thickness together with $\alpha_- = 1$ indicate that the reduction of Ti(IV) at passive titanium occurs by a CB mechanism, and that the energy of the transferring electrons is around E_{cs}. A similar bend has previously been found in the cathodic polarization curves for reduction of $V(OH)_4^+$ [14] and $Fe(CN)_6^{3-}$,[15,21] but it still lacks a commonly accepted explanation. Morrison[1] claims that the bend can be explained by the rate-determining step of electron transfer changing from charge transfer across the oxide/electrolyte interface to charge transfer across the metal/oxide interface as the cathodic current density increases. Schmickler and Schultze,[2] on the other hand, claim that the same bend is due to the participation of resonance tunneling. Unfortunately, the present data are insufficient to distinguish between these two possibilities.

The presently studied redox couple [Ti(III)/Ti(IV)] shows quite simple reaction orders. Such simple behaviour is expected from the energy-level model of charge transfer,[1,2] but has previously not been found to apply to the redox couples $VO^{2+}/V(OH)_4^+$ and $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ [15] at passive titanium electrodes. A recent paper on the kinetics

of the $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple at passive tin[22] similarly reports a reaction order of 0.7 with respect to the reactants.

On the other hand, the behaviour of presently studied redox couple is not quite simple with regard to its HSO_4^- concentration dependence [(3a) and (3b)]. However, only two different explanations of this dependence seem reasonable:

1. HSO_4^- ions become adsorbed on the top of the oxide, thus changing $\varphi_{ox} - \varphi_{sol}$ (i.e. the potential drop over the Helmholtz layer) and thereby $E_{cs} - E_t$ (t = ox or red).
2. HSO_4^- ions form complexes with the titanium ions in the solution. These complexes have E_t near E_{cs} (i.e. they play the same role as the $TiOH^{2+}$ ion does).

The first explanation must be rejected since:

(a) Preliminary measurements on the Ti(III)/Ti(IV) couple at passive niobium electrodes reveal a similar effect of HSO_4^- ions. Therefore, it is most likely that the influence of HSO_4^- ions is due to the formation of some sulfate complex with the titanium ions in the solution.
(b) The steady-state passive current of titanium, which depends on $\varphi_{ox} - \varphi_{sol}$,[16,23] is independent of the presence of HSO_4^- ions.[16]

Although the latter explanation of the influence of HSO_4^- ions on the rate of electron transfer is the most likely one, it will only be given a superficial discussion in the present paper. The reason is that a thorough study of the various complex equilibria in the solution is needed before a detailed mechanism can be developed. Furthermore, in such a mechanism the role of $TiOH^{2+}$ ions should not be neglected, although their concentration decreases as the concentration of the sulfate complexes increases. The number of HSO_4^- ions surrounding the titanium ions may be low (1 or 2) for the electroactive sulfate complexes. This assumption is supported by the rate of electron transfer increasing with increasing HSO_4^- ion concentration also in the case of deficiency of HSO_4^- ions (i.e. $[HSO_4^-] \ll [Ti(III)$ or $[Ti(IV)]$. In addition, j_+ seems to be independent of the concentration of HSO_4^- ions when the ratio $\dfrac{[HSO_4^-]}{[Ti(III)]}$ is greater than about 2.

The influence of H_3PO_4 on the rate of electron transfer is even more difficult to interpret than is the influence of HSO_4^-. There is no doubt that H_3PO_4 forms complexes with Ti(III) in the solution since the solution becomes darker on its addition. Moreover, the oxidation product Ti(IV) forms sparingly soluble phosphate precipitates on the titanium electrode, thus explaining the appearance of interference colours at such electrodes. As long as the properties of the phosphate precipitate (i.e. its value of E_{cs} and thickness) are unknown, it is of little interest to pursue the influence of H_3PO_4.

An inspection of the polarization curves for oxidation of Ti(III) and for reduction of Ti(IV) at passive titanium (Fig. 2) and at platinum reveals the huge difference in polarization behaviour between oxide-covered and bare

metal electrodes. The rate of electron transfer at platinum electrodes exceeds that at passive titanium by up to 4 orders of magnitude. In addition, the rate of electron transfer at oxide-covered electrodes is strongly influenced by the presence of highly electroactive species [i.e. species with low values of $E_{cs} - E_t$ (t = ox or red)]. The present data clearly show this influence:

(a) The value of $E_{cs} - E_t$ is "high" for the redox couple H^+/H_2, thus explaining the slow H_2 evolution at passive titanium. At platinum electrodes the current of H_2 evolution is high even at low overvoltages. This explains the great difference in the case of determining the polarization curves for reduction of Ti(IV) at platinum and passive titanium electrodes.
(b) The rate of electron transfer at passive titanium is very sensitive to the presence of electroactive reactant species (Fig. 6). For platinum electrodes the presence of such species is of little importance.

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