JOURNAL OF APPLIED ELECTROCHEMISTRY 6 (1976) 283–291

Electrochemical reactions by tunnel current through thin insulating anodic oxide films on tantalum

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Received 29 August 1974

Tantalum electrodes covered with oxide films, the thickness of which ranged from 40–90 Å, were investigated. Indium or gold was deposited on the oxide film by the vacuum deposition technique to prevent any change of oxide film properties by polarization. Polarization curves of In |oxide film|Ta diodes in a chloride buffer solution of pH 2·3 almost coincided with the I/V curves of them in the solid state. A redox reaction of a ferricyanide/ferrocyanide couple at Au |oxide film| Ta was also perfectly controlled by electron transfer through the insulating oxide layer. Electron conduction with anodic polarization was mainly brought about by the electron tunnelling, while the Schottky emission possibly predominated in the conduction with cathodic polarization. Actual rates of corrosion of indium deposited on the films did not accord with those predicted by extrapolation of polarization curves to the open circuit potential, owing to the high electric resistance of the oxide films.

1. Introduction

Recently, Vetter and Schultze [1, 2] and Kohl and Schultze [3] investigated the rates of electrochemical reaction of some redox systems on oxide covered platinum electrodes and concluded that the reaction rates were influenced by tunnelling probability of electrons through the oxide layers of thickness 5–8 Å. Besides these works, Elliott, Zellmer and Laitinen [4], Memming and Molloers [5] and Petting, Schoppel and Gerischer [6] interpreted their results on electron transfers between semiconductor electrodes and chemical species in solutions by electron tunnelling through a space charge layer of semiconductor surfaces. And, the authors [7] also pointed out the possibility of electron tunnelling to account for the apparently high conductivity of a passive film on nickel.

The subject of electron tunnelling has been studied intensively in solid state physics, and we have no doubt that even an insulating film has an appreciable electronic conductivity when it is very thin [8–12]. Thus a conductor covered by a chemically and electrochemically stable film might be useful as an inert electrode even if the coating film was insulating. It is likely that for such an electrode, rates of electrochemical reaction are influenced by the tunnelling probability of electrons through the film. Therefore, if one succeeds in preparing an electrode coated with a very thin film which is electrochemically stable, the electrode may become useful for electrolyses, especially for reactions of a relatively low reaction rate.

The present study was conducted to clarify the fundamental properties of an electrode coated with a thin insulating film. Experiments were carried out on tantalum electrodes coated with insulating oxide films prepared by anodic oxidation. It is well known that anodic oxide films on tantalum are chemically and electrochemically stable. Electrical properties of the film were reported in [13–16]. The main purpose of this paper paper is to demonstrate the effects of film thickness on the rates of some electrochemical reactions such as the corrosion of deposited indium and the redox reaction of a ferricyanide/ferrocyanide couple on deposited gold.

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2. Experimental

2.1. *Anodic oxidation of tantalum*

A commercial tantalum plate (99·9%, 0·3 mm thick) was cut into 15 x 20 mm pieces. These pieces were degreased, chemically polished with an acid mixture solution [17], and washed thoroughly with de-ionized water. Then, they were immersed in a hydrofluoric acid solution for 10 s to remove the polishing film and finally washed again thoroughly with de-ionized water. The tantalum plates prepared in this way were placed in a wet condition in the electrolytic cell. Film formation was carried out by anodizing the plate at a constant current density of 100 μA cm^{-2} up to a desired potential and then by holding it at that potential for 3 h. During the anodization, a reverse polarity voltage pulse of half the magnitude of the formation voltage was applied twice to the anodizing plate in the way described by Standly and Maissel [15] (Fig. 1). This treatment led to fairly reproducible film conduction properties. During the anodization, tank nitrogen gas was bubbled into 0·5 vol % H_2SO_4 as the electrolyte. The final current at the end of the anodization was as low as 0·1 μA cm^{-2}. After the anodization, the specimen was washed carefully with de-ionized water and was then dried in a desiccator.

2.2. *Oxide film thickness*

The impedance of the prepared film was measured in the forming electrolyte by an impedance bridge (Yokogawa–Hewlett Packard, model BV-Z-1). For the measurements, the edges of the specimen were coated with epoxy resin. Film thickness was estimated on the basis of the measured impedance by using an apparent area as an effective area and 27·6 as the dielectric constant of the film [18].

In-depth analysis of the secondary ion mass spectrometry of TaO^+ was used as another tool to verify the film thickness. As already reported [19, 10], the intensity of sputtered Ta^+ is distinctly high when it originates from the anodic oxide film, rather than from the tantalum substratum, and the rate of sputtering is kept constant when the condition of the primary ion source is held constant. Therefore, it is possible to obtain a qualitative measure of the film thickness from the sputtering period which produces a high intensity of the secondary ion of Ta^+. The same situation was applicable also to TaO^+ as the secondary ion. A Hitachi ion microanalyzer model IMA-S was used as the instrument. Ar^+ was chosen as the primary ion; the acceleration voltage was 7 keV. The primary ion was fixed so as to give a primary ion monitor current of 42 μA.

2.3. *Preparation of film covered electrode*

Either indium or gold was deposited onto the outer surface of the anodic oxide film by the vacuum deposition technique using the arrangement shown in Fig. 2. An electrical contact to the

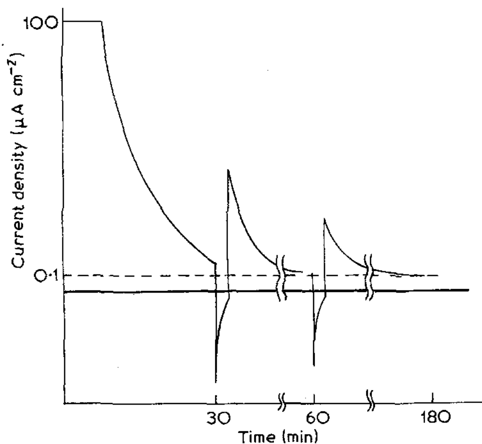


Fig. 1. A typical current-time curve during anodic oxidation by the method of Standley and Maissel.

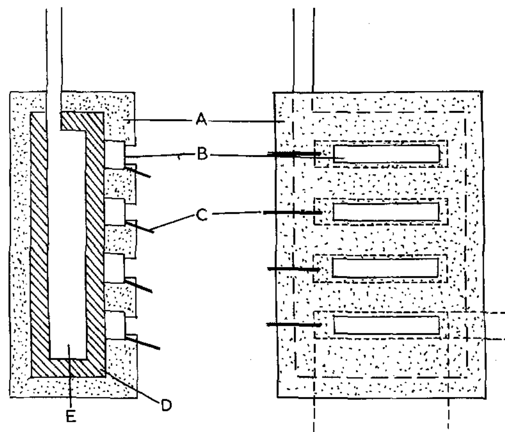


Fig. 2. Schematic illustration of the structure of a metal oxide film tantalum diode. A: epoxy resin, B: metal prepared by vacuum deposition, C: a lead wire, D: anodic oxide film, E: tantalum substratum.

deposited metal layer was made by connecting a lead wire by a silver conducting paint (DuPont No. 4817). A short-circuited metal |oxide| Ta diode could be identified and eliminated by the impedance measurements.

2.4. *Measurements of I/V curves*

The structure of the film-covered electrode is shown in Fig. 2. Only edges of the deposited metal layer were coated with epoxy resin. At first, I/V curves of the In |oxide| Ta and Au |oxide| Ta diodes were measured in the solid state. After that, electrochemical measurements were made on the same diodes. Polarization curves of the In |oxide| Ta diodes were measured in a buffer solution of HCl–KCl mixture of pH 2·3. Corrosion rates of deposited indium in the same solution were determined by polarographic analysis of soluble indium. I/V curves of a ferricyanide/ferrocyanide couple in 1 M KCl were measured at the gold electrode of a Au|oxide|Ta diode. The concentration of the redox electrolyte was 5×10^{-3} M. These measurements were made during nitrogen

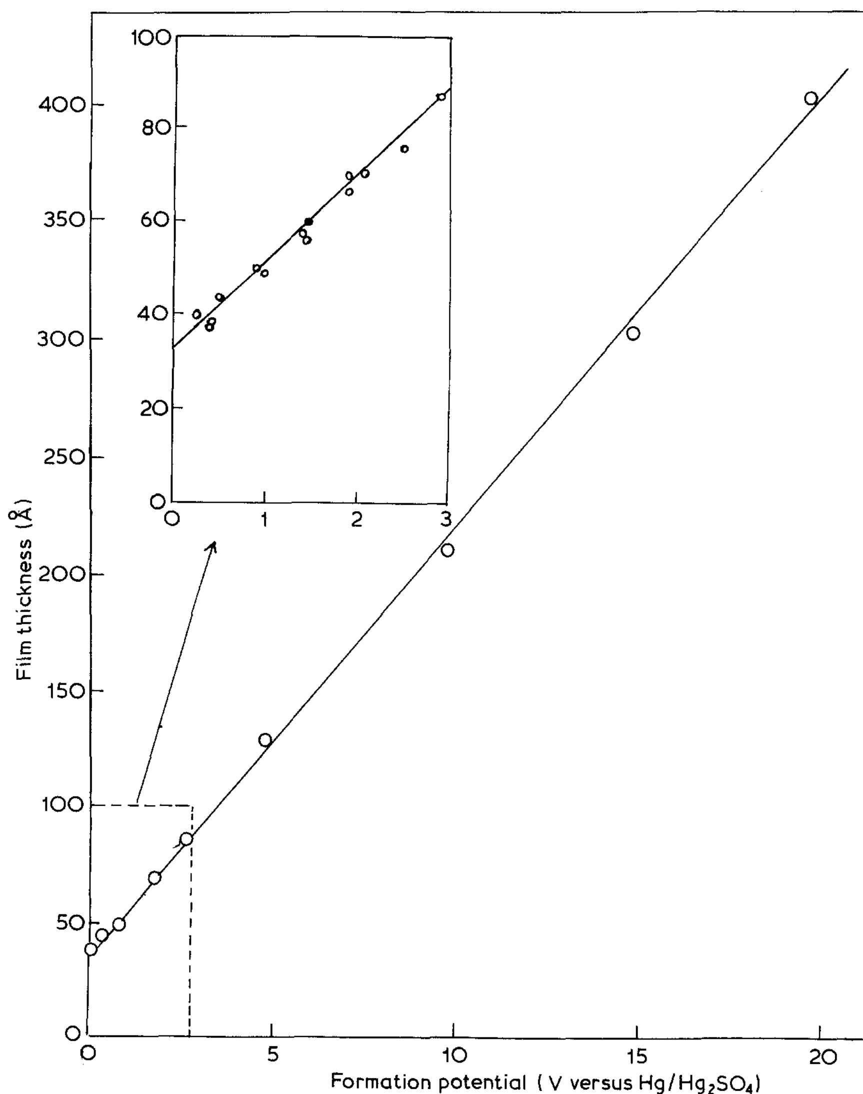


Fig. 3. Thickness of anodic oxide films of tantalum as a function of formation potential. The small frame in the figure shows the correspondence between the behaviour of the film prepared by the method of Standley and Maissel (–○–) and that by a conventional method (–●–).

bubbling at 30° C. An electrometer having an input resistance of 10^{14} (Takeda Riken, model TR-8651) was used as a voltmeter and current was measured by a conventional ammeter or an electronic pico-ammeter (Takeda Riken, model TR-8641). All the measurements of I/V curves of metal |oxide| Ta diodes and of the electrochemical reactions on them were made immediately after the polarization voltage was applied for 2 min.

3. Results and discussion

3.1. *Film thickness of insulating oxide layers*

As already found by many investigators [21–24], a linear relation was found between the reciprocal capacitance of the film and formation potential. Fig. 3 shows the relation between formation potential and film thickness. The relation was formulated as

$$d(\text{Å}) = 20{\cdot}4\,V + 38 \qquad (1)$$

where d and V respectively represent the film thickness and the formation potential against a mercurous sulphate electrode in 0·5 vol % H_2SO_4. The relation in Equation 1 was obtained for the samples prepared by a conventional method, that is, anodizing at 100 μA cm^{-2} at a desired potential and then holding for 3 h at that potential. This relation also held for the samples prepared by the method of Standley and Maissel, as can be seen in a frame of Fig. 3.

If in-depth analysis of TaO^+ was applied to the films formed at various potentials, a signal intensity profile of the secondary ion of TaO^+, as shown in Fig. 4, was obtained. One can consider that the film was sputtered out at the time t_0 in the figure. Plots of values of t_0 against formation potentials gave fairly good linear relations as Fig. 5 shows. This result is qualitatively in agreement with the linear dependence of the film thickness on the formation potential.

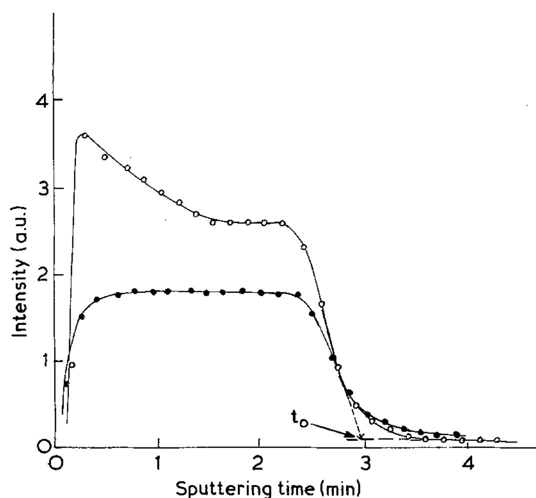


Fig. 4. In-depth analysis of Ta^+ and TaO^+ for the anodic oxide film of tantalum formed at 4 V versus a mercurous sulphate electrode. t_0: sputtering time when the oxide layer is sputtered out. –o– TaO^+, –●– Ta^+.

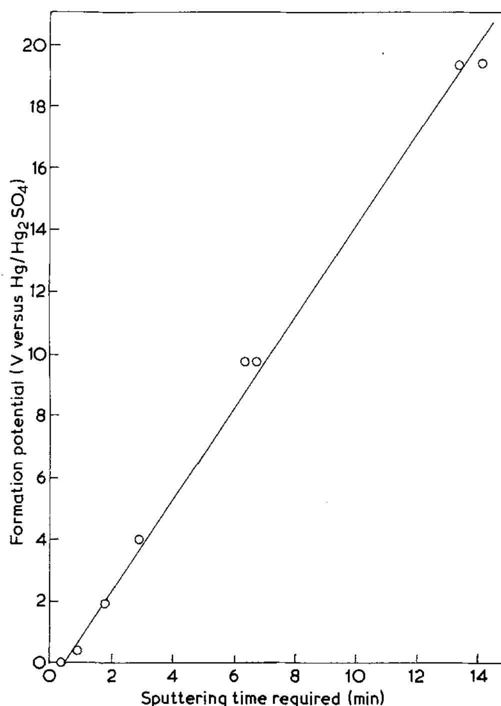


Fig. 5. The relation between the oxide film formation potential and the time required for the film to be sputtered out. Primary ion: Ar^+; Acceleration voltage: 7 keV.

3.2. *Conduction properties in the solid state.*

Fig. 6 shows typical I/V curves of Ta |oxide| In diodes of various film thicknesses. The results of many runs are presented in the figure. Sometimes I/V curves deviating from those of Fig. 6 were obtained. As already pointed out [25–27], the discrepancy might be brought about by inhomogenities in the films, such as flaws and irregularities. In order to eliminate the contribution of the inhomogenities to the conduction properties, the

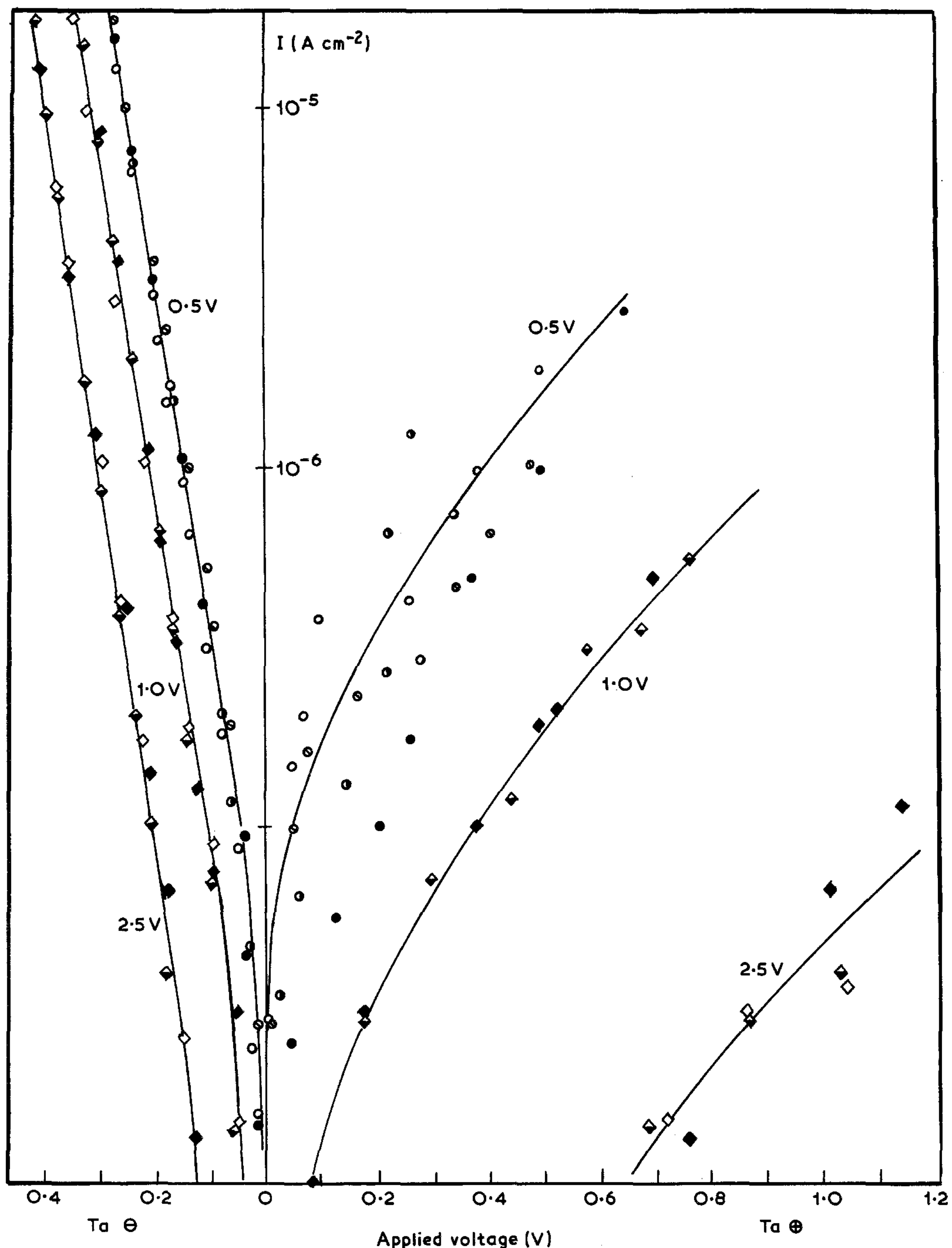


Fig. 6. I/V curves in the solid state of an In |oxide film| Ta diode having oxide films prepared at the various formation potentials indicated in the figure.

electrode area must be the minimum possible. However, very small areas make electrochemical measurements more difficult. Thus the film having typical conduction properties was used for the electrochemical measurements, without restricting the area further.

The I/V curves in Fig. 6 clearly show that there exists a linear relation between log I and applied

voltage when the tantalum substratum is biased negatively ($Ta^{\oplus}$ in Fig. 6 indicates that external voltage was applied to a diode in such a way that the tantalum substratum was biased positively and the counter metal negatively). Similar results have already been reported by other investigators and the difference in electronic conduction behaviour between the bias directions is attributed to different conduction mechanisms in the two cases [12, 14]. On the basis of the conduction theories already discussed [28], it was judged that Schottky emission predominated when the tantalum substratum was biased negatively, while electron tunnelling prevailed through the thin insulating oxide layer when the substratum was biased positively. Our preliminary experiments on the temperature dependence of the I/V curves, which were performed in the temperature range between 5 and 50° C, also supported these conduction mechanisms.

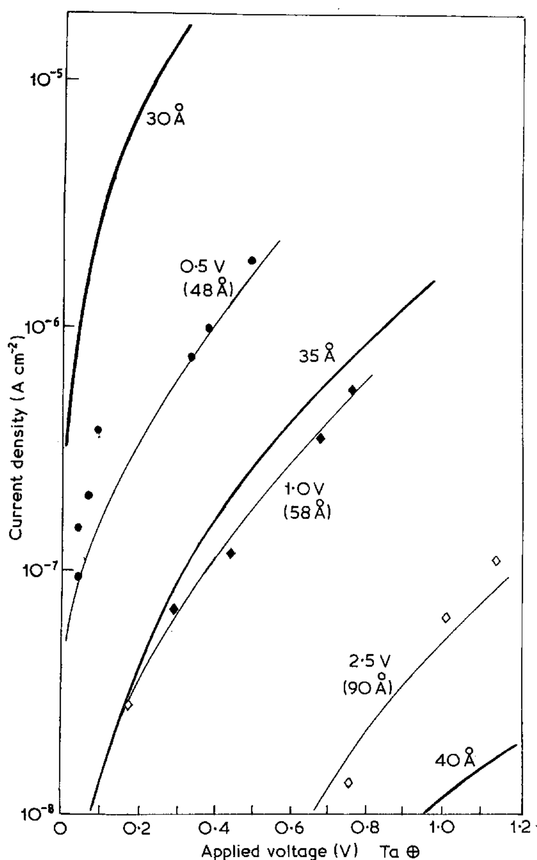


Fig. 7. Comparison of the anodic branches of I/V curves expected theoretically for In |oxide film| Ta diodes with those determined experimentally. Bold solid lines: theoretical curves predicted on the basis of a rectangular potential barrier model. —●—, —◆—, —◇—; curves obtained experimentally on the diodes having oxide films formed at 0·5, 1·0 and 2·5 V, respectively, against a mercurous sulphate electrode.

Fig. 7 shows the anodic portions of the I/V curves obtained experimentally and those predicted by the Fowler-Nordheim tunnel equation,

$$I = (BF^2/\psi) \exp -(\lambda \psi^2 F) \quad (2)$$

where F, B and ψ denote field strength across the film, a constant of $1{\cdot}1q^3/4\pi h$ and the mean potential barrier height at the negatively biased metal/insulator interface, respectively. The theoretical curves in Fig. 7 were derived on the assumption that ψ at the film/indium interface was 0·96 eV. This assumption will be reasonable if a trapezoidal potential barrier is adopted, since the potential barrier at the tantalum/film interface is 1·1 eV [13, 14], and the work functions of tantalum and indium are 4·22 and 4·08 eV, respectively [29]. The shapes of the theoretical and experimental curves were very similar, as Fig. 7 shows, though the accordance of the absolute values of film thickness was rather poor. The similarity of the shapes of the I/V curves also supports qualitatively the postulate that electron conduction due to quantum mechanical electron tunnelling predominated when the tantalum substratum was biased positively.

3.3. *Electrochemical behaviour of indium deposited on the film*

After the solid state conduction properties were obtained, electrochemical measurements were made on one of the four indium layers of a tantalum electrode. For this purpose, the other three indium layers and all the terminal leads connected to the deposited indium layers were coated with epoxy resin. I/V curves in a chloride buffer solution are shown in Fig. 8. The tantalum electrode was polarized positively against a platinum plate counter electrode when the anodic I/V curve of the indium layer was obtained. For the determination of the current density on the electrode whose behaviour is shown in Fig. 8, the apparent area of the evaporated indium layer was chosen as the effective area. This includes the area covered with epoxy resin (see Fig. 2). Such a choice of

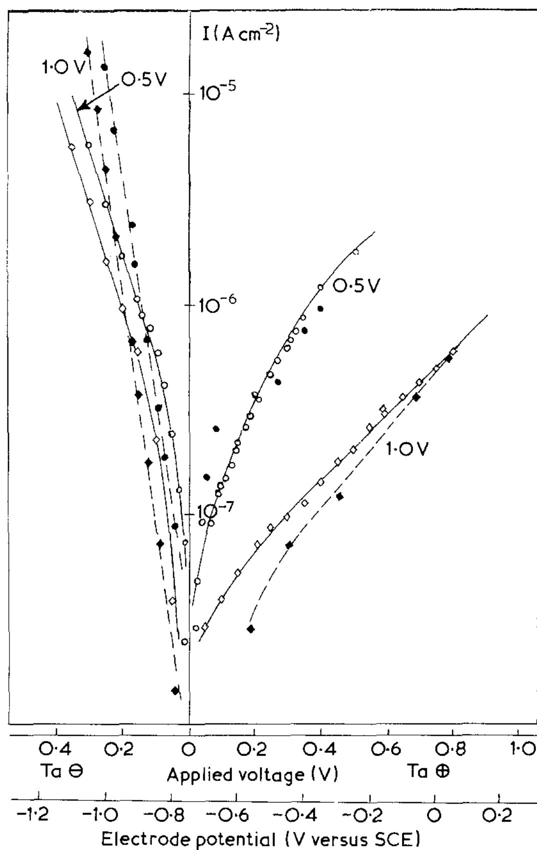


Fig. 8. Comparison of I/V curves of In |oxide| Ta diodes in the solid state with those obtained in a KCl-HCl solution of pH 2·3. —●—, —◆—: solid state I/V curves, —○—, —◇—: polarization curves in a solution of pH 2·3.

effective area is reasonable bearing in mind that current is entirely controlled by tunnelling probability through the film, because the indium layer underneath the epoxy resin can act as an electron sink or source in that case.

When the open circuit potential of the electrode measured against the SCE was superimposed on the origin of the voltage scale of the I/V curves shown in Fig. 6, the I/V curves corresponding to the electrochemical measurements almost coincided with those obtained in the solid state, as shown in Fig. 8. The coincidence of both sets of I/V curves lends confidence to the choice of effective area for the electrochemical measurements. In this regard, it should be noted that current through the epoxy resin in a diode of Ta |epoxy layer| In could not be observed to a measureable extent.

Fig. 8 shows clearly that the electrode reaction was perfectly controlled by the electron conduction through the insulating layer. The cathodic polarization curves, corresponding to hydrogen evolution, deviated from the solid state I/V curves when the current became large. This suggests that the potential drop in the Helmholtz double layer cannot be negligible for these large currents.

The indium electrodes deposited on the oxide films of various thicknesses were dipped into deaerated buffer solutions, and the corrosion rates of indium determined. Before the experiments, the I/V curves in the solid state were obtained. Table 1 shows a comparison of the analytically determined corrosion rates with these expected on the basis of the I/V curves. The latter were determined by extrapolating the cathodic branches of the I/V curves to the open circuit potentials of the electrode. The corrosion rate of a fused mass of indium was also obtained and is shown in the table.

The results show that the actual corrosion rates were not influenced by the oxide film thickness, while the rates predicted by the I/V curves were distinctly dependent on film thickness. Also the current values estimated by the two methods differed by more than two orders of magnitude. However, the discrepancies can be explained on the basis of the insulating oxide layer which exists under the corroded metal and which restricts current flow. This situation is illustrated in Fig. 9.

Table 1. Corrosion rates of indium deposited on anodic oxide films on tantalum

Oxide film thickness (Å)	38	42	48	58	90	0 (In metal)
actual corrosion rate (μA cm^{-2})	38	43·7	45·1	47·4	67·1	9·7
rates by I/V curves (μA cm^{-2})	–*	–*	0·22	0·10	0·04	10·7

* Reliable I/V curves could not be obtained.

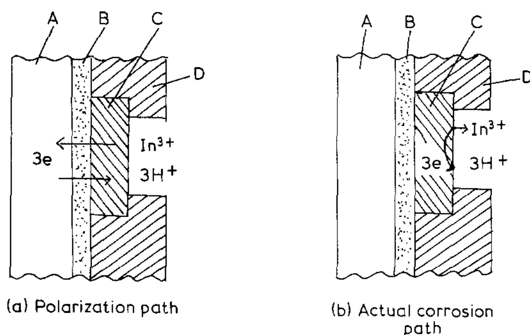


Fig. 9. Schematic illustration of charge transport in a polarization process (a) and in an actual corrosion process (b), A: tantalum substratum B: anodic oxide film, C: indium layer, D: epoxy resin.

Comparison of the actual corrosion rates of the deposited metal layer with that of the fused mass indicates that the roughness factor of the deposited layer was four times larger than that of indium mass.

3.4. *Redox reaction of a ferrocyanide/ferricyanide couple on a gold film on the oxide substrate.*

I/V curves of a ferrocyanide/ferrocyanide redox electrolyte in 1 M KCl were measured on the gold electrode of a Au |oxide| Ta diode. A typical result is shown in Fig. 10. Although the *I/V* curves for the solid state case and the electrochemical reaction do differ, this difference may be ascribed to experimental errors. The exchange current density of the couple on this electrode will be as low as $10^{-7}\,A\,cm^{-2}$ on the basis of Fig. 10, while

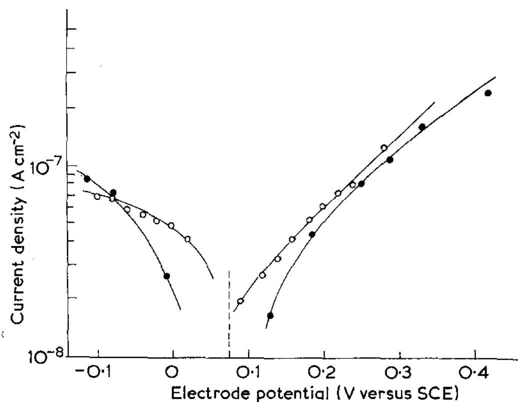
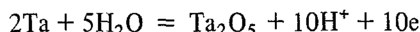


Fig. 10. *I/V* curves of an Au |oxide film| Ta diode in the solid state (—•—) and that of 5×10^{-3} M ferrocyanide/ferricyanide in 1 M KCl on the diode (—○—). Film thickness: 58 Å.

very high values were obtained on platinum and graphite electrodes free from intentionally prepared oxide films [30]. Therefore, the rate of the redox reaction was also probably entirely controlled by the transport of electrons through the film.

Theoretical analysis based on a rectangular barrier model shows that the conduction properties may be improved by two orders of magnitude by a small decrease of film thickness from 35 Å to 30 Å (see Fig. 7). The tunnelling probability in the case of anodic polarization is a function not only of the film thickness but also of mean potential barrier height at the insulator/deposited metal layer interface. Hence, the prediction based on Fig. 7 is probably only true in the qualitative sense. Nevertheless, it will be reasonable to expect that lowering the film thickness still further will improve conduction properties and that electrode reaction rates will increase on an electrode covered by a very thin film of the order of 10–20 Å thick.

The equilibrium potential of the formation of tantalum oxide,



$$2Ta + 5H_2O = Ta_2O_5 + 10H^+ + 10e$$

is $-0{\cdot}84$ V versus SHE in a solution of 0·5 vol % H_2SO_4 (pH = 1·51) [31]. If the film thickness-potential relationship shown in Equation 1 is applied to this potential by taking into account the potential of the mercurous sulphate electrode, a film thickness of 8 Å is obtained. This value indicates that the tantalum plate still had a very thin oxide film at the quoted equilibrium potential even after chemical polishing.

Therefore, it is probably not possible to prepare a film anodically which has a film thickness below 10 Å. Trials were made to prepare an electrode covered with a film of the order of 10–20 Å thick. However, the reproducibility of the solid state conduction properties was very poor. This result indicates that another kind of covering film will be needed to demonstrate the usefulness of an electrode covered with a thin insulating layer.

The gold film on the oxide film was used to prevent film growth by anodic polarization during the measurements of the redox reaction. A covering film such as a polymer, cannot grow with anodic polarization and in this case a metal film would not be needed.

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