# *The Static Electrode Potential Behavior of Tantalum and its Behavior on Anodic Polarisation*

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As is well known, tantalum shows remarkable resistivity towards chemical action and behaves frequently as a passive metal. A study of its static electrode potential behavior and of its anodic polarization would be of importance for obtaining insight into its mode of oxidation leading to the observed resistivity. For this purpose, the electrode potential of tantalum was measured in buffer solutions covering the pH range 1—12 and initially free from its ions. The repetitive oscillographic method was also applied to study its anodic behavior in various media.

## Experimental

The electrodes used in this investigation were pure tantalum wires each 1 cm. long and 1 mm. in diameter. The static electrode potential measurements were performed at 30°C in the Clark and Lub's-Ringer series of buffers covering the pH range 1—12. Before use the electrodes were polished with different grades of emery paper, thoroughly washed with redistilled water and finally rinsed with the solution to be used. Cells and devices were essentially the same as those used in previous papers[1]. A saturated calomel electrode was used as the reference half cell.

The anodic polarization experiments were carried out at 30°C by the repetitive oscillographic method, using the same circuit as that applied by us in a previous publication[2]. The trip voltage of the thyratron valve was always adjusted at 65 V. The electrolytes used were buffer solutions chosen in the acid, the neutral and the alkaline range, together with buffered potassium fluoride of concentrations ranging from $10^{-2}$ to 5 N. Polarization curves were also taken in several unbuffered electrolytes including hydrofluoric, hydrochloric, sulfuric and nitric acid and their neutral salts. All these electrolytes were prepared from the purest Analar products.

## Results and Discussion

**The Electrode Potential Behavior of Tantalum in Solutions Initially Free from its Ions.**—The electrode potential of tantalum in buffer solutions varies with time in such a way that the first steady state values are generally characterised in acid media by considerable drifts towards more negative overnight values. Alternatively, the potentials obtained in neutral and slightly alkaline media show pronounced drifts towards more positive values when the electrodes were left overnight in contact with the electrolytes.

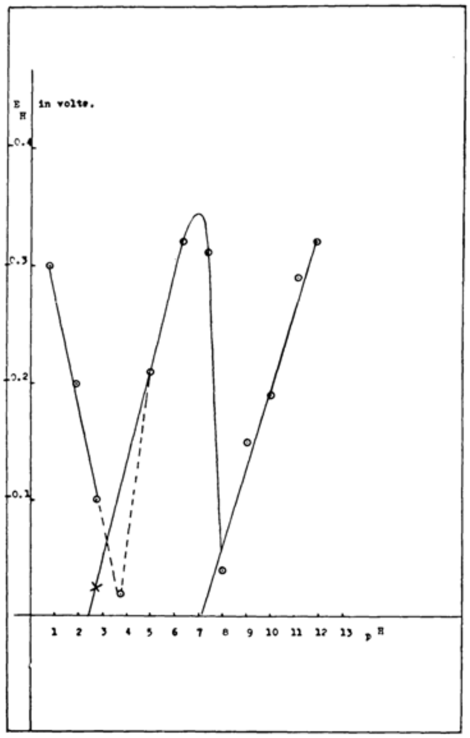

Fig. 1. (×: overnight value)

By plotting the first steady state potentials against pH, a "W"-shaped curve as shown in Fig. 1 is obtained. It consisits of a more or less linear but rather rapid fall of potential within the pH range 1 to 3. The curve then passes through a sharp peak whereupon the potential varies linearly up to pH 7, yielding a coefficient

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[1] A. Riad Tourky and S. E. S. El Wakkad, *J. Chem. Soc.*, **1948**, 740.

[2] W. Machu, E. M. Khairy and M. K. Hussein, *Corrosion*, U. S. A., **11**, 3751 (1955).

of 81 mV per unit pH. Another straight line can be traced along the pH range 8—12, the slope of which amounts to 66 mV per unit pH. By extrapolating the lines running across the pH ranges 3—7 and 8—12, $E'_0$ values are obtained amounting to +0.192 and +0.473 V, respectively.

In order to interpret the phenomena manifested by the tantalum electrode, the thermodynamic potentials of the systems $Ta/Ta_2O_5$ and $Ta/Ta_2O_5/TaO_2^+$ have been computed. According to the calculations reported by Latimer (3), the $E_0'$ value of the former system amounts to −0.8114 V. In order to evaluate the thermodynamic potential of the latter system, the following equilibrium reactions have been considered:

$$Ta_2O_5+H_2O \rightleftarrows 2\,TaO_2^+ + 2OH^- \qquad (1)$$

By applying the relation

$$\log K = -(2\mu^0_{TaO_2^+} + 2\mu^0_{OH^-} - \mu^0_{Ta_2O_5} - \mu^0_{H_2O})/1{,}363 \qquad (2)$$

and using Latimer values for $\mu^0$ potentials of $Ta_2O_5$, $OH^-$ and $H_2O$ which amount to −470.6, −37.596 and −56.690 kcal., respectively it follows that:

$$\mu^0_{TaO_2^+} = -226.050 - 0.682 \log K \qquad (3)$$

Using this value, the $E_0'$ value of the reaction:

$$Ta + 2H_2O = TaO_2^+ + 4H^+ + 5\,e^- \qquad (4)$$

amounts to:

$$E_0' = -0.9763 - 0.0059 \log K \qquad (5)$$

Assuming that the electrode potential of tantalum is determined by the activity of the tantalyl ion in solution, it follows that:

$$E_H = E_{0(Ta/TaO_2^+)} + \frac{RT}{F} \log a_{(TaO_2^+)} \qquad (6)$$

Substituting for $a_{(TaO_2^+)}$ from the relation:

$$a_{(TaO_2^+)} = \frac{K^{1/2}}{a_{(OH^-)}}$$

where $K$ denotes the equilibrium constant of reaction (1), equation (6) transforms into:

$$E_H = -0.9763 - 0.0059 \log K + \frac{RT}{F} \log \frac{K^{1/2}}{a_{OH^-}}$$

$$= -0.9763 + 0.0236 \log K - 0.059 \log \frac{K_w}{a_{H^+}}$$

$$= -0.1503 + 0.0236 \log K - \frac{RT}{F} pH \qquad (7)$$

or

$$E_H = E_0' - \frac{RT}{F} pH \qquad (8)$$

where

$$E_0' = -0.1503 + 0.0236 \log K \qquad (9)$$

The results obtained with the tantalum electrode in buffer solutions initially free from its ions may be explained in view of its decided tendency to acquire the passive state (4). This state is most probably attained when the electrode is covered with an inhibitive film of the pentoxide overlayered with adsorbed oxygen doublets (5). The presence of such a layer together with the passive nature of the surface oxide, accounts for the observed surplus in potential. In the light of the above discussion, one may interpret the $E_H$/pH plot as follows: from pH 1 to 3, the electrode which has been rendered passive by exposure to atmospheric oxygen is subjected to the dissolving action of the electrolyte. This type of attack which takes place through the pores of the pre-immersion film, proceeds with subsequent depolarisation of some of the oxygen doublets, an effect which becomes less pronounced with increase in pH. This makes up for the shift of potential towards more positive values within that range. The electrodic behavior may be conceived under such conditions as that of a metal/metal pentoxide electrode superimposed by varying contributions of overvoltage brought about by the adsorbed oxygen doublets. At pH 3 upwards, the attack is materially diminished and the passive state seems to predominate, the electrode behaving thus as a $Ta/Ta_2O_5/O_2^-$ at a more or less constant overvoltage effect. On comparing the $E_0'$ value obtained within the pH range 3—7 (0.192 V) with the thermodynamic potential of the $Ta/Ta_2O_5$ couple (−0.8114 V), it appears that the overvoltage contributed by the adsorbed gas layer and/or the polarisation brought about the passive nature of the surface film, amounts to as high a value as one volt.

Owing to the complexity of the quinquivalent tantalum ion, it is legitimate to assume that the metal as well as the oxide dissolve in alkaline media in the form of tantalyl ions ($TaO_2^+$), according to the reaction:

$$Ta + 2H_2O = TaO_2^+ + 4H^+ + 5\,e^- \qquad (i)$$

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3) W. M. Latimer, "Oxidation Potentials", 265 (1953).

4) R. Audubert and M. L. Roulleau, *J. Chim. Phys.*, **37**, 101 (1940).

5) G. Gesterheld, *Z. Electrochem.*, **11**, 47, 503 (1905).

and the equilibrium reaction:

$$Ta_2O_5 + H_2O \rightleftarrows 2\,TaO_2^+ + 2\,OH^- \qquad \text{(ii)}$$

Supposing that the behavior along the pH range 8—12 is given by the system Ta/$Ta_2O_5/TaO_2^+$ and assuming that the overvoltage contributed by the adsorbed doublets acquires but little variation with pH, the equilibrium constant $K$ of the reaction (ii) may be evaluated. Thus by substituting for $E_0'$ in equation (9) by the value computed from the slope of the respective straight line from which one volt (the difference between the experimental and the theoretical potential) is subtracted, it follows that:

$$0.473 - 1.0 = -0.150 + 0.024 \log K.$$

Therefore,

$$\log K = 15.7,$$

from which $K = 5 \times 10^{-16}$.

**The Anodic Behavior Investigated by the Repetitive Oscillographic Method.**—The study of the anodic behavior of tantalum by the aid of the cathode ray oscillograph reveals generally the presence of three domains. The first domain comprises two main stages, one of which occurs at a more or less constant negative potential corresponding to the desorption of hydrogen supposedly formed through the cathodic action of the repetitive current. The second stage in this domain consists of a gradual potential rise varying regularly with the applied quantity of electricity, a stage to be described to the building up of the double layer potential. The second domain in these curves includes the stages corresponding to the different states of oxidation of the metal, whereas the third domain covers the regions of attainment of passivity and gas evolution. The results of these polarisation experiments may be outlined as follows:

a) *Experiments in Buffer Solutions*:—The anodic behavior of tantalum was investigated in different buffer solutions within the pH range 1—14. The oscillograms obtained were essentially of the same general form, showing that the electrode maintains its passive nature all over the pH range. Figs. 2—5 contain representative curves taken, successively, in solutions of pH 1, 7, 12 and 14 at the polarising current densities 8.2, 6.2, 13.8 and 7 mA/cm². The appropriate amounts of electricity were supplied by means of a 0.2, 0.4, 1 and 1 μF/cm² condensers, respectively.

On comparing the first domains of these curves, it may be noted that the curve obtained at pH 14, in contradistinction from the other three curves, is characterised by a rather extended stage corresponding to the desorption of hydrogen. This may be explained by assuming that the natural oxide is partially attacked during the initial stages of the anodic process owing to the tendency of tantalum pentoxide to form tantalate in the strong alkaline media. The process takes place with the formation of hydrogen which is sorbed by the metal, together with the

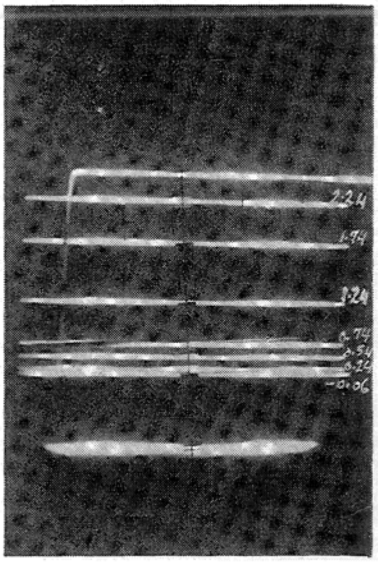

Fig. 2

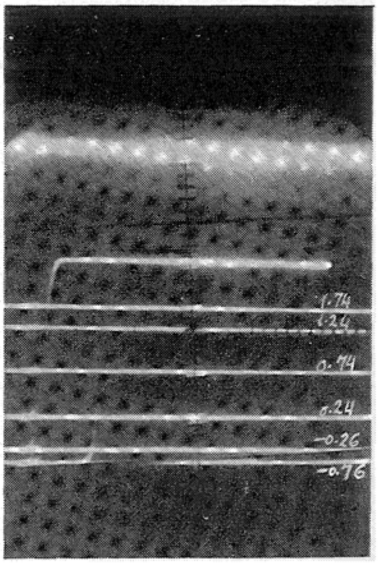

Fig. 3

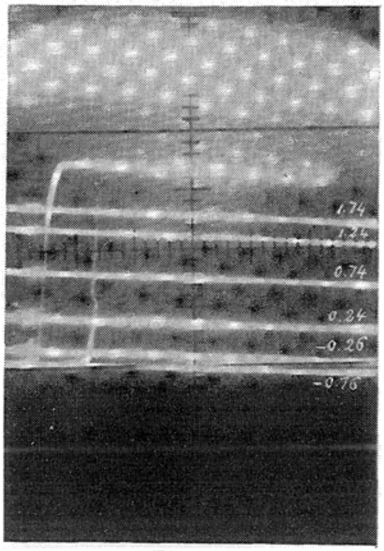

Fig. 4

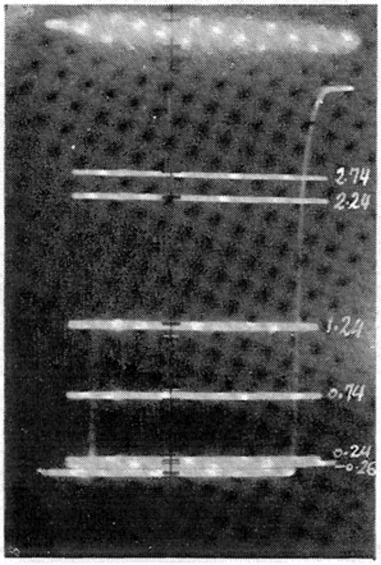

Fig. 5

gas evolved during the cathodic passage of the repetitive current. The removal of the sorbed gas consumes comparatively greater amounts of electricity.

After the process of desorption of hydrogen, the potential jumps abruptly towards appreciably more positive values, attaining a value ranging from 2.5 to 3.5V at which oxygen evolution takes place. This indicates that the electrode surface is passivated by the time the double layer has been fully charged. The capacity of the double layer may be calculated for each curve from the slope of the respective linear potential rise, the horizontal shift of the cathode ray track being proportional to the quantity of electricity and the vertical shift to the acquired potential. The total amount of electricity used up in the overall process is equal to the product of the trip voltage of the thyratron valve (65 V) and the capacity of the applied condenser. The values thus obtained are almost the same averaging around 1 $\mu$F/cm$^2$ of the apparent surface area. The ease with which oxygen is evolved together with the exceedingly low double layer capacities substantiates the passive nature of the electrode surface. This behavior corroborates the results of the static potential measurements regarding the persistence of a naturally present protective oxide film on the electrode surface.

b) *Experiments in Solutions Containing Fluoride Ions*:—Anodic polarization experiments have been carried out in potassium fluoride solutions buffered within the pH range 2—12 with the object of investigating the corroding effect of the fluoride ion when present at lower and higher concentrations ($10^{-2}$—5 M). The oscillograms thus obtained are essentially of the same shape inasmuch as pronounced passivity is achieved in both dilute and concentrated solutions. A representative curve is shown in Fig. 6. It contains two curves "A" and "B" being taken in $10^{-2}$ and 5 M potassium fluoride solutions buffered at pH 7, both at a current density of 9.2 mA/cm$^2$ together with a 0.3 $\mu$F condenser. The potential jumps abruptly after the double layer has been fully charged and oxygen is readily evolved at 3.5 V, consuming the

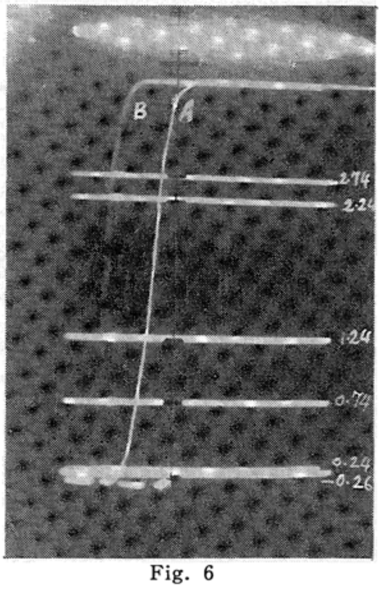

Fig. 6

most part of the applied quantity of electricity. This shows that the fluoride ion introduces no appreciable effect on the attainment of anodic passivity even at the higher concentration. Therefore, it appears legitimate to extend the study to a still higher fluoride ion concentration. For this purpose the electrode was anodically polarized in 10 N hydrofluoric acid, whereupon two oscillograms "C" and "D" were obtained (Fig. 7), taken at 10.5 and 9.4mA/cm$^2$ together with a 0.3, respectively a 1 $\mu$F condenser. Consideration of these curves reveals that when the applied quantity of electricity is relatively small (curve C), the electrode acquires a rather active potential of ~0.2 V after the double layer has been built up, indicating that the corroding effect exerted by the fluoride ion hampers the achievement of passivity. The capacity of the double layer amounts to 30 $\mu$F/cm$^2$ as compared with 1 $\mu$F/cm$^2$ in buffered potassium fluoride solutions, revealing the relative activity of the surface. The electrode behavior may be conceived under such conditions as to be governed by a tantalum/tantalum pentoxide system subject to some overvoltage effect, a picture which conforms to the static electrode potential behavior. Alternatively, prominent passivity is readily achieved on passing higher quantities of electricity. The capacity of the double layer amounts to a value of 3 $\mu$F/cm$^2$ and oxygen is evolved at 3.5 V.

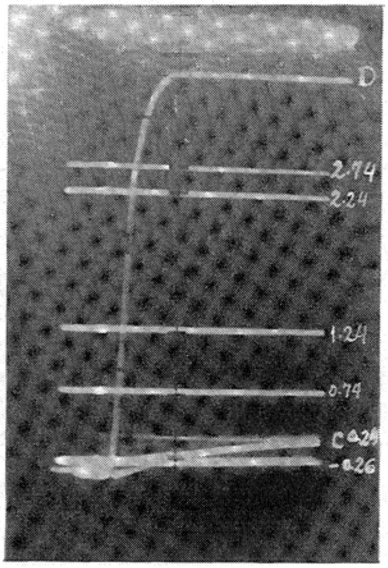

Fig. 7

c) *Experiments in Chloride, Sulfate and Nitrate Media*:—The oscillograms shown in Figs. 8 and 9 were taken in 6 N hydrochloric acid and 1 N sodium chloride solutions. The applied quantities of electricity were 9.7 and 6.5 mA/cm$^2$, using a 0.3 and 1 $\mu$F condenser, respectively. These curves show also that the electrode surface acquires the passive state simultaneously as the double layer has been fully charged, oxygen being evolved at ~4 V. The double layer capacity amounts to 1.5 and 1.1 $\mu$F/cm$^2$ for the acid and the neutral solutions, respectively.

The electrode shows a remarkably

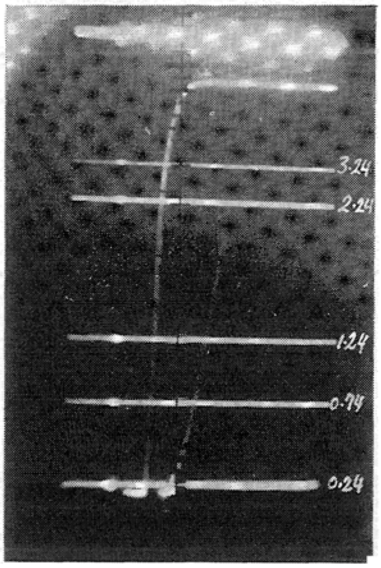

Fig. 8

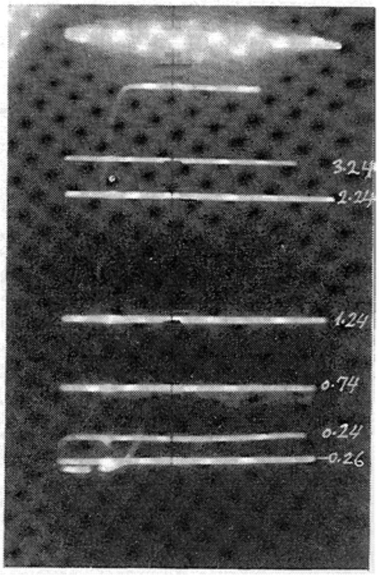

Fig. 9

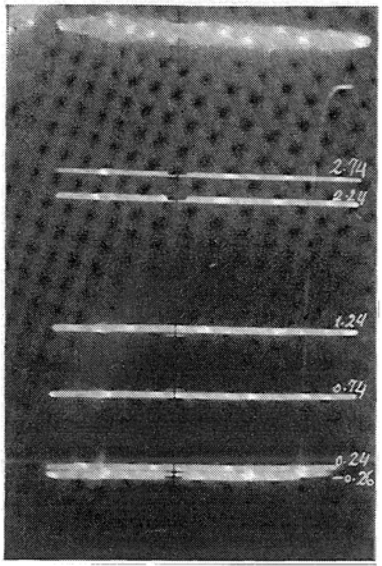

Fig. 10

similar behavior in 1 N sulfuric and nitric acid solutions. A representative curve is shown in Fig. 10 which was taken in 1 N sulfuric acid at 4 mA/cm$^2$ together with a 0.5 $\mu$F condenser. It is apparent that although passivity is rapidly attained, as was the case in chloride media, yet the first domain in this representative curve manifests a rather extended stage which corresponds to the desorption of hydrogen. This indicates that the activation encountered by the repetitive nature of the current is much more effective in sulfuric and nitric rather than in hydrochloric acid. It has to be inferred, however, that on carrying out experiments in sodium sulfate and sodium nitrate solutions, the curves obtained are essentially the same as those given in the sodium chloride solutions (Fig. 9), owing to the diminished dissolving action of these neutral electrolytes.

## Summary

The electrode potential behavior of tantalum is investigated in buffer solutions initially free from the metal ions covering the pH range 1—12. A "W"-shaped $E_H$/pH plot is obtained and the results reveal the existence of a natural passive pentoxide film overlayered with oxygen doublets. The electrode behaves within the pH range 3—7 as a metal-metal oxide electrode subject to an overvoltage of about one volt. From pH 7 to 12 the behavior is given by the system: Ta/$TaO_2^+$ yielding an equilibrium constant $K=5.10^{-16}$.

Anodic polarization experiments by the repetitive oscillographic method have been also utilised in buffer solutions and in other different media. The oscillograms are mostly characterised by sharp potential jumps associating the charging of the double layer, showing the decided resistivity of the surface film. The capacity of the double layer scarcely exceeds 1 $\mu$F/cm$^2$, except in hydrofluoric acid solutions where it attains a maximum value of 30 $\mu$F/cm$^2$.

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