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The differential capacitance of solid tantalum in some aqueous solutions

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The differential capacitance of tantalum has been measured in a number of aqueous electrolyte solutions. The metal is generally covered with an oxide layer in solutions of simple inorganic anions and the electrode capacitance is $\sim 5\text{–}10\,\mu F\,cm^{-2}$. In solutions of oxalate anions the electrode capacitance is much higher and corresponds to that expected for a clean metal in contact with an aqueous solution.

1.Introduction

Tantalum is an important metal in the electrical components industry because of the oxide film, Ta_2O_5, which may be developed in a similar way to the oxide on aluminium. Tantalum in contact with aqueous solutions is often considered to be covered with an oxide film, and it has been suggested [1] that the measurement of the double-layer capacity of a clean electrode surface is not possible. Brodd and Hackerman [2] and also McMullen and Hackerman [3] reported a low value of capacity $\sim 9\,\mu F\,cm^{-2}$ for tantalum in 0·5 M Na_2SO_4 solution. Similarly Isaacs and Leach [4] found the capacity of a tantalum electrode in various carbonate solutions was $\sim 15\,\mu F\,cm^{-2}$.

It is well established that the reversible potential for the reaction

$$Ta_2O_5 + 10H^+ + 10e \rightleftharpoons 2\,Ta + 5H_2O \qquad (1)$$

is inaccessible directly on account of the protective power of the oxide layer which screens the metal from the aqueous solution [5].

However, an examination of the pH–potential diagram for thermodynamic stability indicates that a small region of theoretical stability should exist between the metal and simple uncomplexing ions. The region would be expected to extend in the presence of complexing anions. The relevant data on tantalum complexes given by Charlot [6] indicates that the most effective complexing ion should be the oxalate.

In order to develop the electrochemistry of tantalum in aqueous solutions and to define the conditions under which the kinetics of the aqueous electrochemistry of tantalum may be studied it was decided to search for conditions under which the tantalum electrode is exposed in aqueous solution uncomplicated by oxide films.

The most readily accessible interphase property which may be used for this investigation is the differential capacitance.

2. Experimental

Tantalum (99·99%, Metals Research Ltd) was sheathed in polyethylene to form a working electrode (radius 0·44 cm). The electrolytic cell, polarization circuit, impedance bridges with which either phase or resultant null detection was available, have been described previously [7, 8]. In addition an automatic polarization apparatus was available to provide data from accurately timed measurements [9]. All chemicals were A.R. quality and the water was tridistilled from deionized stock. Before any measurements were made all electrolyte solutions were purified for 72 hours by continuous treatment with specially purified charcoal [7]. All experiments were made under one atmosphere of purified white spot nitrogen.

The electrodes were pre-treated by mechanical polishing, etching in mixed acid [1:5 = $HClO_4$ (specific gravity 1·6): CH_3COOH], then washed to remove etchant before immersion in the electrolyte solutions at − 1·0 V (versus SCE)* to avoid electrochemical film formation.

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* All potentials in this paper are versus SCE.

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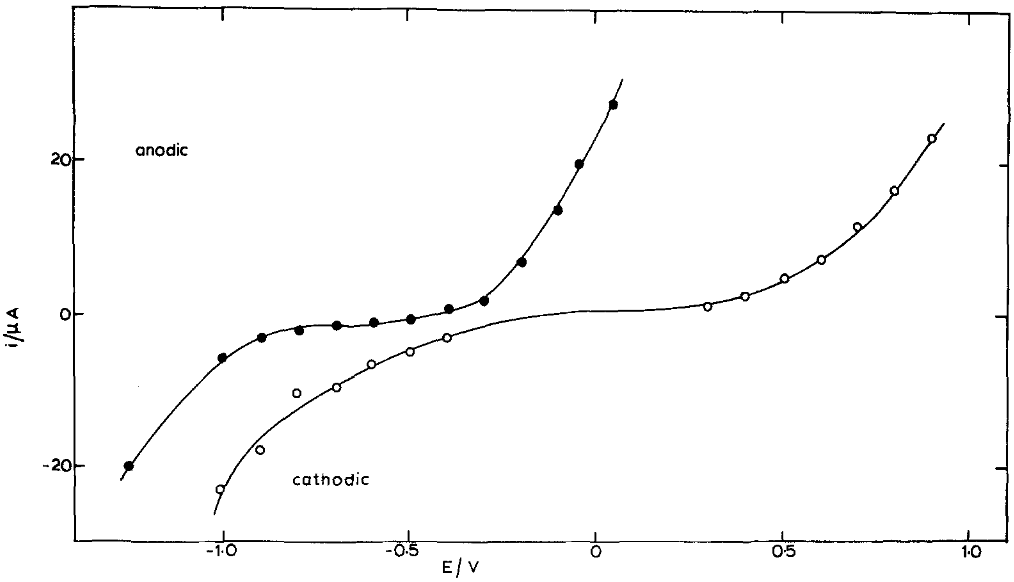

Fig. 1. Faradaic current–potential curve for polycrystalline Ta. Electrode area 0·0152 cm². ○ 1 M KCl; ● 0·5 M oxalic acid. Temperature 23° C.

3. Results and discussion

3.1. *Solutions of simple inorganic ions* (ClO_4^-, SO_4^{2-}, Cl^-)

Fig. 1 shows a polarization curve typical for this group of ions in the concentration range investigated. Between ± 1·0 V (versus SCE) there exists a well-defined polarizable region. At the extremities of this region the current flow and the gas evolution interfere with the measurement of the electrode capacitance. Fig. 2 shows electrode capacitance curves typical of three representative systems. The remarkable feature is the low values

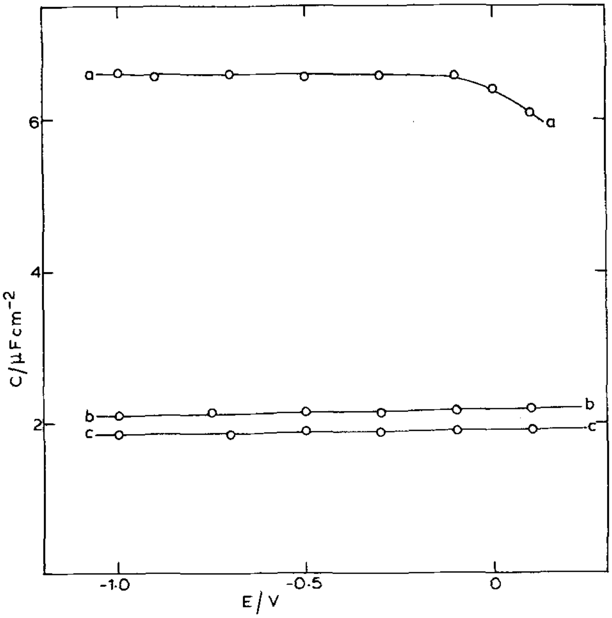

Fig. 2. Electrode capacitance of Ta. (a) 1 M KCl; (b) 0·1 M KCl; (c) 0·01 M KCl. Temperature 23° C.

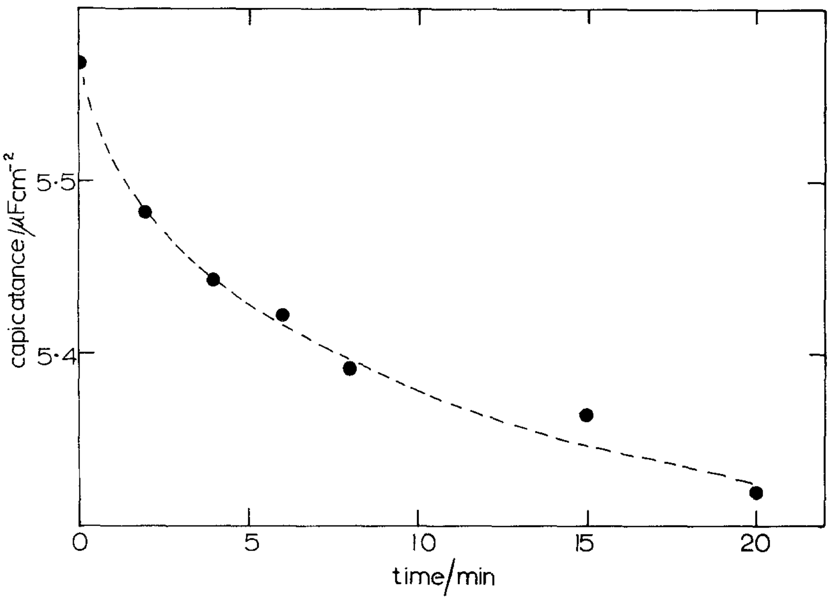

Fig. 3. The decay of electrode capacitance of Ta with time. 1 M KCl, 23° C.

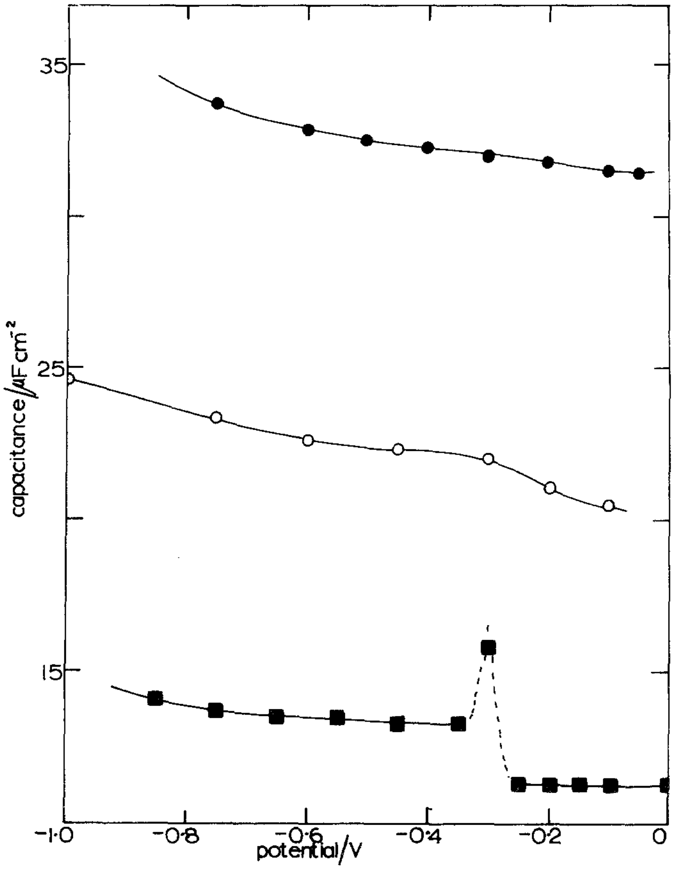

Fig. 4. Electrode capacitance of Ta in oxalic acid solutions. ● 0·5 M; ○ 0·03 M; ■ 0·01 M. Temperature 23° C.

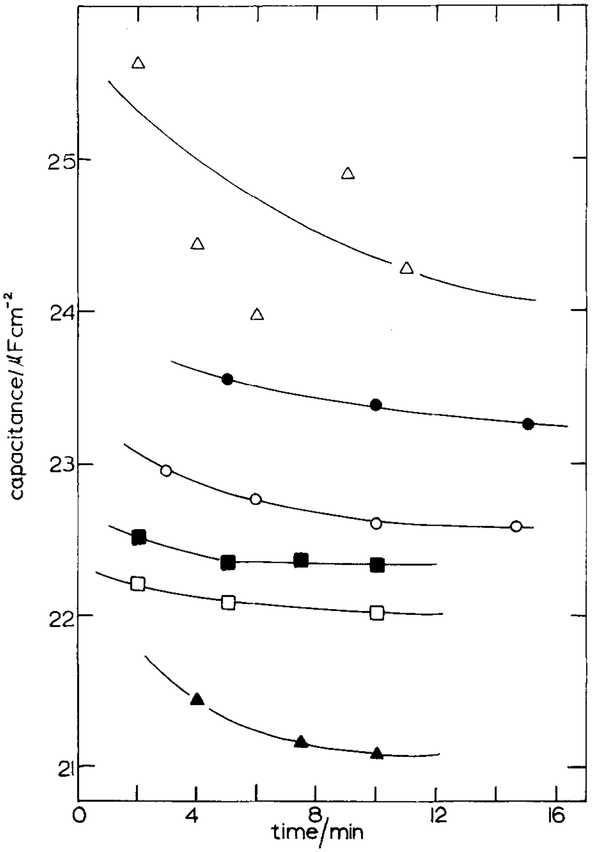

Fig. 5. The decay of electrode capacitance of Ta with time. 0·03 M oxalic acid. △ — 1·0 V; ■ — 0·4 V; ● — 0·8 V; □ — 0·2 V; ○ — 0·6 V; ▲ 0·0 V. Temperature 23° C.

of the electrode capacitances which lie in the range below $9\ \mu F\ cm^{-2}$. As the electrode is driven more positive the capacitance remains relatively constant. However from ~ — 0·1 V the capacitance falls markedly. This fall is interpreted in terms of film thickening at the more positive potentials.

It must be emphasized that there is a considerable time dependence of the capacitance. An experimental decay (Fig. 3) indicates a first-order thickening of the oxide layer presumably by a high field ion conduction process. The thicker the film the lower the capacitance in accord with the flat capacitor formula.

Attempts to force the oxide layer from the electrode by lowering pH were ineffective. Therefore it must be concluded that the Ta_2O_5 film on tantalum is extremely stable.

We are forced to conclude, as did earlier workers [2–4], that with these systems, at all potentials in the experimentally polarizable region the surface of the electrode is covered with an oxide layer.

3.2. *Solutions of oxalate ion*

Fig. 1 also shows the polarization curve for tantalum in 0·5 M oxalic acid. The polarizable region of — 1·3 to 0·2 V is considerably shifted from that observed with the solutions of non-complexing inorganic ions and the shift is in keeping with the exposure of the true metal–aqueous solution interphase inside this region. Fig. 4 shows the corresponding differential capacitance curve together with others for more dilute solutions. It is immediately clear that the magnitude of the capacitance is considerably increased. The value of ~ $30\ \mu F\ cm^{-2}$ in the region — 1·0 V to — 0·3 V indicates that here the true metal surface is accessible for study.

The possibility of the formation of oxides of oxidation states lower that 5 can be eliminated as this would give rise to capacitances much lower than 20–30 $\mu F\ cm^{-2}$. The formation of an adsorbed layer of hydrogen can also be ruled out

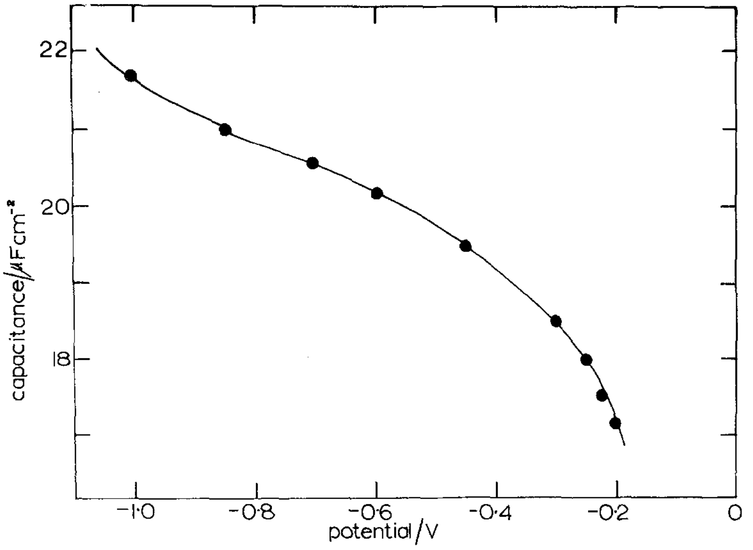

Fig. 6. Electrode capacitance of Ta in 0·5 M potassium oxalate at 23° C.

since this would produce pseudocapacitance peaks of very large magnitude.

At potentials more positive than — 0·3 V the capacitance falls and we can infer that — 0·3 V is the potential limit at which the film is forced off the surface. At very negative potentials the pseudocapacitance due to the HER (hydrogen evolution reaction) obscures the retrieval of the double-layer capacitance. An interesting point concerning the oxalate solutions is seen when the time dependences (Fig. 5) at a range of potentials are compared with those of Fig. 3. The oxalate values became consistent relatively quickly, in keeping with an equilibrium process between metal and solution followed by a prolonged equilibrium. At the most negative potential (— 1·0 V) the erratic changes in capacitance are due to the HER. At the most positive potential (— 0·0 V) the capacitance is low and falls exponentially indicating the development of an oxide layer.

Fig. 6 shows similar data for neutral oxalate solutions. The capacitance measurements again reveal that the metal–aqueous solution interphase is exposed. The resistance of the capacitance magnitude to pH change justifies our choice of oxalate as an effective complexant.

The shape of the differential capacitance curves did not change with concentration. We might have expected to identify the potential of zero charge (p.z.c.) as the potential of the diffuse layer capacitance minimum. This is clearly not possible and indicates that the p.z.c. is not contained in the experimental range: a likely value of the p.z.c. from work function data would place it in the range where the metal is covered with an oxide layer.

4. Conclusion

The true aqueous solution–metal interface is exposed in oxalate solution. It would be expected that oxalate ions would form the ideal solution for the deposition of tantalum (provided that other effects do not interfere). This topic continues to be intensively investigated.

Acknowledgement

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