

Some Aspects of Electrocatalysis

A STUDY OF TITANIUM AND TANTALUM WHEN ALLOYED WITH THE PLATINUM GROUP METALS

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To increase our understanding of the electrochemical processes involved during cardiac stimulation by implanted pacemakers, alloys were prepared containing electrocatalytically active platinum group metals and either titanium or tantalum which irreversibly form very inactive oxides. Our work has shown that alloys with as little as 5 per cent platinum group metals exhibit electrochemical characteristics which are more similar to the platinum group metals than to the valve metals. Under some of the conditions certain of these alloys appear to be better electrocatalysts than the platinum group metals. Alloying titanium and tantalum with small amounts of platinum group metals also appears to prevent anodic dissolution of oxide-free titanium and tantalum.

We define electrocatalysis as the variation of rate of an electrochemical reaction with change in electrode material. An electrocatalyst is thus a heterogeneous catalyst at which charge transfer occurs. In our on-going research programme to understand more fully the electrochemical processes in cardiac stimulation by pacemakers, work with more than thirty metals and alloys considered as possible electrode materials has been undertaken. These studies lead quite naturally to comparisons and correlations of electrocatalytic activity. A significant problem in making correlations with different metals is that even if the overall reaction remains the same, the mechanism is often different on different materials. In one attempt to avoid this difficulty we prepared a series of alloys of titanium and platinum for study. Titanium readily and irreversibly forms an oxide which protects the metal from dissolution, but which also makes it catalytically inactive, at least for the electrochemical processes in which we were interested. Platinum is probably the best electrocatalyst of all metals. In addition to the titanium-platinum series, alloys of titanium and tantalum with iridium and ruthenium were prepared; compositions are given in Table I.

After the studies were carried out, a semi-quantitative analysis of the surface structures of the alloys was made with a Kevex X-ray unit of a Scanning Electron Microscope. Comparisons of the platinum-peak heights indicated the same composition for the exposed surfaces, the surfaces not exposed to solution, and the interiors of the alloys examined after fracturing. Comparison of a tantalum-iridium surface, which had undergone severe electrochemical dissolution, with an unexposed sample indicated that both had the same surface composition. We concluded that the surface compositions of the alloys were essentially the same as those of the bulk compositions.

Experimental Conditions

Wire and rod electrodes were sealed in silicone rubber tubing or teflon tubing, respectively, and all had an exposed geometric area of 0.16 cm^2 . They were mechanically cleaned with silicon carbide cloth, degreased with acetone and rinsed with triple distilled water. Materials which formed an oxygen (or oxide) layer that could not be electrochemically reduced, for example, were mechanically cleaned before every anodic measurement. The alloys

were in the form of rods with a diameter of about 7 mm and their surface areas were fixed using molten polyethylene. Typically a 25 cm² platinum gauze electrode was used as a counter electrode and a Ag/AgCl or a Leeds and Northrop miniature glass electrode was used as a reference, each being calibrated versus a reversible hydrogen electrode (R.H.E.) in the same solution. Details will appear elsewhere (1).

Electrochemical Characterisation Using Cyclic Voltammetry

A qualitative comparison of electrocatalytic activity is readily made from cyclic voltammetry curves, as shown in Figure 1 for results in 1 M sulphuric acid at 25°C and in Figures 2 and 3 for physiological saline solution (0.15 M NaCl) at 37°C.

A number of generalisations can be made from these studies:

1. The cyclic voltammetry features of platinum change significantly in going from sulphuric acid to sodium chloride solution, but this is not the case for the alloys.

2. The peaks for H-adsorption and H-oxidation which are pronounced on platinum in sulphuric acid and absent on titanium, are present on the alloys but not as pronounced. Suitable variation of sweep speed, ν , and limits makes these peaks somewhat more evident. Potentials for these peaks are given in Table II. The positions for the two peaks are essentially the same for titanium-20 per cent platinum, titanium-30 per cent platinum and for platinum.

3. Figures 1(b) and 2(b) for oxide-free titanium show a characteristic anodic dissolution peak on the first anodic sweep followed

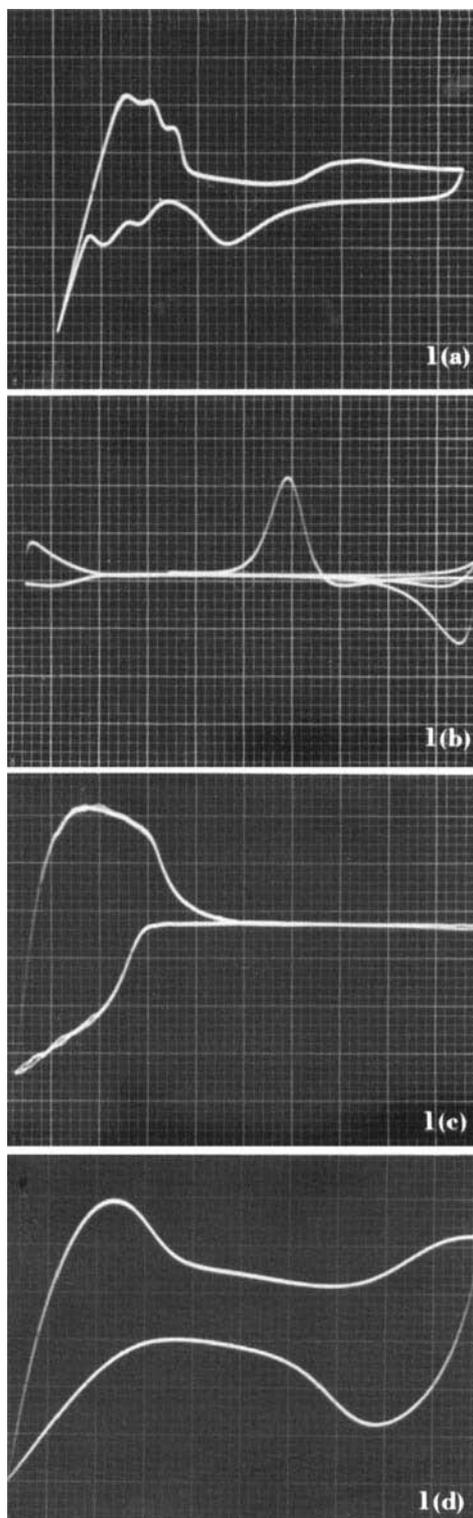


Fig. 1 Cyclic voltammograms in helium-saturated 1M sulphuric acid at 25°C

- (a) platinum wire, $\nu = 5\text{V/s}$, -0.2 to 1.6V
- (b) oxide-free titanium wire, $\nu = 1\text{V/s}$, -0.5 to 1.6V
- (c) titanium-5% platinum, $\nu = 1\text{V/s}$, -0.6 to 1.2V
- (d) titanium-20% iridium, $\nu = 10\text{V/s}$, -0.6 to 1.2V

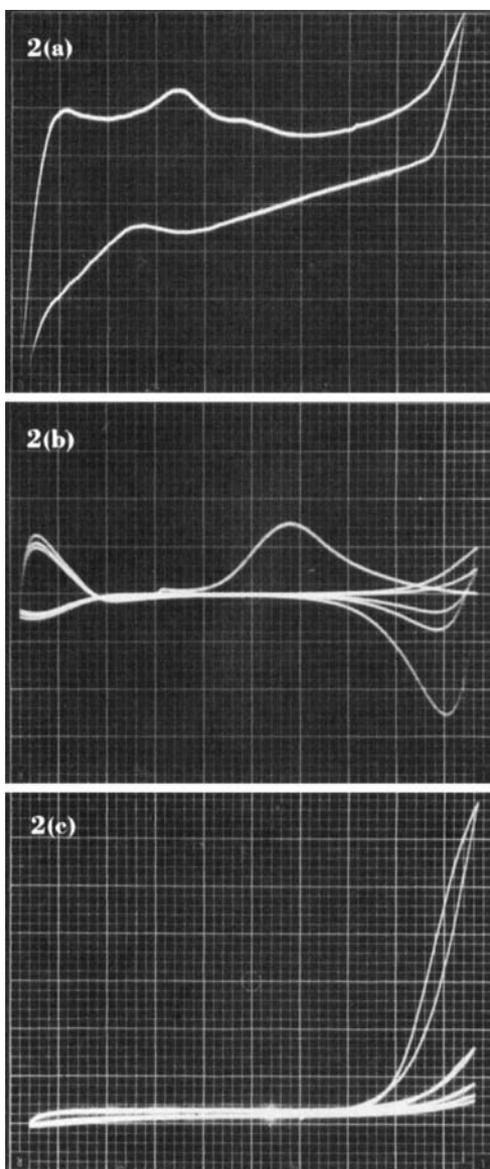


Fig. 2 Cyclic voltammetry curves in helium-saturated physiological saline solution at 37°C
 (a) platinum wire, $\nu = 5\text{V/s}$, -0.5 to 1.5V
 (b) oxide-free titanium wire, $\nu = 1\text{V/s}$, -0.5 to 1.7V
 (c) titanium wire, $\nu = 5\text{V/s}$, -0.5 to 1.5V , detail of 2nd to 5th sweep cycles

alloys when tested in aqueous solutions.

4. Details of the irreversible formation of oxide on titanium are seen in Figure 2(c). The first cycle into the anodic region shows significant change due to oxide formation. Successive cycles show little or no additional oxide formed when the sweep is limited to the same potential limit. When the anodic potential limit is increased by several hundred millivolts, significant change is again seen on the first cycle in the higher potential region. Tantalum behaves in an identical way.

5. The oxides formed anodically on the titanium and tantalum alloys appear to be cathodically reduced, exhibiting behaviour similar to that of the platinum group metals and significantly different from either titanium or tantalum metal.

6. Comparison of the titanium-platinum alloys in Figure 3 suggests the same electrochemical processes occur at each electrode, with a greater degree of reaction and hence greater electrocatalytic activity as the amount of platinum in the alloy increases.

7. The titanium-iridium alloy exhibits a significantly greater electrocatalytic activity in the oxygen region than any of the other alloys; compare, for example, Figures 1(b) and 1(c) with 1(d).

8. Titanium alloys appear to be better electrocatalysts than tantalum alloys. From steady-state measurements it was found that a tantalum-iridium alloy undergoes dissolution at potentials anodic to 1.1V (versus R.H.E.).

Galvanostatic Transient Studies in Physiological Solution

Much of our research programme has involved detailed analyses of some 30 metals and alloys using constant current pulses similar to

by a cathodic peak as the sweep is reversed. This was characteristic of oxide-free titanium and tantalum electrodes. The peak is not present after the first cycle into the anodic region, presumably prevented by oxide formation. None of the alloys, including titanium-5 per cent platinum, exhibits this anodic dissolution peak. Further, no anodic dissolution was observed for any of these platinum-titanium

Table I Alloy Compositions		
Electrode material	Source	Actual composition
Pt	Johnson Matthey	0.03% maximum impurity
Ti	Alfa-Ventron	0.04% maximum impurity
Ta	Alfa-Ventron	0.003% maximum impurity
Ti-5% Pt	Materials Research	5.24% Pt
Ti-10% Pt	Materials Research	9.74% Pt
Ti-20% Pt	Materials Research	20.20% Pt
Ti-30% Pt	Materials Research	29.83% Pt
Ti-20% Ir	Materials Research	19.66% Ir
Ti-20% Ru	Materials Research	20.19% Ru
Ti-20% Pt	Materials Research	19.49% Pt
Ta-20% Ir	Materials Research	19.26% Ir
Ta-20% Ru	Materials Research	20.39% Ru

Table II Potentials of Adsorbed Hydrogen Peaks (vs. R.H.E.) in 1 M H ₂ SO ₄		
Electrode material	H ₁ (adsorption), volts	H ₂ (oxidation), volts
Pt	0.22	0.10
Ti-30% Pt	0.24	0.11
Ti-20% Pt	0.24	0.10
Ti-10% Pt	0.15	0.05
Ti-5% Pt	-0.02	-0.16
Ti	-	-
Ta	-	-0.62
Ta-20% Pt	0.23	0.12
Ta-20% Ir	0.19	0.09
Ta-20% Ru	0.15	0.04

Titanium-iridium and titanium-ruthenium had no observable peaks
H_{ads} peaks are more pronounced as the per cent of platinum in the alloy increases

Table III Electrochemical Parameters for Alloys			
Electrode material	Double layer capacitance, C, μ F/cm	V _{o.c.} (vs. R.H.E.)	b _a (2.3 RT/F) b _c
Pt	20	0.82	2 2/3
Ti	10	0.08	2 2
Ta	12.5	-0.16	2 2
Ti-5% Pt	10	0.17	2 2
Ti-10% Pt	12	0.81	2 2
Ti-20% Pt	19	1.11	2 2
Ti-30% Pt	18	0.92	2 2
Ti-20% Ir	41	0.84	1 1
Ti-20% Ru	22	0.89	2 2
Ta-20% Pt	16	0.70	2 2
Ta-20% Ir	10	0.90	2 2
Ta-20% Ru	9.5	0.73	2 2

V_{o.c.} is the open circuit potential versus the reversible hydrogen electrode established both before and after pulsing in physiological saline solution at 37°C; b_a and b_c are anodic and cathodic Tafel slopes

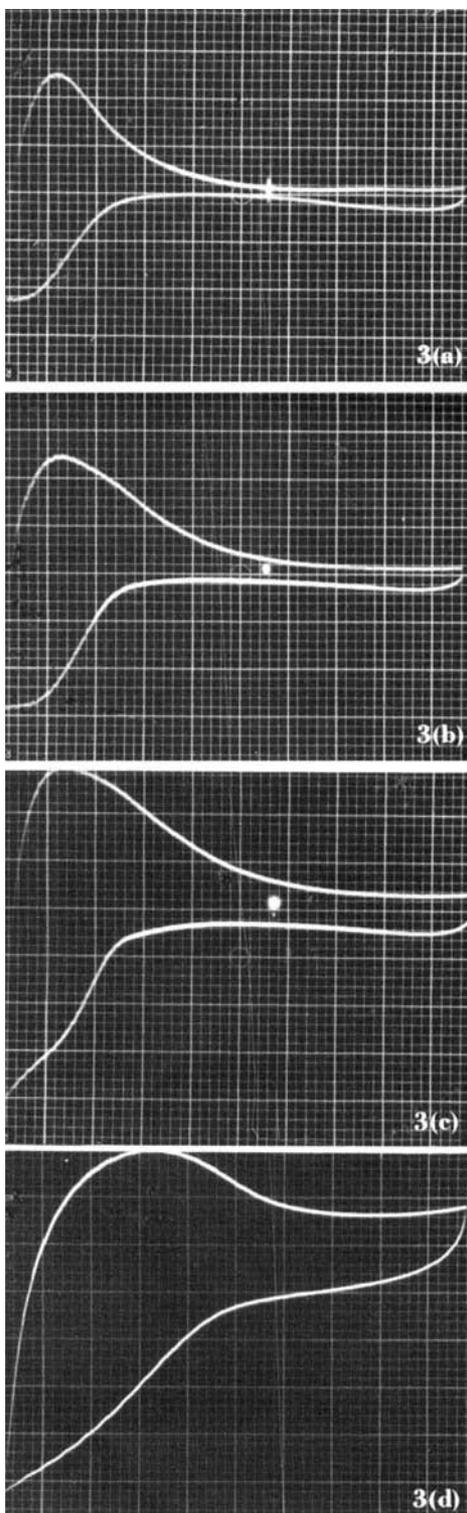


Fig. 3 Cyclic voltammetry curves in helium-saturated physiological saline solution, 37°C, $\nu = 5 \text{ V/s}$, -0.5 to 1.4 V , $i = 1 \text{ mA/cm}$

- (a) titanium-5% platinum
- (b) titanium-10% platinum
- (c) titanium-20% platinum
- (d) titanium-30% platinum

those employed by heart pacemakers. A summary of these results from the perspective of electrocatalysis has been presented elsewhere (1). Typical results for the titanium-platinum alloys in physiological saline solution at 37°C are seen in Figures 4 and 5 for cathodic and anodic pulsing, respectively. (Note that the cathodic pulses have been inverted.) The double layer capacitance was determined for the alloys from the initial slopes of the charging curves, and the values are given in Table III. One unexplained value is the relatively high double layer capacitance for the titanium-iridium alloy.

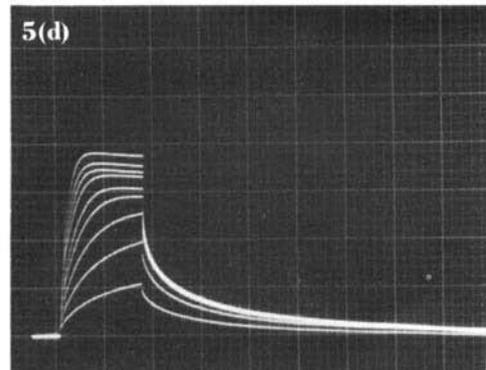
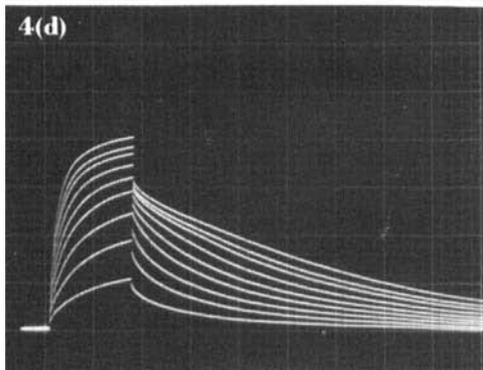
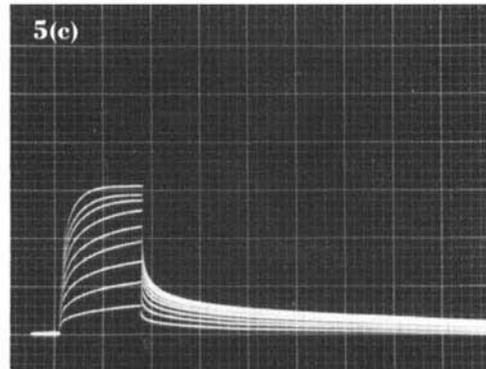
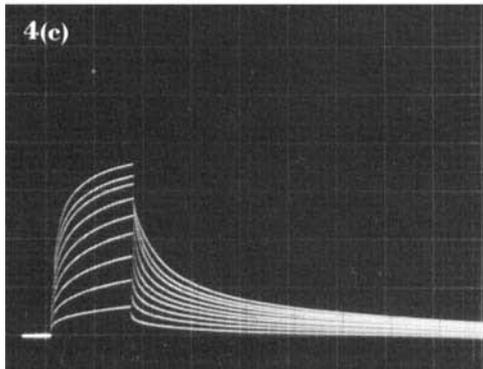
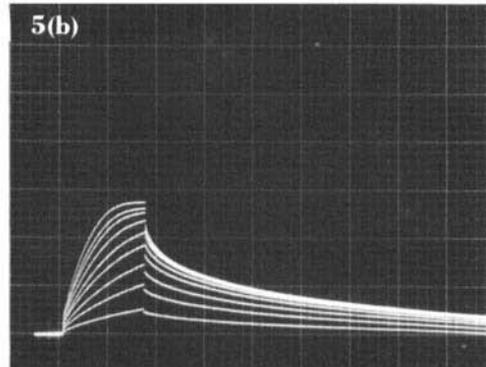
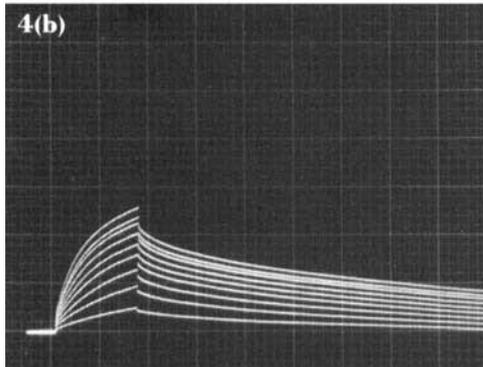
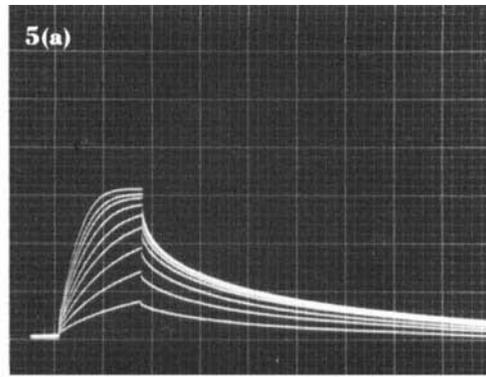
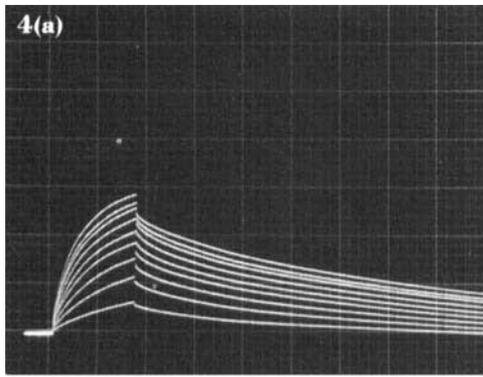
The double layer contribution to the polarisation of the charging curves was subtracted, assuming a constant average value of the double layer capacitance over the potential regions analysed, and Tafel curves were generated from the charging curves. Reasonably good Tafel slope data were obtained and the values are reported in Table III. Identical values of Tafel slopes for the titanium-platinum alloys tend to suggest that the mechanisms for the electrochemical processes are the same and that electrocatalytic comparisons are meaningful.

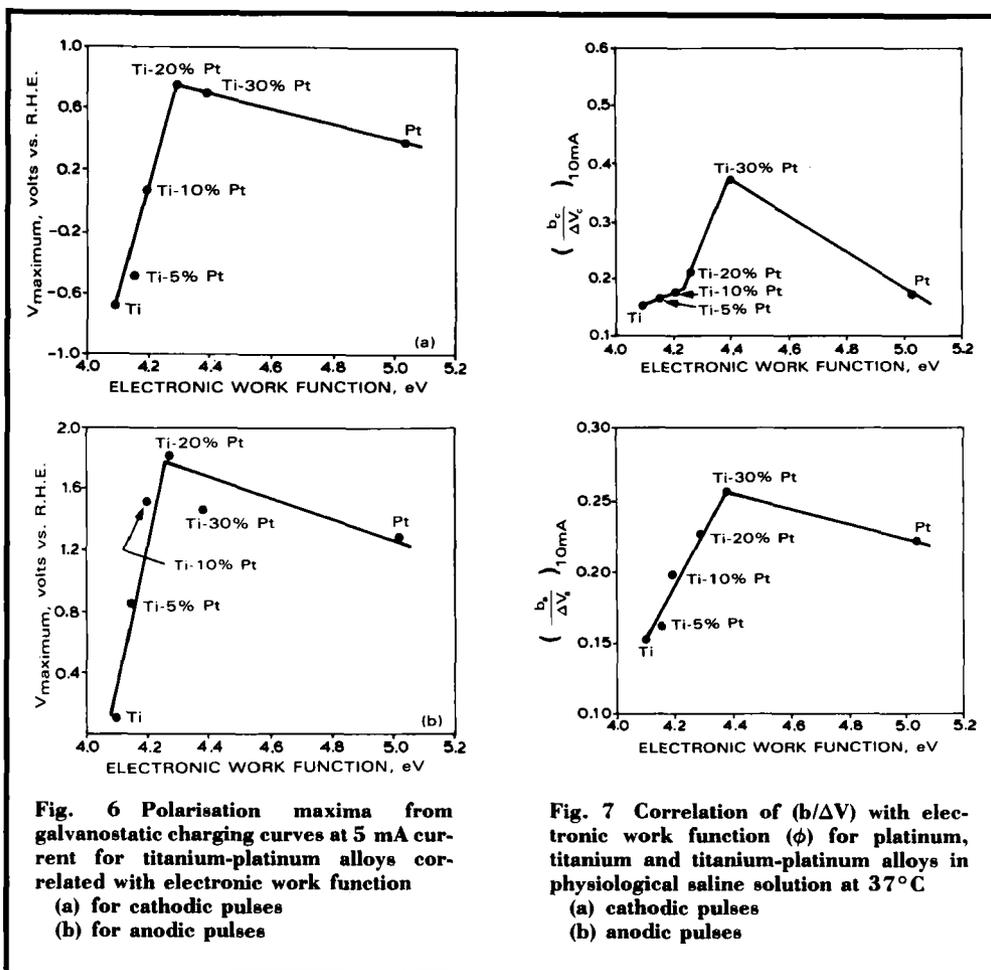
A simple approach to electrocatalysis is to compare the maximum polarisation of the

Fig. 4 (Right) Cathodic galvanostatic charging curves (1 to 9 mA pulses in 1 mA increments) in helium-saturated physiological saline solution, 37°C, 0.16 cm^2 electrode areas. Voltage scale (vertical) is 0.5 V/cm , time scale (horizontal) is 1 ms/cm . The pulses have been inverted

- (a) titanium-5% platinum
- (b) titanium-10% platinum
- (c) titanium-20% platinum
- (d) titanium-30% platinum

Fig. 5 (Far right) Anodic galvanostatic charging curves, all other conditions identical to Figure 4





electrodes at a given current density and pulse length. Figure 6 correlates the maximum values for polarisation of the titanium-platinum alloys, at a current of 5 mA (current density of 31 mA/cm²) with electronic work functions, ϕ , calculated assuming a linear relationship between work function and the composition of the alloy. A definite volcano-type relationship is evident for both cathodic and anodic processes. The open circuit potentials, except for titanium and tantalum which are indicative of dissolution, are typical of potentials established on platinum group metals in solutions with very low oxygen concentrations, and hence electrodes free of oxide on the surface. The cathodic process is reduction of water to form

adsorbed hydrogen atoms with eventual hydrogen evolution at higher currents or longer times of polarisation. The anodic process is oxidation of adsorbed chloride ions to chlorine atoms with eventual chlorine evolution.

An alternative approach is to make correlations of electrocatalytic activity with $\log i$, where i is the current density. From the Tafel equation, taking a potential difference V in place of the overpotential η (which is not precisely defined here), $b/\Delta V$ (where b is the Tafel slope) is proportional to $\log i$. The correlation of $b/\Delta V$ with electronic work function is made in Figure 7 for cathodic and anodic processes in physiological saline solution at 37°C. We observe a volcano-type relationship

with titanium-30 per cent platinum showing maximum electrocatalytic activity for both cathodic and anodic processes.

Electrocatalysis in Ethylene Oxidation

The anodic oxidation of ethylene at platinum electrodes has been studied for more than 20 years as a model for electrocatalysis particularly relevant for fuel cell reactions (2). We have re-examined ethylene oxidation, partly because of some disagreement with our initial mechanism proposals (3, 4), but primarily to make an electrocatalytic study with the titanium-platinum alloys. The measurements were made in 1 N sulphuric acid at 80°C with ethylene at 1, 0.1 and 0.01 atmospheres partial pressures using steady-state potentiostatic techniques. Steady-state Tafel behaviour was observed for platinum and for each of the titanium-platinum alloys with slopes of $2RT/F$. The linear Tafel region decreased as the amount of platinum in the alloy decreased, for example, titanium-20 per cent platinum showed linear Tafel behaviour between 0.4 and 0.8 V (versus R.H.E.), while titanium-10 per cent platinum gave linear behaviour between 0.6 and 0.8 V. A negative pressure dependence of the current, and hence a negative order of reaction with respect to ethylene, was observed for platinum and for each of the titanium-platinum alloys, provided the measurements were made at potentials below the limiting current regions. The potential at which a limiting current is observed decreases as the partial pressure of ethylene is decreased.

A typical response of anodic current with change of ethylene partial pressure is given in Figure 8 for titanium-30 per cent platinum. These results are consistent with the earlier suggestions that the anodic oxidation of water to form OH radicals (which then react with adsorbed ethylene molecules) is the rate limiting step (2, 5).

One method of comparing the electrocatalytic activity for ethylene oxidation is to compare the current densities at a given potential in the linear Tafel regions. Figure 9, which correlates

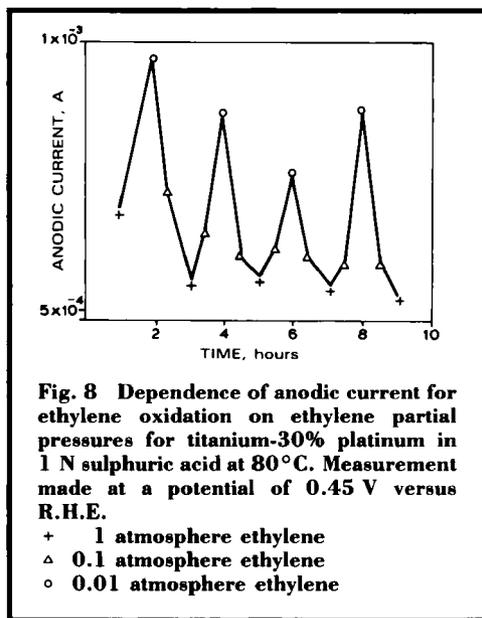


Fig. 8 Dependence of anodic current for ethylene oxidation on ethylene partial pressures for titanium-30% platinum in 1 N sulphuric acid at 80°C. Measurement made at a potential of 0.45 V versus R.H.E.

- + 1 atmosphere ethylene
- Δ 0.1 atmosphere ethylene
- o 0.01 atmosphere ethylene

the current densities versus electronic work function at a potential of 0.6 V, exhibits a surprisingly good volcano-type curve with a maximum for electrocatalytic activity occurring between titanium-20 per cent platinum and titanium-30 per cent platinum. These results strongly indicate that some titanium-platinum alloys, particularly those ones with compositions between 20 to 30 per cent platinum, may

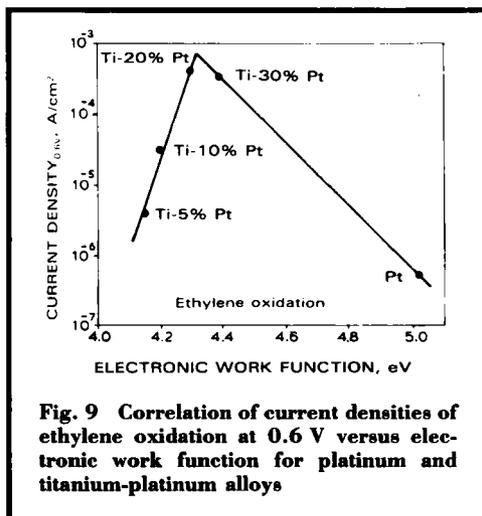


Fig. 9 Correlation of current densities of ethylene oxidation at 0.6 V versus electronic work function for platinum and titanium-platinum alloys

Table IV
Electrochemical Windows on Titanium and Tantalum Alloys
in AlCl₃-MeEtImCl Melts

Electrode material	Electrochemically stable region, volts	
	Basic melt (mole fraction AlCl ₃ = 0.4)	Acidic melt (mole fraction AlCl ₃ = 0.6)
Pt	0.90 to -0.15	2.00 to 0.70
Ti-5% Pt	-0.2 to -0.7	1.30 to 0.00
Ti-10% Pt	-0.2 to -0.45	1.1 to 0.6
Ti-20% Pt	none	none
Ti-30% Pt	none	none
Ti-20% Ir	-0.15 to -0.30	1.2 to 0.7
Ti-20% Ru	0.25 to -2.0	none
Ta	0.40 to -1.0	1.9 to 0.5
Ta-20% Pt	-0.1 to -0.8	1.05 to 0.3
Ta-20% Ru	1.25 to -1.7	2.3 to -0.1
Ta-20% Ir	0.8 to -1.5	1.95 to -0.05

All potentials are referred to an aluminium wire in the acidic (0.6) melt

be better electrocatalysts for organic oxidation reactions than platinum alone.

Electrochemical Behaviour in a Room Temperature Molten Salt System

Room temperature (20°C) highly conducting melts of AlCl₃ with 1,3-dialkylimidazolium chlorides were reported in 1982 (6). These melt systems appear to be of particular interest as electrolytes for high energy density batteries. We were able to examine the behaviour of the titanium and tantalum alloys in these melt systems and the preliminary results were published as a U.S. Air Force Technical Report from the Frank J. Seiler Research Laboratory (7). The stability of the alloys in AlCl₃-methylethylimidazolium chloride melts was examined using cyclic voltammetry. The potential region in which the electrode is stable, that is where it does not undergo dissolution, and in which the melt is electrochemically unreactive, is termed the electrochemical window. These were determined for melts with an AlCl₃ mole fraction of 0.40 which behaved as Lewis bases, and with an AlCl₃ mole fraction of 0.60 which behaved as Lewis acids. The cyclic voltammograms, taken at a sweep rate of 50 mV/s, indicated that all of the titanium alloys were

subject to dissolution in both basic and acidic melts. Aluminium deposition could be observed only from acidic melts and only for platinum and titanium-5 per cent platinum electrodes. In contrast the tantalum alloys demonstrated much greater stability in the melts, in fact tantalum-20 per cent ruthenium gave the widest electrochemical window in basic melts of all the electrode materials examined.

The results of these studies are summarised in Table IV. The electrocatalytic activity can be inferred in the sense that the wider the electrochemical window observed, the lower is the electrocatalytic activity of the electrode.

Conclusions

Studies with electrodes of titanium and tantalum alloyed with platinum group metals have led to a number of interesting observations. Under many conditions the electrochemical behaviour of the alloys is more like that of the platinum group component than that of either titanium or tantalum, even when the platinum component is smaller. For several reactions, namely: hydrogen evolution, chlorine evolution and ethylene oxidation, some of the titanium-platinum alloys appear to be better electrocatalysts than platinum, with a maximum

in activity for the alloys containing between 20 and 30 per cent platinum. From some considerations, titanium-20 per cent iridium ap-

peared to be the most active, and tantalum-20 per cent ruthenium the most stable and least active of the alloys studied.

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Joining Ceramics to Metals by Reaction Bonding

Some of the newer ceramic materials have superior physical properties which may enable them to replace metals in certain applications. However these ceramics are relatively expensive and their fabrication costs exceed those for metals. It therefore seems probable that their use will be restricted to particular areas, such as those subjected to high wear or thermal stress. For many years the solid-state bonding of metals to ceramics has been studied at the C.S.I.R.O., Division of Chemical Physics, Clayton, Victoria, Australia (1), and recently a review of reaction bonding has been presented by workers at that establishment (2).

A large number of bond combinations have been studied, including detailed examinations of the bonding of platinum to alumina and palladium to magnesia. By high resolution electron microscopy it has been established that the reaction between palladium and magnesia involves a liquid-like phase, and proceeds at a temperature lower than the melting point of either material. However, micro-diffraction to within 10Å of the metal/oxide interface shows no evidence of any material other than pure palladium or pure magnesium oxide.

When non-noble metals form part of the combination, solid state bonding appears to involve a totally different mechanism with metal diffusing into the ceramic and reaction zones forming. With some metals it may be difficult to produce strong, reliable bonds directly to a ceramic, but the use of an appropriate metal interlayer enables bonding to be successful. Platinum foil is a suitable interlayer for high temperature applications. Platinum-alumina bonds have been tested up to 1100°C, both vacuum-tightness and strength being retained.

Biomedical devices, for implantation, are

constructed from materials such as ceramics, stainless steels, titanium and titanium alloys, and often platinum or iridium. The individual materials must be biocompatible, as must any metal/ceramic joints; hence reaction bonding can be advantageous. Here the inert noble metals may be used on their own, or as interlayers to facilitate the bonding of ceramics to metals such as titanium.

Reaction bonding is a versatile process which will be used increasingly as new applications are found for the superior properties of the newer engineering ceramics. For use under arduous conditions it is likely that noble metal bonds will be required.

I.E.C.

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Optimising Fuel Cell Cathodes

As phosphoric acid fuel cells move towards commercialisation capital cost is one of the factors influencing their economic viability. Platinum metals catalysts are used in the power section where the conversion of chemical fuel into electric energy takes place, and efforts to improve the performance of the catalysed electrodes continue. Interestingly, a recent study of platinum on carbon catalysts made at Stanford University, suggests that the optimum crystallite diameter for the most efficient use of platinum in fuel cell cathodes is about 3 nanometres ("Oxygen Reduction on Small Supported Platinum Particles", M. Peuckert, T. Yoneda, R. A. Dalla Betta and M. Boudart, *J. Electrochem. Soc.*, 1986, **133**, (5), 944-947).