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*Oxygen reaction on titanium catalysed by gold, platinum and palladium**

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Electrocatalytic properties of titanium surfaces coated with small amounts (0.025–0.6 mg cm^{-2}) of Au, Pt, Pd and their mixtures, with respect to both oxygen evolution and reduction in alkaline solution have been investigated. It was found that all the samples exhibited higher electrochemical activity than the corresponding compact metal surfaces. This could be ascribed to a larger specific surface area of the dispersed catalysis than that of the smooth metal surfaces. The best performance was obtained with dispersed palladium, the potential gap between oxygen evolution and reduction at 1 mA cm^{-2} being reduced to 0.66 V.

1. Introduction

Titanium is known to be a very suitable electrode material for industrial electrochemical applications especially for anodic processes involving gas evolution. In attempts to carry out the reverse cathodic reduction processes, e.g. in fuel cells, other materials have been used such as carbon or other more expensive metals (nickel, silver) with significantly higher specific weight. Since carbon cannot be used for rechargeable batteries of the fuel cell or hybride type (e.g. metal–oxygen cells) a metal carrier becomes unavoidable. In spite of its obvious advantages, no attempt to use titanium as a base for gas diffusion rechargeable electrodes, has so far been published. Since porous titanium bodies can be obtained by sintering titanium powder without difficulty, it was considered worthwhile to investigate the possibility of finding materials which would make the titanium surface catalytically active for both the anodic and the cathodic process in the electrochemical reaction of oxygen in alkaline solutions.

Much work has been reported in the field of electrocatalysis of the oxygen reaction not only with respect to types of catalysts but also to modes of preparation, the latter having a major effect on performance (e.g. [1]). However, in the work cited the emphasis has been on reducing polarization and increasing stability in either the cathodic or the anodic process. Little attempt has been made to investigate the problem of dual function of the electrode, i.e. to overcome or reduce the potential gap between cathodic and anodic polarization and investigate stability under such changing directions of current.

In the present work the whole noble metal group of catalysts, chemically deposited on titanium, was scanned, but only results obtained with gold, platinum and palladium are reported here.

Investigation has been undertaken of the behaviour of the metals alone or in mixtures deposited on compact titanium surfaces in small amounts ranging from 0.025 to 0.6 mg cm^{-2}.

The structure of the deposits has been investigated by X-ray and electronic microscopy.

Electrochemical investigations involved obtaining

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(a) potential sweep voltammograms both for electrodes in the absence of any electrochemically active gas, and in the presence of oxygen in solution;

(b) steady-state potentiostatic polarization curves for both oxygen reduction and oxygen evolution on titanium plated with gold, platinum, palladium and their mixtures.

Since palladium exhibited the most promising properties, some additional electrochemical investigations have been performed with this metal.

2. Experimental details

Compact commercial grade titanium was made in the form of flat cylinders (8 mm in diameter) for use in a rotating disc electrode assembly. For structural investigations the discs were mirror polished by the usual techniques prior to depositing the catalysts. The adherence to such surfaces was, however, rather poor so that catalysts could not withstand anodic polarization for more than a few hours. Therefore, for electrochemical investigations, the polished surface of the cyclinders was etched in a mixture of 10% HCl and 10% $H_2C_2O_4 \cdot 2H_2O$, and then in 5% HNO_3 for 30 min. This made the surface evenly dim.

The noble metal catalysts were introduced to the titanium surfaces from corresponding acid aqueous solutions of their chlorides (of concentration 2–5 mg cm^{-3}) spread by means of a micropipette in a volume sufficient to deposit a desired amount of metal. After evaporating water and acid, the samples were heated in a laboratory kiln open to the atmosphere at 500°C for 3 h. Mixed noble metal catalysts were made by mixing solutions in the desired proportion before spreading.

X-ray analysis of the surface structure was made with a Phillips PW 1730 X-ray assembly with a vertical goniometer PW 1050 and a non-rotating sample holder. The Bragg method was applied using a copper tube at 35 kV (20 mA) with the radiation filtered through an AMR graphite monochromator. The identification was done using ASTM tables.

Scanning electron microscopy of the sample surfaces was carried out with a JSM-35 JEOL instrument, with magnification ranging from 200 to 30 000.

Electrochemical properties were assessed by recording potential sweep voltammograms and steady-state polarization curves under well defined hydrodynamic conditions provided by rotating the electrode.

Potential sweep investigations were performed using Stonehart BC 1200 and PAR M 173 potentiostats with a universal programmer PAR M 175 and a Hewlett-Packard 7015 B X-Y recorder.

The same equipment and a Hewlett-Packard 412 A voltameter was used for steady-state potentiostatic investigations.

The electrochemical cell was fitted with a home-made rotating disc electrode assembly. A Hg/HgO reference electrode in the same solution was connected to the rotating disc via a Luggin capillary. The cell was closed and insulated from the atmosphere in the usual manner.

The solution was 1 M in NaOH made up using triply distilled water. The potential sweep voltammogram for platinum was used as a criterion of purity.

Gaseous nitrogen, purified through molecular sieves and over copper turnings, was bubbled through the cell for measurements made in the absence of oxygen. For those made in the presence of the latter, oxygen gas was also purified through molecular sieves.

The temperature was maintained at 25°C.

3. Results

3.1. *X-ray*

The X-ray reflections obtained with different catalytic surfaces are summarized in Fig. 1. Besides the titanium base and its surface oxide, they revealed the presence of pure noble metal phases as well as some mixed phases (intermetallic compounds and solid solutions) of all the noble metals with titanium [2]. The alloy of gold with platinum and palladium also gave some weak reflection.

There was some proportionality between the amount of all the deposited metals and the intensities of their reflections. No such proportionality was found for the $AuTi_3$ phase however. The intensity of reflections from that phase was more or less constant, indicating that it is formed only at the roots of the noble metal grains.

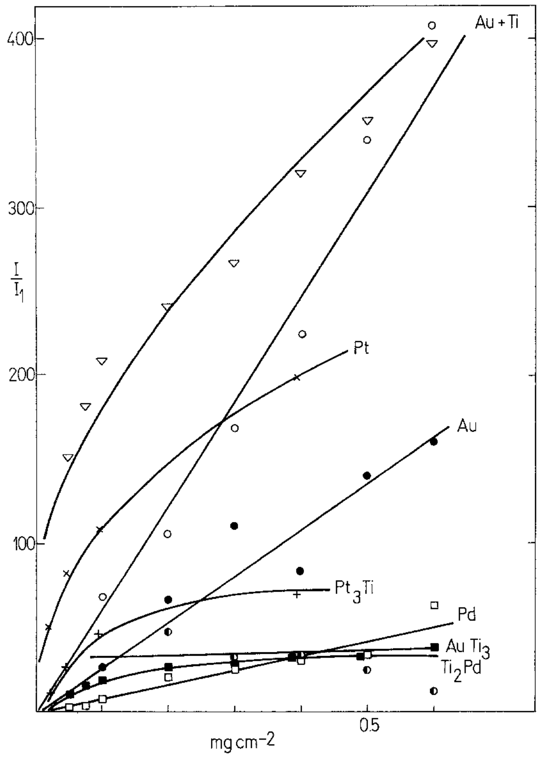

Fig. 1. X-ray analysis of electrodes of titanium catalysed by noble metals. (I/I_1 = ratio of intensity of the given phase to that of titanium base.) ● Au; ○ Au + Ti; ◐ $AuTi_3$; × Pt; + Pt_3Ti; □ Pd; ■ Ti_2Pd; ▽ Pd + Ti.

3.2. *Electron microscopy*

The granular structure of the deposit could be particularly well seen by scanning electron microscopy in the case of gold, as shown in Fig. 2. Tulip-form gold particles were of the order of 1–2 μm in diameter. The deposit of palladium was of a finer grain structure while in the mixed palladium–gold deposit, separate gold particles could be seen although of almost an order of magnitude smaller in size than in the case of pure gold.

3.3. *Potential sweep voltammograms in the absence of oxygen*

The voltammograms obtained with titanium coated by the three pure noble metal catalysts are compared in Figs. 3–5 with those for the corresponding compact metals.

It is seen that in the case of gold some inhibition of oxide formation arises.

Conversely, in the case of platinum and palladium the metal dispersed on titanium exhibits considerably higher activities both in the oxidation and reduction of the noble metal as well as for hydrogen evolution. For palladium a new peak appears at − 0.5 V vs standard hydrogen electrode (SHE). In the anodic direction there are two peaks corresponding to oxidation of hydrogen at − 0.67 and − 0.45 V vs SHE (compared to a single peak at − 0.4 V for compact palladium) and an oxidation wave with $E_{1/2} = 0.2$ V.

Voltammograms for titanium coated with mixed catalysts, obtained by mixing gold solution with those containing Pt and Pd are shown in Fig. 6.

Combinations of gold with platinum and palladium are seen to give voltammograms in which those of pure metals seem to be superimposed upon each other.

It is worth noting the potentials of the peaks for the reduction of the noble metal oxides as given in Table 1, since they determine whether the oxygen reduction should take place on oxide covered or bare metal surfaces.

3.4. *Potential sweep voltammograms in the presence of oxygen*

The voltammograms for gold-plated titanium are shown in Fig. 7, compared to that for compact gold [3]. It is seen that the catalyst plated on the polished titanium surface exhibits smaller activity (reduction current at a given potential) than the compact metal. That plated on the etched surface, however, exhibits a larger activity.

Characteristic are two reduction waves. The height of the second wave at a given rotation speed is the same as those obtained on platinum or palladium (cf. Figs. 8 and 9) while that of the first wave tends to be half that of the second wave. The half-wave potentials are listed in Table 2. There is little difference between those obtained with the cathodic and the anodic sweep. The catalyst at the etched titanium, however, exhibits a higher catalytic activity (more positive half-wave potential) than compact gold.

The same applies to platinum [4] coated on etched titanium as seen in Fig. 8. The higher catalytic activity (cf. Table 2) coincides with increased pseudo-capacitance, higher oxide

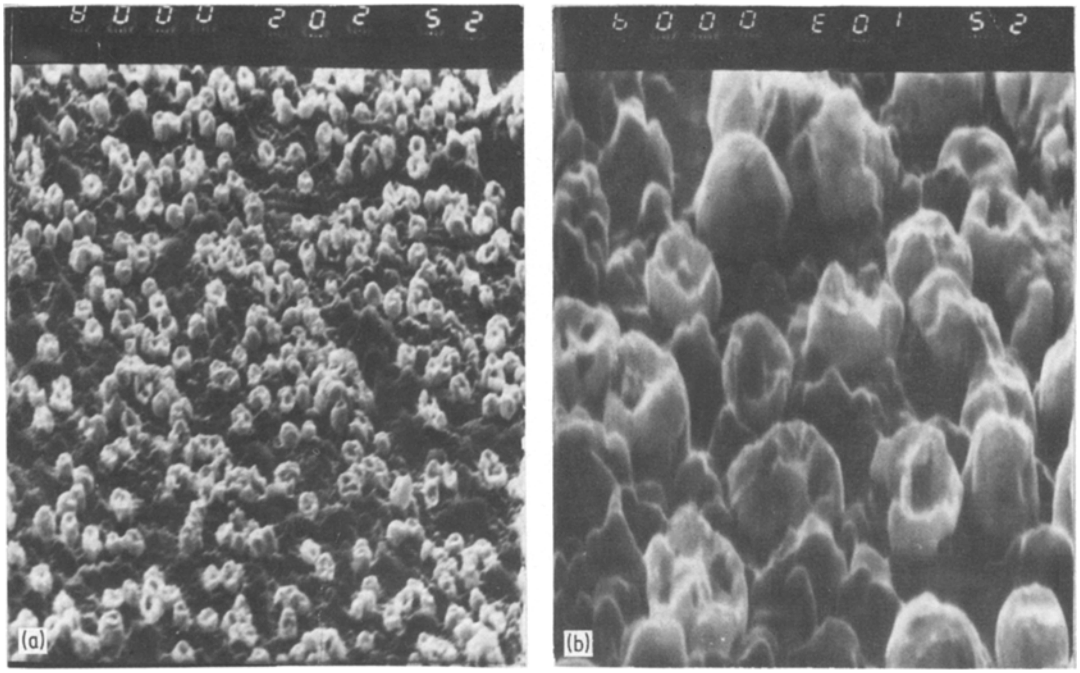

Fig. 2. Scanning electron micrograph of titanium surface covered by gold particles: (a) 2000×, (b) 10 000×.

reduction peaks and an increased diffusion limiting current of almost 50%, reflecting the effect of surface roughening on the hydrodynamics of the rotating disc. There is not much difference in $E_{1/2}$ between the cathodic and the anodic sweep although the large difference in the beginning of the limiting current plateau indicates that the reduction of the oxide in the cathodic sweep occurs only at potentials more negative than $E_{1/2}$.

The opposite case is found with palladium [5], as shown in Fig. 9. There, the $E_{1/2}$ for oxygen reduction on the oxide covered surface (cathodic sweep) is significantly more negative (about 200 mV) than that on the reduced surface (anodic sweep). Reduction of the oxide on palladium is well expressed as the peak in the cathodic sweep. In the anodic sweep the dip in the oxygen reduction limiting current plateau is due to the reduction of hydrogen imbibed during hydrogen evolution at the cathodic limit of the sweep.

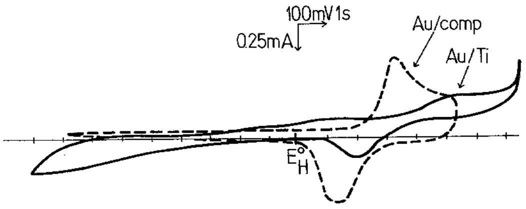

Fig. 3. Potential sweep voltammograms for compact gold and gold deposited on titanium in 1M NaOH in the absence of oxygen (sweep rate of 100 mV s^{-1}).

On both platinum and palladium a single reduction wave is observed.

It was considered interesting to discover to

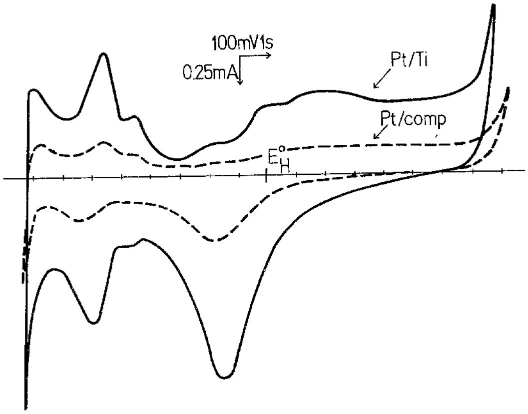

Fig. 4. Potential sweep voltammograms for compact platinum and platinum deposited on titanium in 1M NaOH in the absence of oxygen (sweep rate 100 mV s^{-1}).

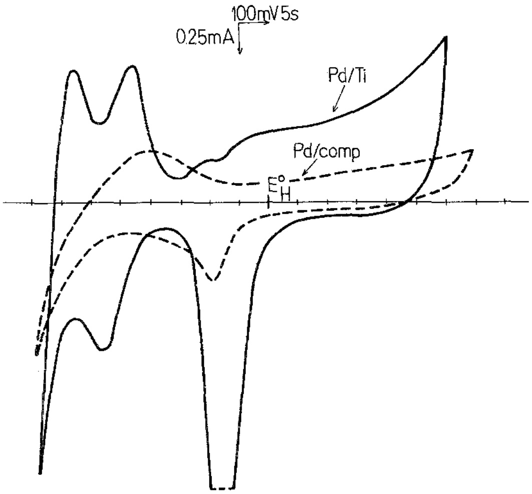

Fig. 5. Potential sweep voltammograms for compact palladium and palladium deposited on titanium in 1M NaOH in the absence of oxygen (sweep rate 100 mV s^{-1}).

Table 1. Potentials of the reduction peaks of oxides

Sample	E_p *(V vs SHE)*	*Recorded at sweep rate (mV s^{-1})*	*Remarks*
Au(Comp)	+ 0.22	100	well defined
Au(Ti)	+ 0.21	100	well defined
Pt(Comp)	− 0.135	100	well defined
Pt(Ti)	− 0.20	20	well defined
Pd(Comp)	− 0.19	20	well defined
Pd(Ti)	− 0.29 to − 0.18	20	increased, depending on anodic limit

what extent the amounts of Pt and Pd on titanium can be reduced without significant loss of the catalytic activity. Hence, the contents of these metals were varied, from 0.6 mg cm^{-2} downwards. It was found that half-wave potentials did not change with contents of 0.07 and 0.05 mg cm^{-2} of Pt and Pd respectively. However, sharp changes in the negative direction occurred beyond these limits.

Potential sweep voltammograms for mixed noble metal catalysts are shown in Fig. 10.

Addition of platinum and palladium to gold is seen to eliminate the first wave. Hence, the diffusion limiting currents become similar to those for pure palladium and palladium catalyst. Other characteristics of the voltammograms for the latter two metals (cf. Figs. 10 and 11) also mask those of gold except for the reduction peak of the oxide of the latter which is seen clearly before the beginning of the oxygen reduction wave. The catalytic activities (cf. Table 2) of the mixed catalysts are higher than that of pure gold but lower than that on pure platinum and palladium.

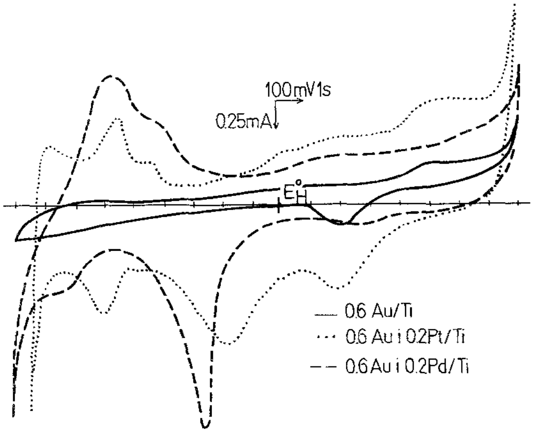

Fig. 6. Potential sweep voltammograms for compact gold and combination coatings of titanium with gold and platinum and gold and palladium, in 1M NaOH in the absence of oxygen (sweep rate 100 mV s^{-1}).

The effects of varying the metal-to-metal ratio in the case of Au–Pd mixtures are seen in Fig. 11. The effect of gold is seen in the fact that the surface is more active in the cathodic sweep than that with pure palladium. The height of the oxide reduction peak at the beginning of the diffusion limiting current plateau is proportional to the palladium content in the mixture.

The catalytic effect in the anodic sweep seems to pass through a minimum with the $E_{1/2}$ changing from +30 through +10 to +60 mV vs SHE for palladium contents of 0.2, 0.4 and 0.6 g cm^{-2}, respectively.

3.5. *Steady-state polarization measurements*

As already indicated by the potential sweep voltammograms, transport of oxygen from the bulk of solution in the cathodic reduction process leads to a diffusion limited current density. The latter was well defined, as has been proven by the fact that it followed closely the Levich dependence

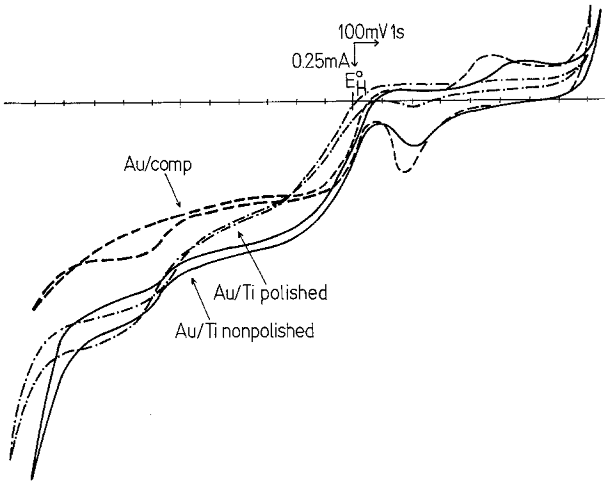

Fig. 7. Same as Fig. 3 but in the presence of oxygen in solution.

on the square root of the speed of rotation of the disc electrode [6]. Hence, in making the steady-state polarization plots this effect has been corrected for, by using corrected current density values, i_c,

$$i_c = \frac{i}{i_D - i} i_D \qquad (1)$$

where i_D is the diffusion limiting current density, and i is the measured current density value.

In such a way Fig. 12 was obtained for pure noble metal catalysts. It can be seen that gold exhibits the lowest catalytic activity of the three metals. At low current densities it gives linear Tafel functions with slopes of RT/F in both cathodic and anodic directions. In both directions there is appreciable curving at higher current densities which cannot be ascribed to difficulties in transport. The most active catalyst for both the anodic and cathodic process is palladium plated on titanium, giving linear Tafel functions in both directions with 120 and 40 mV decade^{-1} slopes, respectively. The cathodic Tafel line seems to start at the peroxide reduction potential, since the anodic lines also tend to a reversible potential other than that of O_2 reduction at low current densities (dashed line).

In general, metals plated on titanium gave larger current density values at a given potential than the compact metals alone. The polarization in the case of mixed Au–Pd catalysts was between those of pure gold and palladium. Table 3 lists

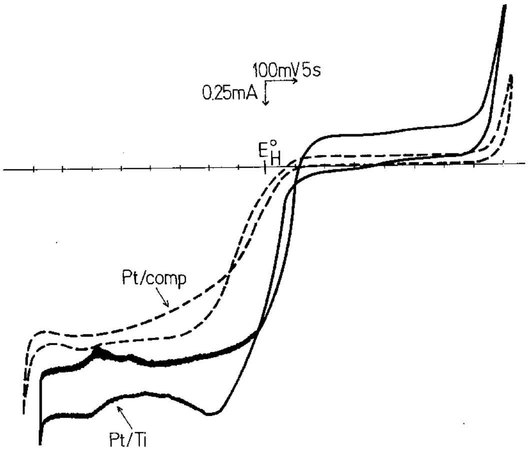

Fig. 8. Same as Fig. 4 but in the presence of oxygen in solution.

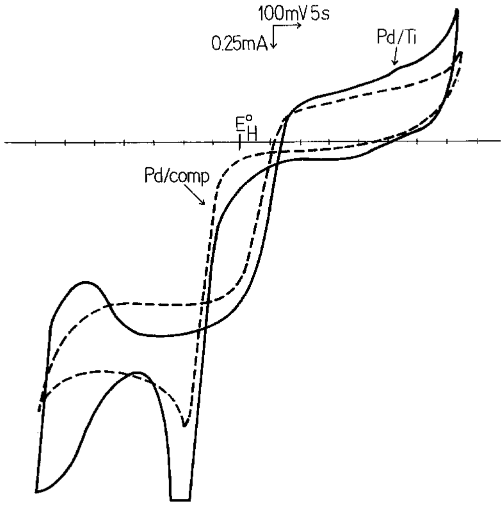

Fig. 9. Same as Fig. 5 but in the presence of oxygen in solution.

Table 2. Half-wave potentials of oxygen reduction in 1M NaOH at different catalytic surfaces $E_{1/2}$ *(mV vs SHE)*

Surface	*On oxidized surface*	*On reduced surface*
Au-compact	–	− 50
Au (0.6*) on Ti	–	+ 20
Pt-compact	− 30	− 20
Pt (0.4) on Ti	+ 10	+ 50
Pd-compact	− 100	+ 60
Pd (0.6) on Ti	− 100	+ 110

current densities at typical anodic and cathodic potentials as well as the potential gap at a common current density of 1 mA cm^{-2}.

4. Discussion

The noble metals are seen to plate upon titanium with some interaction with the substrate, or with each other when plated in a mixture. The interaction with titanium seems to provide a well conducting contact and satisfactory adhesion, especially when the titanium surface is roughened by etching.

However, in most cases these interactions seem to play little role in the electrochemical behaviour of the catalyst. This could be concluded by inspection of the potential sweep voltammograms.

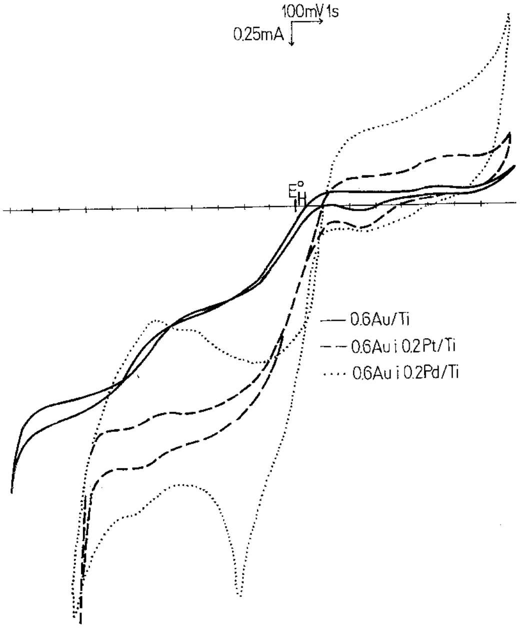

Fig. 10. Same as Fig. 6 but in the presence of oxygen in solution.

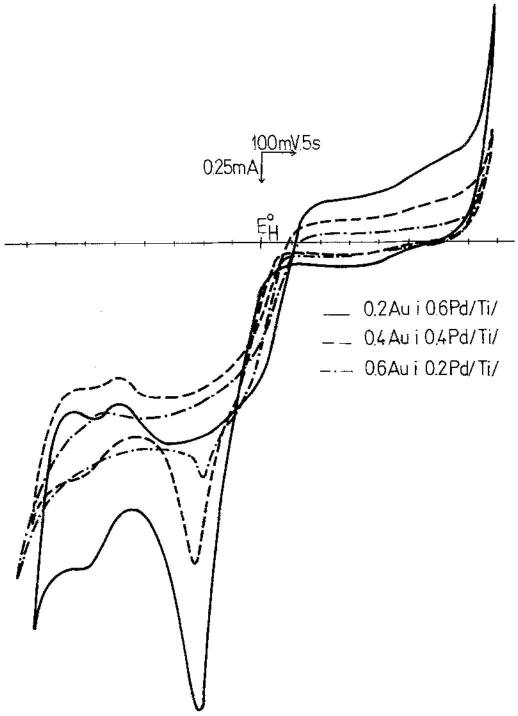

Fig. 11. Potential sweep voltammograms of titanium covered by mixed noble metal catalysts of varying metal-to-metal ratio in 1M NaOH in the presence of oxygen in solution (sweep rate 100 mV s^{-1}).

In the absence of oxygen in solution, with the exception of palladium, the voltammograms for the catalysts dispersed upon the titanium surface in qualitative aspects reproduce those of the corresponding compact metals. Neither new peaks nor significant shifts of peak potentials are found.

In the case of palladium, interaction with the substrate seems to play a significant role. The changes in the voltammogram compared to the compact metal could hardly be accounted for by assuming a high degree of dispersion (increased surface roughness factor) of palladium.

The fact that no new features are found with mixed metal catalysts compared to pure metals, indicates that their alloying plays no significant role. Similarly the slopes of the Tafel plots indicate that oxygen reduction and evolution on catalysts dispersed on titanium follow the same mechanism as on the corresponding compact metal surfaces. The activities of the dispersed catalysts, however, differ significantly from those

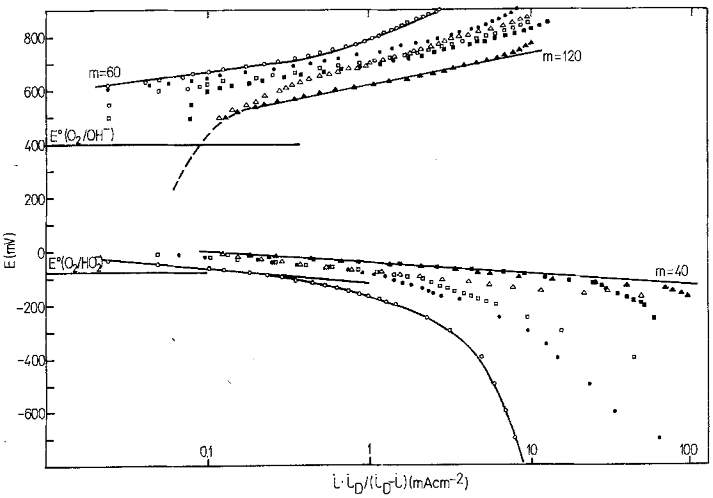

Fig. 12. Steady-state polarization measurements of oxygen evolution and reduction on compact gold, platinum and palladium as well as on those deposited on titanium, in 1 M NaOH. ○ Au; ● Au(Ti); □ Pt; ■ Pt(Ti); △ Pd; ▲ Pd(Ti).

of the compact metal, in most cases being higher at the former. It is questionable if they are accounted for by merely an increase in surface roughness.

Palladium is seen to be the best catalyst of the three metals investigated as far as the electrochemical properties are concerned. The problem of its stability was outside the scope of this work, but within hours of its investigation no indication of a fast degradation was found.

Even though the investigated metals proved to be rather good catalysts for both reduction and evolution of oxygen, the potential gap could not be said to have been overcome. It is a likely consequence of the different mechanisms of the cathodic and anodic processes. The deviations of the anodic polarization curves at low current densities towards a potential more negative than the thermodynamic reversible potential of oxygen (denoted in Fig. 12) indicates that the open circuit potential is determined basically by the reaction of the peroxide present in the vicinity of the electrode.

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Table 3. Current densities at constant potentials and potential gap at a constant current density for different catalysts

Catalyst	i_{an} *(700 mV vs SHE) (mA cm^{-2})*	i_{cath} *(−100 mV SHE) (mA cm^{-2})*	ΔE*(1 mA cm^{-2}) (V)*
Au(comp)	0.22	0.28	0.94
Au(Ti)	0.46	1.28	0.82
Pt(comp)	0.88	1.78	0.79
Pt(Ti)	1.27	12	0.74
Pd(comp)	1.09	2.01	0.78
Pd(Ti)	4.6	8.40	0.66
0.6 Au + 0.2 Pd(Ti)	0.3	1.1	0.84
0.4 Au + 0.4 Pd(Ti)	0.64	1.2	0.82
0.2 Au + 0.6 Pd(Ti)	1.6	2.0	0.72