

Platinum Metal Alloys in Electrocatalysis

By E. W. Brooman, Dip. Tech., and T. P. Hoar, Sc.D.

Department of Metallurgy, University of Cambridge

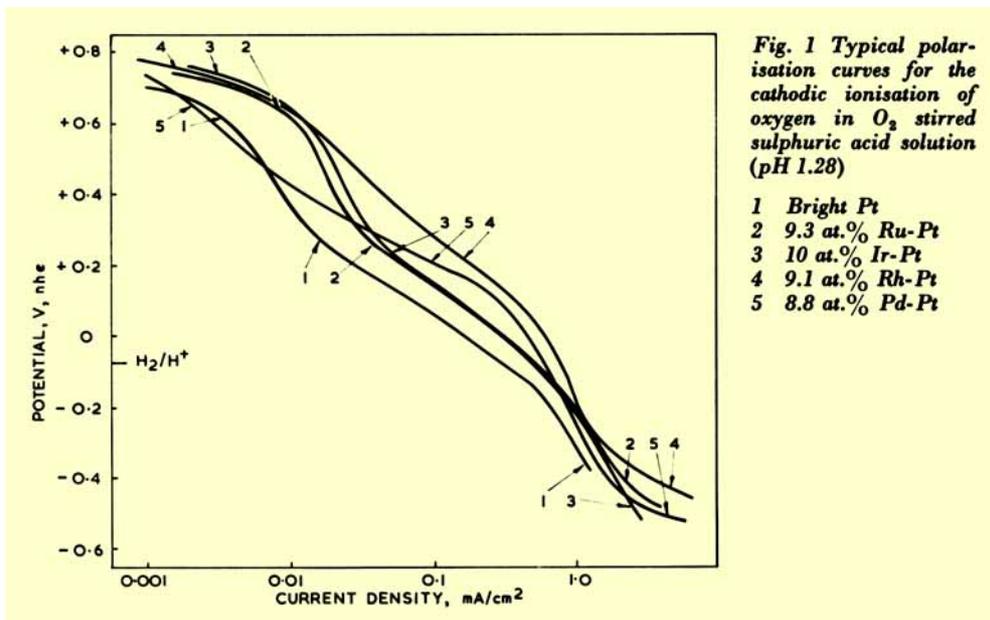
A systematic study of the electrochemical behaviour of platinum alloyed with other platinum metals has not previously been attempted. Some recent research directed to this end is briefly reported here, and shows the enhanced electrocatalytic activity of the alloys studied compared with bright platinum itself for the electrochemical reduction and evolution of oxygen in acid solution.

In heterogenous catalysis in both the liquid and vapour phase the increased activity of various platinum metal alloys over that of either component alone has been reported. In hydrogenation reactions Kowaka (1) noted an increased activity with certain silver-palladium alloys, while Nishimura (2) found that in his studies with platinum, rhodium, rhodium-platinum alloys and their oxides certain alloys were more active than either metal or oxide alone. More recently Bond and Webster (3) reported the high activity of co-reduced mixed ruthenium-platinum oxides, and Rylander and Cohn (4) have also reported marked synergistic effects with mixed ruthenium-palladium catalysts. In the isomerism of *n*-pentane Gray, Masse and Oswin (5) found that with the very wide range of noble metal alloys studied certain compositions of each alloy showed a maximum activity. As a final example, platinum alloyed with 10 to 25 per cent ruthenium was found by McKee and Norton (6) to have the highest specific activity for methane-deuterium exchange.

In the field of electrocatalysis there is less available information on the activity of similar noble metal alloys when used as electrodes. It might be reasonably assumed that direct comparison between simple heterogeneous catalysis and electrocatalysis is possible. For several reasons this may not be so. Reactions occurring at electrode/solution interfaces are

usually more complicated, and often involve numerous successive or competitive processes. The electric field across the interface and the structure of the double layer which play an important part in electrocatalysis do not have analogues at the metal/gas interface in ordinary catalysis. Finally there is also the possibility of potential-dependent reactions occurring between the electrode and the environment which can intervene (either beneficially or detrimentally) in the reaction sequence.

With these facts in mind it is interesting to note that some alloys are indeed proving more electrocatalytically active than the pure metals. Brabers (7), for example, found that hydrogen was more easily electrodeposited on palladium-gold alloys, and Hoare (8) found that the hydrogen reaction also occurred more easily on α - (or β -) Rh-Pd-H alloys containing about 5 atomic per cent rhodium. For fuel cell applications Feuillade (9) cites the activity of some rhodium-platinum alloys, while palladium-platinum alloys were found more active by Grimes, Murray and Spengler (10) for hydrogen and methanol fuels. Frumkin has described results obtained with ruthenium-platinum alloys for methanol/air cells, and Holt and Horowitz emphasised the activity of ruthenium-platinum and molybdenum-platinum alloys in the oxidation of methanol (11). With research also progress-



ing on more effective catalyst supports, possibilities of more efficient and less expensive noble metal electrode systems now seem feasible.

At the moment, however, selection of suitable electrode systems is haphazard and mostly empirical. In order to remedy this to some extent systematic data on these alloys must be collected and made available. For this reason, a research programme, part of which is presented here, was instigated. Preliminary work was carried out on the ionisation and evolution of oxygen at alloy electrodes. This system was chosen for reasons of relative simplicity of apparatus and technique. In comparison theoretical analysis is very difficult and will not be attempted here.

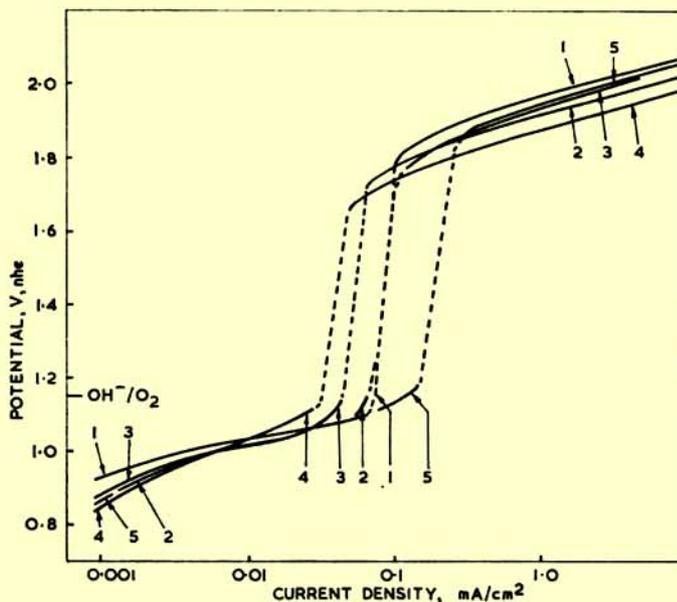
Galvanostatic measurements were carried out at 25°C in very pure, flowing sulphuric acid solutions through which oxygen (at one atmosphere) was bubbled. The specimens were in sheet form about 2 cm² in area (geometric), and were taken from material supplied by Johnson Matthey. They were carefully prepared to give reproducible, phase-oxide free surfaces. Potentials are given on the hydrogen scale and represent

near steady-state conditions (Experimental points shown represent a change in potential of less than 5 mV in 15 minutes). A detailed account of the experimental conditions and procedure is given elsewhere (12).

Alloying addition atomic per cent	Enhancement ratio at 0.68 V, nhe	Enhancement ratio at 0.10 V, nhe
0 (bright Pt)	1.00	1.00
1.9 Ru	1.9	3.0
3.8 Ru	4.6	3.9
9.3 Ru	2.7	2.8
1.1 Ir	2.2	1.7
2.0 Ir	3.5	3.2
5.1 Ir	5.6	2.7
10 Ir	4.2	2.6
1.6 Rh	1.3	4.7
3.7 Rh	1.8	7.4
9.1 Rh	3.4	7.2
17 Rh	4.6	8.9
1.6 Pd	1.02	7.5
3.6 Pd	1.0	7.1
8.8 Pd	1.0	4.5
20 Pd	—	6.3

Fig. 2 Typical polarisation curves for the anodic evolution of oxygen from O₂ stirred sulphuric acid solution (pH 1.28)

- 1 Bright Pt
- 2 1.9 at. % Ru-Pt
- 3 1.1 at. % Ir-Pt
- 4 1.6 at. % Rh-Pt
- 5 1.6 at. % Pd-Pt



Four series of alloys, Ru-Pt, Ir-Pt, Rh-Pt and Pd-Pt, were studied with compositions ranging from 0 to 20 atomic per cent. Typical cathodic polarisation curves, representing the ionisation of oxygen, with eventual hydrogen evolution at the highest current densities, are shown in Fig. 1. The inflections in the curves were caused by the presence of an adsorbed intermediate, but as this was reproducible and was found with all the alloys qualitative and semi-quantitative observations could be made. From these curves it can be seen that all the alloys were, to varying extents, more active electrochemically than bright platinum for this particular reaction. The results are summarised in Table I, where an enhancement ratio is given as a measure of the activity. This enhancement ratio is defined as the current sustained by alloy compared to the current sustained by bright platinum at a given potential. The potentials chosen were 0.68 V, nhe (which corresponded approximately to the end of the first Tafel range), and 0.10 V, nhe (which was just before the limiting current for oxygen reduction). In the range of potentials likely to be encountered in industrial applications

rhodium-platinum and palladium-platinum alloys were found to be superior, giving enhancement ratios of between 4 and 9 in the composition ranges studied.

The anodic behaviour of the alloys proved quite straightforward. Definite oxide formation began at a potential of about 1.10 V, nhe, the alloys as a whole being slightly less polarised than bright platinum. Oxygen evolution began at a potential of about 1.8 V, nhe, for all except the rhodium-platinum alloys, where it began at about 1.7 V, nhe. Thus for the oxygen evolution reaction the rhodium-platinum alloys were by far the most active. The other alloys behaved similarly to each other, all being also slightly more active than bright platinum. Typical anodic polarisation curves are given in Fig. 2, while the results are summarised in Table II. Enhancement ratios are given for 1.9 V, nhe, for all except the rhodium-platinum alloys, where the potential chosen was 1.8 V, nhe. These potentials were 0.1 V above the respective potentials at which oxygen evolution apparently commenced.

In conclusion all the alloys studied showed an increase in activity over that of bright

Table II Activity of some platinum-platinum metal alloys for the electrolytic evolution of oxygen (pH 1.28)		
Alloying addition atomic per cent	Enhancement ratio at 1.8 V, nhe	Enhancement ratio at 1.9 V, nhe
0 (bright Pt)	1.00	1.00
1.9 Ru	—	2.5
3.8 Ru	—	1.0
9.3 Ru	—	1.8
1.1 Ir	—	1.9
2.0 Ir	—	2.2
5.1 Ir	—	2.2
10 Ir	—	1.9
1.6 Rh	2.5	—
3.7 Rh	2.7	—
9.1 Rh	4.5	—
17 Rh	7.9	—
1.6 Pd	—	1.4
3.6 Pd	—	1.4
8.8 Pd	—	1.1
20 Pd	—	1.6

platinum itself. Of the alloys studied rhodium-platinum appeared to be the most active either as cathode or anode. The reason for the improved electrocatalytic activity is not known. Synergistic effects are unlikely as all the alloys examined consisted of a single phase, although miscibility gaps do occur in some of the systems under equilibrium conditions. However, the latter are not usually obtained in practice. Application of the electron theory, with the catalytic activity of a metal depending on its d-character, may be applied with limited success to reactions involving simple sorption and desorption from the gas phase. Its application to electrocatalysis, where there exists a much more complicated state of affairs, does not seem either helpful or promising. A better knowledge of the electronic structure of metals and alloys in the condensed state, and of the effect of an applied field on the electrons, is desirable first.

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Thermodynamic Data for Platinum

A CRITICAL ANALYSIS

Platinum, it has only recently been recognised, exhibits a characteristic known as 'recoilless resonance' when bombarded by 99 keV gamma rays; so that measurements of the absorption of the radiation afford a means of studying what is termed the lattice dynamics of the metal. Analysis of the results of these experiments involves a term known as the Debye temperature θ_{DW} , which relates to the behaviour to be expected from an ideal, homogeneous, isotropic elastic body; and in a recent paper (1) J. R. Harris and his colleagues at Rutgers University, New Brunswick, New Jersey, have reported a value $\theta_{DW} = (234 \pm 6)^\circ\text{K}$ at 0°K . It is also possible to calculate the value of θ_{DW} from a knowledge of the specific heat, thermal expansion, and compressibility of the metal. J. L. Feldman and G. K. Horton, of the same University, have accordingly (2) made a critical examination of the available measurements, determining how closely they can be fitted into one curve for θ_{DW} from 0° to 300°K . The paper must be consulted for details. This analysis yields a value for θ_{DW} of (232 ± 3) at 0°K .

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