Platinum Metal Alloys in Electrocatalysis

A FURTHER EVALUATION OF RELATIVE ACTIVITIES

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The relative electrocatalytic activities of some binary platinum alloys for the oxidation and ionisation of hydrogen and the anodic oxidation of methanol are briefly described. For the hydrogen electrode reaction in acid solution the ruthenium-platinum and rhodium-platinum alloys are generally not as active as bright platinum itself. This is also found for the anodic oxidation of methanol in acid solution. At the low voltametric "sweep" rates used in the latter experiments the activities are somewhat greater on the reverse scan, from high to low positive potentials, than on the forward scan.

A previous paper (1) described the relative electrocatalytic activities of some binary platinum-platinum metal alloys for the oxygen electrode reaction. In the composition ranges studied it was found that all the four series of alloys (Ru-Pt, Rh-Pt, Pd-Pt and Ir-Pt) are more active than bright platinum for both anodic and cathodic polarisations. This present paper describes the activities of the same series of alloys for the hydrogen and the methanol half-cell reactions, again in a sulphuric acid supporting electrolyte.

The literature shows that alloying additions may increase or decrease the activity of the electrodes for these particular reactions, but that little work has been carried out at homogeneous alloy electrodes such as those used in the present experiments. Adlhart and Heuer (2), cited by Bockris and Wroblowa in a review of electrocatalysis (3), made a comprehensive study of various platinum base alloys and found that some Ru-Pt, Ru-Ta-Pt and Ru-Mo-Pt alloys had a lower overpotential for the electro-oxidation of methanol in sulphuric acid solutions. Petrii (4), and his co-workers (5) have also noted the activity of composite electrodeposits of Ru-Pt and Ru-Pd for the anodic oxidation of methanol in sulphuric acid and potassium hydroxide solutions. Conversely, at Au-Pt heterogenous electrodes oxidation of methanol only occurs at the platinum-rich phase (6). The activity of these alloys is decreased with respect to platinum itself, and this has also been found for Cu-Pt alloys (7).

Lewis, Flanagan, Carson and co-workers have in a series of papers (8) discussed the absorption and adsorption of hydrogen at Pd-Pt, Pd-Rh and Pd-Ag alloy electrodes, and have also discussed proton transfer effects. They were not primarily interested in electrocatalytic activities, and their results cannot directly be correlated to fuel cell evaluation studies. The limiting currents for hydrogen ionisation in sulphuric acid electrolytes have been determined at dispersed Pd-Pt and Pd-Rh alloys, as well as at Pd-Cu, Pd-Ag and Pd-Au alloys (9). Hydrogen adsorption and oxidation has also been measured at heterogeneous Au-Pt alloys (10, 11), and these results may be compared with results at similar alloys for methanol oxidation (6).

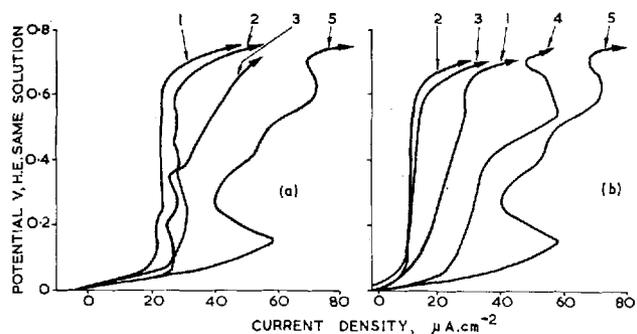A systematic evaluation of the effects of

alloying additions to platinum is desirable. Towards this end the results obtained at alloys with 1, 2, 5 and 10 wt. per cent rhodium, palladium or iridium, and 1, 2 and 5 wt. per cent ruthenium are described.

Experimental

Essentially the same equipment and glass ware were used in both series of experiments. The specimens were discs 12 mm in diameter cut from samples kindly supplied by Johnson Matthey & Co Limited. These were chemically cleaned (1) before the insertion in the Teflon specimen holder which exposed 0.385 cm² to the electrolyte. This holder had a standard B.40 taper on its side to enable it to be plugged directly into the cell, the lower end of which terminated in a B.40 socket. It also incorporated the reference half-cell (Hg/Hg₂SO₄/1N H₂SO₄),

capillary to specimen, and counter electrode of coiled platinum wire. In both series of experiments very pure 1N sulphuric acid solution was used as the supporting electrolyte, and this was de-aerated by a method after Gilroy and Mayne (12). It was circulated by means of a Watson-Marlow flow inducer using an inert silicone rubber elastomer shielded with nitrogen (13). The electrolyte was held at 30 ± 0.5°C with a glass heat exchanger in the solution scrubbing vessel.

Hydrogen gas at atmospheric pressure was admitted as very small dispersed bubbles through a sintered glass disk in the solution line just before it entered the cell. In the methanol oxidation experiments a de-aerated stock solution of 1M methanol was added to the supporting electrolyte to give a concentration of 0.1M methanol. The solutions
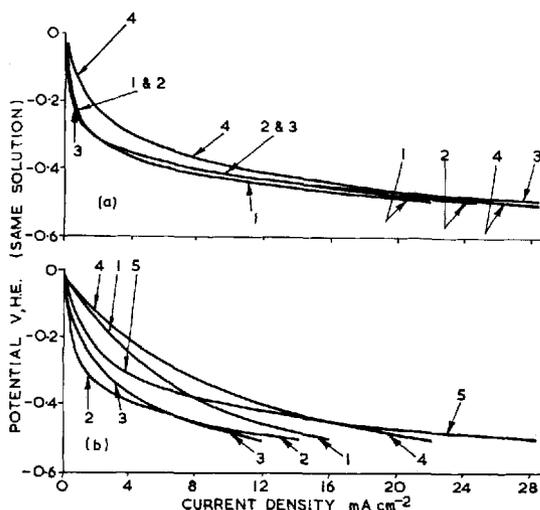
were then further de-aerated. The hydrogen line was disconnected for these latter experiments. Specimens (working electrodes) were further cleaned and activated in the cell during de-aeration by cycling between hydrogen and oxygen evolution as described elsewhere (1), to produce a phase-oxide free surface with a very low concentration of adsorbed impurities. As experiments were usually not carried out until half an hour later (to free solution from the gases evolved during activation) any hydrogen on the surface had time to desorb. This was usually confirmed by the open circuit potential attained before each run.

A stepwise voltametric technique was used for both experimental series. A Tacussel ASA.4 potentiostat impressed known potential on the working electrodes in 50 mV increments every 60 seconds. The currents corresponding to these potentials were recorded. For the experiments with hydrogen the potential ranges studied were 0 to +0.80 V, and 0 to −0.50 V. (All potentials quoted are versus the hydrogen electrode in the same solution.) For the anodic oxidation of methanol the range investigated was +0.40 to +1.40, back to +0.40 V.

A more detailed description of the experimental apparatus, procedure and techniques will be published elsewhere (14).

Results

(a) **Hydrogen Electrode:** The anodic polarisation characteristics of the two series of alloys in hydrogen saturated acid solution are compared with those of bright platinum in Fig. 1a and 1b. The results obtained are suitable for the *on load* evaluation of anodes for possible applications, because of the slow voltage "scanning" rate used. Curves have been drawn through the experimental points to facilitate the interpretation of the data and when this is done they appear similar to those already reported for platinum. There is first a range in which adsorbed hydrogen is anodically oxidised on bare metal, then, especially on the alloys, the current becomes
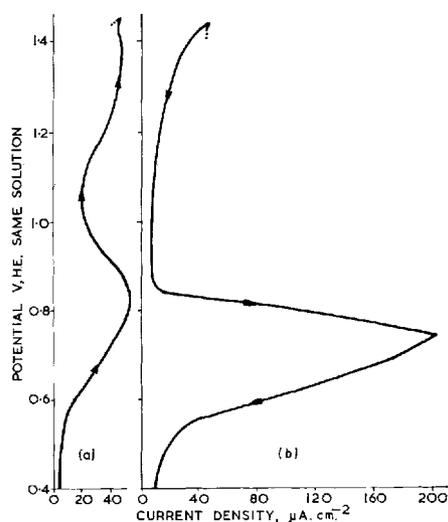

Fig. 3 Potentiodynamic anodic polarisation data for the electro-oxidation of 0.1 M methanol in de-aerated 1N sulphuric acid electrolyte at 30°C at bright platinum: (a) forward and (b) reverse scan: 50 mV steps every 60 seconds

limited, probably when the surface is less saturated with hydrogen molecules and atoms. At around +0.75 V, there is a rapid rise in current corresponding to the onset of rapid oxygen chemisorption and the oxidation of hydrogen molecules or atoms via the chemisorbed oxygen or (at the highest potentials) the low-potential oxide itself.

The Ru-Pt alloys, Fig. 1a, are a little more active than the Rh-Pt alloys, Fig. 1b, and both are less active than bright platinum.

The cathodic polarisation data are shown in Fig. 2a and 2b. In general, the alloys are less active for this reaction than is bright platinum; there is little variation in activity with change in composition of the Ru-Pt alloys (cf. Fig. 1a). Some of the Rh-Pt alloys are a little more active than bright platinum at low polarisations.

(b) **Methanol Electrode:** Fig. 3 shows curves obtained at bright platinum during the anodic oxidation of 0.1 M methanol in 1N sulphuric acid at 30°C. The impressed potential was increased in 50 mV intervals every 60 seconds from ca. +0.40 V, to ca. +1.40 V (Fig. 3a): then without pause was

decreased in similar intervals back to ca. +0.40 V (Fig. 3b). The experimental points have been joined to simplify the presentation. The lower peak corresponds to the fastest possible low-potential oxidation of methanol, as investigated by Pavela (15). The current then falls because of oxygen sorption and the beginning of oxide formation, and increases again with increase in potential, representing the oxidation of methanol on the oxidised surface. There may be cyclic formation of oxygen-containing layers (oxides)* followed by their reduction by methanol. In the reverse scan, Fig. 3b, more rapid low potential oxidation is evident, probably because the oxygen containing layers formed in the forward scan have been reduced to give a more active electrode surface. There is no high potential oxidation of methanol in this "scanning" direction.

Figs. 4 and 5 show the oxidation of methanol at the two series of alloys compared with that at bright platinum. The curves are similar in shape, and the peaks exist at approximately the same potentials suggesting that the alloying additions do not affect the overall oxidation mechanisms. The Rh-Pt alloys, Fig. 5, are not as active as bright platinum. The activities of the alloys of higher ruthenium content are of the same magnitude as platinum, Fig. 4.

Discussion

If the alloying addition used in this investigation produced heterogeneous and not homogeneous electrode surfaces then it would be tempting to explain the variations in activity according to the individual activities of the two components, as has been done with some success by Breiter for the adsorption and oxidation of hydrogen and methanol at Au-Pt alloys (6, 10).

*Even though the solutions were thoroughly de-aerated the formation of these layers is still possible because of the partial electrolysis of water.
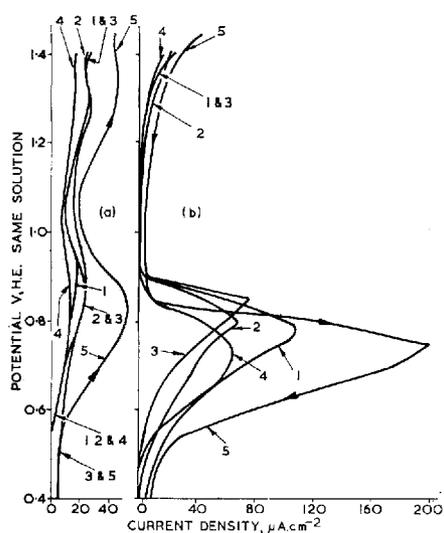
Fig. 4 Potentiodynamic anodic polarisation data for the electro-oxidation of methanol at the Ru-Pt alloy electrodes: same conditions as Fig. 3

1	1·6 at.% Ru	3	9·1 at.% Ru
2	3·7 at.% Ru	4	17·4 at.% Ru
		5	bright Pt

Fig. 5 Potentiodynamic anodic polarisation data for the electro-oxidation of methanol at the Rh-Pt alloy electrodes: same conditions as Fig. 3

| 1 | 1·9 at.% Rh | 3 | 9·3 at.% Rh |
| 2 | 3·8% at.% Rh | 4 | bright Pt |
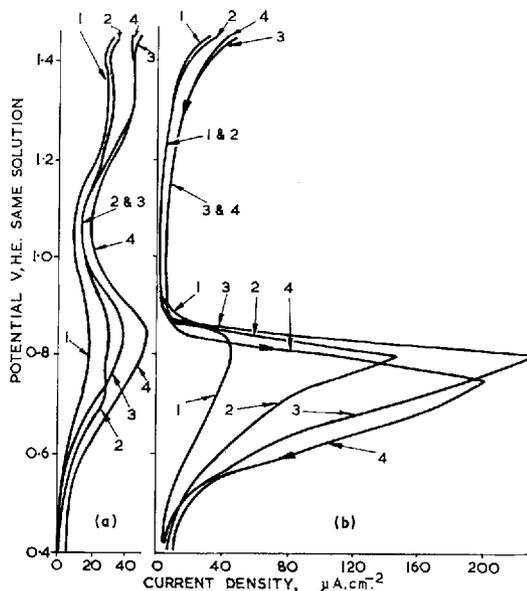
Because of the widely different electro-chemical properties of the two metals this was relatively simple, and he was able to show that the reactions only occurred at the active platinum-rich phase.

There is little available physical data on homogeneous platinum alloys, and even less electrochemical data. Correlation of activity with changes in lattice parameters, lattice strain energies, surface excess energies, work functions and properties dependent on these is thus difficult. It may well be that the addition of ruthenium (c.p.h. lattice) to platinum (f.c.c. lattice) introduces a greater lattice strain than the addition of rhodium (f.c.c. lattice); or it may change the lattice parameter in such a way as to affect the sorptive properties, and hence the oxidative properties are also altered. These arguments are purely hypothetical and only emphasise the need for systematic data on these alloy systems.

Conclusions

For the oxygen electrode reaction the alloys were (1), in the composition ranges studied, more active than bright platinum. The results presented here indicate that, with the exception of some Ru-Pt alloys, the activity for the hydrogen electrode reaction, and the electro-oxidation of methanol, is decreased with respect to platinum. Other results obtained at Pd-Pt, and Ir-Pt alloys are similar to those obtained at the Rh-Pt alloys, and will be described elsewhere (14).

References

1 E. W. Brooman and T. P. Hoar, *Platinum Metals Rev.*, 1965, **9**, 122

2 O. J. Adlhart and K. O. Heuer, "Fuel Cell Catalysis", Final Report, Contract No. DA 36–039, SC 90691, U.S. Army Electronics R & D Labs.

3 J. O'M. Bockris and H. Wroblowa, *J. Electroanal. Chem.*, 1964, **7**, 428

4 O. A. Petrii, *Dokl. Akad. Nauk SSSR*, 1965, **160**, 871

5 O. A. Petrii, B. I. Podlovchenko, A. N. Frumkin and Hira Lal, *J. Electroanal. Chem.*, 1965, **10**, 253

6 M. W. Breiter, *J. Phys. Chem.*, 1965, **69**, 3377

7 R. P. Buck, L. R. Griffith, R. T. Macdonald and M. J. Schlatter, Quarterly Reports 1–4, California Research Corp., Contract No. DA 49–186–502–ORD–929, Diamond Ordnance Fuze Labs., Ordnance Corps, Dept. of U.S. Army, Washington 25, D.C.

8 *Nature*, 1959, **183**, 39; *ibid.*, 1961, **192**, 649; *ibid.*, 1963, **197**, 1293; *Trans. Faraday Soc.*, 1960, **56**, 181, 363; *ibid.*, 1964, **60**, 2234; *Naturwiss.*, 1960, **47**, 177; *J. Electrochem. Soc.*, 1961, **108**, 473

9 I. P. Tverdovskii *et al.*, *Tr. Gosud. Inst. Prikl. Khim.*, 1960 (46), 221, 229, *ibid.*, 1962 (49), 183

10 M. W. Breiter, *Trans. Faraday Soc.*, 1965, **61**, 749; *Z. Elektrochem.*, 1965, **69**, 612

11 A. I. Lapteva, T. I. Borissova and M. G. Slinko, *Zh. Fiz. Khim.*, 1956, **30**, 61

12 D. Gilroy and J. E. O. Mayne, *J. Appl. Chem.*, 1962, **12**, 382

13 D. C. Mears and G. P. Rothwell, *J. Sci. Instrum.* 1965, **42**, 446

14 E. W. Brooman and T. P. Hoar, in the Press

15 T. O. Pavela, *Ann. Acad. Sci. Fennicae, Ser. A, II Chem.*, 1954, No. 59

Activated Platinum Electrodes for Fuel Cells

In the search for economical catalytic electrodes for fuel cells much effort has been expended in trying to achieve the maximum surface area and activity for a given amount of platinum. The use of very fine platinum "blacks" and the dispersion of platinum on charcoal or other types of carbon currently seem to hold the field. A new approach has now been suggested by two workers in the Direct Energy Conversion Operation of the General Electric Company, H. J. R. Maget and G. F. Wheeler, in a paper presented briefly at the Washington, D.C., meeting on fuel cells in 1964 but only just published (*Electrochem. Technol.*, 1966, **4**, (7–8), 412) describe the results of etching with aqueous hydrofluoric acid on first titanium and secondly titanium-tantalum alloys containing up to 10 per cent of platinum. This treatment produced activated surfaces with increased surface concentration of platinum, on of course a metallic conducting substrate reasonably resistant to surface oxidation, capable of supporting relatively large cathodic oxygen reduction currents in acid electrolytes. The latter eventually attacked titanium in the binary alloy but the ternary alloy was much more stable.