Platinum Metals in Electrochemistry

PAPERS AT THE MOSCOW CONFERENCE

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At the fourteenth meeting of the International Committee for Electrochemical Thermodynamics and Kinetics (CITCE) in Moscow in August interest in the platinum metals as "inert electrodes" continued to be manifest. Electrochemists have long used platinum as an "inert" basis for hydrogen, oxygen and halogen gas electrodes, as well as for many redox electrodes such as the ferrocyanide/ferricyanide couple. It proved to be very difficult to set up a reversible oxygen/hydroxyl-ion electrode on platinum; as long ago as 1933 I summarised the then scanty knowledge of this system, and gave experimental evidence (1) that the platinum acquires an oxide film that renders it a poor catalyst for the $O_2+2H_2O+4e \rightleftarrows 4OH^-$ change, as compared with the rather good catalytic action of unoxidised platinum for the hydrogen-electrode reaction, $2H^+ + 2e \rightleftarrows H_2$. It may be worth recalling that this evidence was, to say the least, somewhat sceptically received in "pure" electrochemical circles; to the pure all was pure—certainly the surface of platinum.

Today, with the greatly increased technical interest of "inert" platinum metal electrodes in such fields as fuel cells, chlorine and persalt production, and cathodic protection, a very intensive study of the behaviour of the platinum metals is being made. It is now generally agreed (2, 3, 4) that a platinum surface is far from being "inert", but can be oxidised under several kinds of conditions; only the form of the oxidation is in some cases uncertain.

At the Moscow meeting, much attention was paid to the influence of the surface state of platinum on its effectiveness as a basis for several technically important reactions. Thus V. S. Bagotzky pointed out that both oxygen reduction at a platinum cathode and organic oxidations at a platinum anode are inhibited by oxidation of the electrode surface. E. V. Kasatkin and A. A. Rakov showed that persulphate production at a platinum anode in cooled sulphuric acid solution is inhibited by oxidation of the anode; such oxidation is accompanied by an increase of the a.c. resistance and a decrease of the a.c. capacitance of the electrode, typical behaviour when very thin oxide films are formed. Also, the current-density changes at the platinum anode when its potential is fairly rapidly varied (the chronopotentiometric technique) depend on its pre-history. Likewise, Gonzalez, Capel-Boute and Decroly reported that the state of the platinum surface is important for sulphur dioxide anodic oxidation. M. W. Breiter, in one of a long series of papers, noted that the anodic oxidation of methanol becomes less easy on a series of platinum metals in the order Pt>Pd>Rh>Ir and that it is much reduced on oxidised surfaces. The anodic oxidation of methanol on oxidised and "bare" platinum was examined in detail by J. E. Oxley, G. K. Johnson and B. T. Buzalski of Leesona Moos Laboratories, New York, who found little or no reaction unless the platinum was "bare". Finally, S. Toschev and B. Mutaftschiew of the Bulgarian Academy of Science reported that mercury will electrodeposit around the ⟨111⟩ poles on platinum single crystals, but not around the ⟨100⟩, unless the initial oxide film is removed cathodically or by drastic pickling: then, nucleation at the ⟨100⟩ poles is even faster than at the ⟨111⟩. Evidently,

the surface of platinum may be vitally affected by oxidation.

Adsorbed anions and neutral molecules, as well as oxide films, markedly influence reaction rates on platinum electrodes by becoming adsorbed thereon. Thus, at Moscow, L. Müller and L. N. Nekrassov pointed out that the overall $O_2 \rightarrow OH^-$ change (which, as they demonstrated by rotating-disc experiments using the Frumkin "ring", goes through an intermediate H_2O_2 stage on platinum) is increasingly inhibited by anion adsorption in the order $SO_4^{2-} < Cl^- < Br^-$. Chu Yung-Chao reported that, in anodic persulphate formation, F^-, Cl^-, SCN^- and $CS(NH_2)_2$ have little effect on persulphate formation but markedly reduce the concomitant oxygen evolution; NH_4^+ also inhibits oxygen evolution and seems actually to stimulate persulphate formation. Breiter, in a further paper, gave evidence for increasingly strong adsorption of the halide ions in the order $Cl^- < Br^- < I^-$ and noted also that this type of adsorption inhibits both the formation and the reduction of the oxidised platinum surface, as well as inhibiting desired reactions on the platinum. Adsorption of I_2 rather than I_3^- or I^-, in a system containing all three entities, was discussed by R. A. Osteryoung, G. Lauer and F. C. Anson of the North American Aviation Science Centre, California.

With the intense interest in the surface state—especially with regard to oxidation and adsorption—of the platinum metals apparent in so many of the Moscow papers, it may be natural that the inner electronic structure of the metals received less attention than it deserves. However, J. Brenet of the University of Strasbourg pointed out that since the primary function of an inert basis for any electrode reaction is to act as an electron donor or acceptor, the distribution of electron energy levels in the inert basis must clearly have profound significance.

References

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2 T. P. Hoar .. .. *Proc.* Eighth Meeting CITCE, Madrid 1956, p. 439. Butterworths, London (1958)
3 J. O'M. Bockris and A. M. K. S. Huq .. *Proc. Roy. Soc.*, 1956 **A237**, 227
4 A. Damjanovic and J. O'M. Bockris .. Private communication, 1963

The CITCE papers will be published shortly in *Electrochimica Acta*

A High Temperature Waveguide Termination

PLATINUM AS BOTH GUIDE AND HEATING ELEMENT

In measuring the output from various noise sources by means of a radiometer, a standard noise source is required to calibrate the instrument. This generally takes the form of a hot load, i.e. a termination of known temperature connected to the radiometer by a suitably matched waveguide. For most microwave receivers, a load immersed in boiling water can be used.

Because of the high noise level of microwave receivers in the short millimetric band, a relatively high output is also necessary from the standard noise source if accurate calibration of the radiometer and hence the receiver is to be achieved. This makes it necessary to operate the hot load at an extremely high temperature. In a recent paper, Q. V. Davis of the Royal Radar Establishment, Great Malvern, describes (*J. Sci. Instr.*, 1963, **40**, (11), 524) a hot load that has been developed for operation at 1250°C. This load comprises a one inch long, conically tapered rod of pyrophyllite operating at this temperature in a heated circular waveguide.

In the construction of this waveguide assembly platinum sheet 0.005 inch thick is formed around a mandrel to make the round waveguide 0.143 inch in diameter, the ends of the sheet being extended parallel to each other to copper blocks. The platinum is resistance heated by a current of 500 amp passed through the copper blocks. The whole assembly is enclosed in laminated asbestos to reduce heat losses. J. G. W.