

Activated Platinum Surfaces

ELECTROCHEMICAL STUDIES OF TREATED ELECTRODES

Overvoltage effects at platinum electrodes may often be reduced by "activating" the surfaces by alternate oxidising and reducing treatments. The "activity" so produced soon deteriorates, and the phenomena are now ascribed to a thin unstable layer of disoriented platinum atoms which are formed on the surface and then rapidly reorient themselves.

It is well recognised that the behaviour of a pure platinum electrode in many electrolytes is influenced in a subtle and imperfectly understood manner by the character of the platinum surface. In particular, the overpotential that must be applied in an electrochemical process may be greater for a clean smooth reflecting platinum surface than for one that has been first oxidised (generally by the action of anodically liberated oxygen in an electrolytic cell) and subsequently reduced either electrochemically or chemically.

The oxidising treatment is simple and there is general agreement that it can be quickly achieved in a reproducible manner. The surface of a platinum electrode is readily oxidised by introducing the specimen as anode in a cell containing an electrolyte such as pure dilute sulphuric acid and passing a current of about 25 milliamperes for about 5 seconds. A covering of oxide is immediately formed and rapidly builds up to a remarkably steady maximum. A completely oxidised platinum electrode has been calculated to have 1.3×10^{-8} micro equivalents of platinum oxide per square centimetre of surface area.

Among the earlier workers who have studied activated platinum surfaces J. J. Lingane (1) is particularly associated with the view that their special characteristics are due to the retention after reduction of a small quantity of oxide in the coating. Lingane assumed that the residual oxide was reduced with much more difficulty than the majority of the platinum oxide. Later F. C. Anson (2) presented evidence which indicated that the

small wave which they both noted at the foot of chronopotentiograms is due not to platinum oxide but to the presence of freshly formed finely divided platinum metal, the results of alternately oxidising and reducing a platinum electrode. Anson emphasised that a layer of finely divided platinum so produced must be extremely thin. If such a layer is present it must surely increase the true surface area, but he points out that the effect of this will be observable only if the depths of the hills and valleys are of the order of the diffusion layer in thickness. It is evident that their depths are not so great as this since no effect attributable to an increase in surface area has yet been noticed.

A Japanese investigator, S. Shibota (3), has independently suggested that when an electrode is oxidised and then reduced a thin layer of "unstable platinum atoms" may be formed. The novel feature of Shibota's proposal is that he supposes that these unstable surface atoms, which account for the high activity of the treated platinum surface, quite rapidly aggregate and presumably start to recrystallise at ambient temperatures. This conception has been developed in order to explain the large drop in activity of an activated platinum surface if it is allowed to remain for a short time in a completely oxygen-free pure electrolyte.

Two investigators at the University of California, William G. French and Theodore Kuwana (4), have now studied more intensively some of the consequences of this view, which they have accepted to the stage

of introducing a new symbol, Pt*, which they use to designate an "activated" or "platinised" surface.

In order to establish whether the film formed by activation is metallic platinum (rather than a mixture of metal and oxide), the approach which they adopted was to measure in coulombs the energy consumed first in the oxidation of the platinum and then in the reduction of the platinum oxide. A special quartz cell was used for the chronopotentiometric measurements, and elaborate precautions were taken to degas the cell and its contents before each test and to guard against any leakage of air.

Cyclic Activation

The platinum surfaces were activated by cycling clean platinum foil or wire electrodes between 0 and 1.00 volt in 1*F* H₂SO₄ or between -0.50 and +0.50 volt in 1*F* Na₂CO₃ solution that had previously been degassed. After ten to fifteen cycles a steady state was reached. The shape of the polarisation curves was on the whole reproducible, and was independent of speed of the scan rate between 0.13 and 0.195 volt per second.

It may be helpful to note that the nomenclature "1*F* H₂SO₄", which appears to be increasingly favoured by many chemists in America, probably refers to a concentration of 1 formula gram weight of sulphuric acid in 1 kilogram of solution. There seems to be no general agreement here, however, and in some instances the expression is used to refer to a solution of 1 formula gram weight with 1 kilogram of water.

A freshly activated platinum surface, it was confirmed, behaves in a remarkable and characteristic manner when used as a cathode in either dilute sulphuric acid or dilute sodium carbonate solutions. As the potential is increased, there is a sudden surge of current which then falls away just before the voltage is reached at which hydrogen is evolved. This is the chronopotentiometric prewave recognised by several previous workers.

By using a somewhat complex cycling technique, French and Kuwana have been successful in measuring the total energy involved both in oxidising and in reducing the oxide films and show that the average ratio is essentially unity – the average of a number of tests in both solutions being reported as 0.970 ± 0.050 . This seems to dispose of the view that the reduced surface layer contains residual oxide.

Deterioration of Activity

Further tests were made to determine the rate at which an activated platinum surface deteriorates when allowed to remain in a pure and thoroughly degassed solution. Here, again, a cycling technique was used, and it is shown by a number of careful tests that the return to a more stable thermodynamic state is very rapid. The average half-life of the activated surface state is recorded as of the order of 46 minutes only.

All these results lead the authors to the conclusion that on the surface of an activated platinum electrode there is a "truly dislocated" layer of metal, either atomic in form or consisting of very small crystals. On standing, these are thought to migrate by surface movements and by reorientation to fit into a larger crystalline lattice below.

In many respects this somewhat unsophisticated view of the nature of the surface of an activated platinum electrode invites comparison with the conception of amorphous layers fashionable half a century ago. Shibota in Tokyo in 1963 may seem a far cry from Sir George Beilby in his garden workshop in Glasgow in 1903; but there are interesting parallels between the mental approach of each, working in their different fields, to the surface mobility of metal atoms.

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References

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