

# Platinum Metals Predominate as Electrocatalysts in Fuel Cells

## PAPERS AT LONDON AND BRUSSELS CONFERENCES

Developments in fuel cell technology were extensively discussed at two large meetings held recently, one in London by the American Institute of Chemical Engineers jointly with the Institution of Chemical Engineers and the other in Brussels by the Société d'Etudes de Recherches et d'Applications pour l'Industrie (SERAI). This note reviews some of the more important papers presented.

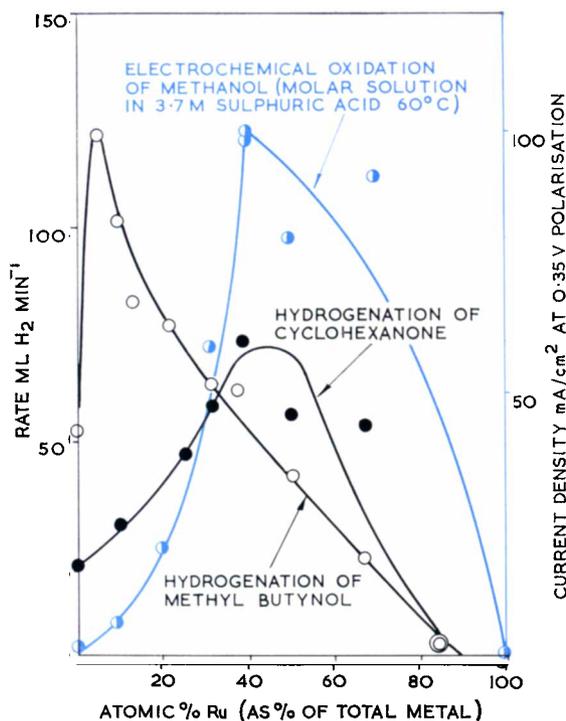
At both meetings a high proportion of the contributions dealing with cell electrodes or electrocatalytic studies related to structures containing platinum or other platinum group metals. It is widely recognised among the many research workers in this field throughout numerous countries that the platinum metals provide the best electrocatalysts for fuel cells designed to operate at or near ambient temperatures and to use simple hydrocarbon or partially oxygenated hydrocarbon fuels. The principal problem that remains is to increase the effectiveness of the platinum metal electrocatalyst so as to obtain more economic utilisation of the metal than has been achieved with the most promising fuel electrodes devised to date.

A number of ways to achieve this end are being investigated. All of them take into account that the nature of the platinum metal catalyst surface is of paramount importance, and research is aimed either at extending it or at modifying it by the introduction of alloying constituents. While it is necessary to obtain a significant increase in activity, this must be brought about without any reduction in the corrosion resistance of the catalyst, or of its electrical conductivity.

A paper illustrating this approach was presented by Dr C. E. Heath and described the work of the Esso Research and Engineer-

ing Co, Linden, N.J., in modifying platinum catalysts used in a methanol-air fuel cell (1). In this work, the platinum surface was altered by alloy formation or metal oxide inclusion to increase its area, disturb the electronic structure of the metal, introduce surface defects, or to form an immobile redox couple. The catalysts were prepared by the co-reduction of aqueous solutions of chloroplatinic acid and metal salts with sodium borohydride; alloy powders of small particle size were produced using gold, iridium, nickel, copper, cobalt and iron as alloying additives. Not all alloys gave increases in activities, but significant improvements were given, in particular, by iron and gold at current densities up to 50 mA/cm<sup>2</sup>. At higher current densities pure platinum appeared superior. Substantially better results were obtained when molybdenum or ruthenium were incorporated in the platinum catalyst surface. The increased activity is thought to be due to the formation of a redox couple on the surface, Mo<sup>5+</sup>/Mo<sup>6+</sup> in the case of molybdenum, ruthenium dioxide in the case of ruthenium. The activities of ruthenium-platinum catalysts were particularly sensitive to composition. Increasing the ruthenium content from 10 to 40 atomic per cent increased the current density at 0.35 volt by over sixteenfold. Higher ruthenium contents caused a reduction in activity, and ruthenium alone lacks any appreciable activity.

These results are shown in the figure overpage and accord well with work carried out by Bond and Webster in the Johnson Matthey Research Laboratories on ruthenium-platinum mixed oxides used in liquid-phase hydrogenation reactions (2). In the latter work ruthenium-platinum oxides, co-produced, and



Graph showing the effects of varying the ruthenium content of ruthenium-platinum catalysts in the electrochemical oxidation of methanol as demonstrated by Heath and in two liquid phase hydrogenation reactions (Bond and Webster)

with varying ruthenium-platinum compositions, were compared with pure platinum oxide (Adams catalyst) in the hydrogenation of a series of unsaturated compounds. As in the electrocatalytic oxidation reactions, substantial increases in activity over that of pure platinum were observed with increasing ruthenium content—maxima in the activity/composition curves occurring in each instance and varying in position with the particular reaction examined. These results are reproduced in the graph for comparison with those presented by Heath.

In both the hydrogenation and the electrocatalytic oxidation reactions the enhanced activities are thought to result from inherent catalytic effects rather than from mere increases in catalyst surface area. The latter had shown increases, but these were not sufficiently high to explain fully the observed

increments in catalyst activity. A study of the electrodes using cyclic voltammetry in the absence of fuel revealed major differences between the electrochemical characteristics of platinum and ruthenium-platinum catalysts. Effects associated with platinum surface oxidation were greatly enhanced by the addition of ruthenium, and this surface oxide is postulated to participate in the electrochemical oxidation of the fuel. In terms of a surface redox approach to fuel cell catalysis, it would be the ruthenium oxide—the redox entity—that is electrochemically formed, and then chemically reduced by the fuel; the process is continuously repeated while the electrode is in operation.

A hydrogen-oxygen fuel cell that produces its hydrogen requirements by *in-situ* steam reforming of methanol and subsequent diffusion of the hydrogen through a silver-palladium membrane which simultaneously acts as the fuel electrode was described by Hartner and Vertes (3). In this cell, developed by the Leeson Moos Laboratories, Great Neck, N.Y., methanol and water vapour react in a catalyst compartment within the fuel cell to produce a mixture of carbon dioxide and hydrogen. The latter is continuously removed from the reaction zone by diffusion through a silver-palladium alloy membrane at about 200°C. The membrane also acts as the anode in a cell using KOH electrolyte and a nickel oxygen electrode. Power densities up to 150 mW/cm<sup>2</sup> at 0.94 volt have been achieved with thermal and electrochemical efficiencies of 90 and 85 per cent respectively.

A review of problems associated with the construction of electrodes and cells was presented by K. R. Williams and J. W. Pearson, of "Shell" Research, who described the use of plastics in several cells that employ platinum metal electrocatalysts (4). Dr H. A. Liebhafsky, of General Electric, Schenectady, N.Y., reviewed a number of research problems that impede fuel cell development, including the need to establish a firm understanding of the nature and function of platinum metal electrocatalysts (5).

T. J. Gray and his co-workers at Alfred University, Alfred, N.Y., presented the results of a detailed study of the gold-palladium and palladium-platinum electrocatalyst systems, and demonstrated the importance of unpaired d-electrons in the catalyst. This work was carried out in conjunction with galvanostatic measurements that elucidated the nature of the electrical double layer and the adsorbed species on an electrode in operation (6).

A. Küssner, of Siemens-Schuckert, described the irreversible changes observed in silver-palladium alloys when the latter were repeatedly charged with hydrogen and operated as fuel anodes. Failure of such electrodes after extensive and repetitive use was attributed, in part, to metallurgical changes resembling fatigue resulting from cyclic mechanical loading. Hardening the alloys and increasing their mechanical strength by the addition, for example, of boron has been shown to overcome some of these difficulties (7).

Numerous other papers presented at the Brussels meeting dealt with the applications of the platinum metals as fuel cell electrocatalysts. C. Berger described the use of platinum on ion-exchange membranes in hydrocarbon fuel cells (8). A paper by Professor Bianchi outlined the construction of a cell to operate on the oxidation of hydrogen by chlorine with an aqueous 20 per cent hydrochloric acid electrolyte (9). In this cell, the hydrogen anode consisted of a graphite structure on which platinum black was deposited. The electrode could operate satisfactorily at current densities up to 100 mA/cm<sup>2</sup>, and when coupled with a graphite chlorine electrode current densities up to 50 mA/cm<sup>2</sup> at 1 volt were achieved with thermal efficiencies exceeding 80 per cent.

Raney-platinum catalysts were used in cells to operate with methane, ethane and propane in 3N sulphuric acid solutions, and were described by H. Binder and his colleagues at Battelle, Frankfurt (10). In these cells it was also found that ethylene would react to yield ethane at the anode. The electrolyte,

however, proved useful only up to 3-molar concentrations; at higher concentrations some of the sulphuric acid was reduced. Experiments carried out under comparable reaction but with phosphoric acid electrolyte demonstrated that the latter was significantly less useful. With propane fuel, for example, power outputs could not be achieved at 155°C that were easily obtained at 100°C using the 3N sulphuric acid electrolyte. Mme Bloch and her co-workers at the Institut Français du Pétrole presented a paper describing studies aimed at producing optimum performance platinum black electrodes for use in a methanol fuel cell (11). In this work platinum was electrolytically and chemically deposited on a variety of supports by different methods and the resulting electrode activity investigated by plotting current density/potential curves.

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#### References

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