

The Platinum Metals in Fuel Cells

ECONOMIC FACTORS IN THE CHOICE OF ELECTROCATALYSTS

Much effort has been expended in recent years on the development of low-temperature fuel cells. The principal obstacle yet to be overcome is the selection of electrocatalysts whose activity and reliability is so high, whose life is so long and whose cost is so low that power can be generated at an economic value.

Electrochemical Society Symposium

The abstracts of the papers presented to the Battery Division of the Electrochemical Society at their autumn meeting in Washington in October indicate the extent to which attention is concentrated on the metals of the platinum group. Of the thirty-four papers presented, no less than twenty-four refer to studies, mainly of a fundamental electrochemical character, of the use of these metals and their alloys.

The high inherent cost of the platinum metals requires that they be employed with the utmost efficiency, and much work is directed to this end. Among the techniques reported are the use of Raney platinum by Binder, Köhling and Sandstede of Battelle, Frankfurt, and by Maget and Wheeler of General Electric, and of charcoal-supported metals adhering to porous nickel (Clark, Darland and Kordesch of Union Carbide), or to a waterproofed acrylic paper (Barber and Woodberry of American Cyanamid). Effort is divided comparably between investigations on hydrocarbon fuels and partially-oxygenated fuels, especially methanol. The former are economically attractive, but their oxidation requires vigorous conditions which are generally strongly acidic. Nitrogenous fuels such as hydrazine also command attention.

Three papers in particular focused attention on the choice of the most appropriate metal or alloy to act as electrocatalyst for each par-

ticular fuel. Grimes, Murray and Spengler of Allis Chalmers reported studies of the use of platinum-palladium mixtures: because of the lower cost of palladium, its partial substitution for platinum is attractive provided no loss of efficiency results. In fact mixtures of the two metals generally show efficiencies greater than those of either metal alone, optimum Pt: Pd ratios being 1:3 for hydrogen and methanol, but 10:1 for ammonia. Pure palladium has the highest efficiency when hydrazine is used as fuel.

Oswin, of Leeson Moos Laboratories, discussed his reasons for believing that no better catalyst than platinum can be found for use in fuel cells. These may be summarised as follows: (i) the heat of chemisorption of hydrogen is low, the Pt-H bonds are weak and the absorbed H atoms are mobile; (ii) platinum is also able to dissociate N-H and C-H bonds, which processes are important in the electro-oxidation of ammonia, hydrazine and saturated hydrocarbons; (iii) significant coverages by weakly-bonded OH radicals encourage surface oxidation reactions; (iv) the Pt=O group is formed only at high potentials and is readily reduced back to Pt-OH, and (v) platinum is resistant to corrosion and dissolution in almost all electrolytes that are likely to be used.

Holt and Horowitz of Esso Research and Engineering stated that alloys of platinum with either gold, nickel, copper or cobalt prepared by reducing aqueous solutions of their salts with sodium borohydride all gave perfectly linear Tafel plots when tested in acidic methanol at 60°C. The slopes of these plots, however, varied quite widely (50 to 90 mV per decade), although the electrocatalytic activity of the alloys was surprisingly constant. The phenomenon is likened to the compensation effect in heterogeneous catalysis. Atten-

tion is drawn to the greater activity of ruthenium-platinum and molybdenum-platinum alloys in comparison with pure platinum for methanol oxidation.

In a paper from the General Electric Research Laboratories, Cairns and Holm reported measurements on the oxidation of propane using aqueous caesium carbonate as electrolyte at about 130°C, and stated that equivalent performances were found with platinum, palladium and ruthenium-platinum alloys, although this suggests that the electrocatalytic reaction was not rate-limiting.

Fourth International Symposium on Batteries

Recent developments in the technologies of electrical energy generation and storage were also discussed at the Fourth International Symposium on Batteries, organised by the Inter-Departmental Committee on Batteries at Brighton. Among the papers that were presented concerning the direct conversion of chemical energy to electricity in fuel cells, a number dealt with the role of the platinum metals as catalysts in the construction of electrodes for use in a range of systems.

A methanol/air fuel cell with an alkaline electrolyte and platinum-impregnated fuel electrodes has been brought to the field-trial stage by Brown, Boveri & Co, Baden, Switzerland, and was described by Vielstich. The cell was developed for marine signalling devices and employed about 5 mg platinum per cm² of electrode surface area. Single cells in laboratory tests gave continuous discharges exceeding 10,000 hours and conversion efficiencies around 145 A-hr/mol methanol (compared with a theoretical efficiency of approximately 160 A-hr/mol).

Some of the problems encountered in the development of multiple units of low temperature fuel cells were described by Williams, Pearson and Gressler of "Shell" Research. This paper gave considerable data on the mechanical construction of a small hydrogen/oxygen fuel battery employing

noble metal electrodes, and referred also to methanol and hydrazine fuel cell systems.

A hydrogen/oxygen cell system using an acid electrolyte was described by Ruetschi and his co-workers. This cell employed microporous gas-diffusion electrodes consisting of platinum-activated titanium for the oxygen reduction, and platinum-activated tantalum for hydrogen oxidation in 3-molar sulphuric acid. A particular feature of this study was the establishment of these metals as the most corrosion resistant electrode substrate under the chosen operating conditions.

There were three contributions from the U.S.S.R. Professor A. N. Frumkin described results obtained with ruthenium-platinum mixtures co-deposited electrolytically on to nickel substrates when these were employed as fuel electrodes in a methanol/air cell using a sulphuric acid electrolyte. Marked improvements over pure platinum activation were observed, with an optimum ruthenium:platinum ratio around 1:9 in the deposit. The two other papers examined at some length the mechanisms occurring at fuel cell electrodes, in particular the chemisorption of ethane and ethylene on platinum surfaces and the ionisation kinetics of hydrogen and oxygen on platinum, palladium and silver palladium foil electrodes in alkaline solution.

The Symposium papers will be published in full, with discussions, by the Pergamon Press Limited, Oxford.

Conclusion

It appears inevitable that the present massive research and development effort must lead to the economic use of the platinum metals or their alloys as fuel cell electrocatalysts on a considerable scale. It is of interest that ruthenium-platinum alloys are mentioned three times in the contributions here reviewed, while their extraordinary catalytic properties are the subject of another article in this issue of *Platinum Metals Review*.

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