

# Catalysts for Fuel Cell Applications

## FUTURE AVAILABILITY AND MANAGEMENT OF PLATINUM

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*Phosphoric acid fuel cells are approaching commercial reality, especially in the United States of America and Japan. Without exception they are catalysed by platinum-containing catalysts; in view of the probable future development of such cells and the predicted size of the market for them it is necessary to consider the availability of platinum for this purpose. This article is based, in part, upon a paper presented at an international workshop on trends in research and applications of fuel cells, which was organised by Unesco in co-operation with the Commission of the European Communities, held at Ravello, Italy, during June. It examines the scale of this potential requirement against a background of existing applications of the metal and the way in which it will be used and recycled. Having discussed some recent developments it concludes that supplies will be adequate to meet even the most optimistic projections of fuel cell market penetration.*

Most of the electrical power used today is generated by alternators driven by steam turbines. The steam is produced in boilers which may be heated by the combustion of a variety of fossil fuels such as coal or hydrocarbons, or by nuclear fission. When converting fuel into heat, heat into steam, and steam into electricity, each process involves efficiency losses. According to the Carnot cycle (1) the maximum theoretical efficiency of a thermal power station is about 66 per cent, but in practice the maximum efficiencies achieved by even the largest and most modern plants are only about 36 per cent. It is also significant that efficiency is equated to size, since it is simple to transmit electrical power; however, it is very difficult to distribute heat in a useful form. A 2000 MW power station will produce upwards of 3500 MW of heat, which is generally discharged wastefully to the atmosphere or the sea, for it would clearly be impractical to pipe perhaps 35 kW of heat to each of 100,000 homes.

Much of the current incentive for fuel cell development is thus the possibility of constructing comparatively small units giving upwards of

38 per cent fuel to bus-bar efficiency. The deployment of small modular units would enable relatively minor increases in demand for electrical power, which would not justify the construction of a conventional power station, to be met rapidly. It would also increase the possibility of utilising by-product heat for industrial processes or for local domestic consumers.

A fuel cell converts fuel (usually hydrogen) and oxidant directly to electricity, and, because it is an engine rather than a battery, it will continue to operate as long as fuel is fed to it. It is also inherently safer than a battery, since fuel and oxidant are stored separately and only combined at the reaction sites. Although the principle has been known since the middle of the last century (2, 3) it is only during the past twenty years that intense effort has resulted in the development of commercially oriented systems. The initial requirement was for light-weight and highly efficient electric power generators for space applications.

Early space-craft fuel cells, such as the Apollo and Gemini units, used alkaline



**Fig. 1** The 4.5 MW fuel cell power plant in Tokyo was constructed by United Technologies Corporation and installed by Toshiba in less than three years. Since April 1983 it has been operated at between 25 and 100 per cent of rated output. The power section, in the foreground, contains platinum catalysts supplied by Johnson Matthey

(potassium hydroxide) and solid ion exchange membrane electrolytes. For larger scale terrestrial systems phosphoric acid electrolyte has been widely adopted. Although this acid has several drawbacks, including poor conductivity and being highly corrosive, it does have the advantages of good stability and very low vapour pressure.

Phosphoric acid electrolyte avoids problems of carbonation of the cathode when using atmospheric air, and by operating the cell at temperatures above 150°C it is possible to use hydrogen contaminated with carbon dioxide and carbon monoxide derived directly from steam reformed hydrocarbons. By generating hydrogen immediately adjacent to the fuel cell in an integrated system, the difficulties associated with transporting large quantities of gas are eliminated.

Fuel cell systems therefore consist of three principal components: a reformer to convert natural gas or liquid hydrocarbons to hydrogen, the fuel cell power section where the conversion of chemical fuel into electrical energy takes

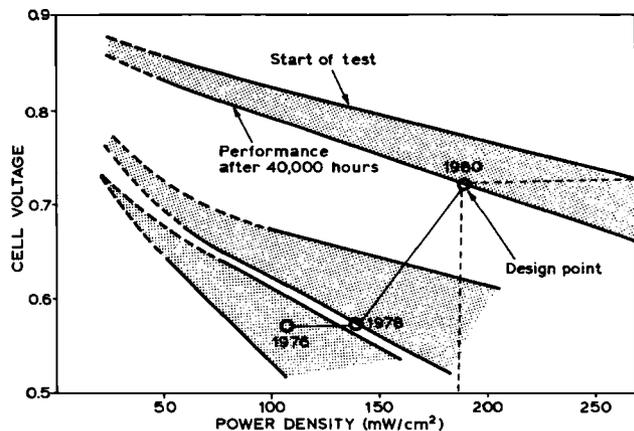
place on platinum catalysed electrodes connected in series to form stacks, and an inverter to convert the DC power produced into alternating current. This can then be transformed into voltages suitable for distribution and use by the consumer.

### **The Current Status of Phosphoric Acid Fuel Cells**

These generators are being considered mainly for two types of application. The first is for electric utility plants of 5 to 30 MW output suitable for localised areas of population, possibly with piped heat distribution forming a Combined Heat and Power (CHP) system. Secondly, individual buildings and factories can be supplied with power and heat from units of 200 to 500 kW. Two user groups have been formed from electric and gas utilities in the U.S.A. and Japan to evaluate and demonstrate the two systems.

Two 4.5 MW powerplants have been constructed by United Technologies Corporation (U.S.A.), one in Manhattan, New York, and the

**Fig. 2** Over the past decade there has been a noteworthy improvement in the performance of phosphoric acid fuel cells. The data presented here relate to United Technologies Corporation fuel cells (from Ref. 6)



other in Goi, Tokyo, for Tokyo Electric Power Company (TEPCO). The New York installation suffered from a series of delays resulting from problems in obtaining approval for installation and from various teething troubles. Prolonged storage of the power section caused it to deteriorate, and it is no longer intended to commission this plant. The Tokyo installation was completed in 1982, two years after the start of construction, first producing power in April 1983. It has since been operated extensively at between 25 and 100 per cent of full power.

The success of the Tokyo plant, which is shown in Figure 1, has encouraged the development of two more advanced systems in the United States. The first is an 11 MW plant being developed by United Technologies, and the second is a 7.5 MW system being evolved by Westinghouse.

United Technologies Corporation and Toshiba have recently announced the formation of a joint company, International Fuel Cells Corporation, which initially will construct three 11 MW plants by 1989, and subsequently a further twenty semicommercial units by 1992. In Japan, the Ministry of International Trade and Industry (MITI) are sponsoring the development of 1 MW systems by 1986. Two consortia, namely Hitachi/Toshiba and Mitsubishi/Fuji Electric, are competing to construct these, in collaboration with various electric utilities.

At present various American and Japanese

gas utilities are sponsoring a demonstration of some 40 units each with an output of 40 kW, running on reformed natural gas. These have been installed in hotels, swimming pools and telephone exchanges. The units have been run for periods of up to a year, giving electrical efficiencies of 40 per cent and an overall efficiency of 80 per cent when recovered heat is included.

Currently, the Gas Research Institute, representing the utilities, is sponsoring development of units of 200 to 400 kW size (5).

### Future Platinum Requirements

The major factor influencing the market size of fuel cells is their capital cost. The various benefits such as efficiency, modular construction and freedom from pollution would, however, create a vast market provided that costs could be brought down. Present indications are that they become an economic proposition for electric power utilities at about \$1000/kW, or \$850 to \$1250/kW for the gas utilities' applications. With mass production, manufacturing costs as low as \$350/kW have been predicted. At an installed cost of \$600/kW, the electric utilities in the United States forecast an upper requirement of 45,000 MW to the year 2005. If we assume that all this capacity is implemented during the 15 years 1990 to 2005, an average of 3000 MW per year is required.

In Japan, the MITI announced in December

1984 that the requirement for the Japanese market during this period could amount to 35,000 MW, comprising 25,000 MW for power utilities and 10,000 MW for small combined heat and power units. This would average a further 2333 MW per annum of added capacity. The combined needs for the U.S.A. and Japan therefore amount to 5333 MW of new capacity each year for the fifteen-year period. If we assume that the rest of the world will require an equal capacity increase, the total becomes 10,666 MW per annum. The question arises whether the world reserves of platinum will meet this requirement.

The current state of the art, see Figure 2, indicates that a realistic performance figure is 700 mV at 200 mA per square centimetre of cell area for a phosphoric acid fuel cell (6). Generally accepted platinum loadings for the anode and cathode are 0.25 mg/cm<sup>2</sup> and 0.5 mg/cm<sup>2</sup>, respectively, giving a requirement of 5.36 kg of platinum per megawatt of power. The maximum forecast world demand for fuel cells (10,666 MW) therefore corresponds to a demand for 57.2 tonnes of platinum per annum.

Current world production is approximately 80.5 tonnes, of which 24 tonnes (30%) is used in the jewellery trade, 22.6 tonnes (28%) is used in car exhaust pollution control, 19.3 tonnes (24%) is used in chemicals, glass, petroleum and electrical products, and 5.6 tonnes (7%) is used for investment. Another 8.9 tonnes is used for a variety of other industrial purposes. Although the possible requirement for fuel cells is very large, the platinum industry has historically responded to changes in demand very rapidly. For example, the market for pollution control catalysts grew up within a few years and the supplies rose to meet this requirement. Estimated reserves in the Merensky Reef in South Africa alone amount to 300 years' supply at current extraction rates.

Hence, should fuel cells achieve the most optimistic predictions for implementation it should be wholly feasible to meet the increased demand for platinum for this purpose.

The 11 MW plants currently under construction are quoted as having an efficiency of 8300

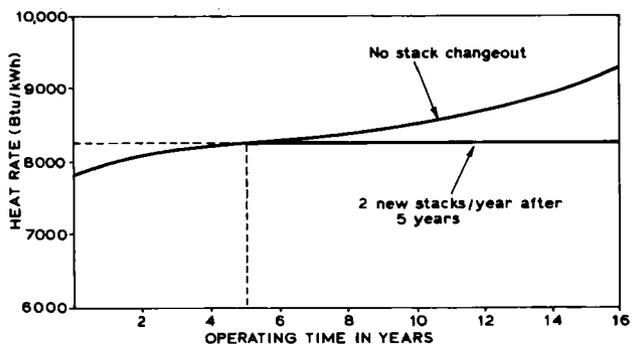
Btu/kWh (7). When, after five years of use, efficiency begins to fall below this level the overall performance of the plants can be maintained by periodically replacing 10 per cent of the stacks during routine maintenance, see Figure 3 (8). It is anticipated that the noble metal content of the cells will be recovered and re-used; indeed the noble metal industry already has a highly effective recycling system. Recovery of the platinum is an added benefit as it reduces the overall cost of fuel cell power plant operation. Considerable quantities of fuel cell catalysts have already been used to develop manufacturing techniques, and recovery of scrap is completely feasible.

### Transport Applications for Fuel Cells

It has long been recognised that electrically propelled vehicles offer numerous benefits in terms of quietness and freedom from pollution. A number of studies are in progress to determine the type of fuel cell most suitable as a source of motive power for such vehicles. The Los Alamos Laboratories have compared phosphoric acid, superacid and solid polymer electrolyte (SPE) systems with alkaline electrolyte cells, and some of the essential requirements for electrical vehicle powerplants have been listed by Gonzalez and Srinivasan (9). These include a high power density (greater than 130 mW/cm<sup>2</sup>) high efficiency (better than 30 per cent), fast start-up time (less than 5 minutes), fast response to transient loads, and a lifetime of 5000 to 6000 hours. Srinivasan has postulated the use of methanol or ethanol as the most viable fuel for mobile applications (6). In this case, the alcohol is reformed to provide hydrogen as fuel for the cell, using phosphoric acid cells as the powerplant. Shell and Alstom-Exxon (10) have also developed direct methanol fuel cells where the liquid fuel is consumed at the anode.

The Elenco consortium in Belgium and Holland has developed alkaline fuel cells running on pure hydrogen and atmospheric air (11). Elenco has now developed a research vehicle, a Volkswagen Microbus, powered by

**Fig. 3** As fuel cell stacks age their conversion efficiency tends to decrease. Correspondingly the heat rate, that is the ratio of the calorific content of the fuel input to the electrical energy generated, rises. By renewing two of the twenty stacks in an 11 MW fuel cell annually the rated efficiency of 8300 Btu/kWh can be maintained



fuel cells with compressed hydrogen stored in cylinders. At present, there is a surplus of hydrogen from existing chlorine production plants which is presently burned purely for its calorific value, and which would suit Elenco's requirements.

A recent Canadian survey indicates that by the year 2000 hydrogen could be generated economically by water electrolysis using hydroelectric or nuclear power (6).

Elenco have selected platinum as catalyst, their extensive experience having indicated that very low loadings of noble metals are more economic than higher loadings of base metals or silver, and offer improved durability.

In France, Alsthom/Atlantique, financially supported by Occidental Chemical Corporation, is developing an alkaline fuel cell. The stack is based on low-cost conducting and non-conducting plastics, mainly polypropylene, and uses a platinum on carbon electrocatalyst (12). The system is also being evaluated using acid electrolytes.

### Catalyst Properties

In order to improve phosphoric acid fuel cell performance, there has been a progressive increase in operating temperatures and pressures. Initially, cells were run at about 150°C and atmospheric pressure. Currently, depending on the manufacturer, cell temperatures range up to about 205°C and pressures up to 8.2 atmospheres. Some idea of these effects in terms of performance improvements is shown in Figure 2.

This has resulted in higher voltages being reached at the cathode, not only at normal operating currents, but particularly under "no load" conditions. In turn, there is a requirement for catalysts that would be resistant to corrosion at ever-increasing temperatures in phosphoric acid under oxidising conditions.

Early fuel cells used platinum black catalysts, that is, highly dispersed metal crystallites. These gave good activities, but required rather high metal loadings. The maximum metal area, resulting from highly subdividing the metal, was about 30 m<sup>2</sup>/g of platinum, and this was rapidly reduced by sintering. Greatly improved utilisation and sinter resistance is given by supporting the platinum on a conducting support, a carbon or a graphite normally being used. The nature of this support is critical to the operation of the catalyst, and in turn to the performance of the fuel cell. By suitable choice of carbon and method of metal deposition the platinum dispersion may be varied almost at will to produce a catalyst specifically suited for the application. Metal areas of up to 150 m<sup>2</sup>/g of platinum can be obtained routinely in large-scale production. Perhaps more importantly, a uniform dispersion of metal over the support can be obtained, giving a high degree of resistance to sintering during use, due to spatial separation of the platinum crystallites. In addition, there are a number of other criteria for the catalyst. These include good electrical conductivity and a combination of surface characteristics giving partial wettability to the electrolyte. Now, for the catalyst support a

combination of corrosion resistance and high surface area is difficult to achieve, especially in the oxidising environment at the cathode. The main advances have been obtained by graphitising the carbons and various thermal treatments have been used to obtain degrees of ordering of the carbon structure (13, 14).

The major portion of the polarisation of the fuel cell under load occurs at the cathode, the hydrogen oxidation reaction being much more facile. Various alloys have been proposed to improve the activity of the anode, including both platinum/palladium (15) and also platinum/ruthenium. The activity of cathode catalysts is markedly improved by incorporation of base metal elements to form intermetallic compounds (16, 17). Such work is likely to lead to substantial improvements in the utilisation of platinum group metals in the near future.

To summarise, a huge effort to develop and demonstrate fuel cell systems for gas and electric utilities applications is in progress in both the U.S.A. and Japan. All of these programmes nearing commercialisation use platinum catalysts for the vital power section, most of these being supplied by Johnson Matthey. If fuel cells fulfil the promising forecasts for implementation over the next twenty years, the supply of platinum should prove adequate to meet the requirements. In the meanwhile, Johnson Matthey is continuing to further the technology by contributing noble metal expertise to collaborative efforts being made with a number of fuel cell developers.

## Osmium-Platinum Alloys

### HIGH STRENGTH PROPERTIES AT HIGH TEMPERATURES

Searching for new platinum alloys for use in industry under stress and at high temperatures metallurgists at the Academy of Sciences of the U.S.S.R. in Moscow have carried out a full investigation of the osmium-platinum system (L.I. Voronova, V.P. Polyakova and E.M. Savitskii, *Metally*, 1984, (5), 191-193). The phase diagram is a simple peritectic type with no intermediate phase, the maximum solubility of osmium being around 25 atomic per cent.

Alloys with 10 atomic per cent osmium were ductile at room temperature and both wires and foils were successfully prepared, but the most remarkable finding was the very considerable increase in hardness at high temperatures in alloys with up to 27 atomic per cent osmium, even up to 1600°C, the authors stating that this property was increased by from 20 to 40 times. Creep rates at 1200 and 1400°C were also found to be appreciably lower.

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