Fuel Cells for Vehicle Propulsion

PLATINUM METAL CATALYST USED IN ALKALINE UNITS

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A detailed study of future electric vehicle developments has identified an opportunity to use city buses and delivery lorries as a first market for fuel cell traction powerplants. Suitable cells employing a platinum metal catalyst on the electrodes have been developed and a substantial production facility has been set up. Trials with a mobile test bed are continuing and it is anticipated that rapid commercialisation will follow once the system has been fully demonstrated.

It has long been recognised that electrically propelled vehicles offer considerable benefits in terms of quietness and freedom from pollution. In the United Kingdom the electric milk delivery van is a familiar sight, and battery driven vehicles are finding an increasing use for local deliveries. In the longer term, it is essential to seek alternatives to petroleum as an energy source for traction purposes since supplies of fossil fuels are limited. Because of the high investment in vehicles and infrastructure, any changes will inevitably be slow. Even if an alternative was immediately available the 10 to 20 year working life of buses and lorries would ensure that a considerable period elapsed before these vehicle fleets were completely replaced. The current over-supply of petroleum products is masking the true long term prospects, for example North Sea oil supplies are expected to peak in 1985 and to decrease steadily thereafter.

It is well known that the development and the commercialisation of electric vehicles is limited by the intrinsic properties of the secondary batteries used as power sources; these being short driving range, long recharging time and high weight. Improvements in secondary batteries may reduce these but will not eliminate them completely. In that respect, the use of fuel cells offers the potential of a more fundamental breakthrough, as one significant difference between the fuel cell and a battery is that the former is an engine which continues to generate power as long as fuel and oxidant are fed to it. The reservoirs of fuel can therefore be as large as necessary, indeed the larger they are, the higher the energy density achieved by the system.

Thus the fuel cell is a device for continuously converting fuel and oxidant directly to electricity. In its simplest form, its operation is the reverse of the electrolyser, in which a current is passed between two electrodes immersed in a suitable electrolyte, and water is split into hydrogen and oxygen. On the other hand, in a fuel cell these gases are supplied to the catalysed electrodes and current is generated. This effect was discovered in 1839 by Sir William Grove, who found that the process of electrolysis between platinum electrodes could be reversed, with a resultant generation of electric current and production of water (1).

In contrast with heat engines such as the internal combustion engine, the fuel cell is not restricted by the Carnot cycle, which, because of achievable temperature, limits heat engines to a theoretical efficiency of about 60 per cent. In practice this results in very much lower efficiencies, only about 25 per cent for petrol

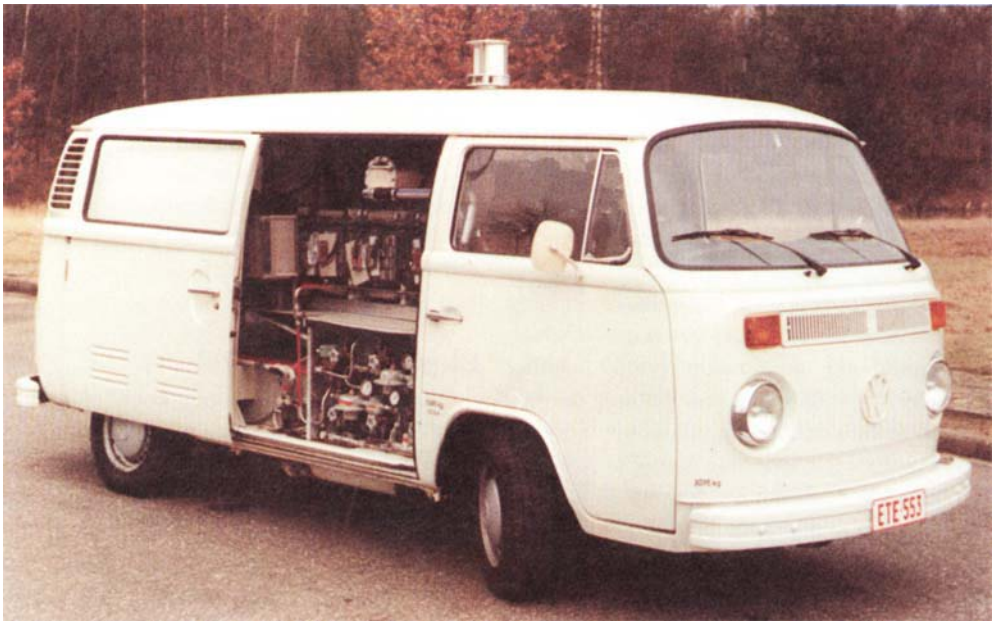

Fig. 1 This Volkswagen van is propelled by a hybrid fuel-cell battery system and was first used on the road in 1982. Currently it is employed as a mobile test bed. The electrodes of the alkaline fuel cell are catalysed with platinum and the unit is fed with air and hydrogen, the latter being stored in high pressure containers which permit a driving range of 200 km

engines and 30 to 35 per cent for traction diesels, compared to the 40 to 60 per cent which is typical of fuel cells (2).

The major development work which established the fuel cell as a viable power source was carried out for the space programme in the United States. This was due to the realisation that the amount of electrical energy required for the various space missions would require a prohibitively heavy mass of batteries. Similar criteria apply to terrestrial applications for motor vehicles.

Work on fuel cells in the United States has been focused mainly on gas and electric supply utilities, and other stationary applications, and most of this work is devoted to phosphoric acid and molten carbonate fuel cells (3). The former employ platinum catalysts, and most of the major development efforts use materials supplied by Johnson Matthey. In addition, several programmes in Europe have been directed towards vehicle applications and development efforts have been mainly on alkaline fuel cells (4). This choice is logical, because the operational features of alkaline cells make them much more attractive for vehicles than those of phosphoric acid cells. These include an operating temperature of 65°C instead of the 150 to 200°C required for the latter, easier and faster starting up of the cells and a higher electrical conversion efficiency of 50 to 60 per cent instead of 40 to 50 per cent attainable with phosphoric acid cells. On the other hand, alkaline cells require the fuel and oxidant reactants to be of higher purity. The amounts of carbon monoxide and carbon dioxide have to be limited, although the exact amounts which can be tolerated depend on the type of electrodes used.

For a number of years Elenco has conducted market research on the fuel cells it has under development for electric propulsion of various types of vehicles (5). In the first phase at least, gaseous hydrogen will be produced away from the vehicle, the tank of which will have to be replenished periodically. Thus it is anticipated that fleet vehicles of various kinds will offer the first areas of application. Examples of such

vehicles are city buses, refuse collecting trucks and other types of vehicles in city services, also forklift trucks and some vans.

From an analysis of the use of fuel cells as power sources in vehicles, it appears that the best approach for building the traction system is the adoption of a hybrid power source (6). The fuel cell delivers approximately the average power required during the driving cycle, and another power source in parallel with the fuel cell provides for the short power peaks which are typical for acceleration periods. Either batteries or a flywheel can be used as this second power source. The utilisation of such a hybrid system not only constitutes an economic advantage by lowering the fuel cell investment cost, but it also offers the benefit of recovering in the batteries or the flywheel the energy from braking, thus increasing the overall efficiency of the system. The vehicle shown in Figure 1 is currently in use as a mobile test bed for such a hybrid fuel cell-battery traction system.

In evaluating such a fuel cell hybrid electric system with respect to other traction systems, two basic comparisons can be made: first with other electric systems, and secondly with internal combustion engine systems. Comparing the fuel cell electric traction system with other electric systems (essentially storage batteries and trolleys collecting power from an overhead wire), results show that in many situations the overall cost per kilometre is lower with the fuel cell system. On the other hand, comparison with combustion engine systems shows that at the present state of the technology and the cost of energy, a cost penalty for the fuel cell system is unavoidable (7). However, this penalty will become smaller in the future as technological development of the new system continues. In some cases however, present cost penalties could become acceptable for environmental reasons or to reduce dependency on imported oil. Commodity hydrogen is presently obtained as a byproduct from the chlorine industry, and large tonnages are produced as intermediates in the petroleum refining industry. In the longer term, it is possible that supplies may be obtained by coal gasification, or by electrolysis using off peak nuclear or hydroelectric power. The use of hydrogen therefore confers flexibility on the fuel cell as a traction power source, and this may become increasingly important in the future.

To summarise, it can be said that in Elenco's opinion there is a sufficient potential in electric propulsion of vehicles to justify further technical efforts towards the implementation of fuel cells in vehicles.

Electrodes and Catalysts

The fuel cell is in many ways deceptively simple, since it involves no moving parts except for peripheral air and electrolyte pumps (8). The electrodes must support catalysed surfaces to create large areas of interface between the reactant gases, the liquid electrolyte, and the solid electrode. By mixing hydrophobic materials, such as polytetrafluoroethylene (PTFE) with hydrophilic carbon supporting the platinum catalyst, a porous structure can be created, combining liquid and gas filled pores. The degree of hydrophobicity is adjusted to create the maximum stable interfacial area between the three solid, liquid and gas phases.

Gases and electrolyte must be arranged to flow uniformly over the surfaces of the electrodes, and current must be conducted away from the catalytic reaction sites with the least possible ohmic resistance loss. This requires electrodes having good electrical conductivity, together with corrosion resistance in concentrated electrolyte over a wide range of electrochemical potentials. In addition, electrodes must be as thin as possible to allow diffusion of gases to the reaction sites, and transport of ions within the electrolyte.

Johnson Matthey has collaborated for many years with a number of fuel cell producers, including Elenco, to formulate suitable platinum metal catalysts. There are many requirements imposed on fuel cell catalysts which are critical to the successful operation of the cell. Normally, carbon or graphite is used as the catalyst substrate material, since it combines conductivity with good corrosion resistance. A wide spectrum of carbonaceous

materials has been evaluated, ranging from activated charcoals with very high surface areas and porous structures, through furnace black, or lampblack materials with medium surface areas, to synthetic graphites. Each of these has very individual characteristics, and being derived from natural sources requires strict quality control. Frequently carbons are manufactured on a large tonnage scale, as for example motor tyre filler materials, and detailed specifications of the carbon for specialised catalyst applications are not available. Standard methods of characterisation include electron microscopy, and chemical, surface area and particle size analyses.

Knowledge of the carbon surface chemistry is vital in understanding the deposition processes in preparing the catalyst. It is feasible to deposit uniform dispersions of platinum crystallites of 1 to 2 nm given a suitable substrate. Metal dispersions of better than 150 m^2/g of platinum, as determined by carbon monoxide chemisorption, are regularly made as production catalysts.

The surface chemistry of carbon also determines its hydrophobicity, and hence contributes to the overall electrode hydrophobic structure, while the particle size and pore size distribution also exert a significant fundamental influence.

Wood charcoals can be obtained which retain the tubular structure corresponding to the original wood, while at the other extreme flake graphites occur as dense lamellar plates, and unless subjected to specialised pretreatments tend to have very low surface areas. Most fuel cells currently being produced use carbons somewhere between these extremes in order to obtain a balance between surface area and corrosion resistance. Typical of these are graphitised furnace black carbons, where a relatively amorphous structure is partially ordered by thermal treatments, which may be carried out at up to 3000°C. Figure 2 is a transmission electron micrograph taken at a magnification of approximately ×190,000, showing a 5 per cent platinum on graphitised carbon black. In this, the graphitic structures are visible as 'skeins' of ordered carbon.

Status of Elenco's Alkaline Fuel Cell Development

Formed in 1976 specifically for the development of fuel cell power sources, Elenco N.V. is a consortium of three equal shareholders; Bekaert, one of the largest metallurgical groups

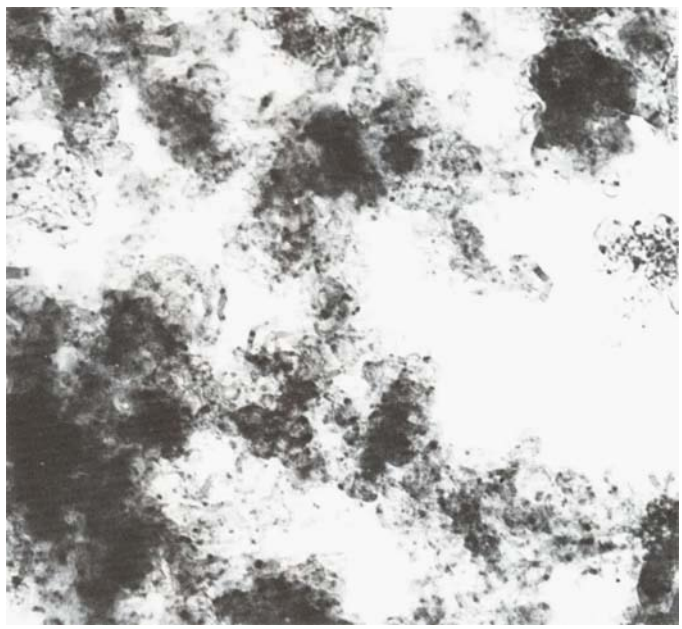

Fig. 2 Electron photomicrograph of 5 per cent by weight platinum on graphitised furnace black carbon powder showing, as minute black dots, the fine platinum crystallites uniformly dispersed over the diffuse carbon. This has been structurally ordered by a high temperature graphitisation process to increase oxidation and corrosion resistance ×190,000

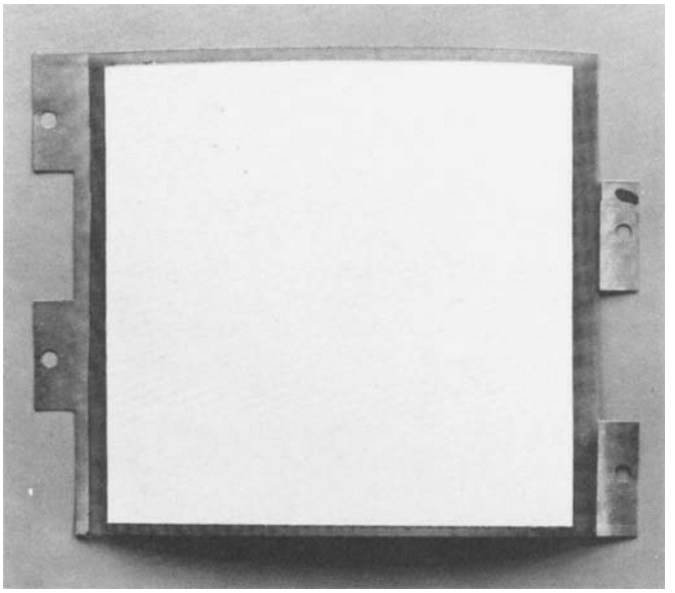

Fig. 3 Fuel cell electrode showing the nickel mesh current collector and inter-cell connectors. The white porous hydrophobic layer prevents loss of electrolyte from the system while allowing the gases to diffuse to the platinum catalysed layer beneath

in Belgium, SCK/CEN, the Belgian Nuclear Research Centre and the chemical manufacturers, D.S.M. Its alkaline fuel cell development programme was started on the basis of fundamental electrode research carried out from 1969 onwards by SCK/CEN, in Mol.

For the electrodes (both anodes and cathodes) the decision was made to use platinum on carbon catalysts, rather than trying to use non-noble metals, although of course the latter approach is in principle possible for alkaline cells. The electrodes are of the gas diffusion multilayer type, using a nickel mesh for the current collection. The cells use a circulating 30 per cent potassium hydroxide solution as the electrolyte and coolant. The nominal operating temperature of the electrolyte is about 65°C, but even at ambient temperature the cells can generate about 50 per cent of their nominal power at 65°C.

Elenco has developed and optimised an electrode, shown in Figure 3, which is suitable for mass production. To demonstrate this an automated manufacturing plant has been built, capable of making sufficient electrodes for 2500 kW of fuel cells a year. This has now been operational for almost three years. In addition, fuel cell block construction technology has been developed, based on rapid techniques for framing the electrodes with a plastic material and for building the frames into blocks. At present the specific weight of the Elenco fuel cell blocks, operating with hydrogen and air, is of the order of 10 kg/kW, and block units incorporating 48 electrodes are being used, see Figure 4. Such block units, with a power rating of 0.5 kW, can be assembled into larger stacks, depending on the power required. For example the unit shown in Figure 5 has a 4 kW rating.

Defining the appropriate conditions for the operation of fuel cells is of course very important to achieve optimal performance levels and cell lives. Therefore, extensive experiments were carried out on numerous 0.5 kW units. Continuous nominal power tests were generally carried out for 5000 operating hours, and in a few cases for up to almost twice that time. The target set for stability, namely 80 per cent of the initial power at the same voltage after 5000 hours of operation, was reached in 1983. Test regimes with intermittent patterns of operation were initially devoted to the comparative effects of different conservation modes between operating periods. On the basis of that work it has now been possible to define operation and conservation modes for intermittent

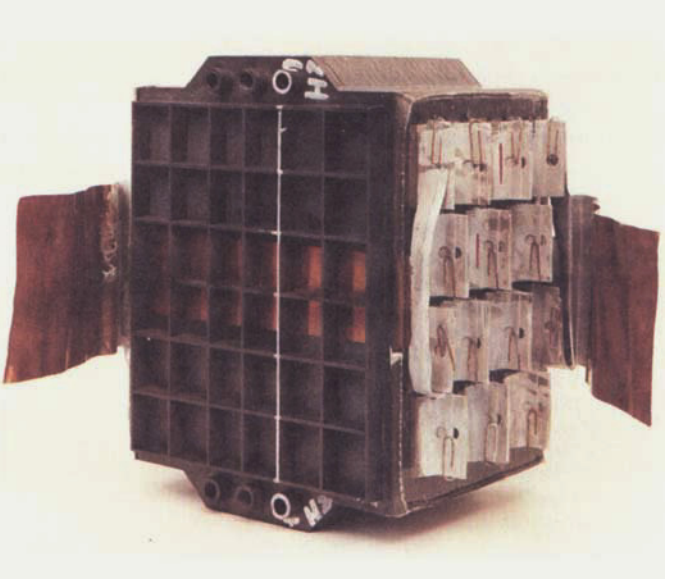

Fig. 4 This 500 watt fuel cell block unit incorporates 48 electrodes and the construction is suitable for automated mass production. The ports at the top and bottom serve to supply and remove the gases and the electrolyte

operation which yield lifetimes comparable to those for continuous operation.

From the start of the programme vehicle applications were envisaged, so an electric van with a hybrid fuel cell system was seen as a necessary part of the research and development work. An electric Volkswagen van was obtained from the manufacturer, the batteries were then removed and replaced by a hybrid fuel cell-battery system, and some additional power electronics were also built in. The van, which is illustrated in Figure 1, made its first short journeys on the road in November 1982, and a longer one of about 100 km in May 1983, driving from the premises of Elenco's partner D.S.M. in Geleen to Mol. The van carries 3.6 kg of hydrogen, stored in high pressure steel containers, which give it a driving range of 200 km. The van is intended to be a mobile test bed, rather than a showroom prototype.

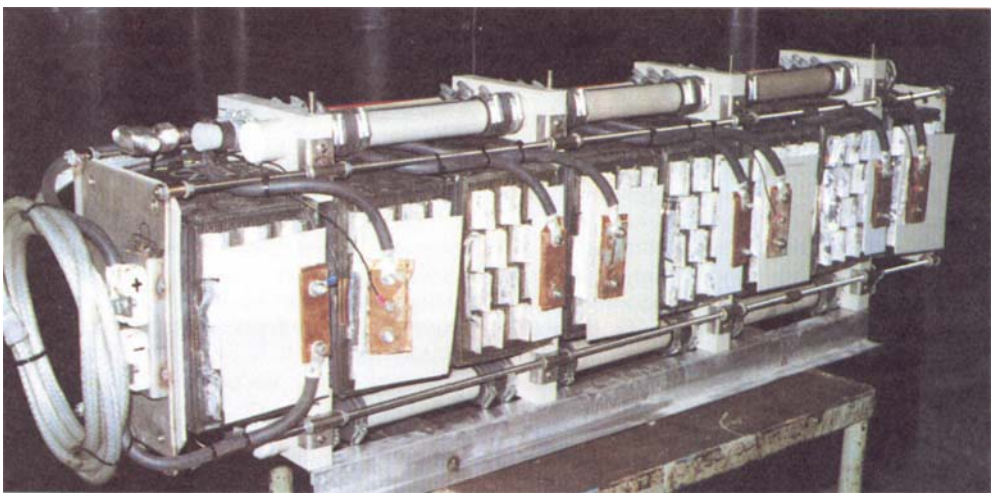

Fig. 5 Simple connections enable 500 watt fuel cell blocks illustrated in Figure 4 to be built into larger stacks capable of providing proportionally higher power outputs. The assembly shown here has a 4 kW rating, the units sharing common gas and electrolyte supplies

Elenco has recently started a programme aimed at the construction of a 40 kW fuel cell unit, to be used by the Belgian Geological Service. At the same time, tests with the Volkswagen van and with smaller fuel cell units will continue.

The construction of a production facility concurrently with the evaluation and testing of the fuel cell is probably unique, and will, it is hoped result in rapid commercialisation of the system once it has been fully demonstrated.

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Recent Achievements in Catalysis

Catalysis Volume 6. EDITED BY G. C. BOND AND G. WEBB, Royal Society of Chemistry, London, 1983, 234 pages, £26 to members, £43 to non-members

Among the Specialist Periodical Reports published by the Royal Society of Chemistry, this volume reviews the recent literature published up to mid-1982 in a field that has become of increasing importance to the chemical industry. As the editors emphasise, it is more and more appreciated that new and better catalysts, often one or other of the platinum metals, can reduce the energy input into chemical processes, improve product yields, minimise by-products and thus lead to a reduction in processing costs. The seven reviews here include "Oscillatory Phenomena in Heterogeneous Catalysed Oxidation Reactions" from C. N. Kenney and his colleagues at Cambridge, "Strong Metal-Support Interactions" by Geoffrey Bond of Brunel and Robbie Burch of Reading University, and "The Catalytic Hydrogenation of Organic Compounds" by M. D. Birkett, A. T. Kuhn and G. C. Bond in which the authors explore the connection between catalysis and electrochemistry. Further reviews come from three workers at the Istituto di Chimica-Fisica in Turin; from Gwendoline Berndt of the Edinburgh School of Agriculture who reports on recent developments in radiotracer methods for catalytic investigations; from B. A. Murrer and M. J. H. Russell of Johnson Matthey on recent achievements in hydroformylation and lastly from E. K. Poels and Vladimir Ponec of the University of Leiden a major article on the production of oxygenated species from synthesis gas.

Tantalum-Iridium Films

A requirement for electronic devices capable of operating at elevated temperatures for extended times has identified a need for a thermally robust metal-semiconductor contact which is not subject to the diffusion that would otherwise degrade its electrical characteristics. Even at relatively low temperatures grain boundaries act as effective diffusion channels for the conventionally used metals, so amorphous metal films have been used to provide a barrier between the primary metallisation and the semiconductor.

Now a letter from the GEC Research Laboratories (M. J. Kelly, A. G. Todd, M. J. Sisson and D. K. Wickenden, *Electron. Lett.*, 1983, **19**, (13), 474–475) describes the relative enhancement of the thermal stability of Schottky barriers on both silicon and gallium arsenide that can be achieved by the use of suitable amorphous thin films, and reports that tantalum-iridium has proved to be superior in all respects to any other material used to date.