

# Fuel Cells – Science and Technology 2002

SCIENTIFIC ADVANCES IN FUEL CELL SYSTEMS REPORTED IN AMSTERDAM

By Donald S. Cameron

The Interact Consultancy, Reading, U.K.

The first of a new series of biannual European fuel cell conferences was held on the 25th and 26th September, 2002, in Amsterdam. These conferences are to be alternated with the Grove Symposium, giving a balance between the scientific and commercial aspects of the technology. The conference theme: 'Scientific Advances in Fuel Cell Systems', was chosen to focus on the scientific challenges posed by the introduction of these novel power generators. Authors from around the world were invited to submit oral papers and posters detailing their progress in the field.

The meeting was fully subscribed with 247 participants from 33 countries, representing universities, research organisations, and fuel cell and system manufacturers worldwide. Forty oral papers, chosen from the original submitted abstracts, and over a hundred high quality poster presentations were made. Most of the oral papers and many of the posters are to be published in a special edition of the *Journal of Power Sources*.

The meeting was organised as a series of six sessions entitled: 'Materials' (2 sessions), 'Stack and cell engineering', 'Balance of plant and advanced fuel cell systems', 'Electrocatalysis and fuel processing' and 'Modelling and engineering'. The importance of materials to the advancement of the technology was emphasised by their featuring in no less than three of the sessions. The first of the two Materials sessions concentrated on developments in hydrogen storage, membrane technology and membrane electrode assemblies. The second Materials session was mainly concerned with corrosion-resistant materials for high and low temperature fuel cells. From such a wide range of topics, this brief review focuses on a selection of presentations that make use of the platinum group metals (pgms).

In his keynote talk, Professor Robert Selman (Illinois Institute of Technology, U.S.A.) empha-

sised the role of science in fuel cells, and enumerated some of the most important developments since the principle of the fuel cell was discovered in 1839 (1). A wide range of approaches are being used to reduce the cost of fuel cells and to make them commercially attractive, including performance improvements in terms of power density, durability and component costs. Improved techniques to exploit the pgms are playing an important part in enabling more compact and less expensive fuel cells and hydrogen generator systems to be constructed. They are also making direct oxidation of organic fuels, such as methanol, feasible.

## Hydrogen Generation

An efficient and compact source of hydrogen or a suitable means of storing the gas are critical to the success of most fuel cell systems. The development of fuel cells with a wide range of power outputs has led to a number of hydrogen generation routes being explored. It has become evident that for many applications, such as polymer electrolyte membrane (PEM) fuel cells, high purity hydrogen is required, since impurities, such as carbon monoxide (CO) can lead to rapid performance deterioration.

## Reformers

In the paper 'High temperature hybrid steam-reforming for hydrogen generation without catalyst', Phillipe Marty (l'École des Mines d'Albi-Carmaux, France) proposed the use of hybrid steam reforming. This incorporates partial combustion of the fuel with injected air to generate heat for the endothermic reforming reaction. Experiments are at a relatively early stage, mainly with fundamental reaction studies. Possibly – because of the high temperatures needed in the absence of catalysts – the typical reaction product is only 30% hydrogen, with the balance being

made up of nitrogen from the atmosphere, 15% CO and carbon dioxide (CO<sub>2</sub>).

In his talk entitled 'A new generation of water-gas shift catalysts for fuel cell applications', Wolfgang Ruettinger (Engelhard Corporation, U.S.A.) described the limitations of the existing copper/zinc oxide-based reformer catalysts, and Engelhard's attempts to develop replacement materials that are more thermally stable and less pyrophoric. In their current reformer system a desulfuriser (to remove sulfur from natural gas) is followed by an autothermal reformer. Here, oxidation of a small proportion of the fuel produces heat to reform the remainder – to a gas containing hydrogen plus 6–10% CO. This passes to a water gas shift reactor (which reduces the CO content to 1–5%). By then injecting 1–2% oxygen and passing the gas through a partial oxidation catalyst, the CO content can be reduced to less than 10 ppm. Engelhard's newly developed Selectra™ Shift catalyst has somewhat lower activity than the mixed oxide-based reformer catalysts but greatly reduced sensitivity to oxygen ingress. The water gas shift reaction demands a large reactor vessel, but to make the system more compact, it is likely to be replaced by a monolith-supported pgm catalyst; no details of this were given. Similarly, in order to reduce the CO content of the product, a two-stage partial oxidation system that contains pgm catalysts which incorporate inhibitors to prevent methane formation, is being introduced. This is likely to enable space velocities in excess of 30,000 volumes per hour in the future.

In her talk 'Advances in fuel processor catalysts', Jessica Reinkingh (Johnson Matthey Fuel Cells, U.S.A.) described the development of reformers mainly for PEM fuel cell systems. These are intended for mobile applications, with the capability of operating on a variety of fuels including natural gas, propane and higher hydrocarbons, although for small portable systems, hydrogen stores or methanol reformers are likely to be used. However, for mobile systems, an autothermal-type reformer system has been adopted to minimise volume and weight. There is a fuel pretreatment reactor mainly to remove sulfur, and reforming followed by a water gas shift reactor. Finally, the

addition of 1–2% oxygen before a last reactor selectively oxidises CO to CO<sub>2</sub>.

For mobile systems, which are weight and volume critical, in order to produce sufficient hydrogen for a 75–100 kW system from a reactor of volume less than 2 litres, space velocities of over 100,000 volumes per hour are necessary. A reformer system fuelled by gasoline has already been demonstrated, functioning at 140,000 per hour space velocity for over 500 hours; after that period it still retained 99.8% of its efficiency. In order to achieve this, it is necessary to use advanced monolith support materials with very high surface areas and to reduce sulfur impurities in the fuel feed to low levels. For the water gas shift reactor, operating at a space velocity of over 50,000 per hour, Johnson Matthey have developed high performance pgm-based catalysts. These exhibit high activity at less than 300°C and avoid the possibility of methane formation.

The Johnson Matthey FP05 prototype reformer, weighing 75 kg and of volume 470 litres, has operated on natural gas for over 2000 hours with over 100 start-up and shut-down cycles. Start up currently takes 20 minutes, although it should be possible to reduce this to around 5 minutes.

## Hydrogen Storage

Most of the fuel cell powered passenger vehicles and buses currently under development rely on hydrogen stored under pressure for their operation. In his talk 'FUCHSIA: Fuel cell and hydrogen store for integration into automobiles', Professor Rex Harris (University of Birmingham, U.K.) described an international cooperative project going on in Germany, Switzerland and the U.K. He reviewed the various types of hydrogen store currently being developed under the EU Fifth Framework Programme. Hydrogen stores which reversibly retain over 7% of their weight of gas are now available. Liquid hydrogen has a very high energy density, but thermodynamics dictate that over 30% of the heating value is used to liquefy the gas. Compressed gases are currently being stored at extremely high pressures in advanced composite cylinders, in the solid state as hydrides, and adsorbed on carbon or glass microspheres.

Work at the University of Birmingham, U.K., indicates that the kinetics of absorption and desorption of hydride systems, based on magnesium-nickel alloys, can be substantially improved using dispersions as low as 0.1% by weight of ruthenium (Ru) and palladium (Pd).

## Electrocatalysis and Direct Fuel Cells

In a talk entitled 'New fuel cell electrocatalysts based on mesoporous precious metals', Anthony Kucernak (Imperial College, London, U.K.) described their techniques to produce pgm and pgm alloy catalysts in the aqueous phase in the form of small, nanoparticulate spheres. Metal areas of  $35 \text{ m}^2 \text{ g}^{-1}$  (Pt) and  $40 \text{ m}^2 \text{ g}^{-1}$  (Pt-Ru) can be produced for unsupported catalysts, while metal areas of  $50\text{--}90 \text{ m}^2 \text{ g}^{-1}$  can be produced on mesoporous carbon support materials. When used to oxidise carbonaceous fuels, the type of catalyst structure appears to affect CO absorption. The catalysts are extremely effective for the direct anodic oxidation of methanol, formic acid and formaldehyde in fuel cells. Catalysts of Pt-Ru alloy have been found to be more active for this purpose since they are less affected by strongly chemisorbed carbonaceous species.

Graham Hards (Johnson Matthey Fuel Cells, U.K.) in a paper entitled 'New catalyst and MEA developments for high performance PEM fuel cells', gave details of the latest Johnson Matthey oxygen reduction and hydrogen oxidation catalysts that have tolerance to CO and  $\text{CO}_2$  impurities. In order to obtain high catalytic activity, the pgms are highly subdivided, yielding surface areas of up to  $150 \text{ m}^2 \text{ g}^{-1}$ , compared to the surface area of atomic dispersions of around  $200 \text{ m}^2 \text{ g}^{-1}$ . However, the nature of the PEM fuel cell demands that the catalytic layer is kept as thin as possible to provide a narrow boundary between reactant gases and electrolyte. To obtain reasonable metal loadings in these thin layers means that the catalyst must be applied, either as the pure metal or as high concentrations, on conducting substrates such as high surface area carbon blacks. Typically, 40–50 wt.% Pt by weight of catalyst is applied to a cathode (oxygen reduction) catalyst. With new deposition routes, even at 70 wt.% Pt on carbon, metal areas

of over  $90 \text{ m}^2 \text{ g}^{-1}$  can be obtained. The PEM fuel cell performance of MEAs employing these new catalysts is significantly improved over the current materials. Alloys of Pt and Ru, at an atomic ratio of 1:1, have been used for some time to provide resistance to CO poisoning as anode catalysts. These catalyst provide good tolerance to levels of CO of only 100 ppm and below. More recently a new anode combination of Pt-Ru and Pt-Mo has demonstrated extraordinary levels of fuel cell performance tolerance with reformat fuel containing up to 2000 ppm CO.

Further improvements in catalyst performance can be obtained by increasing the intrinsic activity of the catalyst metal particles. These can be achieved by alloying the pgm with elements such as chromium, iron and manganese, using thermal treatments to form true alloys. Even though the resulting alloys tend to have lower metal areas after heat treatment, higher intrinsic activities (that is, activity per unit of surface area) more than compensate for surface area losses. The use of alloy catalysts has been well established in phosphoric acid fuel cells over many years.

In his talk 'Improving the tolerance of PEM fuel cells for reformat gas: results and perspectives', Gaby Janssen (Energy Research Centre of the Netherlands (ECN)) enlarged on the variety of techniques available for reducing the effects of impurities in hydrogen on cell performance.

Reformat gas typically contains nitrogen,  $\text{CO}_2$ , CO and water, as well as hydrogen. One reaction that can occur at the anode is the reduction of  $\text{CO}_2$  by hydrogen to form more CO. By incorporating a small proportion of oxygen (1–2%) in the reformat gas and passing it over a suitable catalyst, much of the CO in the fuel can be oxidised to  $\text{CO}_2$ , although the reverse reaction must be prevented in the cells. A second option is to periodically starve the fuel cell of fuel, so that the anode compartments reach oxidising potentials sufficient to oxidise any CO chemisorbed on the surface. However, this technique is less desirable since it entails temporarily closing down the fuel cell. ECN have examined a series of carbon-supported Pt-Pd alloy anode catalysts in PEM cells for oxidation of CO in contaminated hydrogen

fuel at 80°C. Those with higher Pd concentrations have reduced coverage by CO. ECN have demonstrated 20 cell stacks with up to 500 hours of stable operation in reformat gas without an air bleed.

Considerable work has been carried out to develop direct oxidation fuel cells. In his talk 'Direct 2-propanol fuel cells', Zhigang Qi (H-Power Corporation, U.S.A.) described their work on fuel cells that operate on various fuels, including methanol, ethanol, 1-propanol, 2-propanol and ethylene glycol. Fuel concentrations of 0.5–2.0 molar and temperatures of 70–100°C are typically used. The use of 2-propanol in conjunction with a polymer electrolyte membrane reduces some of the problems due to organic crossover to the air cathode encountered with more volatile organic fuels. In small (25 cm<sup>2</sup>) cell tests, current densities up to 200 mA cm<sup>-2</sup> have been obtained at 0.5 V, compared to the 0.3 V typical of direct methanol cells. Voltage decay, caused by impurities adsorbed on the catalysts during operation on the organic fuel, recovers on standing at open circuit voltage or on reversing the polarity of the cells.

A different approach that is being adopted at the University of Newcastle, U.K., was described by Professor Keith Scott in his talk 'Direct methanol fuel cells: solutions to the problem of crossover'. When using 2 mg cm<sup>-2</sup> pgm (Pt-Ru) anode catalysts and 2 mg cm<sup>-2</sup> Pt cathode catalysts in conjunction with Nafion polymer membrane (60–120 µm thick) at 100°C, substantial methanol oxidation occurs at the air cathode. Various cathode catalysts which exhibit selective oxidation properties towards methanol have been assessed. These include cathode catalysts of iron tetramethoxyphenylporphyrins, (Fe TMPP) and Ru-based compounds, such as Ru-Se. To reduce methanol crossover, techniques such as using low methanol concentrations can be used combined with lower-permeability radiation-grafted polymer materials.

## Modelling and Engineering

The importance of optimising fuel cell systems in areas such as thermal balance was emphasised in the final session. Advanced studies are being carried out on hybrids of high temperature fuel cells (such as solid oxide and molten carbonate cells) in

combination with gas turbines to produce systems having almost 70% overall efficiency. This is achieved by using the fuel cell as the combustion stage of gas turbines, with the compressor supplying high pressure oxidant, and utilising the waste heat from the fuel cells to drive the compressor. The main applications for these are as stationary generators providing combined heat and power.

The conference was concluded by the award of four prizes. The best submitted oral presentation was won by Klaus-Dieter Kreuer (Max-Planck-Institut, Germany) and the best poster prize by Adi Aharon (Tel Aviv University, Israel). The prize for the most original contribution was won by Eric Middleman (Nedstack, The Netherlands) for a talk on self-organising nanostructures in PEM fuel cell electrodes that incorporated strings of catalyst and wetproofing agent. Whitney Collella (University of Oxford, U.K.) won the best student contribution.

## Conclusion

The variety of presentations, diverse range of science and high quality of work, demonstrate the wide support that is helping to bring fuel cell technology to the consumer.

## Reference

- 1 W. R. Grove, *Phil. Mag.*, 1839, 14, 127; *ibid.*, 1842, 21, 417

### The Author

Don Cameron is an independent consultant on the technology of fuel cells and electrolyzers. As well as the scientific aspects, his interests include the standardisation and commercialisation of these systems.

## Eighth Grove Fuel Cell Symposium

The Eighth Grove Fuel Cell Symposium will be held at ExCeL in London, from 24th to 26th September, 2003. The theme of the meeting will be 'Building Fuel Cell Industries' to reflect the rapidly growing infrastructure needed to support the technology as commercialisation proceeds. The venue was chosen so that displays of stationary generators, vehicles and the refuelling techniques being developed could be viewed in comfort.

Details of the symposium can be obtained from <http://www.grovetfuelcell.com> or from Sarah Wilkinson: Tel: +44 (0)1865 843691.