

Fuel Cells – Science and Technology 2004

SCIENTIFIC ADVANCES IN FUEL CELL SYSTEMS REPORTED IN MUNICH

Reviewed by Donald S. Cameron

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“Scientific Advances in Fuel Cell Systems” (1) was the theme of the second in a series of biannual European meetings on fuel cells, that are held in alternate years to the Grove Symposia (2). The conference reported here was held on the 6th and 7th October 2004 at the Hilton Munich Park Hotel, Munich, following the first meeting in Amsterdam in 2002 (3). Organised by Elsevier, these conferences provide a balance between the scientific and the more commercial aspects of the technology. Authors from around the world had submitted oral papers and posters for this technically-orientated programme. The meeting attracted 320 delegates from 39 countries including Germany [76], Japan [47], the U.K. [35], Italy [22] and the U.S.A. [13]. These represented universities, research organisations, and fuel cell component and system manufacturers.

Besides almost 60 oral papers, there were 170 high quality poster presentations, and many of these will be published in a special edition of the *Journal of Power Sources* in May 2005. The symposium consisted of eight sessions, on membrane science, fuel processing, materials science, electrochemistry and catalysis, cell and stack technology, and systems and applications. For this review, only work that involves the platinum group metals (pgms) is being reported.

Performance Targets for Transport

The conference began with a Plenary Session and a keynote talk. In this, Frank Preli of UTC Fuel Cells, U.S.A., outlined some of the performance targets for transport applications, compared to what is currently achievable with fuel cells. These can be summarised by five interrelated characteristics: power density, operability (including factors such as cold starting and the range of acceptable ambient conditions), efficiency, durability and cost. Small passenger vehicles are likely to

need a power output of around 85 kW, while buses will need 100–200 kW. To compete successfully with the internal combustion engine, stack power density will need to be over 1.6 kW litre⁻¹, while the complete system will need to provide more than 0.5 kW litre⁻¹ to minimise intrusion into the passenger space. High overall thermal efficiency implies a cell voltage in excess of 0.750 volts, with a decay rate of less than 2 mV per 1000 hours for adequate lifetimes. Performance will need to be maintained over 17,000 start-stop cycles despite adverse operating conditions, such as less than 60% relative humidity at the air inlet. In addition, stacks will need to have the ability to start up quickly from the frozen state for up to 1000 times without damage.

PEMFCs to Achieve these Goals

Proton exchange membrane fuel cells (PEMFCs) operating at relatively low temperatures and catalysed by pgm catalysts offer the best chance of achieving these goals. The cost objective for wide-scale applications in transport is set at \$35 kW⁻¹. Currently, the cell stack plates and membrane electrode assemblies (MEAs) account for 50% of the cost of the whole system, and various means to reduce this proportion are being considered. These include using injection moulding techniques for the inter-cell plates. For high stack power density, the internal resistance of individual cells needs to be reduced, to provide power densities upwards of 0.7 volts per cell at 0.6 A cm⁻². Water management within the membrane has been identified as one of the principal limiting factors to cell performance.

For comparison, the stationary 200 kW PC25 phosphoric acid fuel cell system made by UTC costs \$4,300 kW⁻¹. Several hundred of these highly developed units have accumulated over 6 million operating hours. Laboratory trials indicate that

marginally reducing the operating temperature of the fuel cell stack has a marked effect in reducing sintering of the platinum catalyst, enabling stack lifetimes to be doubled to over 80,000 hours or 10 years. In the past few years the life of PEMFCs has also been extended from a few hundreds of hours to over 10,000 hours and laboratory tests indicate that these can be extended to over 20,000 hours.

Progress in PEM Technology

In a later keynote talk, Charles Stone, of Ballard Power Systems, Canada, also discussed the technical challenges and progress made in PEM technology. The performance and durability of PEMFCs are already established, and products being evaluated by the public include 30 buses in the Clean Urban Transport for Europe (CUTE) programme, with 9 more in California, Australia and China. Hydrogen has evolved as the fuel of choice, and a supply infrastructure is being developed in several parts of the world. Power densities over $2.2 \text{ kW litre}^{-1}$ are achievable for stacks operating at 0.6 volts per cell. However, component costs need to be reduced, while technology needs to be developed for the rapid start of frozen cell stacks, for water management and for resistance to impurities in the reactant gas. In particular, air cathodes that can operate at over 1 A cm^{-2} need to be developed.

In the longer term, modelling and measurement tools should enable more rapid progress in optimising systems. Membranes with increased durability have been developed; these have resistance to peroxy radical attack and reduced weight loss with time. Degradation of the anode catalyst carbon support has been greatly reduced, thanks to a programme jointly carried out by Ballard and Johnson Matthey, and new catalysts have demonstrated up to 500-fold greater stability.

For cathode catalysts, graphitised Vulcan carbon supports provide greatly improved stability and durability. Considerable progress has been made in reducing the pgm content of PEMFCs. Platinum loadings have been reduced to around 1.0 mg cm^{-2} for electrodes made using screen printing, compared to loadings of $8\text{--}10 \text{ mg cm}^{-2}$ Pt that were common ten years ago. These are pro-

jected to fall further to $0.3\text{--}0.5 \text{ mg cm}^{-2}$ using roll coating techniques, and ultimately to 0.1 mg cm^{-2} with chemical vapour deposition methods. Improved current collector plates and MEAs with new gas diffusion layers have helped to improve water management and hence performance.

Stone emphasised the need to carry forward improvements to all the interrelated aspects of the technology. Several of the subsequent papers highlighted the efforts being devoted to understanding and developing models of various aspects of PEMFC operation including water management, low temperature start-up, and the quest for improved catalyst and membrane materials.

Membrane Science

Direct oxidation of methanol in fuel cells has made considerable advances in recent years to the point where several are on the verge of being manufactured commercially. In a talk entitled '0.5 W/cm² PCM-based methanol-air fuel cell – recent progress at Tel Aviv University', A. Aharon provided details of a novel and inexpensive ($\$4 \text{ m}^{-2}$) nanoporous proton conducting membrane, consisting of a non-conducting ceramic powder mixed with a polymer binder and an acid. This is extremely permeable to water penetration during cell operation.

One of the problems of direct methanol fuel cells (DMFCs) is the undesirable migration of solvated water through the membrane, associated with protons, with up to 18 molecules of water transferred for each molecule of methanol oxidised. This has been identified as a major reason for cathode flooding and performance loss at high current densities. The high porosity of the Tel Aviv University membrane enables surplus water to permeate back through the membrane to the anode compartment. Substituting trifluoromethane sulfonic (triflic) acid for sulfuric acid yields performances of 0.5 volts at 0.8 A cm^{-2} with a platinum loading of 4 mg cm^{-2} . These performances have been demonstrated on small scale cells which are being increased in size to 50 cm^2 bipolar cells, and a 12 W cell is being built which will occupy 900 cm^3 .

Water transfer across the membrane is also

accompanied by loss of methanol into the cathode compartment by migration. Another approach to the problem of methanol and water diffusion in DMFCs was presented by L. Pitol-Filho, of the Universitat Rovira I Virgili, Spain. Composite membranes were made from mixtures of polysulfone (PSf) and poly(ethylene glycol) (PEG) and used to study the rates of transfer of reactants. PEG contains OH⁻ hydrophilic groups which combine with hydrated protons, and experimental data confirmed that higher PEG concentrations assisted proton transport, with a plateau of about 50% PEG. At this ratio, the ratio of H⁺ : methanol was about 8.8 : 1 compared to 4.0 : 1 for membranes containing 20% PEG.

Fuel Processing

A paper by Q. Li of the Technical University of Denmark, 'Integration of high temperature PEMFC with a methanol reformer' emphasised the need for high PEMFC stack operating temperatures to facilitate integrating the reformer into a system. Newly-developed thermally stable polymer membranes such as acid-doped polybenzimidazole membranes allow PEMFCs to operate at up to 200°C. Using platinum/ruthenium alloy anode catalysts, raising the operating temperature from 80 to 200°C increases the tolerance to carbon monoxide in the fuel gas from 100 ppm to over 30,000 ppm (that is, 3%). The CO impurity content in the hydrogen from a methanol reformer is typically less than 1% by volume, and hence reformat can be directly used to fuel the PEMFC. So far, small (10 cm × 10 cm) fuel cell stacks working at 170°C combined with methanol reformers operating at 210°C have demonstrated performances of up to 50 A at 750 mV per cell.

Electrochemistry and Catalysis

Work by the Energy Research Centre of the Netherlands ECN, has confirmed that carbon dioxide, which is present in reformat fuel in concentrations of up to 25%, can have a detrimental effect on fuel cell performance that goes beyond the dilution effects associated with an inert gas. In his talk 'Carbon dioxide poisoning on proton-exchange-membrane fuel cell anodes', G. J. M.

Janssen explained that these poisoning effects arise from the reverse of the water gas shift reaction: CO₂ is reduced by hydrogen to a reduced form (most likely carbon monoxide) which is adsorbed preferentially on the catalyst. Carbon monoxide is a well-known poison for pure platinum catalysts at low temperatures, the catalyst becoming inactive for hydrogen dissociation. From kinetic data, it is evident that some bimetallic catalysts also catalyse the oxidation of the adsorbed species to CO₂. Hence catalyst poisoning can be mitigated by using bimetallic alloy catalysts such as supported Pt/Ru, which has a high CO electrooxidation rate constant.

In a talk entitled 'Novel high performance platinum and alloy catalysts for PEMFC & DMFC', Y. Tsou of the E-TEK Division of De Nora North America Inc., reviewed the status of their products, including catalysts, gas diffusion electrodes, and membrane electrode assemblies (MEAs). In a departure from their traditional platinum sulfite route for catalyst preparation, E-TEK have developed new platinum chemistry to provide materials with a more homogeneous particle size and higher surface area. This enables increased metal loadings on carbon to be achieved while maintaining high metal surface areas. Using thermal treatments, true bimetallic alloy catalysts such as Pt/Ru can be produced with up to 50% metal loading on carbon. When used in PEMFCs, these exhibit resistance to CO poisoning. Alloy catalysts with a ratio of 80% Pt to 20% Ru have been found to provide optimum performance for DMFCs, while other carbon-supported alloy catalysts such as Pt/Mo, Pt/W and Pt/Sn can be prepared.

In his talk 'Ultra-low Pt loading anode for DMFC application', A. S. Aricò of CNR-ITAE Institute, Italy, described work undertaken to reduce the ppm requirements for DMFCs. A preparation procedure allowing the surface decoration of unsupported Ru catalysts by Pt nanoparticles has been developed. These have been examined by electrochemical stripping voltammetry to compare their electrocatalytic activity to state-of-the-art carbon supported Pt-Ru (1 : 1) alloys and bare unsupported Ru catalysts. Suitable performances have been achieved with

ultra-low Pt loadings on DMFC anodes at temperatures of 80–130°C. Reducing the anode Pt loading by a factor of twenty produces a loss of power density of about 35%. Catalysts containing small amounts of Pt nanoparticles on the surface of a less expensive metal, such as Ru, may prove a useful route to reducing catalyst costs for DMFC devices.

However, Aricò emphasised that improvements to catalytic activity are dwarfed by the effects of temperature in increasing the reaction rate. With an anode loading of 0.1 mg cm⁻² of platinum, and 1 molar aqueous methanol solution, raising the operating pressure and the temperature to 130°C could increase the current density from less than 0.6 A cm⁻² to almost 4.0 A cm⁻² at 0.4 volts per cell.

Stack and Cell Technology

In view of the current activity in commercialising micro fuel cells for electronic and consumer applications, a paper entitled 'Miniaturised proton exchange fuel cell in micromachined silicon surface' by G. D'Arrigo of CNR-IMM, Italy, was of particular interest. In this work, PEMFCs were fabricated using technology developed for ultra-large scale integrated (ULSI) microchips. The fuel cells consist of two symmetrical structures fabricated on 2.2 cm × 1.9 cm porous silicon wafers. Miniature rhomboidal microchannels, several microns below the surface, are formed by surface micromachining and etching processes. The rhomboidal trenches thus formed are closed up and formed into microchannels by depositing a surface layer of silicon using chemical vapour deposition. These microchannels distribute fuel and oxidant across each electrode. A patterned gold layer is used to define permeable porous sector areas and to collect the current.

Metallic clusters of Pt or Ru catalysts are deposited inside the porous silicon skeleton by electrodeposition, while the proton exchange membrane is deposited on the patterned porous membrane by a spinning process. The structures represent a novel method of miniature cell construction and possibly a new application for the electronics industry.

Poster Exhibition

The large number of posters concerned with ppm catalysts reflects the intense interest in direct methanol and direct ethanol fuel cells, and CO-tolerant catalysts for PEMFCs. A wide variety of catalysts are being investigated, including alloys of platinum with ruthenium, rare-earths, selenium and tin. These are supported on materials ranging from titanium mesh to carbon nanotubes, mesoporous carbon and acetylene carbon black.

In their poster 'Towards shape selective PEMFC/DMFC catalysts: Dependence of CO oxidation on Pt nanoparticle shape', S. Kinge *et al.* (Max-Planck-Institut für Kohlenforschung, Germany) describe how a "seeding method" has been developed to produce shape-specific nanocrystallites. This was used to deposit 4 nm truncated octahedral platinum nanoparticles on Vulcan XC72 carbon (20 wt.% Pt). Examination of these catalysts by cyclic voltammetry in a rotating disc electrode method shows two peaks corresponding to two different sites of CO oxidation, with peaks assigned to the {111} (0.72 V NHE) and {100} (0.83 V) crystallographic planes of the platinum particles.

A poster entitled 'A new direct methanol fuel cell by a membrane electrode assembly zigzag folded down' is self explanatory. This novel design for a micro DMFC is proposed by M. Shibasaki *et al.* of Tokyo University of Science. A membrane is folded into a 3-dimensional zigzag shape with electrodes inserted into the folds. Methanol is fed from one side of the assembly, and air diffuses into the cathode side via a porous insulator layer. Overlapping cathode supports provide inter-cell connectors to enable multiples of cells to be connected in series. A cell with an active area of 16 cm² × 2 has demonstrated 3 mW cm⁻² power density, operating on 2 M methanol and at ambient temperature.

Poster Prize Awards

Of the 170 posters presented at the conference, twelve were highly commended and, after a short presentation to the final selection panel, four of these were chosen to receive a prize. In the Low Temperature Fuel Cell category, W. Y. Lee *et al.*

(Korea Institute of Energy Research, Korea, (ROK)) received a prize for the poster 'Effect of micro-layers in gas diffusion layer on the performance of PEMFCs'.

In the Systems and Applications category, M. Oszcipok (Fraunhofer Institute for Solar Energy Systems, Germany) was awarded a prize for the poster 'Statistic analysis of operational influences on the cold start behaviour of PEM fuel cells'.

In the High Temperature Fuel Cells category, K. Sugiura (Osaka Prefectural College of Technology, Japan) gained a prize for the poster 'Evaluation of volatile behaviour and the volatilization volume of molten salt in DIR-MCFC by using the image measurement technique'.

Finally, in the Fuel Processing and Storage category, G. O. Alptekin (TDA Research Inc., U.S.A.) was awarded a prize for the poster 'Selective sorbents for natural gas desulfurization'.

Conclusions

The increased attendance at the conference compared to the one held in 2002, particularly by the academic community and research students indicates a higher level of interest in the technical aspects of fuel cells. The tremendous variety of papers and posters provides ample evidence that new ideas and innovative designs continue to advance fuel cell technology, and are rapidly overcoming the remaining barriers to producing commercial devices. Perhaps most significantly, development of modelling and other experimental techniques will make it possible to study the complex interrelated characteristics of cells, stacks and systems to enable even more rapid strides to be made in future.

References

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- 3 D. S. Cameron, *Platinum Metals Rev.*, 2003, 47, (1), 28

The Reviewer

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