

Fuel Cells: Science and Technology 2002, 25/26 September 2002, Amsterdam

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Fuel cells are energy generators which provide a combination of high efficiency combined with low pollutant emissions, based on the direct electrochemical oxidation of hydrogen or hydrocarbon fuels to provide an electric current, and at the same time forming water. They can be built in a wide range of sizes ranging from power for mobile telephones and laptop computers, through to multi-megawatt power stations. After decades of development and large scale trials, fuel cell generators are now entering commercial service to provide electricity and heat for individual homes, or district schemes. In addition, virtually all the world's major vehicle manufacturers are demonstrating electrically propelled passenger vehicles or municipal buses.

The conference had the theme "Scientific Advances in Fuel Cell Systems", with the aim of highlighting the technical challenges posed by the introduction of these new power generators. Together with the well established Grove Symposium series, it was intended to emphasize the scientific and the commercial aspects of the technology. The conference was fully subscribed, with 247 participants from 33 countries representing universities, research organisations, and manufacturers. Almost forty oral papers were chosen from the submitted abstracts, and in addition there were over a hundred high quality poster presentations. Most of the papers and many of the posters will be published early next year in a special edition of the *Journal of Power Sources*.

Recent developments of supported gold catalysts described at the Conference and elsewhere (1) indicate that there are numerous potential applications in fuel cell technology for gold materials. These include generation of hydrogen by reforming hydrocarbons and the subsequent water-gas shift reaction, and also in the purification of the resulting gas mixture by selective oxidation of carbon monoxide. Finally, there could be opportunities to exploit the properties of gold in the form of catalysts, particularly for low temperature proton exchange membrane (PEM) fuel cells, which are one of the most widely developed forms of generator and also the most susceptible to poisoning by impurities in hydrogen fuel.

The conference consisted of six sessions, covering the materials used in fuel cells, generation and storage of hydrogen fuels, modelling studies and engineering aspects. Materials and catalysis featured in three of the sessions, which served to emphasize their importance to the technology. For the purposes of this brief review it has been necessary to select topics presenting opportunities for the use of gold.

Hydrogen Generation

An efficient and compact source of hydrogen is essential for the operation of most fuel cells. Development of systems 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 PEM fuel cells, high purity hydrogen is required, since even 10 parts per million of carbon monoxide can lead to rapid performance deterioration.

In a talk entitled "A New Generation Of Water-Gas Shift Catalysts For Fuel Cell Applications", Wolfgang Ruettinger of Engelhard Corporation in the USA described the limitations of existing copper/zinc oxide based reformer catalysts. Engelhard have developed replacement materials with improved thermal stability and without the tendency to

become pyrophoric when exposed to atmospheric air. In the Engelhard system, natural gas is passed through a reactor to remove traces of sulphur, followed by the addition of a small proportion of air and passage through an autothermal reformer to produce hydrogen with 6-10% carbon monoxide. In the reactor, combustion of some of the fuel with the injected air provides heat for the endothermic reformer reaction. A water gas shift reactor then reduces the carbon monoxide content to 1-5%. Finally, by injecting a further small percentage of oxygen and passing the gas mixture through a selective oxidation catalyst, the CO content can be reduced to less than 10 parts per million.

The newly developed Engelhard "Selectra Shift™" catalyst has somewhat lower activity than traditional mixed oxide reformer catalysts, but greatly reduced sensitivity to oxygen ingress. However, the water gas shift reaction requires a large reactor vessel, and to make a more compact system it is likely to be replaced with a monolithic honeycomb supported catalyst. To further reduce the CO content of the hydrogen produced, a two stage partial oxidation system is being introduced.

In a talk entitled "Advances in Fuel Processor Catalysts", Jessica Reinkingh of Johnson Matthey Fuel Cells also described the development of reformers for PEM fuel cell systems. These are light, compact units intended for mobile applications, with the eventual capability of using a variety of hydrocarbon fuels including natural gas. In order to minimize volume and weight, an autothermal reformer system has been adopted. This entails using a pretreatment reactor to remove sulphur, then adding some air to the fuel and reforming, followed by a water gas shift reactor. Finally, a small proportion of air is again injected, and the fuel passes through a selective oxidization catalyst to convert carbon monoxide to carbon dioxide.

In order to construct very compact systems, space velocities of at least 100,000 volumes per hour are required for the reformer. Natural gas reformer systems have been run at a 140,000 hourly space velocity which retained 99.8% of their efficiency after 500 hours of operation. This was achieved using monolith support materials with very high surface areas. For good durability, it is essential to reduce sulphur impurities in the system to very low levels. For the water gas shift reactor, where it is necessary to operate at over 50,000 hourly space velocity, platinum on ceria catalysts are used. These exhibit high activity at less than 573 K and avoid the possibility of methane formation. The Johnson Matthey FP05 prototype, with a weight of 75 kg and volume of 470 litres produces sufficient hydrogen for a 75-100 kW fuel cell. This has operated on natural gas for over 2,000 hours with over 100 start-up and shut-down cycles.

In a poster entitled "FTIR study of methanol

decomposition on gold catalyst for fuel cells", Prof. Flora Boccuzzi *et al* of the University of Turin gave details of their study of the interaction of methanol, methanol-water and methanol-water-oxygen on Au/TiO₂ catalysts by in situ infrared spectroscopy and quadrupole mass spectrometry at different temperatures. The aim of the work is to elucidate the nature and abundance of the surface intermediates formed in different experimental conditions and to understand the mechanism of methanol decomposition, steam reforming and of combined reforming reactions. In the presence of oxygen, there is a direct conversion of methoxy species in formate species adsorbed on gold. It is proposed that oxygen absorbed on gold particles near oxygen vacancies of the support take part in the oxidative dehydrogenation of methanol. Studies such as this are leading to a better understanding of the role of gold in a range of supported gold catalysts examined by other authors including Fe₂O₃, ZnO, ZrO₂, TiO₂, Fe₂O₃, Fe₂O₃-ZrO₂ (1).

A poster by the World Gold Council entitled "Gold's Future Role in Fuel Cell Systems" listed some of the many potential uses for gold catalysts in fuel cell technology, including the use of supported gold catalysts in the water gas shift reaction. Research has shown that gold supported on iron oxide is more active at lower temperatures than the mixed copper/zinc oxide catalyst currently used commercially. In addition, the effectiveness of gold catalysts for the removal of carbon monoxide impurities from hydrogen streams from reforming reactions has already been demonstrated. Preferential oxidation of carbon monoxide in hydrogen-rich reformer gas can be achieved by gold on iron oxide catalysts which are significantly more active at lower temperatures than commercial catalysts such as the Pt on Al₂O₃ currently used. Gold has also been used in conjunction with the platinum group metals for the direct oxidation of hydrocarbon based fuels such as methanol. Other applications for gold in fuel cells were also described including their use as corrosion resistant materials in high temperature fuel cells, and the incorporation of gold catalysts to provide improvements in electrode conductivity (2).

Electrocatalysis

Dr. Anthony Kucernak, of Imperial College London, described techniques to produce platinum group metal and alloy catalysts in the form of small, nano-particulate spheres in a talk entitled "New Fuel Cell Electrocatalysts Based On Mesoporous Precious Metals". The technique can be used to produce unsupported platinum catalysts with metal areas of up to 35 m²g⁻¹ Pt. Combined with the use of mesoporous carbon supports which provide spacial dispersion of the metal crystallites and reduce sintering, metal areas of up to

90 m²g⁻¹ Pt can be obtained. The direct anodic oxidation of carbonaceous fuels appear to be structure dependent, affecting the mechanism of carbon monoxide absorption, and the technique produces catalysts which are very effective for the oxidation of methanol, formic acid and formaldehyde. Platinum-ruthenium alloy catalysts are less affected by strongly chemisorbed carbonaceous species which act as a poison.

The commercial viability of low temperature fuel cells, particularly proton exchange membrane (PEM) types has been transformed by developments in precious metal catalysts. In a paper entitled "New Catalyst and MEA developments for high performance PEM fuel cells," Graham Hards of Johnson Matthey Fuel Cells described advanced oxygen reduction catalysts, and also hydrogen oxidation catalysts which exhibit improved tolerance to carbon monoxide impurities. The structure of the PEM fuel cell requires catalyst layers as thin as possible to minimise the boundary between reactant gases and electrolyte. This means that catalysts must consist of pure metal, or high concentrations on conducting substrates such as carbon, and oxygen reduction (cathode) catalysts typically consist of 40% platinum. For hydrogen oxidation (anode) catalysts, a mixture of platinum and ruthenium has been found to be resistant to carbon monoxide adsorption, and typically 20% Pt / 20% Ru supported on carbon is used. For resistance to high levels of carbon monoxide, reference was made to bi-layer electrodes, which may be used in conjunction with additions of oxygen to the hydrogen fuel. In this case, selective oxidation of CO to CO₂ occurs on the surface of the electrode. This could be a further potential use for supported gold catalysts, deposited on the electrode surface, with their high activity for CO oxidation at low temperatures.

Gaby Janssen of the Energy Research Centre of the Netherlands (ECN) reviewed some of the techniques available for reducing the effects of impurities in hydrogen on cell performance in a talk entitled "Improving the tolerance of PEM fuel cells for reformat gas: results and perspectives". In addition to hydrogen, reformat gas contains nitrogen, carbon dioxide, carbon monoxide and water. By adding a small amount of oxygen (1-2%) and passing it over a catalyst, much of the remaining carbon monoxide in the fuel can be oxidized to carbon dioxide.

A second technique is to consume raw reformat gases, and allow the fuel cell to be partially poisoned by the carbon monoxide. By then periodically starving it of fuel while drawing a current, the anodes become polarised to the extent that they reach oxidizing potentials. This is sufficient to oxidize and liberate carbon monoxide chemisorbed on their surface. However, this technique is not favoured since it

requires regularly shutting down and restarting the fuel cell. Thirdly, by using palladium-rich carbon supported Pd/Pt alloy catalysts which have exhibited tolerance of carbon monoxide at 353 K, ECN have been able to operate small PEM fuel cell stacks for up to 500 hours in reformat gas without an air bleed. At present, other electrode modifications, such as the inclusion of CO filter layers, are under investigation. In the longer term, increasing the operating temperature of the PEM fuel cell to 423-473 K would provide greatly improved CO tolerance, and facilitate heat removal from the stack, but this requires the development of a new generation of proton exchange membranes.

The conference was concluded by the award of four prizes for the best submitted oral presentation and poster, the most original and the best student contribution. Overall, it served to emphasize the vital importance of science and technology to the successful commercialisation of fuel cells by reducing their cost and improving their performance and durability. A tremendous research and development effort is in progress, with the most advanced low temperature systems which use solid polymer electrolyte also requiring the highest purity hydrogen. This represents an excellent opportunity for gold catalysts for use in gas purification, both for the water gas shift reaction and to oxidize carbon monoxide at low temperatures.

Even though they have been used for many years in specialised low temperature alkaline electrolyte fuel cells, gold catalysts have not been widely investigated. There is evidence that pure gold has electrocatalytic activity in a wide range of applications, as well as forming alloys with the platinum group metals. In particular, the electrocatalytic properties of highly dispersed small particles are largely unexplored. Hence there are at least three areas in fuel cell technology with potential for using gold catalysts: in the formation and clean-up of hydrogen fuels, and as constituents of the fuel cell electrodes. In addition, the excellent corrosion resistant properties of gold could lead to other applications in the demanding environment of molten carbonate fuel cells. The conference was generally agreed to be highly successful, and is likely to be held again in Europe during September 2004.

Reference

- 1 Donka Andreeva, *Gold Bulletin* 2002, 35/3 .
- 2 D Cameron, R.J. Holliday and D.T. Thompson to be published in special edition of *Journal of Power Resources*, 2003