Advances with HotSpot™ Fuel Processing

EFFICIENT HYDROGEN PRODUCTION FOR USE WITH SOLID POLYMER FUEL CELLS

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Fuel cells, invented in the last century, have only in the past twenty years come under intense development and attention (1). There are several types of fuel cell, but the successful technological advances achieved with the solid polymer type fuel cell (SPFC) have given it a prominent position. SPFCs function as the prime mover for automotive propulsion and stationary power generation. The basic SPFC is an electrochemical device, which converts the chemical energy within a fuel directly into electricity in a single step. By comparison, a conventional combustion engine converts the chemical energy in a fuel into electricity indirectly in three steps:

• by converting the chemical energy into heat energy by combustion

• by converting the heat into mechanical energy in a piston or a turbine engine, and

• by converting the mechanical energy into electrical energy in a generator. By eliminating the two inefficient intermediate steps a fuel cell can produce electricity significantly more cleanly and efficiently.

The fuel for a fuel cell, usually in the form of a hydrogen-rich stream, is fed to the anode, and air is fed to the cathode. At the anode, the hydrogen is oxidised and the resulting flow of electrons are channelled into an external circuit. At the cathode, oxygen is reduced, using the electrons returning from the external circuit. Between the anode and the cathode is a solid polymer membrane which transports the ions (protons) produced by the oxidation and consumed by the reduction, thus closing the circuit. The electric current flowing in the external circuit is the prime motive power for mobile or stationary applications.

Because electrical power is generated (in one step) without the heat generating step, the fuel cell is not restricted by the Carnot efficiency limit which affects all combustion engines. The efficiency of a fuel cell electrochemical engine is therefore much higher than that of a combustion engine. Carbon dioxide emissions are reduced and no other pollutants, such as sulphur dioxide, nitrogen oxides or particulate matter, are produced. The core fuel cell component, the stack, has a long life and very low noise emissions, and with no moving parts does not require maintenance. These advantages make fuel cells attractive as a replacement for combustion engines, for instance for automotive propulsion and small- to micro-scale stationary power generation applications (2).

However, while it has advantages over conventional combustion engines, the SPFC engine requires hydrogen as fuel. For certain niche applications, the use of hydrogen fuel is acceptable, but for the most important automotive and stationary mass market applications, it is necessary to use conventional fuels, such as natural gas, liquid petroleum gas (LPG), gasoline or methanol. The fuelling issue is a potential barrier to its commercialisation and to overcome this problem, a fuel processor has been developed to produce hydrogen cheaply and efficiently from a range of conventional fuels. This missing "link" will enable propulsion and generation systems to evolve from present day combustion systems into more efficient and environmentally-acceptable technologies.

HotSpot™ Technology

HotSpot™ technology provides an efficient means of producing hydrogen from a hydrocarbon fuel on a scale that it is required for many fuel cell applications, see Figure 1 (3). The hydrogen-generating technology needed by small-scale fuel cell systems is very different to that of the large-scale industrial units which currently generate hydrogen. Traditionally, hydrogen is generated on a large scale using one of two basic processes: steam reforming or partial oxidation.

Fig. 1 The P2 prototype fuel processor: the top section contains the HotSpot™ reformer, capable of producing enough hydrogen for a SPFC to generate 7 kW of electricity. The lower section houses the Demonox™ CO clean-up unit where the CO content of the reformate is reduced to below 10 ppm. The inlets and outlets are contained within the central section. The reformate emerges from the processor via the largest of the tubes that can be seen on the right of the unit. Also visible on the front of the central section are connections for a number of thermocouples; these are to provide useful diagnostic information about this prototype unit

Steam reforming is an efficient process for the production of hydrogen, as up to 4 molecules of hydrogen can be produced per atom of carbon in the case of methane. As this reaction is kinetically slow, large catalytic reactors are required. The reaction is also endothermic, so a large amount of energy must be put into the process.

Partial oxidation is a fast reaction and can be carried out with or without a catalyst. It is exothermic so no external energy input is required. The maximum amount of hydrogen that can be produced is 3 molecules per carbon atom but this process also includes a water gas shift reaction to convert the carbon monoxide (CO) produced in the process. The water gas shift reaction is quite slow and thus the reactors can be very large. The partial oxidation reaction also creates high temperatures which may cause problems, especially in small-scale units designed for domestic use.

Instead of this, HotSpot™ technology uses autothermal reforming which is a combination of partial oxidation and steam reforming on the same catalyst particles. This has the advantage that the overall reaction rate is quite fast, so the catalyst bed can be small. The exothermic and endothermic reactions can be balanced so no external heat needs to be supplied to the system. Using this technology it is also possible to produce over 3 molecules of hydrogen per carbon atom. Hydrogen is thus being generated both from the water and from the natural gas.

Reformer Catalyst

The reformer catalyst developed for HotSpot™ was required to activate the hydrocarbons over a range of temperatures and to withstand relatively high temperatures without deactivation. The reformer catalyst also had to be active for steam reforming and partial oxidation and be resistant to coking. Inside the reformer section of the
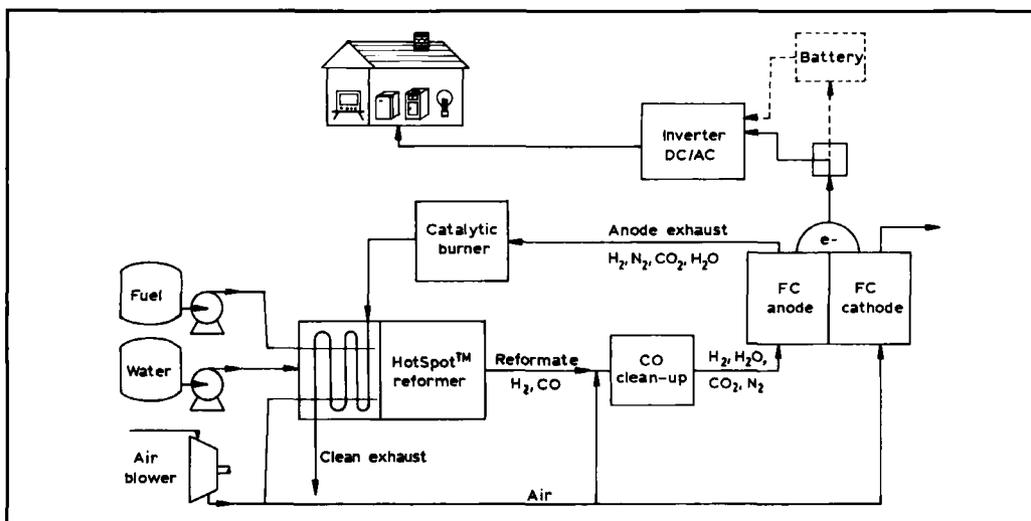
Fig. 2 The three-part system of the fuel processor which produces pure hydrogen for supply to a fuel cell. The HotSpot™ produces hydrogen from hydrocarbon fuel using autothermal reforming. The CO clean-up unit removes CO which would otherwise poison the fuel cell catalysts. The catalytic burner burns the hydrogen left over from the fuel cell, recycling the energy. All these units contain platinum group metals catalysts

HotSpot™, besides the catalyst, are heat exchange components essential for the efficient operation of the fuel processor. Their integration with the catalyst section allows the reformer to be operated over a wide range of outputs with high efficiency and to handle transients without notably changing the composition of the reformate being produced. This is important if a combined heat and power (CHP) system is to cope with changing electricity demands.

CO Clean-up

When the reformate emerges from the reformer section of the fuel processor, it contains a small amount of CO which must be removed before it can be used to power a fuel cell. CO is a poison to solid polymer fuel cell electrodes as it preferentially adsorbs to the catalyst dramatically reducing the performance of the cell. There are a number of ways in which CO can be removed and selective oxidation was chosen as the best. However, the selective oxidation of CO presents a number of challenges, as reducing CO levels to less than 10 ppm when hydrogen is present at concentrations of up to 50 per cent, requires a catalyst of very high selectivity. To achieve this a range of platinum group metals catalysts were developed. These catalysts exhibited high selectivity but only over a

specific temperature range. As the reaction is exothermic, a new engineering system was devised in which a multistage reactor is used with interstage temperature control. This Demonox™ system can reliably reduce CO levels from over 3 per cent to less than 5 ppm over a range of throughputs. The heat produced in the Demonox™ system is recovered and can be used – either for heating in a cogeneration (CHP) system or internally in the fuel processor.

Anode Exhaust Gas Burner

The final part of the system is the anode exhaust gas catalytic burner. Between 10 and 20 per cent of the hydrogen fed into the fuel cell passes through unreacted. This hydrogen must be recovered if the system is to be efficient.

The hydrogen is therefore burnt catalytically and the heat is used to generate the steam required in the reformer. Any traces of CO and unconverted hydrocarbons are also burnt at this stage to ensure that the only emissions from the fuel processor are carbon dioxide and water. In order to do this, a new catalyst was developed. This catalyst is active enough for the hydrogen to react with oxygen (air) at room temperature, and catalyse the combustion of CO and hydrocarbons at relatively

low temperatures while being itself thermally stable.

The Johnson Matthey fuel processor combines these three new catalytic systems and novel reactor designs into a single efficient unit and enables SPFCs to be used successfully for micro-cogeneration applications, see Figure 2.

Micro-cogeneration

Micro-cogeneration is the simultaneous generation of electric power and heat by a generating device at the site where both are required. All generators produce waste heat, so producing one small enough to be located in residential or light commercial environments, means that the byproduct heat can be immediately used, thus improving the overall efficiency. Many different types of conventional combustion-engine cogeneration systems exist, but few are practical or economical at such micro-scales. Fuel cell and fuel processor technologies are highly suitable technology for micro-cogeneration systems, being compact, quiet, efficient, responsive, inherently low-maintenance and non-polluting.

The development of novel fuel cell-fuel processing technologies is expected to increase the number of micro-scale distributed generation sites. Regions where price differences between electricity and natural gas, especially where electricity costs 4 times or more than gas, where natural gas, LPG and compressed natural gas (CNG) are more readily available and where there is a lack of an extensive electrical transmission and distribution infrastructure are likely beneficiaries.

Micro-scale fuel cell generation and cogeneration systems of output less than 50 kW are expected to be used for small units, for example, as backup power, uninterruptible power and high quality power, for sensitive sites such as computer data centres, hospitals and power generation in remote sites, while mass use is expected, for residential and light commercial use.

Conclusions

Fuel processing enables the potential of SPFCs to be realised. The Johnson Matthey fuel processor has been successfully tested with a number of fuel cells and supplied to developers of fuel cell systems for transportation and stationary applications. The fuel processor has been developed to a much smaller scale than previously thought possible, and can be used in a range of applications not previously accessible with conventional technology. These advances in micro-scale fuel processing technology are expected to encourage the development of further catalysts and catalyst systems to exploit the benefits of fuel cell technology. The system is now in the advanced development phase, with a commercial product planned in the near future.

References

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Cryo-Imaging of Palladium Colloids

A team of researchers from Lund University in Sweden have succeeded in imaging the aggregation behaviour of palladium nanoparticles in solution, at different values of pH and ionic strength, by low-electron dose cryo energy-filtered transmission electron microscopy (cryo-EFTEM) (J.-O. Bovin, T. Huber, O. Balmes, J.-O. Malm and G. Karlsson, *Chem. Eur. J.*, 2000, 6, (1), 129–132).

Palladium colloids, covered by sodium sulfanilate protective ligands, were rapidly cooled by plunge-freezing to avoid particle rearrangement. Elemental mappings were taken at low energy and short exposures to prevent damage. Shapes, sizes, structural defects and distances between the agglomerated colloids were visible. A two-window method (jump ratio imaging) identified the palladium colloids. The colloids were always present as a mixture of single nuclei and aggregates in solution. The number of single particles in solution could be increased by lowering the ionic strength and raising the pH, but some agglomerates of two (or more) nuclei still remained.

This technique may be used to determine the best deposition conditions for the palladium/ligand and other metal/ligand systems and to study the chemistry of solids interacting with liquids.