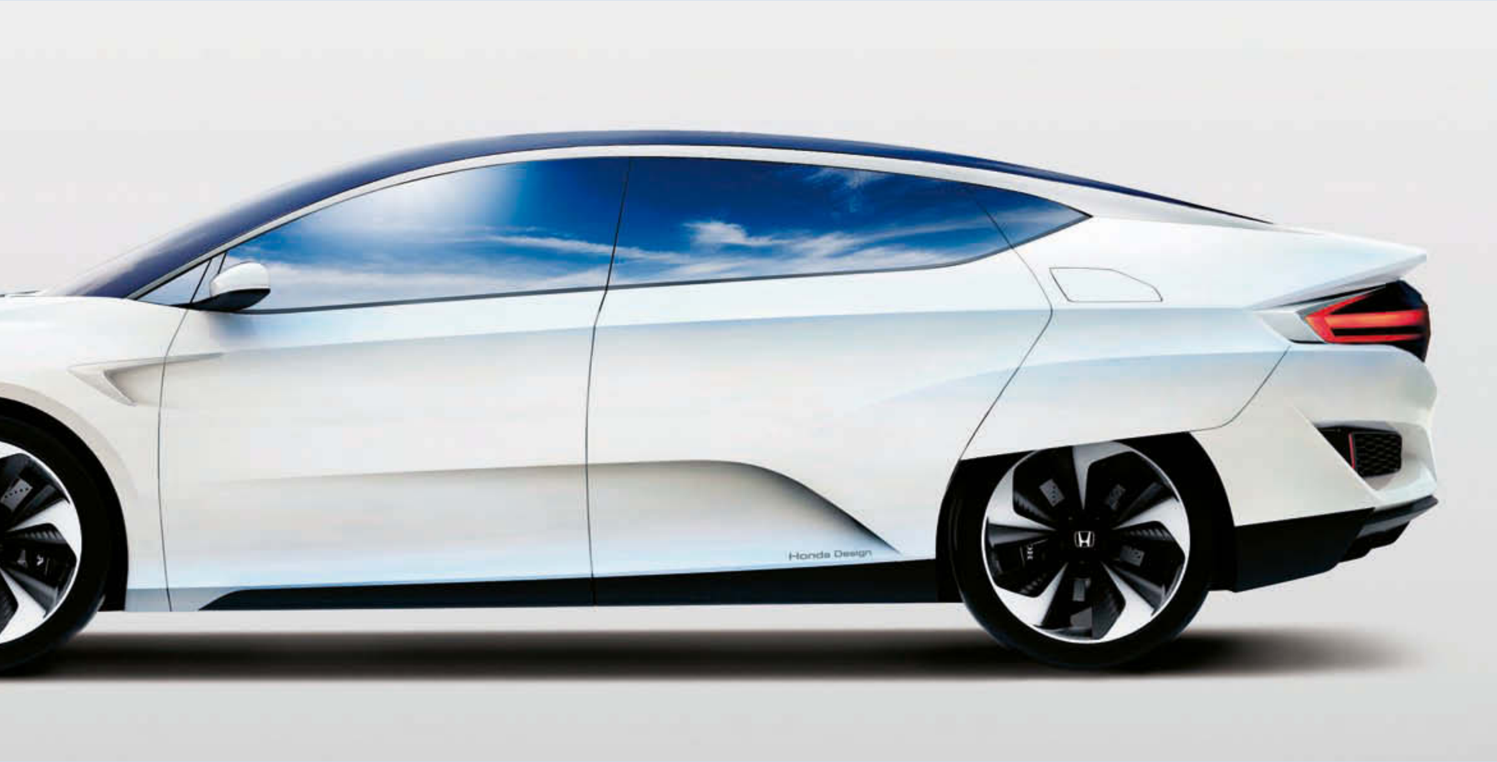
ETHANOL FUEL CELLS

Resident expert Phil Thane takes a look at the research going in to fuel cell technology and why widespread production is still some years away.

During December 2014, two major motor manufacturers announced new models powered by fuel cells running on hydrogen, the Honda FCV and the Hyundai ix35. The obvious snag, apart from the price, is that the UK has just 15 hydrogen fuelling points. In October last year, the Government announced plans to provide up to £11million support to facilitate the roll-out of hydrogen fuelled vehicles and associated infrastructure across the UK, and this includes the creation of 15 more fuelling points. But is hydrogen really a sensible choice?

HYDROGEN, THE PLUS POINTS

Burn hydrogen in air and it combines with oxygen to produce water and a lot of heat. React hydrogen and oxygen in a fuel cell and you get rather less heat, and the 'missing' energy appears as electric current which can be used to drive an electric motor. The combination of hydrogen fuel cell and electric motor, as used by Honda and Hyundai, is significantly more efficient than an internal combustion engine and the exhaust gas is pure water. Fuel cells combine well with kinetic energy recovery systems, that can store braking energy in batteries for a short burst of extra power when needed.



THE HYDROGEN ECONOMY IS ON TRACK THEN?

Not yet. The petroleum industry has developed over a hundred years or so, to produce and refine crude oil, and distribute petrol and diesel. They have thousands of storage tanks, hundreds of thousands of miles of pipelines, refineries, ships and road and rail tankers, as well as hundreds of thousands of forecourts worldwide, with tanks, pumps and safety systems. Road vehicles have been designed to use these fuels; engines, tanks, pipes, pumps and engine management systems all optimised for well known fuels. Now imagine replicating that infrastructure worldwide for hydrogen – it's not going to happen quickly.

The other elephantine issue in the debate is where does

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hydrogen come from? Hydrogen is the most abundant element in the universe, but it is so light and so reactive that any naturally occurring hydrogen on earth simply drifts away into space, or reacts with something else. Most hydrogen is either in the form of water or in one of hundreds of hydrocarbon compounds. Hydrogen is widely used in industry and most is made by steam reforming natural gas. So although a hydrogen powered car emits only water vapour, somewhere a lot of fuel is being burnt to raise steam to react with a lot of gas.

There are other ways to make hydrogen, electrolysis of water for one. But it's expensive using conventional electricity (from coal), doing it with 'green' electricity on a large scale is never likely to be feasible.

Splitting water into hydrogen and oxygen without electricity might turn out to be the answer. Researchers at Purdue University, Indiana, demonstrated in 2007 that an alloy of aluminium and gallium in water does the trick, the aluminium is oxidised to alumina releasing hydrogen. The gallium catalyst can be re-used and the alumina regenerated into aluminium – using quite a lot of electricity.

In April 2013, a team of Virginia Tech researchers, led by Dr. Y.H. Percival Zhang, announced that they had created a novel biocatalyst that can produce hydrogen from xylose – the second-most abundant sugar in plants. Neither process is likely to be developed on a commercial scale for many years, though.

HOW DO FUEL CELLS WORK?

At its simplest, a fuel cell consists of two chambers separated by a membrane which acts as an electrolyte, with an electrode in each chamber. Hydrogen enters one chamber, and oxygen, or more usually air, enters the other. On the hydrogen side, a catalytic reaction on the surface of the anode splits hydrogen atoms into positively charged ions and negatively charged electrons.

The electrons are conducted out via the anode as useful electric current. The membrane is impervious to gas molecules, but permeable to hydrogen ions, which pass through to the other chamber. The electrons flow into the cell on the oxygen side via the cathode, where another catalytic reaction re-unites them with the ions and the resulting hydrogen reacts with the oxygen to make water (and heat).

In practice, the electrodes are either porous or etched with fine channels to create the widest possible contact area in the smallest space. Platinum is usually used as a catalyst, deposited as a thin layer on the electrode surface. Direct Ethanol Fuel Cells (DEFC) are much the same, but with detail changes. The anode side has to be engineered to accept a liquid rather than a gas, it is still the hydrogen ions and electrons that provide the power, but the carbon and oxygen in the fuel have to be dealt with. Earlier indirect fuel cells had a separate reactor, where ethanol was converted to hydrogen and CO_2, but in the direct cell it all happens at the anode. First the catalyst needs to be able to split ethanol, and there is plenty of research into that still to be done.

Separated from hydrogen, the carbon and oxygen would naturally combine to form carbon monoxide, because there is insufficient oxygen to form dioxide. CO is highly toxic, but it also poisons the catalyst and stops it working. The best solution so far is to add water to the

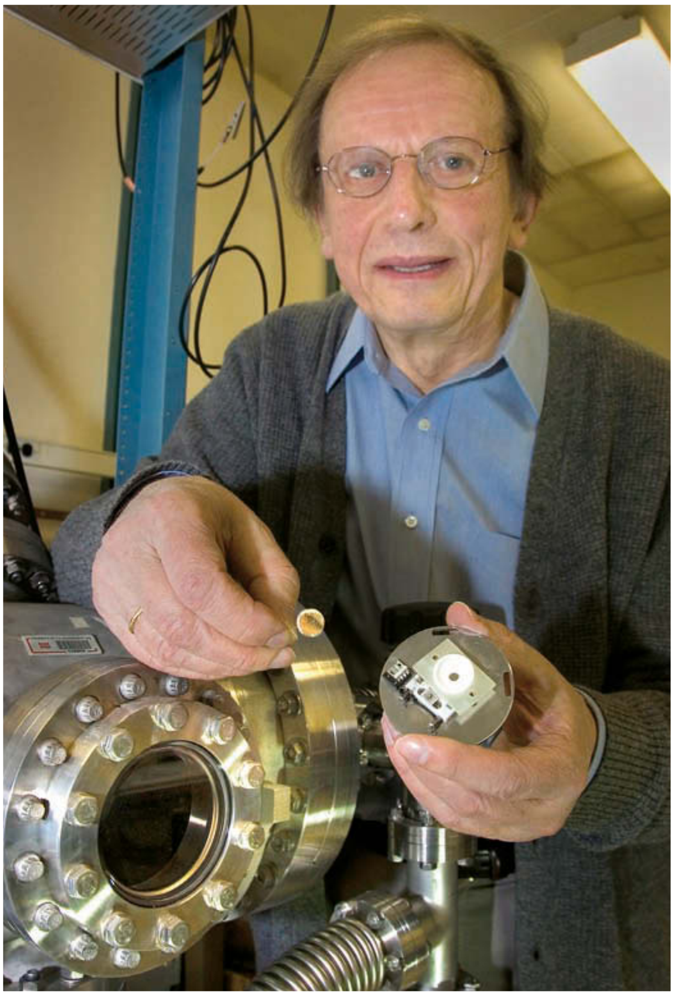
SO WHY ETHANOL?

Ethanol and methanol are types of alcohol, ethanol (CH3CH2OH) is present in alcoholic drinks and methanol (CH3OH) is used in hardware store 'meths' to render ethanol undrinkable. Both contain a lot of hydrogen, with a little carbon and oxygen, and can be used in fuel cells. Both are liquid, which makes them a lot easier to store, transport and pump into a vehicle than hydrogen. In 2009, Toshiba announced small scale methanol fuel cells to recharge phones and other gadgets 'off-grid', but they never caught on.

Ethanol is currently the favourite with researchers because it is more energy-dense than methanol and much less toxic. Ethanol is already made in quantity as a biofuel additive to conventional petrol, so the oil industry and distribution network would find it relatively easy to deal with compared with hydrogen. Biofuel ethanol is generally produced from sugar or grain, synthetic ethanol is produced from petrochemicals. Brazil, with an awful lot of sugar cane, is the only country in the world that produces enough bio-ethanol to power a significant proportion of its transport. However, even if fuel cell cars ran on petroleum-derived ethanol, the increased efficiency compared with internal combustion engines would help reduce greenhouse gas emissions.

AN ETHANOL ECONOMY?

Maybe, one day. Bio-ethanol faces the same problem as biodiesel, either the industry takes agricultural land from food production, driving up food prices and creating shortages in poorer countries, or it adds to greenhouse gas problems by cutting down forest and draining swamps to press more land into production. There is a lot of research into alternative means of production; micro-organisms that can ferment waste materials for example. As ever there are no quick easy answers in the alternative fuels business.



ethanol, which is split into hydrogen and oxygen. The oxygen ensures that CO_2 is produced as waste gas, and the hydrogen behaves just like the hydrogen from the ethanol. In a practical system, waste water from the cathode would be condensed and returned to the anode side. Splitting water and moving extra hydrogen ions through the membrane reduces the efficiency of the cell, an issue known as water drag.

Radoslav Adzic, Senior Chemist at the Department of Chemistry, Brookhaven National Laboratory in Upton, New York state, is one of the world's leading experts on catalysts for fuel cells, and author of several papers on the subject. Many catalysts have been tried by different and varied research groups, but Adzic's group have concentrated on improving the performance of platinum by manipulating it at an atomic level.

Solid slabs of platinum are expensive, and only the outer surface can take part in the reaction, so they are focussed on making 'mono-layers' on other materials, ie a layer that is just one atom thick. They realised that because different metals have atoms of different sizes, the platinum atoms can be either squashed closer together or stretched further apart than they normally would be in a piece of solid platinum, depending on the type of metal they are deposited on. This straining of the mono-layer increases the performance of the catalyst giving more current per cm^2 of surface.

So far the best catalysts are made of three materials – a base of tin, coated in gold, then platinum. The tin provides the support, and is relatively cheap. The platinum is the active catalytic layer, and the gold puts the platinum under strain. Fortunately, the layers are so thin that Adzic estimates that a stack of cells big enough to provide 100kW – plenty for a decent car – would use about as much precious metal as a current generation catalytic converter.

Phil Thane

USEFUL LINKS

If you want to read more about DEFC, try here:

BNL
www.bnl.gov/chemistry/see

BNL Press release about DEFC
www.bnl.gov/newsroom/news.php?a=1898

Paper by Cai & Adzic about fuel cell catalysts
www.hindawi.com/journals/apc/2011/530397