

Making Fuel Cells More Affordable

With oil near \$50 a barrel, alternatives to gasoline, such as fuel cells, have found their way into experimental power systems for laptop computers and into many experimental cars. The main drawback to the commercialization of fuel cells has been their cost. For example, an automotive fuel cell engine can cost as much as \$100,000 apiece — nearly 25 times the cost for a gasoline engine of equal power. In proton exchange membrane (PEM) fuel cell engines, the membrane itself can cost almost as much as the entire gasoline engine. Additionally, today's fuel cell membranes require replacement every year or so.

PolyFuel, Inc. (Mountain View, CA; www.polyfuel.com) has developed a hydrocarbon membrane technology for hydrogen-based automotive fuel cells that are said to cost about half as much per square meter as the conventional perfluorinated PEM membranes. "Current products, such as DuPont's Nafion will let enough protons slip through to generate about 6.5 kW/m, but our hydrocarbon membrane will generate more than 7 kW," explains Jim Balcom, PolyFuel's president (A car would require 50 to 75 kW). Furthermore, PolyFuel's hydrogen membrane technology has demonstrated a 35–50% increase in durability when compared to its perfluorinated counterparts.

The backbone of the Nafion membrane is formed from relatively weak polytetrafluoroethylene (PTFE)-like polymer fibers. Conductive clusters of water form at the ends of side chains extending from the PTFE backbones. "The side chains have sulfonate groups

on the ends, which are hydrophilic, so they attract water," explains Balcom. Protons follow a winding path from cluster to cluster while crossing the membrane (Figure 1); between clusters, it is forced to use fewer free water molecules as a conductive pathway. Since the conductive clusters are relatively far apart, large amounts of free water (*i.e.*, a higher level of humidification) are required to keep conduction going. At elevated temperatures, the PTFE-like backbone expands, pulling the conductive groups farther apart. Some of the free water also evaporates. Together, these effects reduce membrane conductivity.

In contrast, the PolyFuel membrane consists of alternating structural hydrocarbon blocks and conductive sulfonated blocks. The structural blocks bind together, causing the conductive blocks to line up (Figure 2). Water is attracted to these blocks because of their molecular structure, and forms a continuous conductive pathway for the protons from the fuel side of the membrane to the air side. Balcom notes that the nature of the hydrocarbon backbone structure makes the PolyFuel membrane 16 times stronger than perfluorinated membranes, even at elevated temperatures. "Because the conductive blocks are closely aligned, the membrane exhibits good conductivity at low humidification as well as at higher temperatures — at 95°C and 50% air-relative humidity — a performance

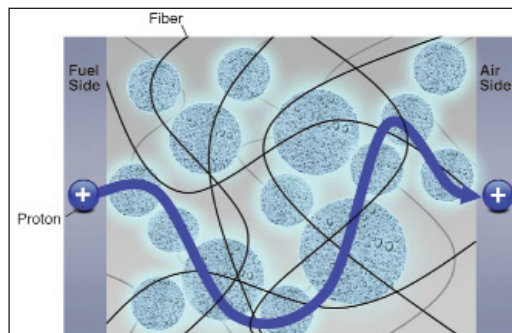


Figure 1. The perfluorinated membrane is a spaghetti-like maze of twisting, winding conductive paths that break down as they dry out or heat up.

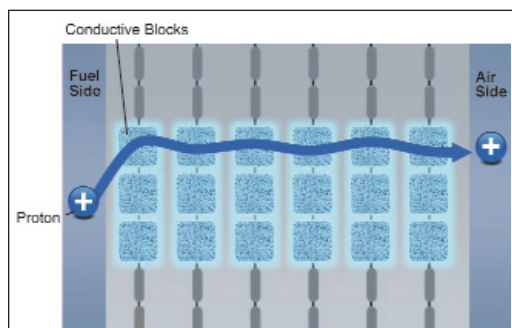


Figure 2. The PolyFuel membrane is a nanostructured array of highly conductive proton superhighways held together by strong structural hydrocarbon blocks.

combination that has never been achieved before with other materials," he explains. "It also works well at low temperatures (around 32°F), while fluorine-based membranes produce very little power at such low temperatures," Balcom continues.

There are problems that need to be resolved before PolyFuel's membrane reaches the marketplace, including the logistics of producing hydrogen and transporting it to fuel-cell vehicle filling stations (see p. 16). Nearer-term commercialization is possible for the firm's hydrocarbon membranes, which are directed at portable direct methanol fuel cells (DMFCs), for which PolyFuel is planning to launch commercial tests in 2005. "Unlike Nafion membranes, which are designed for a hydrogen environment, PolyFuel's membrane is robust in the presence of methanol, resulting in only 1/3 of the methanol crossover seen in conventional perfluorinated membranes at the same output level," says Balcom. This allows portable fuel cell systems based upon the DMFC membrane to be

PEM Primer

Proton exchange membranes comprise a stack of cells, each of which has two bipolar plates and a polymer membrane. One plate acts as the anode and the other as the cathode. Surface channels in the plates distribute hydrogen and air to the membrane between them. A thin layer of platinum catalyst on the membrane dissociates hydrogen into protons (positive hydrogen ions) and electrons, which pass through the membrane to the cathode, and electrons, which exit the stack as an electrical current before reaching the cathode, where they react with the protons and oxygen in air to form water and heat.

about 1/3 smaller, lighter and less expensive, as well as up to 35% longer running on the same amount of fuel. "We anticipate early commercial launch of the portable DMFC membranes in 2006 and a full-scale launch in 2007," says Balcom.

Meanwhile, Ticona (Florence, KY; www.ticona.com), the technical polymers business of the Celanese Group (Kelsterbach, Germany), has lowered the fabrication costs of PEM fuel cell bipolar plates by at least 50% with a new model that is made solely of injection-molded thermoplastics (IMTs) vs. other materials (*e.g.*, aluminum, gold-coated stainless steel, graphite or thermoset-graphite blends), and cuts the cost per kilowatt needed to operate the stack from \$4,000/kW to \$1,050/kW. Frank Reil, Ticona's market development manager, points out that the use of IMT components represents significant progress in meeting the European Union's target cost of \$665/kW by 2010 for 2-kW residential units.

The 17-cell prototype features injection-molded bipolar plates (measuring 150 mm × 150 mm × 2.5 mm thick) fabricated of Ticona's Vectra liquid crystal polymer (LCP) and end plates made of Fortron polyphenylene sulfide (PPS; Figure 3). The bipolar plates are produced in volume (currently by SGL Carbon; Meitingen, Germany), the end



Figure 3. Ticona's prototype proton-exchange membrane fuel cell, designed with injection-molded bipolar plates, reduces the production cost of this model by 50%.

plates are manufactured by Ensinger (Nufringen, Germany), the membranes by PEMEAS (Frankfurt, Germany) and the stack assembly by ZSW (Ulm, Germany). "With a cycle time of just 30 s, the bipolar plates are produced in volume without the labor- and cost-intensive machining and other finishing steps needed to form their intricate channels when other materials are used," says Reil. "Further, the LCP's ability to carry a carbon loading of over 80% and still process well exceeds the performance capacity of nearly any other engineered thermoplastic." Both polymers are known to withstand the aggressive media found in fuel cells,

while remaining dimensionally stable, even at temperatures as high as 200°C. Fortron PPS can also be used in peripheral components to further reduce costs, as can other injection-moldable engineering polymers, such as Celcon acetal copolymer.

Improving stationary fuel cells

Stationary fuel cells, possibly the next generation of boilers — are usually operated by natural gas, which contains a high proportion of hydrogen in the form of methane, and generate electricity and heat with an overall efficiency in excess of 80%. With power outputs between 10 kW and 250 kW of electrical energy and power efficiencies of 30–50%, they already match the efficiency levels of those exhibited by large coal and gas power plants. An obstacle to the commercialization of stationary fuel cells is attributed mainly to the pretreatment of natural gas to obtain pure hydrogen feed.

Engineers at BASF AG (Ludwigshafen, Germany; www.basf.com) have simplified these reactions by switching from so-called autothermal reforming (reacting the methane with air and steam) to steam reforming (reacting the methane with steam only) to produce hydrogen. "This eliminates some of the catalytic steps involved in performing the conversion, thereby cutting production costs by as much as 30%," says Markus Hoelzle, BASF product manager for fuel-processing catalysts.

Hydrogen generation by autothermal reforming is a six-step process that involves: desulfurization of the natural gas feed; reforming of the natural gas in a gas mixture of hydrogen and carbon monoxide (CO) at 750–900°C over a platinum/rhodium (Pt/Rh) catalyst; three catalytic reaction steps at decreasing temperatures to convert the CO into CO₂ (high-temperature CO removal (350–400°C) over a Pt catalyst, low-temperature CO removal (170–250°C) over a Cu catalyst, and fine purification by CO oxidation at 100–200°C over Pt/Rh catalyst); and a final stage involving a catalytic reactor with a Pt/Pd catalyst to incinerate fuel cell off gases. "Most

Stabilizing Metal-Oxo Catalysts

Metallic platinum has long been known to be an excellent catalyst for oxidations of organic compounds. However, further improving the reactivity of platinum in catalytic materials including fuel cell electrodes and/or using less platinum in these systems remains a goal of both fundamental and practical importance. In context with better understanding of platinum-oxygen interactions and reactivity, the first platinum-oxo complex has been prepared and characterized by a team spearheaded by Craig Hill at Emory Univ. (Atlanta, GA; www.emory.edu).

This complex, formed by reaction of platinum(II) with oxygen in the presence of metal oxide clusters (polytungstate units), which serve as ligands to the platinum, contains an unprecedented double bond between platinum and oxygen. "These Pt-oxo units are likely intermediates in many platinum-based oxidations," says Hill. In the Emory compound, the Pt-oxo unit is stabilized by the donation of antibonding electrons (electrons in higher *d* orbitals) to the tungsten atoms of the ligands. "This electron donation (or "backbonding") phenomenon strengthens the platinum-oxygen bond," explains Hill.

Examination of platinum and other metal-oxo compounds of the late-transition-metal elements that would serve as electrodes will facilitate probing the features that control the rates and selectivities of oxygen-based oxidations catalyzed by these metals.

of these stages are necessary to remove carbon monoxide, which is a strong poison for the catalysts in the fuel cell,” says Hoelzle.

Switching from autothermal to steam reforming requires less expensive catalysts for reforming (Ni/Rh vs. Pt), eliminates the need for precise dosing of air, cuts out the initial high-temperature reaction required for CO removal, purifies CO at 100–200°C over Ni/Ru catalyst and incinerates thermal off gases at 600–800°C.

Finally, a simplified setup compared to the initial five catalytic reaction steps results, featuring three catalytic reactors and one burner.

Two of these reactors, namely the reactors for CO removal and CO purification, can be linked together by a heat exchanger since they are operating at the same temperature level. And finally, the thermal burner generates the heat for the heat-consuming steam reforming reactor. Hoelzle says the company is working to further reduce costs by improved catalysts for hydrogen generation as well as for the fuel cell electrodes. In the long term, a total substitution of all precious metal catalysts by base metal systems is the ultimate target (sidebar on previous page).

CEP

PROCESS TECHNOLOGY

1-Octene via Selective Tetramerization of Ethylene

The linear comonomers 1-hexene and 1-octene are used in industry to make polyethylene. While several firms have developed highly selective chromium catalysts to make 1-hexene via an ethylene trimerization, the analogous tetramerization to produce 1-octene has remained elusive. The proposed mechanism for trimerization involves a seven-membered metallacycle intermediate consisting of a chromium atom and three conjoined ethylene molecules. Expansion of the ring to the nine members needed to form 1-octene was believed to be unlikely to occur, until now.

A team led by Annette Bollmann of Sasol Technology (Johannesburg,

South Africa; www.sasol.com) explored a variety of Cr(III) catalysts with diphosphine ligands to make 1-octene, finding several combinations that provide nearly 70% selectivity for the olefin [*J. Am. Chem. Soc.*] Optimization led to production rates of more than 500 kg/h of product per kg/h of catalyst. Sasol is increasing production of 1-octene to meet global demand, which is expected to grow at 6–8%/yr.

A Supercritical Route to Hydrogenation

Supercritical reactor technology can benefit many reactions, such as hydrogenation, where the replacement of conventional solvents with supercritical carbon dioxide (CO₂), can greatly increase hydrogen’s solubility and improve yields. However, the generation of supercritical CO₂ requires pressures of around 100 bar and metering gases at the right concentrations and flowrates — a task that is often difficult, expensive and hazardous.

Now, a research group at the Univ. of Nottingham (U.K.; www.nottingham.ac.uk) led by chemistry professor Martyn Poliakoff has developed a supercritical hydrogenation reaction process that renders the storage and metering of high-pressure gases unnecessary. Working with Poliakoff, technology licensor HEL Group Ltd. (Hertfordshire, U.K.; www.helgroup.com) has designed a laboratory-scale reactor measuring 35 cm wide × 30 cm deep × 50 cm high offering flowrates from 0.05 to 50 g/min of total gas. These units are available to industry for testing (Figure 1).

In the lab-scale reactor, formic acid (HCOOH) is pumped through a small, heated piece of tubing (~5 mL) filled with commercially available catalyst containing 5% platinum. The formic acid decomposes into a mixture of CO₂ and H₂ at a ratio of CO₂:H₂ = 1.0 or higher (Figure 2), leaves the tubing at pressures of up to 400 bar, and enters the supercritical reactor, together with the substrate.

At the same time, ethyl formate, is also passed over the catalyst in a separate compartment, decomposing

into CO₂ and ethane, compounds that become supercritical fluids under the same conditions — those in the downstream reactor. “Altering the flowrate of the formic acid and ethyl formate allows us to change the proportion of hydrogen in the gas stream to that needed for the hydrogenation reaction,” says Poliakoff.

In contrast to conventional reactions, which require many process steps to recover the product, followed by treatment or disposal of the solvent, product recovery in the supercritical reactor requires only a reduction of pressure. The supercritical CO₂ changes back into a normal gas, leav-



Figure 1. HEL Group’s supercritical flow reactor measures 35 cm wide, 30 cm deep, and 50 cm high and handles gas flowrates up to 10 g/min.

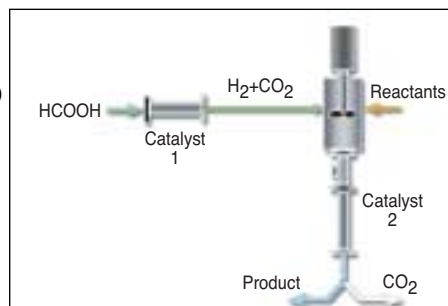


Figure 2. Supercritical fluid hydrogenation technology works without high-pressure gases by using liquids that decompose into CO₂. Both figures courtesy of HEL Group.