Update

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Breaking Ground on the Fuel Cell Frontier

Fuel cells offer promises of near-zero emissions, renewable-fuel usage, and high-efficiency energy for mobile and stationary applications — the question is just when these benefits will materialize. "I see a lot of progress, but we were expecting something to happen by now, and it seems unrealistic to expect something in 2004," says director of energy research Atakan Ozbek at ABI Research (Oyster Bay, NY; www.abiresearch.com). A report from the National Academy of Engineering and National Research Council (both in Washington, DC; www.nationalacademies.org) suggests that the Bush Administration's goal of making H_2-powered fuel-cell cars practical and cost-effective by 2020 may be overly optimistic, and that the H_2 economy is several decades away.

Against this backdrop, chemical engineers are helping to bridge the gap between fuel cells' promise and reality. Proton-exchange membrane (PEM) fuel cells own the largest share of the market, accounting for half the current installations, according to the Freedonia Group (Cleveland, OH; www.freedoniagroup.com) (see Table). In these systems, a H_2-containing fuel passes over the anode, releasing electrons; the H_2 ions pass through a polymer-membrane electrolyte and combine with oxygen at the cathode to form water. Operating at about 80°C, PEMs are attractive for automotive, stationary and portable power-generation applications.

Some PEM manufacturers are focusing their product development efforts on the automobile market, which poses the toughest challenges. "This low-cost, high-volume application has to be very reliable and durable," says Michael Rosenberg, corporate relations manager at Ballard Power Systems (Burnaby, BC; www.ballard.com). "We must deal with vibration, dust, different operating temperatures, and continuously ramp from low to full power," he continues.

Figure 1. Zero-emission Mercedes-Benz Citaro buses, powered by Ballard fuel-cell engines, transport commuters in London, U.K., and Madrid. Spain. These and eight other cities throughout Europe (the others are Amsterdam, Barcelona, Hamburg, Stuttgart, Luxembourg, Porto, Stockholm, and Reykjavik) participate in the European Fuel Cell Bus Project, which puts 30 buses powered by Ballard fuel cells on the road.

Fuel cell technology that was developed for automobiles can be transferred fairly easily to stationary applications, where the fuel cells' efficiency and operating life (about 40,000 h) are more important than their power density and ability to respond to load changes. Ballard, for instance, is introducing a 1-kW residential cogeneration system for the Japanese market this year through a joint venture with EBARA Corp. (Tokyo; www.ebara.com) and Tokyo Gas (Tokyo; www.tokyo-gas.co.jp). The stationary market appeals to fuel-cell makers for several reasons, including higher threshold costs for mass-market penetration (*e.g.*, \$3,000-3,500/kW for stationary vs. \$100/kW for autos), points out Frost & Sullivan (San Jose, CA; www.frost.com) analyst Ravi Krishnaswamy, adding that " the considerable experience and data they gain from their stationary prototypes can be carried over to the automotive segment."

One example of this technology transfer is the 75-kW PEM fuel cell made by auto giant General Motors (Detroit; www.gm.com/company/gmability/adv_tech/index.html), which was installed this past February at Dow Chemical Co.'s (Midland, MI; www.dow.com) Freeport, TX, site (*CEP*, March 2004; p. 14). The system uses H_2 produced by Dow's onsite chlor-alkali process, and will be expanded during the summer months, provided its viability in an industrial setting is proven.

Catalytic converters

H_2, the U.S. Administration's fuel of choice, is required at high-purity levels for PEM fuel cells, since catalyst and membrane materials are easily poisoned or deactivated by sulfur and carbon monoxide. But even at its cheapest — when it is produced from natural gas — H_2 costs four times as much as gasoline. But, chemical engineers are working on making H_2 a commodity.

The removal of sulfur from fuel is crucial in H_2 production for fuel cells. But while desulfurization is old hat to refiners, fuel cells raise the performance bar. "For most refinery or other fuel-processing applications,'low-sulfur fuel' means 15–30 ppm," points out Ke Liu, former task leader at HydrogenSource (S. Windsor, CT; www.hydrogensource.com), a joint venture between UTC Fuel Cells (S. Windsor, CT; www.utcfuelcells.com) and Shell Oil Co. (Houston, TX; www.shellus.com) focused on developing fuel-processing technologies. "PEM fuel cells need sulfur at *ppb* levels," he stresses.

Options include passive adsorption and hydrodesulfurization (HDS), which uses recycled H_2 in the presence of a catalyst to convert sulfur to H_2S,

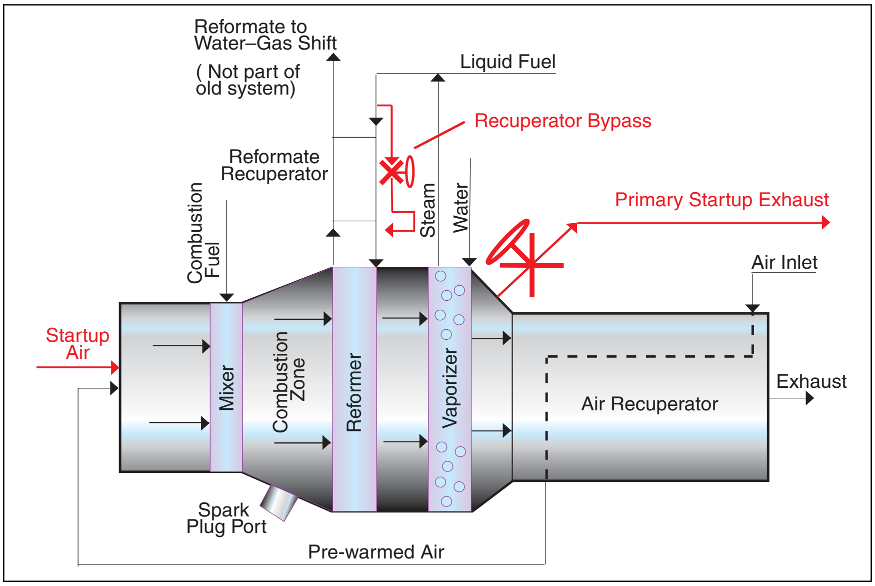


Figure 2. Flow schematics for the Rapid Start reforming system. Previous systems utilized a combustion catalyst to provide the ignition source, which required a ramping of air and fuel flows during a cold start and thus, introduced a lag between initial ignition and full combustion gas flow. Rapid Start features a spark ignition system, which provides rapid ignition as soon as fuel enters the combustion chamber. Red items are active only during the startup transient. Blue items operate only during steady-state operation.

which is adsorbed. Engelhard Corp.'s (Iselin, NJ; www.engelhard. com) selective catalytic oxidation (SCO) process combines fuel with air in the presence of a catalyst to selectively oxidize sulfur to SO_x, which are adsorbed downstream.

The researchers found that sulfur removal of more than 99.9% for both natural gas and liquefied propane gas (LPG) occurs when the oxygen:carbon ratio is 0.03:1.0, and fuel-inlet temperature is 250–270°C, with space velocities below 6,000/h. Unlike passive adsorption and HDS, SCO does not use or generate any toxic or hazardous substances, uses much less adsorbent, and does not require H_2 recycle.

After desulfurization, H_2 can be generated via: catalytic partial oxidation (CPO), in which air is catalytically combined with fuel; steam reforming (SR), which combines fuel with steam, or autothermal reforming (ATR), a combination of the two. Süd-Chemie's (Louisville, KY; www.sud-chemie.com) ATR catalyst comprises a platinum-group metal supported on an alumina washcoat containing rare-earth oxides, applied to a ceramic or metallic monolith. Catalyst performance is affected by the proportions of CPO and SR used in ATR, as well as space velocity — so, the amount of precious metal can be optimized for operating conditions and required performance.

Another important step in H_2 production is water-gas shift (sometimes conducted in separate, high-temperature- and low-temperature-shift steps), in which CO is reacted with water to produce H_2 and CO_2, reducing CO below 1%. WGS is nothing new to industry — the ammonia industry, as Liu points out, has been using Cu-Zn WGS catalysts for over 50 years — but fuel cells have new requirements. Traditional catalysts, with typical gas-hour space velocities below 4,000/h, require huge reactor volumes and are pyrophoric — simply a nuisance in ammonia plants, which shut down fairly infrequently and can use nitrogen blanketing. "But fuel-cell applications mean putting this in people's basements or cars," adds Liu. He says that HydrogenSource's patented process, which uses noble-metal WGS technology from Süd-Chemie, solves the space and safety issues of traditional WGS processes (Süd-Chemie is also developing non-pyrophoric base-metal WGS catalysts).

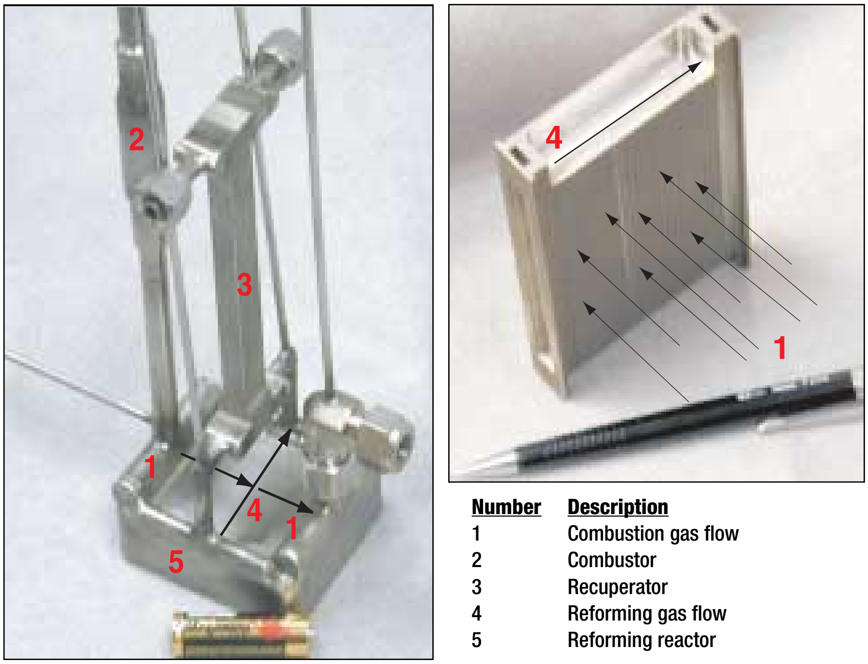
This technology is used in HydrogenSource's 150-kW fuel-processing system, which employs HDS, followed by a proprietary CPO reformer, WGS and preferential oxidation (PrOx, in which the remaining CO is converted to CO_2). "The challenge of developing fuel processing for such a big scale is the turndown ratio, which is 7:1," says HydrogenSource's senior systems engineer Jingyu Cui. "In less than a minute, we can ramp up from 30 kW to 150 kW." (A 7:1 H_2 turndown in the fuel processor translates to a 5:1 power turndown in the fuel cell.)

The CPO and noble-metal WGS technology formed the basis for HydrogenSource's 50-kW, 75-L onboard gasoline fuel processor for cars. "You basically put a H_2 plant underneath the hood," says Liu, who was the system lead for the program. The processor ramps up to full capacity in less than 4 min, during which time the car runs on stored battery power (fuel-cell vehicles are all hybrids at present).

Table. U.S. fuel-cell demand ($ millions).

Item	1998	2003	2008	2013
Total fuel-cell spending	540	1,230	3,550	7,500
% commercial	9.6	8.9	31.0	61.3
Commercial fuel-cell demand by market (total)	52	110	1,100	4,600
Electric power generation	27	62	730	2,250
Military/aerospace	21	22	45	170
Motor vehicles	3	17	60	290
Portable electronics	neglig.	4	130	1,140
Other	1	5	135	750

Source: The Freedonia Group, Inc.



Number	Description
1	Combustion gas flow
2	Combustor
3	Recuperator
4	Reforming gas flow
5	Reforming reactor

Figure 3. The conventional steam-reforming reactor, shown at the left, has been modified to incorporate a new panel configuration (right) with very short flow distance for the heating gas. The flow can be substantially increased during startup without incurring high pressure drop on the combustion gas side.

Consolidation strategies

Rapid startup was also the idea behind Pacific Northwest National Laboratory's (PNNL; Richland, WA; www.pnl.gov) onboard steam reformer, which starts up to produce reformate in 12 s (Figure 2, p. 8). During startup, a significant amount of excess steam is generated to heat a downstream WGS reactor, while reducing CO levels until the WGS reactor reaches operating temperature.

The reformer and water vaporizer are configured as thin panels (Figure 3, right), allowing high combustion flow with low pressure drop. "Flow within the heating gas microchannels is laminar so that a high heat transfer coefficient can be obtained despite the decrease in velocity," explains Greg Whyatt, staff engineer at PNNL.

Previous systems (Figure 3) had a lower flow cross section and greater flow distance for the combustion gas flow. The pressure drop limited the extent to which combustion flow could be increased during startup. "By reducing the pressure drop for normal operation to 1 in. H_2O, the flow can be substantially increased during startup without incurring a high pressure drop, thereby enabling a more rapid startup," Whyatt continues, adding that the design also minimizes the mass of components that require heating prior to reformate production.

Shell International Exploration & Production's (Houston; TX; www.shell.com) integrated membrane steam reforming reactor (MSR; Figure 4) improves considerably on current SR processes, which typically require high-temperature (800–1,000°C) operations, leading to expensive materials of construction, NO_x formation, and furnace volumes of greater than 10,000 ft^3 at the refinery scale (for a 150 kW processor, suitable for stationary or mobile H_2 production, reformer volumes are approximately 5 ft^3), and low thermal efficiencies (typically < 80%).

The SMR shifts reaction equilibrium in favor of H_2 production by continuously removing pure H_2 as fuel and steam flow through the catalyst bed. "In addition, the process achieves fuel conversions above 90%, and generates concentrated, high-pressure CO_2 at selectivities of greater than 98%, which can be sequestered or used for enhanced oil recovery," adds Andreas Matzakos, Shell staff research engineer. The reactor can operate at temperatures as low as 450°C. Shell predicts that a reactor with 10 m^2 area and 0.27 m^3 of catalyst can produce up to 3,700 kg/d of H_2, when membrane permeance reaches its full potential.

"The membrane combines the functions of a steam reformer, high-temperature shift, low-temperature shift, PrOx, and H_2 separation into one operation," says chemical engineering professor Yi-Hua Ma at Worcester Polytechnic Institute (Worcester, MA; www.wpi.edu), leader of the group that developed the membrane. "You save a lot of materials and operating cost, and save room for mobile applications." The membrane comprises a palladium alloy on a porous stainless-steel support; because high-temperature operations can cause intermetallic diffusion, the researchers developed an *in situ* technique for creating an oxide layer on the support before applying the precious metal.

Fuel economy

Molten-carbonate fuel cells (MCFCs), whose electrolyte consists of carbonate salts (usually a mixture of lithium carbonate and potassium carbonate), operate quite differently from PEMs. At the anode, H_2 releases electrons and combines with carbonate ions ($(CO_3)^{-2}$) to form water and CO_2; at the cathode, oxygen and CO_2 combine with electrons to produce carbonate ions (CO_2 is recycled from the anode exhaust to combine with the cathode feed stream). The systems operate at 600–650°C.

The high temperature allows for internal reforming, so the fuel cell can directly use fuels such as natural gas. In addition, MCFCs can function in combined heat and power applications to provide overall energy efficiencies of 75% (electrical efficiency is about 47%). Fuel Cell Energy (FCE; Danbury, CT; www.fuelcellenergy.com) has also developed a hybrid fuel-cell/turbine generator that offers total electrical efficiencies of 70–75%, ac-

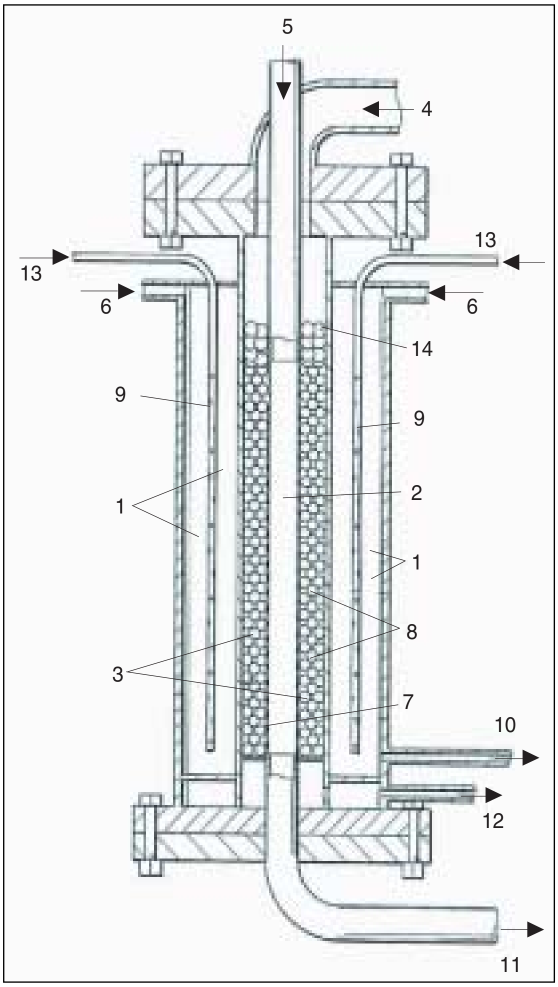


Figure 4. Conceptual drawing of the membrane steam reforming (MSR) reactor: 1. FDC heating section; 2. H_2 permeate section; 3. Catalyst section; 4. Natural gas/steam inlet; 5. Sweep steam inlet; 6. Pre-heated air inlet; 7. Pd-alloy membrane; 8. Catalyst; 9. FDC fuel tube; 10. Flue gas outlet; 11. H_2/sweep steam outlet; 12. CO_2/steam outlet; 13. Fuel inlet; 14. Inert solids. Courtesy of Shell International Exploration & Production.

MORE ABOUT FUEL CELLS

■ U.S. Dept. of Defense's fuel-cell programs; www.dodfuelcell.com

■ U.S. Dept. of Energy's (DOE)
Hydrogen, Fuel Cells & Infrastructure Technologies Program
www.eere.energy.gov/hydrogenandfuelcells

■ U.S. Fuel Cell Council (USFCC); www.usfcc.com

■ Exhaustive information on fuel-cell installations; www.fuelcells.org/charts.htm

■ National Academy of Sciences' report, "The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs," available now from the National Academies Press;Tel: (202) 334-3313 or (800) 624-6242; or visit www.nap.edu to request a copy.

Note: All above organizations' headquarters are located in Washington, DC.

■ AIChE's 2004 Spring National Meeting (April 24–27; www.aiche.org) proceedings. Call (800) 482-4788 or e-mail bzemke@omnipress.com to place an order. Contact name: Crystal

cording to CTO Hansraj Maru. While most of its fuel cells are targeted for stationary applications, FCE is also developing a liquid-fuel system for ships.

MCFC materials of construction tend to be relatively inexpensive: the catalysts are based on nickel; the plates separating the reducing and oxidizing gases are made of stainless steel, as is most of the balance-of-plant equipment. Challenges include: corrosion of metallic components; stability of porous materials used to contain the liquid electrolyte; stability of catalysts, which are in contact with the electrolyte; and thermal-management issues attendant with high-temperature processes. "Then, you have to put all this together to get some meaningful voltage," Maru says, adding that FCE combines four hundred 0.75-V fuel cells in one stack to generate 300 V.

FCE is one of several fuel-cell developers involved in the U.S. Dept. of Energy's (DOE; Washington, DC; www.doe.gov) Solid State Energy Conversion Alliance (SECA; www.seca.doe.gov), a program aimed at lowering stationary fuel-cell costs to $400/kW (DOE; estimates current costs at about $4,500/kW). Another prominent SECA technology is solid-oxide fuel cells (SOFCs): At the anode, H_2 releases electrons and combines with oxygen ions (O^{-2}) to generate water; at the cathode, oxygen combines with electrons to produce oxygen ions. SOFCs, which work at 600–1,000°C, are appealing for their energy efficiency (about 60%) and ability to tolerate relatively impure fuels (they can directly use unreformed CO as fuel).

While SOFCs can have a tubular configuration (the tube consists of electrolyte sandwiched between the cathode and anode materials), much attention has been on planar SOFCs. Because SOFCs' performance losses are largely due to resistance, explains Maru, many developers adopted planar configurations that allowed them to use very thin films. "That cut back the ohmic resistance significantly, allowing higher-power-density operation; this allows the use of lower temperatures without a marked increase in resistivity," he adds. Operating at lower temperatures allows FCE to use many of the same materials used by its MCFCs.

One challenge for high-temperature fuel cells, says Maru, is being able to use a wider range of fuels (*e.g.*, diesel, landfill gas, propane, ethanol), which would allow operation in remote locations . Another challenge is a perennial chemical engineering issue. "We have several heat exchangers in our system, and gas-to-gas heat exchangers can be very bulky," says Maru. "So we are always looking for very compact, efficient heat exchangers that would withstand our service requirements at high temperatures and have long service times."

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