

# Green Hydrogen Production: A Work in Progress

For decades, hydrogen has been touted as a “clean” fuel that could be produced around the world from renewable resources. But the dream of its promoters has remained unfulfilled for lack of competitive technology. Today, however, the outlook for extracting hydrogen from sustainable feedstocks as a viable alternative to petroleum and natural-gas fuels seems much brighter.\* Prodded by the prospect of diminishing petroleum supplies, the U.S. and other countries have been making heavy investments in “green” hydrogen production technologies, with the overarching goal to accelerate the adoption of what is commonly called a hydrogen economy.

President Bush, who expressed his commitment to hydrogen in his State of the Union Address on Jan. 31, 2006, has asked Congress for \$289 million in fiscal year (FY) 2007 (up \$53 million from FY 2006, ending Sept. 30) to support the Hydrogen Fuel Initiative (HFI). Managed by the U.S. Dept. of Energy (Washington, D.C.; [www.doe.gov](http://www.doe.gov)), this Initiative is the host of extensive R&D efforts currently underway at various national laboratories and scores of companies and universities. For its part, industry is investing more than \$1 billion/yr, estimates Steven Chalk, DOE’s hydrogen program manager.

The Initiative calls for an investment of \$1.2 billion over five years, from 2004 to 2008. A basic goal is to develop technology by 2015 that could deliver hydrogen to the market for \$2–3/gasoline gallon equivalent (gge; untaxed, in 2005 dollars), independent of the pathway used to produce and deliver the gas. One gge is roughly equivalent to one kilogram of H<sub>2</sub>.

“A primary objective of the program is to substitute hydrogen for gasoline in vehicles using onboard proton-ex-

change-membrane (PEM) fuel cells as the enabling technology,” says Chalk. In the current budget (FY 2006), \$73 million has been allocated for H<sub>2</sub> production and delivery, \$44 million for fuel-cell research, \$40 million for fuel-cell vehicle demonstrations and fueling infrastructure, \$32.5 million for basic research, and \$34 million for H<sub>2</sub> storage. Storage, of course, is vital to the success of the program (box, p.10).

At present, about 95% of the H<sub>2</sub> used in the world is made by steam-reforming natural gas. The remaining 5% is high-purity H<sub>2</sub> produced by electrolysis, an energy-intensive route for splitting water into H<sub>2</sub> and O<sub>2</sub>. One of DOE’s basic goals is to reduce the cost of extracting H<sub>2</sub> from water, either by improving the economics of electrolysis or by employing other water-splitting techniques. “We are looking for diversity in processes, and we are indifferent as to how hydrogen is made, as long as the technology is domestic, carbon-neutral and economically competitive,” says Chalk.

### High-temperature electrolysis

Conventional electrolysis yields high-purity H<sub>2</sub>, but it is energy-intensive and too expensive for mass production. A promising alternative is high-temperature or steam electrolysis, which operates at a minimum temperature of approximately 800°C. Heat — preferably from an inexpensive source — is added to reduce the electricity requirement for H<sub>2</sub> production. Solar energy and heat from nuclear power plants are the principal sources under investigation. While systems that use solar energy have already been tested, the nuclear option is still years away, pending the development of high-temperature reactors. Six types of reactors are being developed through the Generation IV International

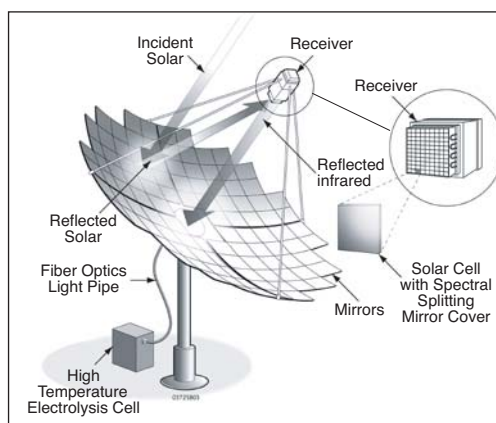


Figure 1. Solar energy is used to produce both heat and electricity for high-temperature electrolysis in this system, patented by Solar Systems Pty Ltd.

Forum, a DOE initiative that coordinates the R&D efforts of 10 nations and the European Commission. Up to three would use the reactor’s heat, or heat and electricity, to make H<sub>2</sub>, explains David Henderson, program manager for nuclear hydrogen research in DOE’s Office of Nuclear Energy Science and Technology (Germantown, MD). DOE’s efforts are focused on the Very High Temperature Reactor (VHTR), cooled by helium, under development by Idaho National Laboratory (INL; Idaho Falls; [www.inl.gov](http://www.inl.gov)). For the longer term, Oak Ridge National Laboratory (Oak Ridge, TN; [www.ornl.gov](http://www.ornl.gov)) is working on a variation of the VHTR, the Advanced High Temperature Reactor, which will use a liquid-salt coolant. Both would operate at 800–1,000°C, versus about 300°C for today’s commercial reactors, says Henderson. He notes that both Japan and China already have reactors that operate at 700–850°C.

### Solar heat

Solar heat has boosted the H<sub>2</sub> output of an electrolyzer by more than 45% in a process developed by Solar Systems Pty Ltd. (Melbourne, Australia; [www.solarsystems.com.au](http://www.solarsystems.com.au)), a manufacturer of

\* For further coverage of the hydrogen economy in *CEP*, see Dec. 2005, pp. 20–22 and Nov. 2004, pp. 4–6.

commercial solar equipment. More significantly, the process promises to achieve 45% efficiency for H<sub>2</sub> production by solar energy — more than five times greater than what has been achieved with conventional solar panels and electrolyzers, says John Lasich, technical director.

In Solar's system, a concentrator delivers high-intensity sunlight to a spectrum splitter that divides the radiation into short and infrared (IR) fractions (Figure 1). Short wavelengths are channeled to gallium arsenide-based, multi-junction solar cells that convert light energy to electricity with an efficiency of 30%, says Lasich. The IR radiation delivers heat energy to an yttria-stabilized zirconia electrolyzer, increasing the electrolyzer's operating temperature to 850°C or more.

Initial tests indicate that the addition of the heat can increase the electrolyzer's hydrogen yield to 1.47 W per watt of electrical input. Lasich notes that a conventional electrolyzer operated at room temperature has an efficiency of about 70%, yielding 0.7 W of H<sub>2</sub> per watt of electricity.

The process has been tested at a scale of only a few watts, but Lasich says the technology is "readily scalable." A "several-hundred-watt" system is slated for testing later this year at the National Renewable Energy Laboratory (NREL; Golden, CO; [www.nrel.gov](http://www.nrel.gov)). If the expected performance is confirmed, Lasich estimates that a commercial plant using a 10-MW electrolyzer could produce 10,000 m.t./yr of H<sub>2</sub> at a cost of \$2.48/kg.

A key element in steam electrolysis is the availability of high-temperature solid-oxide electrolysis cells (SOECs), notes Robert McConnell, a senior project leader at NREL. Initially developed for fuel cells, a solid-oxide electrolyzer is "basically a fuel cell running backwards," he says.

Meanwhile, Ceramtec, Inc. (Salt Lake City, UT; [www.ceramtec.com](http://www.ceramtec.com)) has tapped its fuel cell expertise to develop SOECs of yttria-stabilized zirconia and other materials. The company makes flat sheets that are stacked in series (Figure 2). Joseph Hartvigsen, a se-

nior engineer with Ceramtec, explains that in electrolysis, the H<sub>2</sub> production rate is stoichiometric with the current, so the efficiency of the cell depends only on its operating potential, or voltage. At higher temperatures, part of the total energy is supplied as thermal energy, thereby permitting lower voltages.

So far, Ceramtec has built cells of 10 × 10-cm and is developing 20 × 20-cm cells for high-temperature electrolysis. A 25-cell stack was commissioned in January at INL with an initial H<sub>2</sub> output of 200 normal L/h. After one month of continuous operation, the H<sub>2</sub> production rate dropped to 165 L/h, but "the cell has otherwise performed well, with no leaks," according to Stephen Herring, technical director for high-temperature electrolysis at INL. Investigation into this slow degradation is ongoing. Next year, INL plans to start testing a 15-kW unit, Herring says.

A novel steam-electrolysis system is being developed by SRI International (Menlo Park, CA; [www.sri.com](http://www.sri.com)). Carbon monoxide is fed to the anode side of a solid-oxide cell and depolarizes the anode, thereby decreasing the high-temperature electrolysis voltage from 1 V to 0.2–0.3 V. The use of CO as a depolarizer also generates heat at the anode, says Iouri Balachov, a senior research engineer at SRI, and this would be enough to sustain the reaction temperature of 800–850°C in a 5–10-kW electrolyzer.

Although the process has been tested only in the laboratory, SRI expects that the combination of anodic depolarization with steam electrolysis will reduce electricity consumption to about 20–30% of the value associated with conventional electrolysis, while generating pure H<sub>2</sub> at a cost of \$2–3/gge, vs. more than \$4/gge for conventional electrolysis. SRI believes the process would fit well within or near a chemical process plant or integrated coal-gasifica-

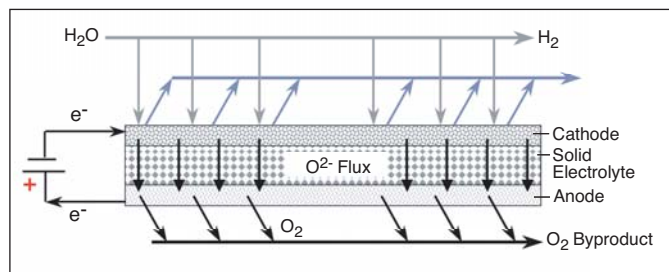


Figure 2. A schematic showing the operation of a solid oxide electrolysis cell.

tion, combined-cycle plant, where CO is readily available and the process could serve as an alternative to a water-gas shift reaction.

### Thermochemical cycles

Solar and nuclear energy are also the major sources of heat for the thermochemical routes to H<sub>2</sub>. A water-splitting thermochemical cycle that uses concentrated solar energy to reduce zinc oxide (ZnO) particles to metallic Zn, then reacts Zn with H<sub>2</sub>O to produce H<sub>2</sub> is being developed by the ETH-Swiss Federal Institute of Energy Technology Zurich (ETH; [www.pre.ethz.ch](http://www.pre.ethz.ch)) and the Paul Scherrer Institute (Zurich; [www.psi.ch](http://www.psi.ch)). ZnO dissociates at above 2,000°C, but the researchers have lowered the reaction temperature to 1,000–1,300°C by adding a reducing agent, such as biomass-based charcoal.

A 300-kW prototype reactor for the carbothermic reduction was tested at the solar tower facility of the Weizmann Institute of Science (Rehovot, Israel; [www.weizmann.ac.il](http://www.weizmann.ac.il)) and produced 50 kg/h of Zn, with a solar-to-fuel energy conversion efficiency of 30%, according to ETH professor Aldo Steinfeld. "A commercial-scale plant of 10 MW should achieve 50% energy-conversion efficiency," he adds.

As for the second step, ETH has developed a process in which Zn nanoparticles are formed and immediately hydrolyzed *in situ* for H<sub>2</sub> production. "The high specific surface area of the nanoparticles enhances the reaction kinetics, and heat and mass transfer," says Steinfeld. "This results in a residence time of less than 1 second." The process has been demonstrated at the laboratory scale in a continuous, tubular aerosol flow reactor.

### The nuclear option

In DOE's nuclear hydrogen program, thermochemical research and development is focused on sulfur-iodine and hybrid sulfur cycles. "Of about 100 thermochemical cycles that had been proposed in the past, these are the most mature technologies," says Henderson. Both processes are expected to meet DOE's goal of making H<sub>2</sub> for under \$2.00/kg at a nuclear plant site. In the S-I cycle, H<sub>2</sub> is formed by the decomposition of hydriodic acid (HI) at 400–500°C. Iodine, the co-product, is reacted with SO<sub>2</sub> and H<sub>2</sub>O at around 120°C to produce HI plus H<sub>2</sub>SO<sub>4</sub> (this is known as the Bunsen reaction). SO<sub>2</sub> is regenerated by decomposing the acid at temperatures up to 900°C.

The development of the S-I cycle, a cooperative effort between DOE and France's Atomic Energy Commission

(CEA; Paris; [www.cea.fr](http://www.cea.fr)), is headed by Paul Pickard of Sandia National Laboratories (Albuquerque, NM; [www.sandia.gov](http://www.sandia.gov)). CEA is working on the Bunsen reaction, Sandia on H<sub>2</sub>SO<sub>4</sub> decomposition, and General Atomics (San Diego, CA; [www.ga.com](http://www.ga.com)) on HI decomposition. An integrated laboratory-scale unit demonstrating the closed-loop operation of the entire cycle is slated to start up at the end of 2007.

Finding materials (*e.g.*, to make heat exchangers and catalysts) that can withstand the hot, corrosive environments of the S-I cycle is "a significant challenge," says Pickard. Another problem is that the Bunsen reaction requires excess I<sub>2</sub> to promote a phase separation of the HI from the H<sub>2</sub>SO<sub>4</sub>. Exacerbating the issue is the presence of excess water, which increases the amount of energy needed to pump and heat up the

process liquid, Pickard notes. INL is developing a membrane system to remove water — a step that would also make I<sub>2</sub> less soluble in the acid.

The hybrid sulfur (HyS) thermochemical process, which is being developed at the Savannah River National Laboratory (Aiken, SC; [www.srnl.doe.gov](http://www.srnl.doe.gov)), combines H<sub>2</sub>SO<sub>4</sub> decomposition with electrolysis. SO<sub>2</sub> from the decomposition step is mixed with dilute H<sub>2</sub>SO<sub>4</sub> and fed to the anode of an electrolyzer. At 25°C, the presence of SO<sub>2</sub> decreases the reversible cell potential from 1.23 V, for conventional water electrolysis, to 0.17 V, says William Summers, program manager for energy security at Savannah River. H<sub>2</sub> evolves from the cathode, while concentrated H<sub>2</sub>SO<sub>4</sub> is generated at the anode and is recycled for decomposition.



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So far, the HyS process has been tested at the single-cell scale at ambient temperature, using a polymer electrolyte membrane (PEM) similar to that used in fuel cells for vehicles. Next year, the laboratory plans to build a cell stack to produce about 120 L/h H<sub>2</sub> at 80°C and 90 psig.

Increasing the pressure and temperature improves the kinetics and lowers the voltage requirements of the process, says Summers. A commercial plant is expected to operate at 300 psig, with a cell voltage of 0.6 V — about one third that of a conventional electrolyzer.

## Hydrogen from biomass

A one-step process to produce H<sub>2</sub> from biomass-derived oxygenated compounds, such as glycerol, glucose and sugar-alcohols, has been developed by Virent Energy Systems (Madison, WI), a spinoff from the Univ. of Wisconsin ([www.uwisc.edu](http://www.uwisc.edu)). Virent's aqueous-phase reformation (APR) uses a precious-metal-based catalyst at 210–250°C and 300–500 psia to convert the sugars to a mixture of H<sub>2</sub>, methane, ethane, propane, CO<sub>2</sub> and steam. The H<sub>2</sub>O is removed by condensation, then H<sub>2</sub> of 99.999% pu-

rity is recovered through a palladium membrane filter or by pressure-swing absorption (Figure 3).

Eric Apfelbach, Virent's CEO points out that APR is simpler than the conventional alternatives, such as producing, then reforming ethanol to obtain H<sub>2</sub>, or gasifying biomass and recovering H<sub>2</sub> from the resultant syngas. A test system is producing 450 g/h of H<sub>2</sub> (about 6 m<sup>3</sup>/h) — enough to power a 5–7-kW fuel cell.

Next year, Virent is scheduled to start up a 50-kg/d unit for DOE. Feedstock will be supplied by Archer Daniels Midland (ADM; Decatur, IL;

## Storage technology: a critical element of a hydrogen economy

The ability to transport hydrogen and store it onboard vehicles is of prime importance in DOE's hydrogen program. "Storage is our number one critical area and is our highest priority," says program manager Steven Chalk.

About \$34 million has been allocated to the R&D of storage materials and systems in the current year's budget. The work is divided into three categories - chemical hydrogen storage, metal hydrides, and carbon materials - each managed by a "center of excellence." Los Alamos National Laboratory (NM; [lanl.gov](http://lanl.gov)) and Pacific Northwest National Laboratory (PNNL; Richland, WA; [pnl.gov](http://pnl.gov)) are lead partners for chemical hydrides, while Sandia National Laboratories (Livermore, CA; [www.ca.sandia.gov](http://www.ca.sandia.gov)) and NREL are respectively partners for metal hydrides and carbon-based storage.

Some 30 universities and laboratories, and several companies, are working with the centers on technology developments, and many more are working under separate DOE contracts. The common goal is to come up with an economical, readily dischargeable and rechargeable system that enables a vehicle to travel at least 300 miles without recharging, while meeting prescribed weight and volume requirements. These conditions present tough challenges that affect each type of technology in different ways.

For example, metal hydrides made of lanthanum-nickel or vanadium "work fine," but they are too heavy to meet the system storage requirement of 6 wt.% H<sub>2</sub>, says James Wang, coordinator for the metal hydrides program at Sandia. To avoid this limitation, researchers are working on alloys that use light elements, such as lithium, magnesium and boron. But, these metals present other problems. Magnesium hydride, for instance, stores 7.5 wt.% H<sub>2</sub>, but won't release it at below 350–400°C, Wang says. Researchers are developing alloys that will release H<sub>2</sub> at a lower temperature.

### Chemical hydrides

Many chemical hydrides are hydrogen-storing liquids that release H<sub>2</sub> in the course of driving. In this concept, spent liquid is returned to the manufacturer for recharging and the vehicle tank is refilled with fresh hydride. The appeal of a liquid is that "it is similar enough to petroleum fuels that it could be transported and delivered through the existing infrastructure of tanker trucks and ser-

vice stations," says Christopher Aardahl, of PNNL, chief engineer for the chemical hydrides center.

One candidate liquid, an aqueous solution of sodium borohydride, has already been demonstrated in a hydrogen-fueled vehicle by Millennium Cell (Eatontown, NJ; [www.millenniumcell.com](http://www.millenniumcell.com)), a partner in the DOE program. Sodium borohydride releases H<sub>2</sub> at a low or neutral pH, so it is stabilized at a high pH with sodium hydroxide. When the H<sub>2</sub> is needed to fuel the vehicle, it is passed over a ruthenium-nickel catalyst that releases the H<sub>2</sub> at high pH. In a related development, Intematix Corp. (Fremont, CA; [www.intematix.com](http://www.intematix.com)) says it has developed metal-alloy catalysts for H<sub>2</sub> release whose cost is less than one tenth that of ruthenium.

However, regeneration of the spent fuel (a mixture of sodium borates) is costly, since it involves the production of sodium metal from sodium chloride by electrolysis. Millennium Cell has developed a less-expensive electrolytic method, but "it is still fairly energy-intensive," says Aardahl. PNNL and its partners are seeking other ways to regenerate sodium borohydride and are investigating other storage compounds, such as boron-nitrogen compounds.

Under a separate DOE program, Air Products and Chemicals, Inc. (Lehigh Valley, PA; [www.airproducts.com](http://www.airproducts.com)) has developed a liquid hydride based on *n*-ethylcarbazole, an organic compound that stores 5.7 wt.% H<sub>2</sub> and is readily regenerable by conventional catalytic hydrogenation. Dehydrogenation is done at 180–200°C over a supported metal catalyst, says Guido Pez, chief scientist. Air Products is investigating other liquids that can carry a higher percentage of H<sub>2</sub> and release it at a lower temperature.

### Carbon systems

R&D managed by the carbon-based storage center at NREL is predicated on the fact that carbon is a lightweight element that can be fabricated in many forms and provide a high-surface-area support for metals that bond with H<sub>2</sub>. Work is being done with various forms of carbon, including nanotubes, says Michael Heben, lead scientist for the center.

So far, researchers have been able to achieve 6 wt.% H<sub>2</sub> storage at 77°K and about 50 bars. "Our main challenge," Heben says, "is to do the same thing at room temperature."

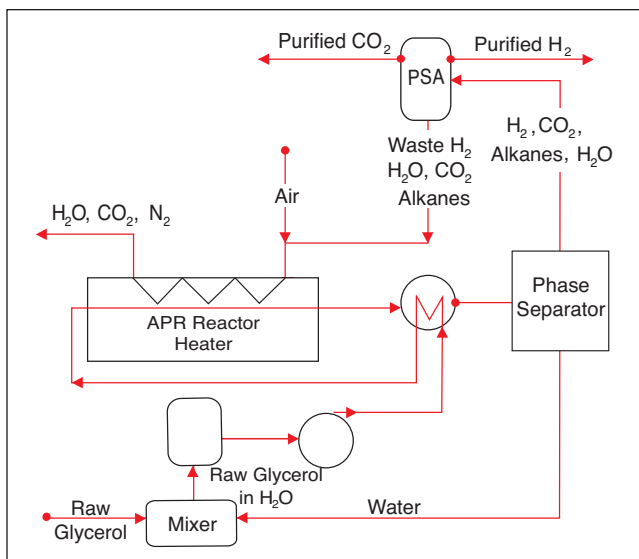


Figure 3. An overview of Virent Energy Systems' process for the production of hydrogen from glycerol (or other biomass-derived oxygenated compounds).

www.adm.com), a major corn processor and Virent's partner in the DOE project. Apfelbach says the process could produce H<sub>2</sub> for \$2–3/gge from sugar streams generated in corn wet-milling.

In a related project, United Technologies Research Center (East Hartford, CT; www.utrc.utc.com) is working on a process to hydrolyze ground-up poplar wood in sulfuric acid, then reform the hydrolyzed biomass at 200–300°C to obtain H<sub>2</sub>. The process has not yet been tested, says staff engineer Sean Emerson, but researchers have identified some candidate precious-metal catalysts and have modeled the process. "We expect to meet the 2010 efficiency target of 50% (energy input vs. H<sub>2</sub> output) at a cost of \$1.75/kg H<sub>2</sub>," Emerson says.

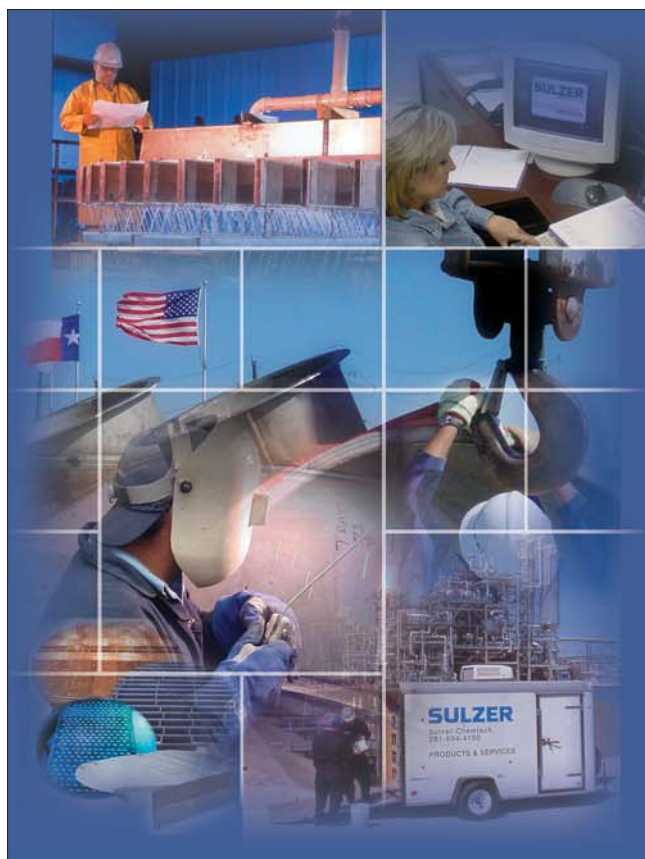
### Using sunlight and water

Photoelectrochemical systems eliminate most of the cost of an electrolyzer by using sunlight to split H<sub>2</sub>O via semiconductors that are immersed in the water. Also, they achieve H<sub>2</sub> production at about 1.35 V, for an electrolysis efficiency of 91%, notes John Turner, a principal scientist with NREL.

However, developing materials that have long-term corrosion resistance is challenging Intematix Corp. (Fremont, CA; www.intematix.com) says it has developed tungsten-based metal-oxide photo-electrode cells that are not corroded by H<sub>2</sub>O.

A photochemical system that is said to yield more than 80% H<sub>2</sub>, vs. 12% for TiO<sub>2</sub>, has been developed by Coastal Hydrogen Energy, Inc. (Stillwater, OK). Water vapor at 115–125°C flows through a cylinder that is coated with a proprietary catalyst. Simultaneously, the vapor is irradiated by an ultraviolet lamp and radiofrequency energy is passed through the vapor, splitting it into H<sub>2</sub> and O<sub>2</sub>. According to Gary Austin, chief science officer, the cost of H<sub>2</sub> production is below \$1/kg of H<sub>2</sub>. CEP

GERALD PARKINSON is a contributing editor with over 25 years of experience writing about the chemical process industries.



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