New Horizons For Hydrogen

Producing Hydrogen from Renewable Resources

These days, you'll likely notice the buzz about hydrogen and fuel cells — in conversations at local coffee shops, in newsstand headlines, and on the nightly news report. The president's Hydrogen Fuel Initiative, unveiled in his January 2003 State of the Union address, has captured the nation's attention by highlighting the possibility of a clean and sustainable energy future based on hydrogen. This vision of a new hydrogen economy "will mean a world where our pollution problems are solved and where our need for abundant and affordable energy is secure… and where concerns about dwindling resources are a thing of the past."-- Spencer Abraham, *Hydrogen Energy Roadmap*, November 2003.

Renewable Hydrogen

Hydrogen is the most abundant element in the universe. And while it doesn't exist by itself on Earth, it can be produced from a wide variety of resources — coal, oil, natural gas, biomass, and water. This versatility contributes to the promise of hydrogen, allowing it to be produced where and when we need it.

About 95% of the hydrogen we use today comes from reforming natural gas. The remainder, high-purity hydrogen from water electrolysis, is primarily produced using electricity generated by burning fossil fuels. But to realize the full benefits of a hydrogen economy — sustainability, increased energy security, diverse energy supply, reduced air pollution and greenhouse gas emissions — hydrogen must be produced cleanly, efficiently, and affordably from domestically available renewable resources.

The ultimate goal is a sustainable cycle of hydrogen production and use. In the first stage of the cycle, hydrogen is produced from renewable resources, such as via photoelectrolysis of water, in which energy from the sun is used to convert water into hydrogen and oxygen. The hydrogen is then used to power a fuel cell, in which hydrogen and oxygen from air recombine to produce electricity, heat, and water. This cycle produces no pollution and no greenhouse gases. Advanced technologies that produce renewable hydrogen as part of this cycle will play a leading role in the future hydrogen economy.

NREL explores several options for producing hydrogen from renewable resources, including biomass conversion; electrolysis using electricity from renewable resources, in particular from wind energy; and direct water-splitting using microorganisms or semiconductors. Some technologies are ready for real-world demonstrations. Others are just emerging and will require long-term R&D investment. But all are focused on the same goal — producing clean, sustainable hydrogen.

Hydrogen from Biomass

Since the Laboratory opened in 1978, NREL has been developing methods for converting biomass to fuels, chemicals, heat, and power. Building on the successes of these efforts, biomass is now one of the best near-term options for producing renewable hydrogen.

Biomass resources are abundant and widely distributed throughout the United States. And because biomass consumes atmospheric carbon dioxide (CO_2) during growth, it can have a small net CO_2 impact compared with fossil fuels, effectively sequestering carbon and reducing our nation's greenhouse gas emissions.

Biomass feedstocks like agricultural and forest residues, consumer wastes, and crops specifically grown for energy production are composed of three interconnected polymeric materials — cellulose, hemicellulose, and lignin. Of the technologies used to break down this biomass structure and produce hydrogen, perhaps the ones closest to being competitive with conventional means are the thermochemical processes of gasification and pyrolysis.

Gasification is a two-step process in which biomass is thermochemically converted into a combustible gas. In the first step, the volatile components of the fuel are vaporized (in the presence of oxygen, air, or steam) at temperatures below 600°C by a set of complex reactions. This yields a mixture of CO_2, carbon monoxide (CO), tar,

hydrogen (H_2), and water vapor (H_2O), with by-products of char and ash. In the second step, the char is gasified at 800°–850°C through reactions with oxygen (O_2), steam, and H_2. This yields a mixture of gases that primarily consists of CO, CO_2, and H_2. Some of the unburned char is combusted to provide the heat needed for the gasification. The overall reaction is:

$$Biomass + O_2 \rightarrow CO + H_2 + CO_2$$

The gas product of this process requires conditioning to remove tars and inorganic impurities. Carbon monoxide is converted to additional hydrogen by the water-gas-shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$
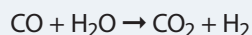
Pyrolysis is a process that thermally degrades biomass to a mixture of gases, char, and an oxygen-rich liquid called bio-oil. Pyrolysis takes place at 500°–800°C in the absence of oxygen. The overall reaction is:

$$Biomass + Energy \rightarrow Gases + Char + Bio\text{-}Oil$$

The relative proportions of the three products depend on the pyrolysis method, the characteristics of the biomass, and the reaction conditions — heating rate, temperature, and residence time. For example, pyrolysis has been used to produce charcoal for centuries. This requires relatively slow reaction rates at very low temperatures to maximize solid yield. Fast pyrolysis is used to maximize either the gas or liquid products, depending on the temperature employed.

The bio-oil and gases are converted to hydrogen using catalytic steam reforming, followed by the water-gas-shift reaction. The catalytic steam reforming reaction takes place at 750°–850°C over a nickel-based catalyst:

$$Bio\text{-}Oil/Gases + H_2O \rightarrow CO + H_2$$
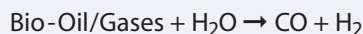
The CO is converted into additional H_2 by the water-gas-shift reaction, resulting in the overall reaction:

$$Bio\text{-}Oil/Gases + H_2O \rightarrow CO_2 + H_2$$
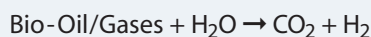
As the final step in both gasification and pyrolysis, the H_2 and CO_2 are separated to yield H_2 that is 99.99% pure, meeting the requirements for use in a fuel cell.

Co-products. Although well understood, the processes of biomass gasification and pyrolysis face challenges. To be competitive,
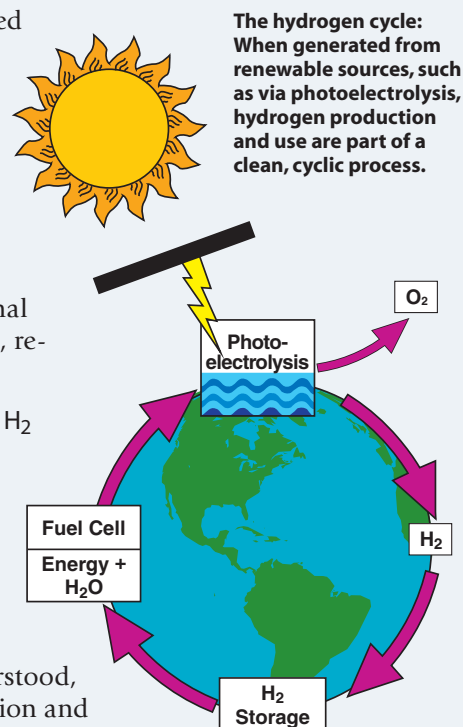
The hydrogen cycle: When generated from renewable sources, such as via photoelectrolysis, hydrogen production and use are part of a clean, cyclic process.
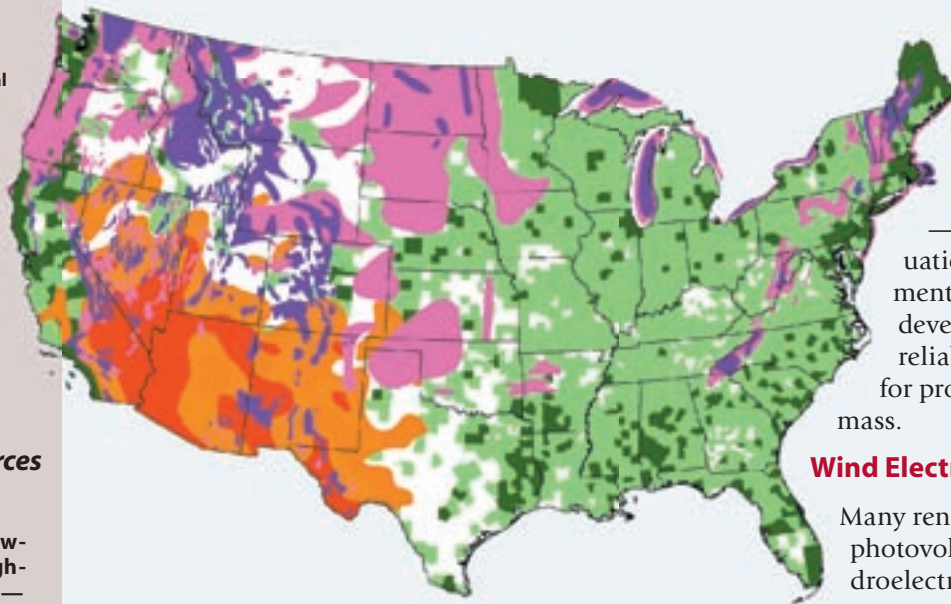
Renewable Resources for Hydrogen

We have enough renewable resources throughout the United States — from wind, solar, biomass, etc. — to meet the energy needs of the entire country. The wide distribution of renewable resources allows the use of decentralized hydrogen production from coast to coast. For example, in Iowa, hydrogen could be produced as a byproduct of the corn ethanol production process; and in Massachusetts, it could be produced from electricity generated by off-shore wind farms. Decentralized hydrogen production using renewable resources available regionally reduces or eliminates the cost associated with hydrogen storage and delivery. (Storage is a major challenge, however — see sidebar "Storing Hydrogen in Carbon Nanotubes," page 8.)

higher process efficiencies and better heat and mass integration are needed. The processes must be flexible enough to handle a range of low-cost feedstocks and their variations in chemical and physical characteristics. Large-scale technology demonstrations of the entire biomass-to-hydrogen process are needed to optimize the process and prove its viability. Plus, we must be able to derive other valuable products from biomass.

This is where pyrolysis has an advantage over gasification. Because bio-oil is made up of two distinct fractions, it can be separated based on water solubility. The water-soluble fraction can be converted to hydrogen via catalytic steam reforming, and the water insoluble fraction can be used to make high-value adhesives. While this approach is not yet cost-competitive, it remains a long-term strategy for converting biomass to hydrogen. Meanwhile, NREL is investigating other coproduct opportunities.

Other feedstocks. In the lab, researchers are evaluating low-cost, potentially high-yield renewable feedstocks — agricultural residues, mixed plastics, trap grease, textiles, and other organic materials in the post-consumer waste stream — for their potential to produce hydrogen using pyrolysis/steam-reforming technology.

New catalysts. Scientists are designing cost-effective, feedstock-flexible reforming catalysts. Commercially available catalysts cannot withstand the harsh conditions required to produce hydrogen from pyrolysis liquids, resulting in catalyst losses of 10%–20% by weight per day. NREL has developed new nickel-based catalysts to withstand reaction conditions. Testing on pyrolysis oils from pine and mixed hardwoods verified that the new catalysts can produce hydrogen with efficiencies as good as or better than those of the best commercial catalysts. These cata-

lysts are being modified for use with other feedstocks.

All of these investigations — co-products, feedstock evaluation, and catalyst development — are contributing to the development of an optimized, reliable, cost-effective process for producing hydrogen from biomass.

Wind Electrolysis

Many renewable technologies — photovoltaics, wind, biomass, hydroelectric, and geothermal — can generate the clean and sustainable electricity needed to run an electrolyzer. But for electrolytic hydrogen production to be cost-effective, we need a low-cost source of renewable electricity. During the past 25 years, advances in wind turbine technology have dramatically reduced the cost of wind power. Today, the cost of wind electricity typically ranges from 3–7¢/kWh for utility-scale projects. This puts wind electrolysis in a good position to be the first economical renewable hydrogen-production system.

In wind electrolysis, the wind turns the blades of a wind turbine, and the blades spin a shaft, which connects to a generator to make electricity. An electrolyzer uses this electricity to separate water into hydrogen and oxygen:

$$2H_2O + \text{electricity} = 2H_2 + O_2$$
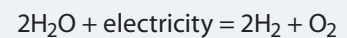
Proton exchange membrane (PEM) electrolyzers, which are being investigated for this application, consist of a membrane sandwiched between two catalyst-coated electrode plates. At the positively charged electrode (anode), water is split into protons (H+), electrons (e-), and oxygen. The oxygen is collected or released, and the electrons move through an external circuit under the influence of an applied electric field. The protons move through the membrane and combine with electrons at the negatively charged electrode (cathode) to form H_2.

Producing both electricity and hydrogen from wind turbines offers the promise of optimizing electrolysis and power-system efficiencies and lowering costs. For example, producing hydrogen with wind power can improve the ability to dispatch electricity when needed, which is a limitation associated with the intermittent nature of wind energy. When the wind turbine is producing electricity, hydrogen can be produced via electrolysis and stored for later use. The stored hydrogen can then be used in a fuel cell

to produce electricity during times of low power production or during peak demand.

Coupling wind turbines with low-cost electrolyzers can also reduce the cost of a system by minimizing redundancy. For example, variable speed wind turbines rely on power electronics to convert the "wild AC" (variable frequency, variable voltage) produced at the generator to DC, which, when connected to the grid must be converted back to AC at grid frequency (60 Hz). Electrolyzers designed for grid-connected operation also incorporate power electronics to convert AC from the grid to DC power required by the electrolyzer cell stack. These power converters represent a significant percentage of the total cost of the wind turbine and electrolyzer.

To make wind electrolysis cost-effective, researchers will have to lower the cost of wind electricity itself, design more efficient electrolyzers, and optimize the wind/electrolyzer integrated system. Once they've done this, they will still need to resolve the logistics of integrating wind electrolyzer systems with utility systems at local, regional, and national levels.

One step toward meeting these challenges is a planned demonstration of integrated electrolysis systems at NREL's Wind Hybrid Test Facility. For this demonstration, NREL is designing a single power-electronics package and controller that will eliminate redundancy in the wind electrolysis system and allow the power output of wind turbines to match the power requirements of electrolyzers. Success here will help pave the way for commercializing the concept.

Direct Hydrogen Production

Direct water-splitting technologies — using photoelectrochemical devices or photosynthetic microorganisms — are the "Holy Grail" of the hydrogen economy. These processes use
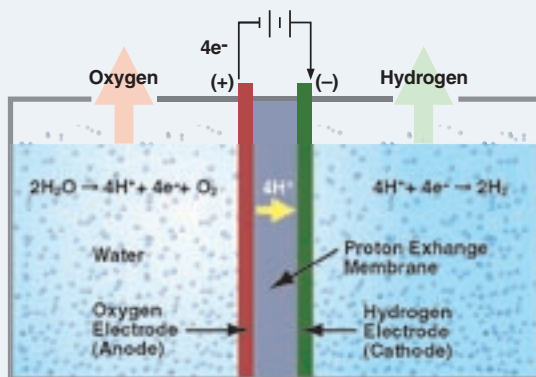
In a PEM electrolyzer cell, water is split into protons (H^+), electrons (e^-) and O_2 at the anode. The protons move through the membrane to the cathode, where they combine with electrons to form H_2.

energy from sunlight to dissociate water into hydrogen and oxygen. They are the ultimate clean and sustainable hydrogen production methods. Although not ready for prime time, photoelectrochemical and photobiological technologies show great promise for the future and are the focus of long-term R&D efforts at NREL.

Photoelectrochemical research. A photoelectrochemical (PEC) hydrogen system integrates photovoltaic (PV) material with an electrolyzer to produce hydrogen directly from water, using only sunlight. This system offers many benefits over two-step processes in which the PV cells and electrolyzer are separate components of the system. Combining the two components in a single PEC device can eliminate most of the electrolyzer costs and reduce semiconductor processing because surface contacts, interconnects, and wiring are no longer necessary. It can also increase the efficiency of the process by 30%, further reducing the cost of delivered hydrogen.

The basic PEC hydrogen production system consists of two electrodes — a semiconductor electrode and a platinum metal electrode — immersed in an aqueous electrolyte. But instead of using electricity from an external source like wind power, the semiconductor absorbs light energy and generates the electrical current that drives the electrolysis reaction, splitting water into hydrogen at the semiconductor surface and oxygen at the metal electrode surface.

Although simple in concept, the challenge is to find a material that can drive this one-step process. For it to be viable, two criteria must be met — the light-harvesting system must have the correct energetics to drive the electrolysis, and the system must be stable in an aqueous environment (see sidebar "The Right Energetics," page 6).

So far, no single semiconductor has been identified that satisfies all of the criteria for use in a hydrogen-evolving PEC system. The most stable semiconductors in aqueous solution are oxides, but their band gaps are too large for efficient light absorption, or their semiconductor characteristics are poor. Semiconductors with better solid-state characteristics are typically thermodynamically unstable with respect to oxidation.

Finding a material that can drive the process is the key to the success of PEC hydrogen production. Materials now under evaluation — gallium nitrides, amorphous silicon, and copper indium gallium diselenide films (CIGS) — build on materials developed for PV. A variety of surface treatments — protective coatings and band-edge engineering — are also being evaluated to

address energetic issues, corrosion problems, and catalysts for the water-splitting reactions.

Gallium nitrides, although expensive, are good candidates for PEC hydrogen systems because they show high efficiencies, are chemically stable, and their band gaps can be adjusted by altering their composition to produce alloys of gallium nitride. Gallium phosphide nitride and indium gallium nitride are being evaluated to determine if they can be tailored to meet the requirements for solar water-splitting.

Amorphous silicon (a-Si) multijunction systems developed for PV offer a lower-cost alternative to gallium nitride materials. Triple-junction a-Si devices have voltages sufficient for water splitting, and the cells can be tailored to produce voltages matched to the energetic requirements of water-splitting, maximizing overall efficiency. But a-Si is unstable in aqueous solutions and must be protected by a corrosion-resistant coating in a PEC-hydrogen system. To maintain the function of the semiconductor, the coating material must be stable, transparent, and conductive. For this, researchers are evaluating silicon nitride compositions.

Semiconductor materials based on polycrystalline thin films, such as CIGS, are also promising alternatives. They are made with inexpensive techniques and can reach efficiencies greater than 15%, both of which help reduce costs. Incorporating sulfur into CIGS increases the band gap into the range required for PEC water-splitting. Making a viable CIGS water-splitting device would greatly decrease PEC hydrogen production costs.

Once we identify a semiconductor material with the ideal band gap and chemical stability, it still won't split water unless the semiconductor band edges overlap the water redox potential. This energetic mismatch can be overcome by using a tandem semiconductor system or by modifying the semiconductor band edges. NREL researchers have demonstrated a solar-to-hydrogen conversion efficiency of 12.4% using a unique structure based on a gallium indium phosphide/ gallium arsenide ($GaInP_2$/GaAs) tandem system. In this configuration, the GaAs cell generates the additional voltage needed to overcome the energetic mismatch between the $GaInP_2$ semiconductor and the water redox reactions. Researchers are investi-

NREL scientist John Turner demonstrates the ability of a PEC cell to produce hydrogen from water using energy from a light source.

The Right Energetics

For a PEC-hydrogen structure, system energetics are a function of the intrinsic electronic properties of the semiconductor material and the electrochemistry at the interface of the semiconductor and the electrolyte.

According to the band theory of solids, which describes the electrical conductivity of solid materials, the available energy levels for electrons in a material form two bands — a valence band and a conduction band. The energy difference between the two bands is called the band gap energy. When a semiconductor absorbs light (photon) energy, electrons from the valence band are excited into the conduction band to generate a current. Only photons with energy equal to or greater than the band gap of the material can free an electron from the valence band to the conduction band. To absorb a large portion of the solar spectrum, the band gap must be less than 2.2 electron volts (eV). For PEC applications, the electrical output must also be large enough to drive the water-splitting reaction (greater than 1.23 eV). The ideal material for a PEC-hydrogen system has a band gap of 1.6–2.2 eV.

In a PV system, a solid-state junction is the active layer where charge transfer occurs. In a PEC system, the interface between the semiconductor and the electrolyte is the active layer. The characteristics of the band edges (i.e., the top edge of the valence band and the bottom edge of the conduction band) at this interface determine whether water splitting takes place. For a given semiconductor material, the energetic positions of the bands at the semiconduc-

gating the effects of adsorption of organometallic compounds on the band-edge properties of GaInP$_2$. In theory, these materials should shift the band edges into the water-splitting range, and speed up the charge transfer rate at the surface. Understanding and controlling the interfacial properties of semiconductor electrodes is key to successfully producing hydrogen from PEC systems.

The development and characterization of new semiconducting materials and systems are critical for the future viability of PEC-driven hydrogen generation. Continuation of the collaborative relationship between PV and PEC hydrogen R&D will accelerate progress in identifying and synthesizing more efficient, lower-cost, and electrochemically stable solid-state materials and systems.

Photobiological research. The green alga, *Chlamydomonas reinhardtii*, is one of several microorganisms that uses sunlight to produce hydrogen directly from water. Like all green plants, this green alga also produces oxygen during photosynthesis. Unfortunately, oxygen inhibits the function of algal hydrogenase, the enzyme in *Chlamydomonas* that catalyzes the release of hydrogen gas. So under normal conditions, i.e., in sunlight, the alga cannot sustain hydrogen production for more than a few minutes.

Before photobiological hydrogen production can become a viable commercial-scale option, scientists need to find ways to control the oxygen sensitivity of the hydrogenase. Researchers are attacking this problem on two fronts — by isolating new forms of the organism that can sustain hydrogen production in the presence of oxygen and by developing processes that separate the oxygen and hydrogen production reactions in the algae.

In the first approach, researchers are using advanced molecular engineering to design hydrogenase enzymes that are more resistant to oxygen inactivation. Past research indicates that the oxygen inactivation occurs when oxygen binds directly to one of the iron species located at the catalytic center of the enzyme. Researchers developed a model of the hydrogenase structure to help identify regions in the enzyme most likely to be involved in access of oxygen to the catalytic site. This led to the discovery that the gas channel, which allows hydrogen to diffuse out of the catalytic center of the enzyme, is large enough to allow oxygen to flow back into the catalytic site and deactivate the enzyme. Researchers inserted bulky amino acid molecules along the gas channel walls to reduce the size of the channel so that hydrogen, but not oxygen, could flow through it. This modified enzyme appears more resistant to oxygen deactivation than the original. Researchers are continuing this molecular engineering approach to further improve oxygen tolerance of the alga.

In the second approach, researchers are identifying and characterizing the process conditions that allow the algae to produce either oxygen or hydrogen, but not both simultaneously. They designed a metabolic switch to cycle algal cells between a photosynthetic growth phase, which produces oxygen, and a hydrogen production phase. The switch is based on withholding sulfur, essential for maintaining normal photosynthesis; without it, the algae decrease their photosynthetic activities to low levels (such that any oxygen evolved is immediately consumed by the respiratory activity of the culture) and become anaerobic in the light. As a consequence, they switch to a different metabolic pathway — one that utilizes the reductants generated by water oxidation — to produce hydrogen gas instead. This pathway, which involves a

In a PEC hydrogen system, a semiconductor cell and a platinum metal electrode are immersed in an aqueous electrolyte. The semiconductor absorbs light energy to generate the current that drives the electrolytic reaction, with hydrogen produced at the semiconductor electrode and oxygen at the metal electrode. For this configuration to work, the band gap of the semiconductor must be between 1.6 eV and 2.2 eV, the band edges must straddle the water redox potential, the system must be stable in solution, and charge must be transferred quickly from the semiconductor surface to the water.

tor surface are fixed. For water splitting to occur, the band edges must overlap the energy levels of the hydrogen- and oxygen-evolving reactions (the water oxidation-reduction potential). Specifically, the conduction band edge must be higher in energy than the hydrogen-evolving half reaction (-0.41 eV), and the valence band edge must be lower in energy than the oxygen-evolving half reaction (0.82 eV).

In addition, charge transfer from the semiconductor surface to the water must occur quickly. If electrons build up on the surface of the semiconductor, they shift the band edges in a negative direction and possibly out of the range required for water-splitting. To accommodate this possibility, band-edge characteristics can be shifted to the required energetic positions through chemical modification of the semiconductor electrode surface.
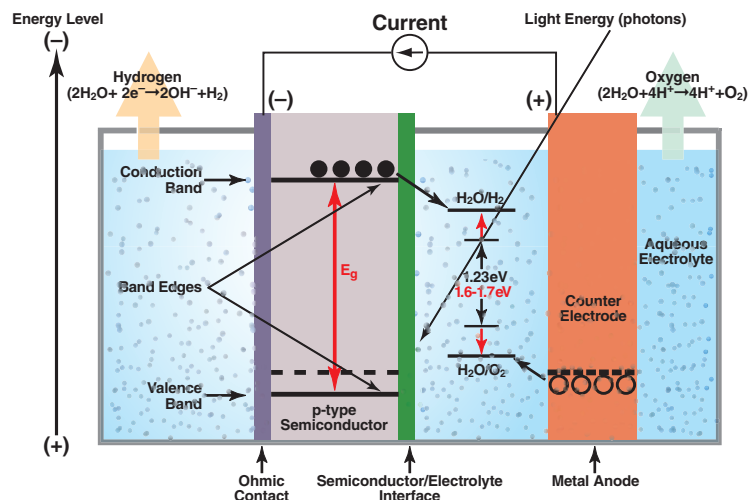
Structural model of the hydrogenase enzyme from the green alga *Chlamydomonas reinhardtii*. The different colored lines depict individual atoms that constitute the enzyme: dark blue for nitrogen, red for oxygen, white for hydrogen, yellow for sulfur, and light blue for carbon. The catalytic center for the hydrogenase — the portion of the enzyme that synthesizes hydrogen gas — is depicted in ball form, showing atoms of iron (green) and sulfur, along with carbon, nitrogen, and oxygen.
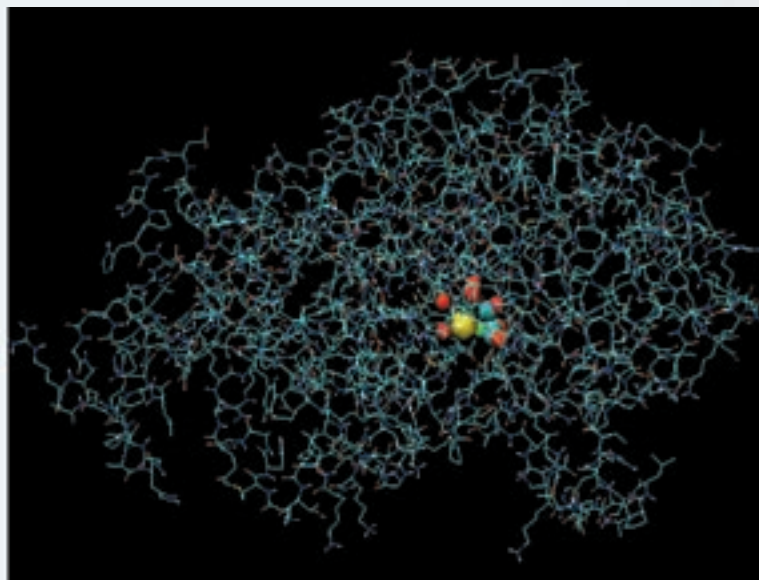
conversion processes, power system integration, electrochemical materials development, metabolic engineering of algae, and more. These advanced technologies are varied and complex, and each comes with its own set of challenges that must be addressed before they are ready for commercialization. It will take the creativity, hard work, and collaboration of scientists, engineers, and analysts from many disciplines throughout the Laboratory to meet these challenges and continue to move toward a sustainable hydrogen future.

hydrogenase enzyme, is responsible for releasing large amounts of hydrogen, even in the presence of limited photosynthetic oxygen evolution.

The process is reversible, and the cycle can be repeated over and over. To optimize hydrogen production, researchers are investigating cell density in the photobioreactors, the level of sulfate deprivation, the light intensity, the pH of the medium, and the presence of organic substrates in the medium.

Researchers are making steady progress in their endeavors to understand and direct the metabolic activity of *Chlamydomonas reinhardtii*, but photobiological hydrogen production is still an emerging technology with much to learn. Further investigation and optimization of both approaches will determine the most cost-effective, efficient route to hydrogen.

Conclusion

The success of renewable hydrogen is directly tied to advances in renewable technologies under development at NREL — thermochemical

For More Information

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Storing Hydrogen in Carbon Nanotubes

Developing safe, reliable, cost-effective ways to store hydrogen — with the ability to carry enough hydrogen on-board a vehicle to enable a 300-mile driving range — is critical to the success of the president's Hydrogen Initiative. But today's methods for storing hydrogen — under high pressure as a compressed gas, or as a liquid at extremely low (cryogenic) temperatures — cannot meet the performance requirements of on-board storage. Promising advanced solid-state materials like complex metal hydrides may provide a breakthrough in hydrogen storage. Another promising avenue, which NREL researchers are exploring, is nanostructured carbon materials that adsorb hydrogen gas reversibly at high efficiencies and energy densities.

The basic mechanism that drives carbon-based hydrogen storage — gas-on-solid adsorption — is a safe, potentially low-cost method. However, high-surface-area carbon materials produced by conventional methods — pyrolysis of coal, biomass, or carbon carrying gases — do not adsorb significant amounts of hydrogen at room temperature. But carbon materials produced at the nanoscale (1 billionth of a meter) have dramatically different characteristics — large surface-to-volume ratios, unique size-specific chemistry, and short bulk diffusion lengths — that favor enhanced hydrogen adsorption.

To optimize the hydrogen adsorption capacity of carbon materials, we must understand the mechanism of the hydrogen adsorption, including the interplay between the chemical and molecular forces in bind-

ing hydrogen to carbon materials. Hydrogen can be adsorbed onto the carbon surface through physisorption, in which the physical attraction between molecular hydrogen and the carbon surface forms a weak physical bond, or through chemisorption, in which molecular hydrogen (H_2) is dissociated into atomic hydrogen (H), forming a strong chemical bond with the carbon surface. To meet DOE's hydrogen storage requirements with this approach, the binding energy must permit strong but reversible immobilization of hydrogen atoms or molecules, and the density of the binding sites must be sufficient to ensure a system weight fraction of hydrogen of at least 8%.

During the past decade, NREL's R&D has focused primarily on the carbon nanostructure known as "single-wall nanotubes" (SWNTs), long, thin cylinders of graphite with a diameter of just a few hydrogen molecules (1-2 nm). The carbon atoms in the graphite structure are connected together in a hexagonal lattice similar to chicken wire. Researchers can control the synthetic conditions to produce tubes of different diameters, with different carbon bonding, and electronic type (semiconducting or metallic, a function of the nanotube lattice). They can also introduce defects, dopants, and catalysts into the nanotube structure to alter properties and tailor the performance of nanotubes.

In 1997, NREL researchers demonstrated that SWNTs can store hydrogen at a range they speculated to be 5%–10% by weight. More recently, they showed that SWNTs can adsorb up to 8% by weight hydrogen when catalytic metal species are present. However, other laboratories have not been able to duplicate these results. To resolve this controversy, NREL is now focused on improving the reproducibility of the measured performance and fully characterizing the SWNTs to understand the mechanism and extent of hydrogen adsorption.

Poor reproducibility is attributed in part to the small sample sizes currently available. Typically, NREL's SWNT samples weigh just a few milligrams. It is difficult to measure the performance of such small samples. NREL has established a group to define and disseminate measurement and sample-handling protocols for carbon nanomaterials. In addition, NREL scientists are developing repeatable and scalable methods for producing larger quantities of active materials.

They are also performing experimental and theoretical studies of carbon nanomaterials to uncover the fundamental science that drives the gas-on-solid adsorption process and to ultimately control and optimize hydrogen storage. As part of this endeavor, they are synthesizing, testing, characterizing, and evaluating a variety of different types of SWNTs and other carbon materials. They are investigating the impact of SWNT electronics and structure on the thermodynamics, kinetics, and capacity of

hydrogen storage, the role of defects and catalysts, and the nature of interactions at the SWNT wall/hydrogen interface. And they are exploring other nanostructured carbon materials, which could provide additional information on what governs adsorption interactions with hydrogen.

A number of new concepts have been proposed to explain and manipulate the hydrogen adsorption characteristics of carbon nanomaterials. One possible approach to increasing the hydrogen storage capacity of SWNTs is to enhance chemisorption with reversible hydrogen spillover. In this approach, a catalyst in contact with the nanotube wall dissociates molecular hydrogen. Because the nanotube is curved, the attractive forces of the carbon atoms in the lattice overlap. This results in a higher number of carbon atoms interacting with the hydrogen, which lowers the activation energy for hydrogen addition and permits surface diffusion of the hydrogen away from the catalyst. Atomic hydrogen diffuses from the catalyst onto the SWNT where it is stored. If the carbon-hydrogen binding energy is not too large, the process could be reversible.

Researchers still have a long way to go before this technology is fully understood. Significant improvements over currently available hydrogen storage technologies are required if hydrogen is to become a viable energy carrier. Innovative new approaches, improvements in synthesis and analysis techniques, and scale-up of optimized cost-effective processes are critical for determining the potential of these materials to store and release adequate amounts of hydrogen under practical operating conditions. Hydrogen storage represents a difficult but exciting challenge — success in unlocking the mysteries of hydrogen storage in nanoscale carbon materials could open the door to the hydrogen future.

One concept for increasing the ability of carbon single-wall nanotubes (blue) to store hydrogen is to use a metal catalyst (silver) in contact with the surface of the nanotube. Here, the catalyst dissociates hydrogen molecules to hydrogen atoms (yellow), which then diffuse into the nanotube lattice and reversibly bond with carbon atoms (blue).