

The Hydrogen Fuel Alternative

G.W. Crabtree (Argonne National Laboratory, USA)

M.S. Dresselhaus (Massachusetts Institute of Technology, USA)

Abstract

The cleanliness of hydrogen and the efficiency of fuel cells taken together offer an appealing alternative to fossil fuels. Implementing hydrogen-powered fuel cells on a significant scale, however, requires major advances in hydrogen production, storage, and use. Splitting water renewably offers the most plentiful and climate-friendly source of hydrogen and can be achieved through electrolytic, photochemical, or biological means. Whereas presently available hydride compounds cannot easily satisfy the competing requirements for on-board storage of hydrogen for transportation, nanoscience offers promising new approaches to this challenge. Fuel cells offer potentially efficient production of electricity for transportation and grid distribution, if cost and performance challenges of components can be overcome. Hydrogen offers a variety of routes for achieving a transition to a mix of renewable fuels.

Introduction

Increased energy use is the universal driver for raising the quality of life in all societies, from developing to developed countries. However, the present reliance on energy from fossil fuels produces unwanted side effects: environmental pollution that threatens human health, carbon dioxide emissions that accelerate global warming, and geopolitical tensions arising from the nonuniform distribution of fossil resources throughout the world. The challenge is to find highly efficient ways to produce, deliver, and use energy that enhance quality of life but do not threaten the environment and climate or strain geopolitical relations.

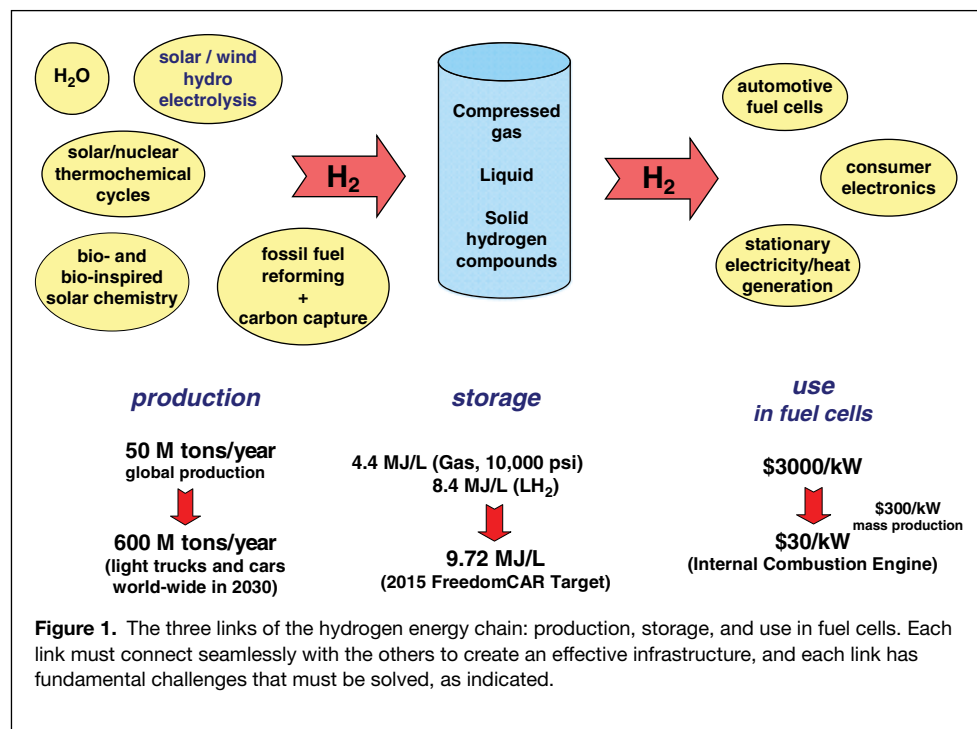
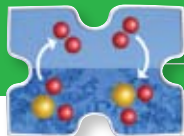
The energy carrier hydrogen is an alternative to fossil fuels with the potential to achieve these goals.^{1–3} Hydrogen is abundant in chemical compounds such as water and the organic compounds of biomass, and its combustion produces only heat and water with no offensive pollutants or carbon dioxide. Hydrogen can be combined with oxygen in the electrochemical reactions of a fuel cell to produce electricity, a clean, versatile carrier of energy enabling many end uses including lighting, refrigeration, communication, information processing, and transportation. The intimate connection between hydrogen and electricity through fuel cells makes hydrogen much more than simply a clean substitute for fossil fuel combustion.

Achieving the promise of hydrogen as an efficient, sustainable, and environmentally friendly fuel requires widespread innovation and development of the means for its production, storage, and use. The energy-chain and technical challenges for creating a viable hydrogen economy are shown in **Figure 1**. The most effective use for hydrogen is conversion of its chemical energy to electrical energy in fuel cells. The high conversion efficiency of fuel cells, up to 60%, makes them attractive compared to other electrical generation alternatives based on fossil fuels, which are about 34% efficient on average. The high efficiency of electric motors (typically well above 90%) makes the fuel cell–motor combination attractive for transportation compared to gasoline engines, typically about 25% efficient. This potential for high-efficiency end use adds additional appeal to the environmental argument for hydrogen: not only is it free of pollutants and greenhouse gases, but it also uses considerably less primary energy for a given energy use.

As shown in **Figure 1**, the cost of the present generation of fuel cells is 100 times that of a gasoline engine; with mass production, the cost differential might fall to a factor of 10. In addition to cost, longevity, frequency of repair, and performance in cold weather are other areas in which fuel cells are not yet competitive with gasoline engines for widespread use in transportation. Lowering cost and enhancing performance present materials research challenges in terms of the cathodes, electrolyte membranes, and catalysts of fuel cells.

Hydrogen storage for transportation presents a major materials research challenge, namely, to find a storage medium that combines a hydrogen density greater than that of the liquid with fast kinetics allowing rapid charging and discharging. Many conventional bulk materials have been explored and rejected as storage media because they do not meet these criteria. However, nanoscience opens new opportunities for addressing this challenge, with the potential for high surface areas and hybrid structures that enable multifunctional performance, such as low-energy dissociation of hydrogen molecules on the surface and rapid diffusion of atomic hydrogen to the interior.

The challenge for production is finding a source of hydrogen that can supply the needs of a full-fledged hydrogen economy and that is not dependent on fossil fuels for feedstocks. Producing hydrogen from natural gas, a widely used established process, in sufficient quantities to power the world's cars and light trucks would strain the world's supply of conventional methane, making natural gas as geopolitically sensitive as oil. Furthermore, the production of hydrogen from natural gas generates as much pollution and carbon dioxide per unit of energy output as burning the gas directly. Aside from fossil fuel, possible sources of hydrogen include reforming the carbohydrates of biomass or splitting water molecules thermally, electrolytically, or photochemically. Although these nonfossil routes to hydrogen production are attractive and potentially viable, they require breakthroughs in materials research to discover effective, robust catalysts that lower the energy barriers to production; to achieve nanoscale integration of the sequential production steps; and to lower cost.



Progress toward a mature hydrogen economy depends on breakthroughs in finding new materials and basic understanding of the nanoscale phenomena that govern the interactions of hydrogen with materials. The ultimate evolution of a hydrogen economy, however, depends on much more than technical feasibility. As with all new technologies, comparisons of hydrogen with a developing mix of alternatives for performance, cost, efficiency, convenience, reliability, and safety will determine its future course. The outcomes of these comparisons are themselves developing, as the costs of fossil fuels and environmental mitigation of their use increase and as engineering and scientific discoveries alter the mix of competing alternatives.

Although a mature hydrogen economy requires technical and economical solutions for production, storage, and use, there is value in implementing any of these without full-blown solutions for the others. Hydrogen fuel cells can be used in large stationary installations for neighborhood heat and power and for small personal electronics without solving the problem of on-board storage for transportation, and hydrogen storage can be used with intermittent sources of renewable energy such as solar and wind without large-scale hydrogen production. As a highly storable carrier of energy, hydrogen offers remarkable versatility, enhanced by its compatibility with electricity, the less-storable energy carrier that forms the backbone of our energy distribution system. Thus, although a full-fledged hydrogen economy encompassing production, storage, and use could be the ultimate goal, a partial implementation of hydrogen as a storable energy carrier for use in stationary and personal fuel cell applications is a desirable outcome on its own merits.

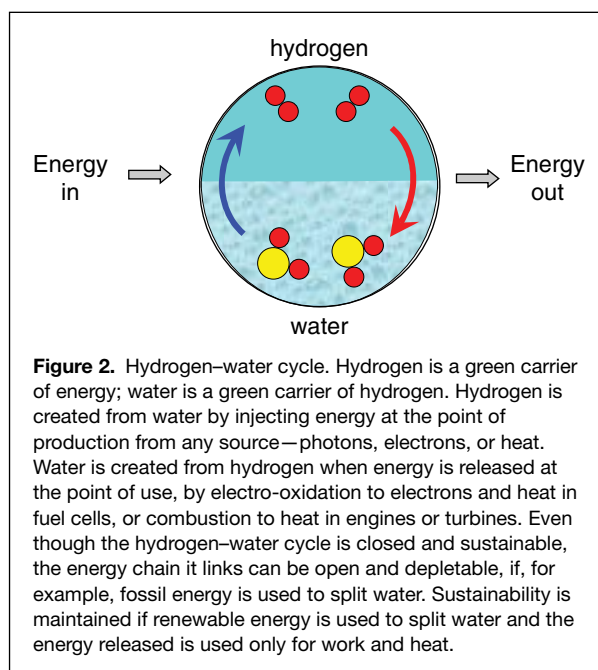
This article presents the current status of and promising research opportunities to overcome the technical and economic challenges in hydrogen production, storage, and end use. Although the focus is on recent developments and future directions, there is a long and distinguished history of hydrogen research that laid the foundations for the current surge of research activity.⁴

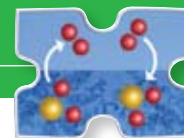
Hydrogen Production

In a mature hydrogen economy, hydrogen could replace fossil fuel for transportation in cars and light trucks, produce electricity for distribution through the grid, and provide portable electricity for personal electronics and other applications. Transportation now consumes about 20% of the world's energy, and electricity about 12%.⁵ About 600 Mt/year of hydrogen will be needed worldwide to power all cars and light trucks in 2030, compared to about 50 Mton/year now produced.² About half of the global supply of hydrogen is produced by reforming natural gas.² The reforming of natural gas, however, is not an attractive production route for a mature hydrogen economy, because the order-of-magnitude increase in demand would deplete our finite reserves and the concentration of gas reserves in a relatively few regions of the world could lead

to geopolitical tension and unstable supplies. Environmental impact is also a major concern, as reforming natural gas to hydrogen produces as much pollution and CO₂ as burning the natural gas directly.

Splitting water renewably, that is, using only renewable energy inputs, is an attractive production route for hydrogen as a fuel of the future. Water is abundant on the surface of the earth and more widely distributed geographically than fossil fuels. The water–hydrogen cycle (see **Figure 2**) is closed, unlike the fossil fuel energy chain that operates on a “once-through” basis,





depleting reserves at the point of production and producing unwanted CO₂ and pollutants as byproducts at the point of use. In contrast, the hydrogen and oxygen produced from the splitting of water are recombined at the point of use to release energy, replenishing the water taken for its production. This closed chemical cycle is a prerequisite for a sustainable energy system—no chemical compounds are created or destroyed once the cycle is complete. There is, however, a net flow of energy through the water–hydrogen cycle—in for water splitting and out upon water formation. If fossil or nuclear energy is used to split water, its once-through chemistry reappears, and the sustainability of the closed water–hydrogen cycle is lost. Using a source of renewable energy to split water, however, eliminates the once-through features and enables a sustainable, closed cycle for energy use.

The efficiency of the water–hydrogen cycle is key to its value. Inevitably, more energy is needed to split water than is recovered on its recombination. Minimizing the energy barriers to water splitting and recombination are high-priority research challenges in catalysis and nanoscale science. Present technology can split water with over 80% efficiency in large electrolyzers⁶ and recover electricity at 60% efficiency upon recombination in combined-cycle turbines or in fuel cells. Although they demonstrate the principle of the water–hydrogen cycle, these production routes and efficiencies are only illustrative. Other options for splitting water by thermal, photochemical, and electrochemical means are now being explored in the laboratory.

The proof of principle and most advanced incarnation of solar water splitting is provided by photosynthesis, in which a complex protein assembly—Photosystem II—collects daylight, channels its energy to a photocatalyst based on Mn₃CaO₄, and orchestrates the physical coordination of two water molecules and the catalyst to produce O₂, protons, and electrons. Water splitting is such a demanding process that nature has evolved only one mechanism to accomplish it, used by all photosynthetic organisms for the past three billion years. Although Photosystem II produces only protons and electrons separately, the enzyme hydrogenase can finish the job by joining protons and electrons to produce H₂.⁸ With high-resolution x-ray and neutron diffraction, we know the structures and some of the working principles of Photosystem II and hydrogenase.^{9–11} The challenge is to use this knowledge to develop genetically modified designer plants that produce hydrogen directly from sunlight and water, and to assemble artificial structures inspired by nature that accomplish the same goal.^{8,10}

A second route to solar hydrogen production uses semiconductors to produce electrons and holes that are, in turn, used to split water with the aid of a catalyst. Wide-bandgap semiconductors such as the oxides TiO₂ and WO₃ are favored substrates because they are inexpensive, are robust in water solutions, and can be created in the form of nanotubes and other nanostructures with large surface areas to promote light harvesting.¹² The challenge is accessing the solar spectrum at energies below the wide bandgap of these oxides. One promising approach coats the oxide surfaces with narrow-bandgap nanodot semiconductors or dyes that transfer electrons excited by low-frequency light to the oxide; another approach dopes the oxides to lower their bandgap.^{13,14} Catalysts are needed as well, to reduce the energy barriers to water splitting.¹⁵ The ability to fabricate, characterize, and understand complex nanostructures is key to success with semiconductor-based water splitting, and impressive progress has been made recently in exploiting nanostructured materials for solar hydrogen production.

Hydrogen production from coal is an intermediate alternative to the present practice of natural gas reforming and the future development of splitting water renewably. Coal is the

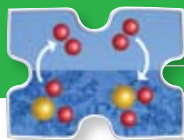
most abundant of fossil fuels and the most able to supply a large quantity of hydrogen without depleting its reserves or inflating its market price. Gasification of coal produces hydrogen and CO directly in syngas, and CO reacts with steam to produce more hydrogen in the water–gas shift reaction. Several approaches are under development for producing hydrogen from coal with CO₂ capture that maintain 60–90% of the original energy content of the coal.^{16,17} The development of membranes for separation of hydrogen from CO and CO₂ is a key materials issue.¹⁸ Coal gasification and the water–gas shift are commercial technologies ready to implement in integrated gasification combined-cycle (IGCC) power plants for generating electricity from coal with CO₂ capture at up to ~40% efficiency, compared to an average efficiency of ~34% for existing electricity production from coal without CO₂ capture. (See the article on coal by Powell and Morreale in this issue.) A relatively slight modification of this process enables coproduction of hydrogen along with electricity and CO₂ capture, and the fraction of production devoted to electricity and to hydrogen can be varied on demand with little or no sacrifice in efficiency.¹⁷ The switchability of production from electricity to hydrogen accommodates the intermittency of renewable sources by producing hydrogen when solar and wind are active and electricity when these sources are dormant. In this approach, the coal plant runs at full production capacity and high efficiency continuously, and no storage of electricity produced by renewable sources is required. The hydrogen coproduced with electricity can be transported for use off the production site or used on-site to produce electricity at efficiencies approaching 60% in combined-cycle turbines or solid-oxide fuel cells for electrical grid distribution. Thus coproduction not only provides a flexible, low-marginal-cost source of hydrogen for transportation and other distributed uses, it encourages the development of hydrogen for electricity production and distribution through the grid.

Any source of heat can be used to split water through thermochemical cycles that require several reaction steps operating at high temperature. Concentrated solar power can produce the high temperatures needed for thermochemical conversion, as can the heat from nuclear reactors. The challenges are discovering and developing the thermodynamics of chemical cycles that split water and finding materials that can withstand the high temperatures and often corrosive environments required by these processes.¹⁹

Hydrogen Storage

The use of hydrogen for transportation, personal electronics and other portable power applications requires an effective hydrogen storage medium. Existing technology for hydrogen storage is limited to compressed gas and liquefaction, both of which are used now in demonstration vehicles. Compressed gas, even at the highest practical pressure of 10,000 psi, is still a bulky way to store hydrogen that requires a significant fraction of the trunk space in a small car to enable a 500 km driving range. Liquid hydrogen takes up slightly more than half the volume of 10,000 psi compressed gas, but it loses 30–40% of its energy in liquefaction. Although gas and liquid storage are useful as temporary options in a provisional hydrogen economy, more compact and efficient storage media are needed for a mature hydrogen economy.

The most promising hydrogen storage routes are in solid materials that chemically bind or physically adsorb hydrogen at volume densities greater than that of liquid hydrogen. The challenge is to find a storage material that satisfies three competing requirements: high hydrogen density, reversibility of the release/charge cycle at moderate temperatures in the range



of 70–100°C to be compatible with the present generation of fuel cells, and fast release/charge kinetics with minimum energy barriers to hydrogen release and charge. The first requires strong chemical bonds and close atomic packing; the second requires weak bonds that are breakable at moderate temperature; and the third requires loose atomic packing to facilitate fast diffusion of hydrogen between the bulk and the surface, as well as adequate thermal conductivity to prevent decomposition by the heat released upon hydriding. Although several materials have been found that satisfy one or more of the requirements, none has proven to satisfy all three. In addition to these basic technical criteria, viable storage media must satisfy cost, weight, lifetime, and safety requirements as well.²⁰

Two recent developments in materials science hold promise for meeting the difficult hydrogen storage challenge. The first is the rapid progress in nanoscience in the past five years. The small dimensions of nanoscale materials minimize the diffusion length and time for hydrogen atoms to travel from the interior to the surface. The large relative surface area provides a platform for dissociation of molecular hydrogen to atomic hydrogen, a prerequisite for diffusion and for chemical bonding with the host. The surface area can be tailored with a monolayer of catalyst to promote dissociation, and surface curvature can be adjusted through the size of the nanoparticles to create unbonded orbitals that promote reactivity with hydrogen.

The second promising development for hydrogen storage materials is the growing ability of density functional theory to numerically simulate material behavior.^{21–24} Density functional theory implemented on computer clusters is now in widespread use for the calculation of the electronic structures, crystal structures, bond strengths, and heats of reaction for many multi-element compounds. The number of compounds that can be simulated and the level of comprehensive information about their structures and stability far exceed what can be determined experimentally by discovery synthesis in the laboratory on the same time scale. This potentially powerful tool for numerically screening materials is now being applied to hydrogen storage compounds. A recent study examined 300 candidate compounds for their structures, hydrogen storage capacities, and hydrogen decomposition temperatures.²³

Hydrogen storage materials employ two complementary strategies for releasing hydrogen for use: thermalization and destabilization. In thermalization, hydrogen is released from the storage media by heating to the decomposition temperature, where some or all of the hydrogen is driven off. This traditional approach emphasizes hydrides with light elements from the first and second rows of the periodic table, to maximize the mass percentage of hydrogen.²⁵ The ternary and quaternary hydrides of these elements have high storage capacities, notably the borohydrides $M^+BH_4^-$ (where M is Li, Na, or K and B can be replaced by Al),²⁶ and the boranes NH_nBH_n , where n ranges from 1 to 4.^{27–29} The borohydrides have significant storage capacities, up to 19% of the mass of the molecule for $LiBH_4$, but they suffer from high decomposition temperatures and large activation barriers to rehydrogenation. Catalysts such as Ti reduce the barriers for both the decomposition and rehydrogenation of borohydrides and alanates, offering a practical route to their use as hydrogen storage materials.³⁰ NH_4BH_4 substitutes the ammonium ion for a simple metal cation in the borohydride structure, packing four more hydrogens into the molecule. The hydrogen mass ratio is an impressive 24%, but not all of the hydrogen can be easily removed thermally. The hydrogen comes off in stages, with about 6% of the mass released for each decrease of n by one, as shown in **Table I**. The first hydrogen comes off at <25°C, making it too unstable for

Table I: Hydrogen Storage Capacity of Amine Borohydrides NH_nBH_n .

Reaction	Wt % H_2	T (°C)
$NH_4BH_4 \Rightarrow NH_3BH_3 + H_2$	6.1	<25
$NH_3BH_3 \Rightarrow NH_2BH_2 + H_2$	6.5	<120
$NH_2BH_2 \Rightarrow NHBH + H_2$	6.9	~155
$NHBH \Rightarrow BN + H_2$	7.3	>500

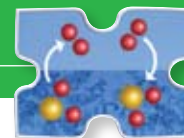
storage under expected operating conditions. The remaining hydrogens come off at <120°C, ~155°C, and 500°C. Thermal decomposition of NH_3BH_3 to $NHBH$ removes the second and third hydrogens and releases 12% hydrogen by mass below 155°C, making it attractive for portable storage. Confining NH_3BH_3 in a nanoporous scaffold lowers its decomposition temperature, speeds its release kinetics, and suppresses undesirable decomposition products. A path for reversibly recharging $NHBH$ has not yet been found and remains a subject of intense research.

Ammonia (NH_3) is a high-capacity storage medium with 17 wt% hydrogen. Its stability is too great to release hydrogen easily, and furthermore, NH_3 is dangerous to the environment. Ammonia can be combined with other compounds that allow NH_3 to be reversibly released and absorbed as a molecule, effectively eliminating the toxic hazard during storage. For $Mg(NH_3)_6Cl_2$, the temperature for decomposition to $MgCl_2$ and NH_3 is 150°C.³¹ The ammine salt $Mg(NH_3)_6Cl_2$ can be formed into nanoporous pellets as shown in **Figure 3**, which could function as a potential carrier for ammonia that would remove its environmental danger if handled by trained personnel. Although decomposition of ammonia to hydrogen occurs at too high a temperature to be viable for low-temperature fuel cells using polymer electrolytes, ammonia can be used directly in solid-oxide fuel cells, where the high operating temperature can be used to decompose it without an energy penalty.

An alternative approach to the thermal release of hydrogen from a storage compound is destabilization of the storage compound by reaction with a second compound. An example is $LiNH_2 + LiH \rightarrow Li_2NH + H_2$, which releases hydrogen at



Figure 3. Pellets of $Mg(NH_3)_6Cl_2$, a carrier for ammonia. The pellets hold NH_3 at nearly its density in liquid ammonia, but at a vapor pressure of only 2 mbar; there is no significant release of ammonia to the environment and the pellets can be handled safely. The pellets are charged at room temperature and release ammonia above ~100°C. After Reference 31.



~150°C, significantly lower than the release temperature for either LiNH₂ (lithium amide, 200°C) or LiH (500°C).^{32,33} The storage capacity of 6.5% for this reaction is substantial, although not high enough for the ultimate storage solution. If Li₂NH could be destabilized to release the remaining H, the storage capacity would be 9.6%, high enough for hydrogen-powered transportation. LiBH₄ and MgH₂ are another destabilization couple, with a storage capacity of 11.5%.³⁴ The promise of destabilized hydrides for storage is the much larger number of paired (or multiple) hydrides than single hydrides might provide effective storage. The advantage of the larger number of hydride pairs is balanced by the challenge of searching this enormous set. Guiding principles are needed to choose likely hydride pairs for which the reaction kinetics and destabilization temperature promise to be favorable. The screening potential of density functional theory simulations plays a crucial role here, potentially short circuiting years of experimental phase diagram work.

Nanostructured materials open broad new horizons for the hydrogen storage challenge. The structural and compositional complexity of nanostructured materials and their diverse surface morphologies enable control not only of the static but also of the dynamic features of the charge/release phenomena. Core-shell composites, for example, enable free exchange of protons between interior environments tailored for bonding to the host and surface environments designed to make and break the molecular H₂ bond. Metal-organic frameworks are open structures that physisorb molecular hydrogen at specific sites within the framework, yet allow easy diffusion to the surface and release hydrogen at low temperature; the richness of their structure-property relationships is just beginning to be appreciated.^{35,36} Nanoporous materials that divide and confine storage media such as NH₃BH₃ in nanoscale units can lower the decomposition temperature and activation barriers for hydrogen release and alter the decomposition pathways and end products.²⁸ Mg(NH₃)₆Cl₂ is naturally nanoporous, accounting for its rapid NH₃ charge/release times.³¹ Combined with the blossoming power of density functional theory to predict reaction pathways and materials properties, nanoscale science represents a new era of hydrogen storage possibilities.

Hydrogen Use in Fuel Cells

Fuel cells converting hydrogen and oxygen to electricity and water are an appealing alternative to fossil fuel combustion engines for their efficiency, versatility, and environmental friendliness. The basic operation of a fuel cell is depicted in **Figure 4**. Fuel cells produce electricity with a potential efficiency of 60%; the electricity can be used directly or converted to motion, light, or heat. In contrast, gasoline engines operate with ~25% efficiency and are used almost exclusively for producing motion. Analysis of results from the first two years of the U.S. Department of Energy's fuel cell learning demonstration based on a fleet of 77 fuel cell vehicles showed that fuel cell efficiency at one-quarter power as tested on a dynamometer reached 52.5–58.1%, close to the target efficiency of 60%.³⁷

Polymer electrolyte membrane (PEM) fuel cells for transportation rely on dispersed Pt nanoparticle catalysts supported on carbon substrates for promoting the reaction of protons, electrons, and oxygen molecules to water. Although Pt is the best-known catalyst for this reaction, it cannot meet the demands of a mature hydrogen economy because of its high cost and relative scarcity. Orders-of-magnitude increases in its catalytic activity are needed to reduce the required quantities, or it must be replaced by an alternate catalyst that is active, abundant, and inexpensive.

A recent breakthrough increasing the catalytic activity of Pt by a factor 10 for the oxygen reduction reaction at the fuel cell cathode reveals a promising new research direction for tuning catalytic activity, as shown in **Figure 5**.^{38,39} The approach is to alter the electronic structure of the subsurface layers of Pt by substitution with a second element, leaving the surface layer intact. The “Pt skin” on the surface maintains the atomic configuration of pure Pt that promotes breaking O–O bonds and forming O–H bonds, while substitution in the first subsurface layer adjusts the electronic structure and bonding strength of the skin by adding or subtracting electrons. Density functional theory³⁹ plays a key role in subsurface manipulation of catalytic activity, describing and predicting its outcomes and providing a quantitative scientific framework for this novel approach.

The membranes for polymer electrolyte fuel cells are based on C–F polymer backbones with sulfonic acid side chains. Proton conductivity is achieved by hopping between the hydrogen sites of neighboring side chains. The hopping process requires hydration of the polymer with water, limiting the operating temperature of the membrane to about 80°C and requiring considerable attention to water management. New membrane materials that eliminate the hydration requirement and enable hydrogen ion conductivity at higher temperatures are needed and are being intensively pursued.^{40,41} One promising direction is the formation of nanocomposite membranes by addition of hydroscopic constituents that retain a high water content at high temperatures, thereby extending the temperature range of conventional proton conduction mechanisms. Another approach is to replace the C–F polymer backbone with a more thermally resistant structure, but retain the same side chain sulfonation to enable proton conductivity. Membranes based on some of these alternate polymers can operate above 120°C. A third creative approach is to replace water with another solvent that assists proton mobility but has a higher boiling point, such as phosphoric acid. Some of these membranes conduct protons at temperatures up to 200°C in the absence of water.⁴² Key issues in all membrane materials include acid loading to provide additional sites for proton transfer, polymer crosslinking to improve thermal and mechanical stability at high temperature, and enhanced surface area to enable effective electrical and chemi-

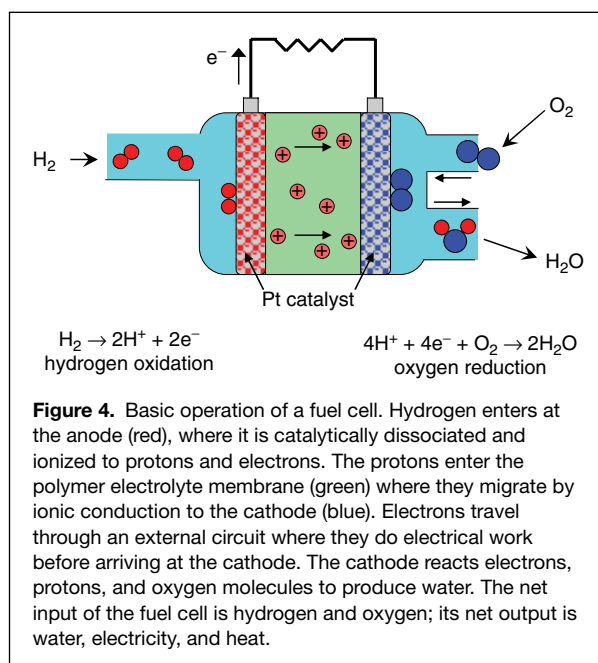
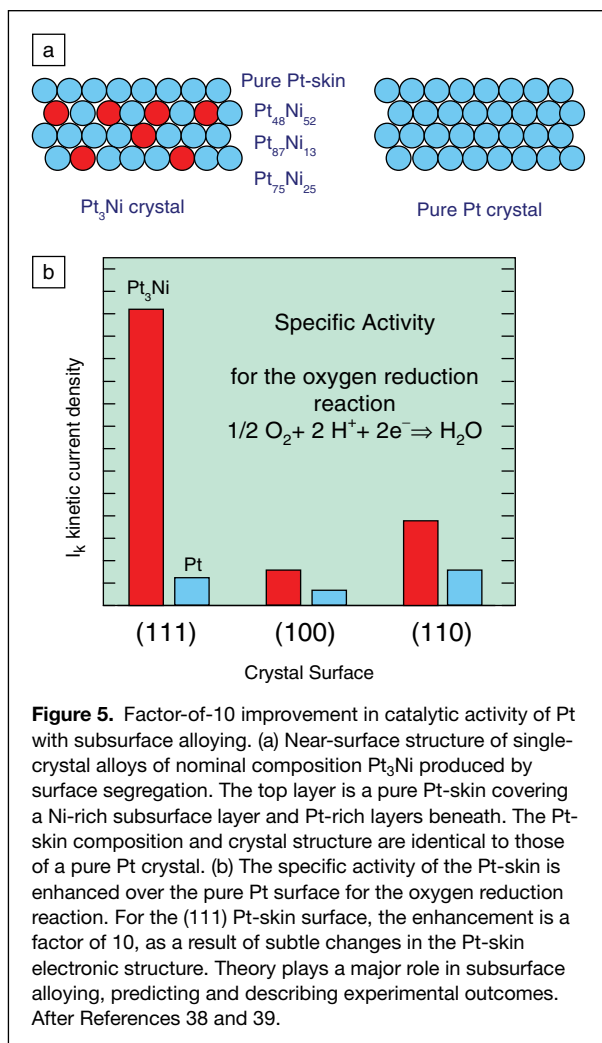
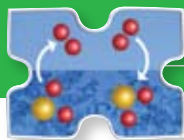


Figure 4. Basic operation of a fuel cell. Hydrogen enters at the anode (red), where it is catalytically dissociated and ionized to protons and electrons. The protons enter the polymer electrolyte membrane (green) where they migrate by ionic conduction to the cathode (blue). Electrons travel through an external circuit where they do electrical work before arriving at the cathode. The cathode reacts electrons, protons, and oxygen molecules to produce water. The net input of the fuel cell is hydrogen and oxygen; its net output is water, electricity, and heat.



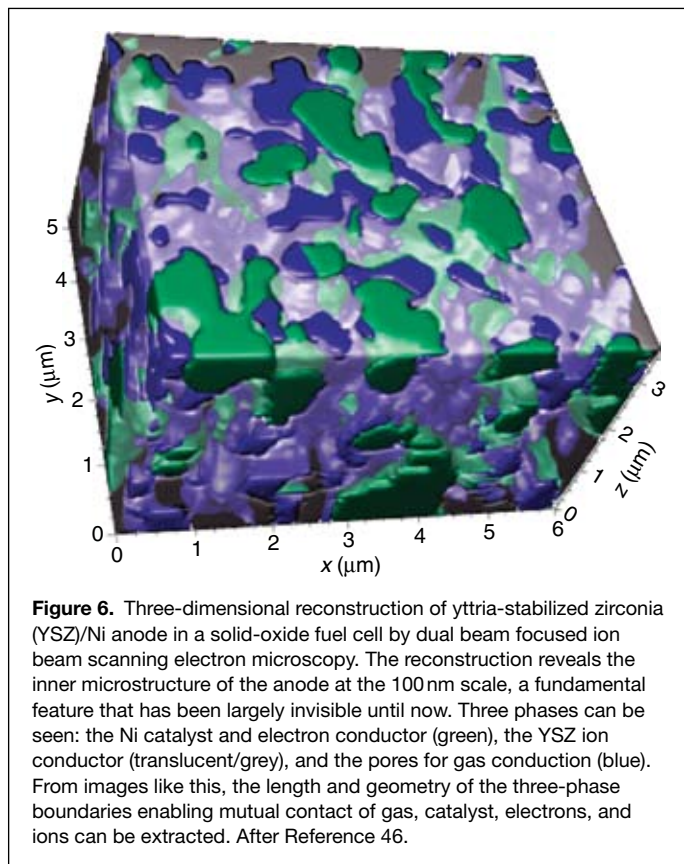
cal exchange with the electrodes. Chemically crosslinking membranes from liquid precursors at low temperature delivers improvements in all of these properties.⁴³

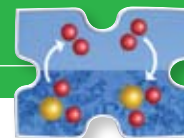
Beyond transportation, hydrogen and fuel cells can make a substantial contribution to clean and efficient energy use for stationary power generation for grid distribution, as battery replacements for personal electronics, and as stationary or portable emergency power. For large-scale stationary applications, solid-oxide fuel cells operating continuously in the range of 800–1000°C are the favored technology for their economies of scale. Here, O²⁻ ions are the mobile species, traveling through a solid-oxide membrane to react with H⁺ ions to produce water. The high operating temperatures required to produce sufficient oxygen ion mobility in the perovskite membrane limit the lifetime of components, create fatigue from thermal cycling, and require long starting and stopping times. Reducing the operating temperature of solid-oxide fuel cells to 400–600°C is a major materials research goal requiring new solid electrolytes with high oxygen ionic conductivities, active catalysts for hydrogen oxidation at the anode and oxygen reduction at the cathode, and electrode materials with suitable ionic and electronic conductivities that are compatible with the electrolyte.⁴⁴ Promising results have been achieved using Ce_{1-x}M_xO_{2-δ} (where M is Gd, Sm, Ca, or Mg) and (La_{1-x}Sr_x)(Ga_{1-y}Mg_y)O_{3-δ} as the electrolytes, in which the oxygen vacancies are controlled by

charge-deficient substitutions on the cation sites. The electrodes facing the electrolyte must have significant ion and electron conductivities at low temperatures, a key research objective. Promising anodes include rare-earth-doped ceria, such as Sm_xCe_{1-x}O_{2-δ}, together with a Ni catalyst,⁴⁵ and cathodes include doped CoO₃, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} and Ba_{0.5}Sr_{0.5}CoO_{3-δ}. High performance of the electrolytes and electrodes depends not only on composition, but also on internal microstructure, a feature that has remained largely hidden until recently. Three-dimensional imaging of fuel cell components using transmission electron microscopy is beginning to reveal the inner microstructure of the three-phase boundary at the intersection of the gaseous environment, the electrode, and the polymer membrane where molecular gases, electrons, and ions meet and exchange. **Figure 6** shows the rich detail that 3D imaging reveals about this three-phase boundary in a yttrium-stabilized zirconia anode of a solid-oxide fuel cell.⁴⁶ Such images yield quantitative information about the volume fractions, surface areas, and connectivities of the various phases and will soon be applied to the electrodes and membranes of many established and emerging fuel cell types.

Evolution of a Hydrogen Economy

Widespread hydrogen-powered transportation requires the simultaneous solution of challenges in production, storage, and use, a much more difficult task than solving any of the three alone. We are far from practical solutions in fossil-free production and in solid-state storage, and the path to these outcomes will not be based on incremental innovations in today's technologies of reforming natural gas or coal, or storage in compressed gases and liquids. Fuel cells are qualitatively different, however: a competitive technology can arise from innovation





on today's approaches and designs. Like the internal combustion engine of a century ago, today's fuel cells can spawn a long line of progeny based on successive innovation of their electrodes, membranes, and catalysts.

The requirement of disruptive innovation for the success of fossil-free production and solid-state storage makes the entrepreneurial approach difficult to launch for transportation. Unlike earlier energy shifts from wood to coal and from horse to internal combustion engine, all of the pieces are not yet in place for hydrogen-powered vehicles to offer an obviously cheaper and higher performing alternative to fossil fuel power. The disruptive innovations that will enable production and storage for a full-fledged hydrogen economy can come only from high-risk, high-payoff basic materials research, rather than incremental approaches.

The value of a hydrogen economy, however, extends well beyond transportation. Hydrogen is remarkably attractive in many applications as an energy carrier. Once produced, it is environmentally friendly, and it is flexibly convertible to other forms of chemical, thermal, or electrical energy at high efficiency. In these respects, hydrogen shares the appealing attributes of electricity, the world's most versatile and fastest-growing energy carrier. Hydrogen and electricity are natural partners, as they can be interchanged at high efficiency through electrochemistry in fuel cells and electrolyzers. Their compatibility is enhanced by their complementary storage characteristics: hydrogen stores energy indefinitely and at high density in chemical form, whereas electricity is typically used at the moment it is produced and lacks a convenient high-density form of storage. The intermittent character of renewable electricity and the diurnal and seasonal fluctuations in demand make local hydrogen storage and interconversion to electricity a powerful and natural option.

The intimate connection between hydrogen and electricity provides attractive routes for the development of a hydrogen economy. Hydrogen in stationary solid-oxide fuel cells produces electricity much more efficiently than do existing coal-fired power plants. Hydrogen for electricity production is available in abundant amounts from the gasification of coal, where CO₂ capture is easier and less expensive than in existing power plants based on the combustion of pulverized coal. The hydrogen produced in this way can be burned at high efficiency in combined cycle turbines to produce electricity, converted to electricity at high efficiency in solid-oxide fuel cells, or transferred off the power plant site for other uses such as transportation. This diversity of deployable options allows the entrepreneurial spirit to operate with present technology, ready to incorporate new scientific discoveries and technological innovations and to respond to changing market opportunities. Because this development route uses known technologies, it is not dependent on disruptive innovation in production and storage. Furthermore, it requires no new infrastructure off the power plant site.

Other attractive routes for hydrogen development are electricity for personal electronics and emergency power. In both cases, performance trumps cost as the top priority, and the portable electricity of fuel cells offers advantages over batteries and fossil fuel generators. Fuel cells can operate for longer times between refueling or recharging than batteries of the same weight and volume. For emergency power, hydrogen and fuel cells produce electricity at much higher efficiency than small fossil fuel generators. They have no moving parts that require lubrication and maintenance when not in use. Large units can be stored at critical sites such as hospitals and communications centers or delivered by truck to neighborhoods. As with utility-scale power generation, these personal electronics and emer-

gency power applications do not require solutions to the production and storage challenges before deployment. Although the relative cost of electricity from portable fuel cells is higher than for battery or fossil fuel alternatives, the differential cost of these applications is small enough that the advantages of size, operating time between charges, efficiency, and convenience could become deciding factors.

The prospects for hydrogen as an energy carrier are intimately connected to the course of energy developments over the next half-century. Global energy demand is expected to double by 2050, and electricity demand to triple, while concern for environment and climate expands. This unique combination of trends creates many opportunities for hydrogen to enter the global energy mix as a complementary energy carrier and natural partner for electricity. Hydrogen and fuel cells operate effectively at all scales, spanning personal, automobile, neighborhood, and utility applications. Hydrogen links chemical and electrical energy with much more flexibility, efficiency, and cleanliness than is possible for fossil fuels. In the transition to new energy sources and uses at mid-century, these advantages will have growing importance and appeal.

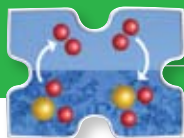
Apart from technical and economic factors, safety plays an important role in the evolution of a hydrogen economy. As for gasoline and electricity, the high energy density of hydrogen creates the possibility of harm to humans and property. Codes and standards need to be developed that enable hydrogen to be handled safely and reliably. As hydrogen becomes more commonplace, these codes and standards need to be disseminated widely to professional hydrogen workers and to the public. This requires a concerted effort in education about the dangers of hydrogen and in safe procedures for its handling. Gasoline and electricity carry similar dangers, but codes, standards, and education have been effective in reducing the incidence of injury from these energy sources and carriers to an acceptable level. A similar and deliberate level of commitment to safety codes and standards will be needed for hydrogen.

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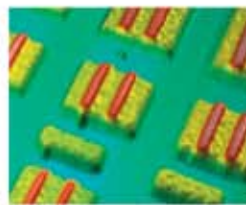
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