Hydrogen Safety

A focus on power generation applications

By Steven F. Rodgers, Shravan K. Vudumu, Scott E. Grasman, Susan L. Murray and Umit O. Koylu

HYDROGEN PROVIDES a unique opportunity to reliably generate power with zero on-site emissions of pollutants or greenhouse gases. While winds do not always blow and the sun is not available at night, energy from hydrogen is accessible on demand. Hydrogen is an energy storage medium; since it does not exist in its elemental state on earth, it must be manufactured (potentially with renewable sources) (Goswami, Mirabal, Goen, et al., 2003) and that takes energy.

In this sense, it is more akin to a battery than a solar panel. As such, it can mediate between the arbitrary nature of some renewable sources and the specific demands of industry as either a backup power unit, for portable or transportation applications, or for running equipment independent from the conventional electricity grid.

Hydrogen releases energy when it bonds with oxygen. This can be achieved through a reaction of hydrogen in an internal combustion engine (in the place of gasoline) for automobiles (Vudumu & Koylu, 2009a) or by an electrochemical reaction in a fuel cell to produce electricity. Combustion reactions convert chemical energy into thermal energy, which can then be used to produce mechanical work and electrical energy, but fuel cells convert the chemical energy directly to electrical energy so less energy is lost in intermediate steps. This energy loss prevents a combustion engine from ever being as efficient as a fuel cell.

For portable or stationary power generation, the most common method of extracting energy from hydrogen is with a fuel cell. Currently, the most common type is the proton exchange membrane (PEM) fuel cell. In a PEM fuel cell, the flow of hydrogen and oxygen is separated by a membrane assembly (Figure 1, p. 40). The membrane assembly consists of the membrane and two gas diffusion layers that contain the catalyst (typically platinum). On the fuel side of the assembly (anode), hydrogen gas (H_2) is split into its constituent hydrogen atoms by the catalyst (as shown on the left side of Figure 1).

The hydrogen atoms are stripped of their electrons leaving just protons. These protons are free to pass through the membrane, but the membrane is impermeable to the flow of electrons. The protons want to combine with oxygen atoms at the cathode to form water, but they lack the electrons to complete the chemical reaction. This compels the electrons to go the "long way" to the far side of the membrane assembly (right side of Figure 1), through whatever electrical circuitry connects the two sides. These electrons flowing through wiring form an electrical current that can be utilized. The waste product of this reaction is pure water, which is the primary state in which hydrogen is naturally found on earth.

Hydrogen power and fuel cells have already begun to become incorporated into the industrial workplace. This includes hydrogen-powered fork-

Abstract: *Hydrogen has the potential to provide clean and secure energy. It can be used to power internal combustion engines or fuel cells. Although hydrogen has long been used in various industrial processes, some myths persist that it is an intrinsically dangerous fuel. This article discusses hydrogen's unique properties and outlines some guidelines for its safe use in many applications.*

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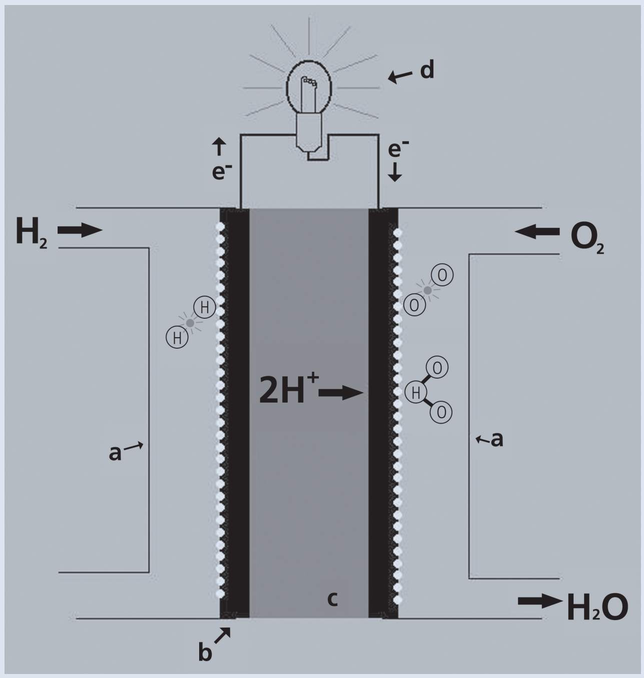
Figure 1

Proton Exchange Membrane Fuel Cell

a) gas channels; b) gas diffusion layer with catalyst; c) membrane; d) external load.



lifts and emergency backup power. Companies such as Nissan, Toyota and Hydrogenics have built test vehicles and are running trials to test their viability in the market (Nissan Forklift Europe B.V.; Toyota Industrial Equipment, 2005; Hydrogenics Advanced Hydrogen Solutions).

A government analysis of fuel-cell-powered forklifts (Mahadevan, Judd, Stone, et al., 2007) concluded:

> PEM fuel cells can provide value over battery-powered forklifts in high productivity environments. When forklifts are operated under conditions of near continuous use, fuel cell vehicles are significantly less expensive than similar battery-powered systems from a life-cycle cost perspective. Advantages of PEM fuel cell systems operating under such conditions include rapid refueling, eliminating time and cost of replacing batteries, constant voltage delivery, increased productivity by eliminating battery recharging time, fewer repairs due to fewer moving parts, and elimination of battery storage/changing rooms and associated costs (p. 139).

Motorola is working with Dantherm Power to equip 100 TETRA base stations with fuel cells for emergency power (Motorola). A fuel cell powered a radio tower in Maryland during the blackouts caused by Hurricane Isabel in 2003, allowing emergency response agencies to coordinate their efforts (DOE Hydrogen Program, 2008). Hydrogen energy continues to improve and prove its usefulness (Thomas, Martin, Cottrell, et al., 2009).

The issue of using hydrogen safely is at the forefront of alternative energy research. If hydrogen use is to become ubiquitous, those involved must analyze current safety standards and ensure that they are adequate. Many researchers (MacIntyre, Tchouvelev, Hay, et al., 2007; Crowl & Jo, 2007; Dahoe & Molkov, 2006) and government organizations (Sandia National Laboratories, 2007) are doing just that. This article summarizes the current state of hydrogen safety and presents key factors to consider in order to use hydrogen safely.

Hydrogen Misconceptions

Hydrogen has been connected with two key technologies of the past century, and the connections have not been positive.

Like the sinking of the *Titanic*, the accounts of the destruction of the *LZ-129 Hindenburg* have transcended generations, due in part to the dramatic footage of its demise and the frantic and impassioned "Oh, the humanity!" radio broadcast of Herbert Morrison (Munchkin Studios, 2009). As a result, some may have associated this event with the destructive potential of hydrogen (Ricci, Bellaby & Flynn, 2008).

The commonly held view of the explosion has been challenged by Addison Bain, a retired NASA scientist. Bain (1999) argued that the cause of the fire was ignition of the zeppelin's skin and that the rapid spread was due to the coating used to seal the cloth skin. Supporting this theory are the facts that fire glowed red (hydrogen flames are blue and nearly invisible in daylight) and that the airship's tail section appeared to remain buoyant for some time after the fire began, suggesting that the hydrogen gas remained secure.

These arguments are refuted by Dessler, Overs and Appleby (2005), who say that "spark ignition [of the fabric] is physically implausible if a natural spark is employed," and that the burning rate of the paint is much too slow to account for the rapid destruction of the *Hindenburg*. The fire's color can be explained by the fact that, even if it did not significantly contribute to the disaster, the airship's skin would be burned, and this would have noticeably changed the hue of the flame. The perceived buoyancy could well have been caused by inertia coupled with the updraft created by the firestorm above the airship's tail.

So what caused the catastrophe? It is suggested that hydrogen was released by either a punctured ballonet (the bladders that contained the hydrogen) or a stuck vent. The passing storm front electrically charged the zeppelin, and the resulting static discharge ignited the hydrogen.

Table 1

Comparison of Properties of Hydrogen, Natural Gas & Gasoline

Characteristic	Hydrogen	Natural gas	Gasoline	Hydrogen has . . .
Lower heating value (kJ/g)	120	50	44.5	More energy per kilogram
Flammability limits in air (vol%)	4-74	5-15	1-7	Wider flammability limits
Density (kg/m^3)	0.082	0.67	4.4	More buoyancy
Diffusion coefficient in air (cm^2/s)	0.61	0.16	0.05	Fastest spread
Stoichiometric flame speed (m/s)	2.1	0.4	0.3	Fastest burning velocity
Minimum ignition energy (mJ)	0.02	0.3	0.3	Easiest ignition

The hazards associated with hydrogen are similar to those associated with other fuels, such as natural gas and gasoline, and they differ where physical characteristics differ.

Is this counter to the earlier assertion that hydrogen is not intrinsically dangerous? The only conclusion that can be drawn is that a mixture of combustible gas and oxygen should not be permitted in proximity to static discharges. In this case, the combustible gas was hydrogen, but the same could be said for any flammable gas.

A second misconception should be addressed as well. The advent of nuclear weapons has instilled a justified fear of annihilation, not just of individuals but of the species and the biosphere. This fear generates an equally justified unease about the tools of potential destruction, one of which is known popularly as a "hydrogen bomb." This has led some to associate hydrogen fuel with mushroom-shaped clouds (Zachariah-Wolff & Hemmes, 2006), but this is unfounded.

The nuclear weapon that uses hydrogen as an energy source releases its energy by fusing the nuclei of two hydrogen atoms together. This process requires large amounts of energy to initiate. In the weapon, this energy is supplied by nuclear fission of plutonium or uranium. In stars, the energy to fuse hydrogen comes from the intense pressure generated by their bulk. In either case, these intense releases of energy are caused by a nuclear reaction. In fuel cell applications, the energy that is utilized results from an electrochemical reaction; there is no possibility of a nuclear explosion or some sort of Chernobylesque meltdown.

Unique Properties & Safety Considerations

The actual dangers of hydrogen must be taken seriously. The hazards associated with hydrogen are similar to those associated with other fuels, and they differ where physical characteristics differ. Table 1 compares some important properties of hydrogen with those of natural gas and gasoline.

One significant difference is hydrogen's very low density. It is the lightest possible molecule with a molecular weight of 2 g/mol. This makes it very buoyant (hence its use to float air vehicles such as the *Hindenburg*). Its high buoyancy makes hydrogen rise more rapidly than other fuels when leaks occur.

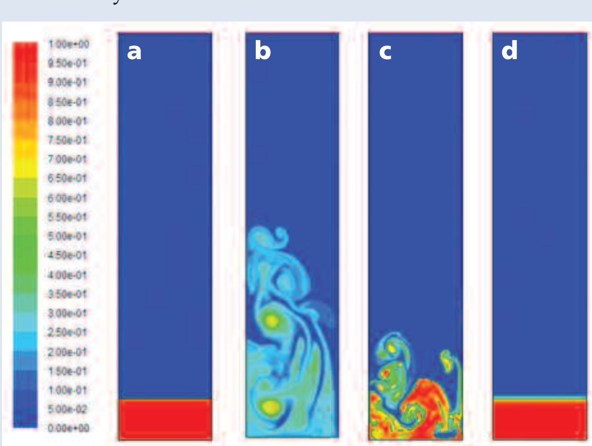
This is illustrated in Figure 2, which shows a simulation of hydrogen (case b) practically launching upward after release, as compared to the more placid spread of methane (case c) and the lethargic diffusion of ethylene (case d) (Vudumu & Koylu, 2009b).

Hydrogen's rapid rise coupled with its wide flammability limits is significant because it implies that even a small leak could lead to accumulation of a flammable hydrogen mixture in partially enclosed areas such as parking garages, road tunnels or between rafters in a building

Figure 2

Transient Mixing Behavior of Gases

a) Initially concentrated in the lower 10% of the cylinder; b) hydrogen/air; c) methane/air; d) ethylene/air mixing 2 seconds after the release of the fuel. Scale is percent fuel in mixture by volume.



The high buoyancy of hydrogen makes it rise more rapidly than other fuels when leaks occur. In this simulation, hydrogen (case b) practically launches upward after release, as compared to the more placid spread of methane (case c) and the lethargic diffusion of ethylene (case d).

Photo 2 (left) shows a flame resulting from the combustion of a gas mixture containing 77% hydrogen and 23% methane, while Photo 3 (right) depicts an acetylene flame.

(Gupta, Brinster, Studer, et al., 2007; Koylu, Vudumu & Sheffield, 2009).

On the other hand, were a fire to occur, it would be more likely to happen overhead (Koylu, et al., 2009), as opposed to at ground level as would be the case with more dense fuels. A hydrogen flame that begins at ground level will rise rapidly; in fact, two-thirds of the *Hindenburg's* passengers survived, as the fire raged over their heads. Those who died were either located at the front tip of the zeppelin (which, as the back sank, became an exit point for hydrogen), jumped or became trapped as the wreckage settled around them, and died as a result of burning diesel fuel (Russell, 2009).

The accumulation of hydrogen is a cause for specific concern, however, since hydrogen (like other flammable gasses) tends to detonate when ignited in confined areas. The wide flammability limits and low minimum ignition energy exacerbate this issue.

The mitigation of this hazard has three distinct aspects: 1) sensors for early detection; 2) ventilation to prevent accumulation; and 3) electrical grounding to avoid static discharges.

Sensors are necessary because hydrogen is naturally an odorless gas. Odorants that are typically added to gasses (such as the methanethiol added to the natural gas used to heat water in homes) cannot be used with fuel cells because they adversely affect the catalyst used to split the H_2 molecules. Sensors must be relied on to warn of any leaks.

Ventilation is possibly the most important aspect of fuel cell safety. The high buoyancy of hydrogen makes this process potentially simpler than it would be for other fuels. Barley and Gawlik (2009) show that even nonmechanical ventilation (no fan or other energy input) can reduce concentrations resulting from even sizeable leaks to safe levels. An open vent in the right location could be sufficient to evacuate hydrogen to the outside environment.

To avoid static charges as an ignition source, fuel cells and other equipment should have electric grounds. This requires proper installation and maintenance of a building's wiring system.

Hydrogen flames are different from flames of hydrocarbon fuels, not just because of hydrogen's properties but also because of the properties of the combustion products. Hydrocarbons such as methane and petroleum products are composed of, as the name suggests, hydrogen and carbon atoms arranged into molecules.

When these are combined with oxygen in combustion, the products include carbon dioxide, carbon monoxide and soot. Hydrogen fires produce none of these.

The dangers of the greenhouse gas carbon dioxide and the toxic carbon monoxide are well publicized (UN Intergovernmental Panel on Climate Change, 2007; Sara, Marcelo & Gordon, 1992). The soot particles become heated by the combustion process.

As they are heated, they begin to glow. (This is the same sort of radiation that occurs when a heated piece of metal begins to glow—electromagnetic radiation—which is distinct from radiation resulting from nuclear processes, although they can both be called radiation.)

This is what gives hydrocarbon flames their characteristic yellow hue. This radiation transfers heat to the surroundings and makes the flame visible. Since hydrogen fires do not produce soot, they are much harder to see and are typically invisible under nor-

Photo 4 (top): Propane and hydrogen flame viewed in daylight.

Photo 5 (bottom): Propane and hydrogen flame viewed through a thermal imaging camera.

Table 2

Relevant Codes & Standards

Code or standard	Topic
NFPA 853	Standard for the Installation of Stationary Fuel Cell Power Systems
NFPA 50A	Standard for Gaseous Hydrogen Systems at Consumer Sites
IEC 62282-2	Fuel Cell Technologies—Part 2: Fuel Cell Modules
ICC IFC-2006	International Fire Code
ANSI/CSA America FC 1-2004	Stationary Fuel Cell Power Systems
UL 2075-2007	Gas and Vapor Detectors and Sensors
CGA P-12	Safe Handling of Cryogenic Liquids
CGA G-5.5	Hydrogen Vent Systems
SAE J2578 (SAE J2578)	Recommended Practice for General Fuel Cell Vehicle Safety
NFPA 55-2003	Standards for the Storage, Use and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks

Several organizations have developed codes and standards for the safe handling and use of hydrogen and hydrogen fuel cells, including NFPA, International Electrotechnical Commission, ANSI, UL, Compressed Gas Association, Society of Automotive Engineers and International Code Council. These standards cover a wide range of possible safety issues.

mal daylight conditions. Photos 2 and 3 compare hydrogen and acetylene flames. The hydrogen flame is only visible because of the low light conditions, while the acetylene flame radiates with enough intensity to be seen at all times.

This is further demonstrated by Photos 4 and 5, which show a hydrogen flame burning just as hot as a propane fire without radiating visible light. Besides reducing the flame's visibility, the lack of radiating soot particles diminishes one's ability to detect a hydrogen fire by sense of touch. A radiating fire can be felt several feet away, not just by the movement of hot air (convection), but by the absorption of the electromagnetic radiation put off by the glowing soot particles.

The practical consideration of this is that a hydrogen flame may not be felt on the skin until a person is nearly within the flame itself. This emphasizes the importance of hydrogen gas sensors that can detect hydrogen leaks before they combust. Firefighters and first responders typically carry handheld thermal imaging cameras to find hydrogen flames, but low-tech methods such as the trusty broom can be used as well: If an individual enters an area with an invisible hydrogen flame, the broom will ignite before the person gets too close, thus providing a clear sense of the fire's location (Pacific Northwest National Laboratory & Los Alamos National Laboratory).

Hydrogen gas also has an effect on some materials through a process known as material embrittlement. The weakening of steels can partially be explained by hydrogen reacting with the carbon in the metal to form methane. All metals are affected to some extent, but the mechanism for this is not completely understood. NASA's hydrogen safety standards (NSS 1740.16, since canceled) offered several recommendations to avoid embrittlement:

1) Aluminum is one of the few metals known to show only minimal susceptibility to hydrogen, so its use effectively eliminates hydrogen embrittlement.

2) Containers with thick walls of low-strength metals will generally contain hydrogen more safely than containers fabricated from similar alloys treated for high strength, subject to appropriate welding techniques.

3) A metal or alloy is almost certain to have a lower resistance to fatigue than if hydrogen were not present if it is exposed to hydrogen and cyclic stresses. Designers should, in the absence of data, assume a substantial (up to fivefold) decrease in resistance to fatigue.

4) The use of metals and alloys with a body

Photo 6: Missouri S&T's mobile hydrogen unit showing a) compressed hydrogen tanks; b) ventilation system; c) warning light; and d) emergency shutoff button. Not visible in this picture are hydrogen sensors and another emergency shutoff device located on the outside of the trailer.

centered cubic crystal structure, such as iron and tungsten, should be avoided whenever practical. Cast iron shall not be used.

5) Hydride-forming metals and alloys should not be used as structural materials for hydrogen service. Their use requires careful consideration of operating temperatures and adverse effects of hydride formation.

Hydrogen embrittlement is a greater issue for those who design safe hydrogen systems than it is for those who operate such systems. However, users should be aware of the effect and watch for any damaged parts in contact with hydrogen, as the fuel could intensify the problem and cause leaks.

Several organizations have developed codes and standards for the safe handling and use of hydrogen and hydrogen fuel cells, including NFPA, International Electrotechnical Commission, ANSI, UL, Compressed Gas Association, Society of Automotive Engineers and International Code Council. These standards cover a wide range of possible safety issues. Table 2 (p. 43) lists standards that can be consulted.

A properly set up hydrogen cylinder system is shown in Photo 6 (p. 43). This is the mobile hydrogen unit (MHU) used by Missouri S&T's EcoCAR Challenge team to produce and store hydrogen for its competition vehicle, a fuel cell plug-in hybrid electric vehicle. Key features to ensure safe operation include the indicated emergency light to warn personnel of a detected hydrogen leak and a fan-driven ventilation system placed at the trailer's highest point. Emergency shutdown buttons are located inside and outside of the trailer.

Conclusion

Hydrogen can help provide clean energy for various uses. However, as a combustible gas, precautions must be taken in its application. Hydrogen has many properties that make it unique, including high buoyancy, wide flammability limits and low flame visibility. With knowledge of these hazards, hydrogen and fuel cells can be used safely in working environments. ■

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