

HYDROGEN FUEL CELLS

AN ALTERNATIVE FOR FUTURE

Abstract— Electrochemical and other process industries frequently vent or flare hydrogen by products to the atmosphere. 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. Also summarized are the fundamental principles of fuel cell thermodynamics and of fuel cell power plant engineering. Throughout the paper, current and future perspectives regarding thermodynamics and sustainable development are considered.

Keywords—Hydrogen; energy; fuel-cell; thermodynamics; sustainable development; energy conversion.

I. 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 non uniform 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. 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 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. 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, nano science 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

FAISAL KAMRAN

Department of Electrical and Electronics National Institute of
Technology-Puducherry Karaikal

AMAN JAIN

Department of Electrical and Electronics National Institute of
Technology-Puducherry Karaikal

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 non fossil 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.

I. PRODUCTION OF HYDROGEN

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. About half of the global supply of hydrogen is produced by reforming natural gas. 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 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 by products 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 electrolyzers 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. 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. 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 favoured 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. 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. Catalysts are needed as well, to reduce the energy barriers to water splitting. 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. The development of membranes for separation of hydrogen from CO and CO₂ is a key materials issue. 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. 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. The switch ability 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.

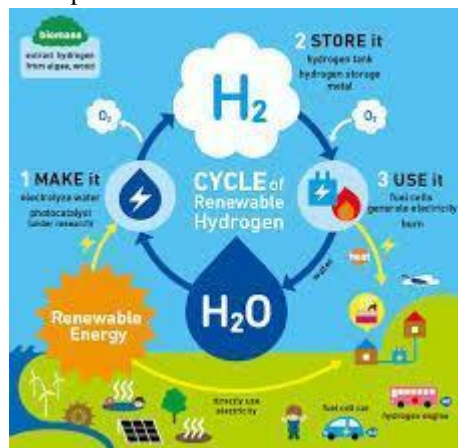


Fig.1: HYDROGEN CYCLE

II.STORAGE OF HYDROGEN

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. 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 behaviour. 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. 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. 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) and the boranes NH_nBH_n , where n ranges from 1 to 4. 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. 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. The first hydrogen comes off at $<25^\circ C$, making it too unstable for storage under expected operating conditions. The remaining hydrogens come off at $<120^\circ C$, $\sim 155^\circ C$, and $500^\circ C$. Thermal decomposition of NH_3BH_3 to $NHBH_2$ removes the second and third hydrogens and releases 12% hydrogen by mass below $155^\circ C$, 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 $NHBH_2$ 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 $150^\circ C$. The ammine salt $Mg(NH_3)6Cl_2$ can be formed into nanoporous pellets, 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 $\sim 150^\circ C$, significantly lower than the release temperature for either $LiNH_2$ (lithium amide, $200^\circ C$) or LiH ($500^\circ C$). The storage capacity of 6.5% for this reaction is substantial, although not high enough for the ultimate storage solution. If Li_2NH could be destabilized to release the remaining H, the

storage capacity would be 9.6%, high enough for hydrogen-powered transportation. $LiBH_4$ and MgH_2 are another destabilization couple, with a storage capacity of 11.5%. 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 H_2 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. Nanoporous materials that divide and confine storage media such as NH_3BH_3 in nanoscale units can lower the decomposition temperature and activation barriers for hydrogen release and alter the decomposition pathways and end products. $Mg(NH_3)6Cl_2$ is naturally nanoporous, accounting for its rapid NH_3 charge/release times. 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.

III. HYDROGEN AS 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 Fig. 1. 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 $\sim 25\%$ 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%. 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. 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 theory 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 neighbouring 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. 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. Key issues in all membrane materials include acid loading to provide additional sites for proton transfer, polymer cross linking to improve thermal and mechanical stability at high temperature, and enhanced surface area to enable effective electrical and chemical exchange with the electrodes. Chemically crosslinking membranes from liquid precursors at low temperature delivers improvements in all of these properties. 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-d} (where M is Gd, Sm, Ca, or Mg) and (La_{1-x}Sr_x)(Ga_{1-y}Mg_y)O_{3-d} 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-d}, together with a Ni catalyst and cathodes include doped CoO₃, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d} and Ba_{0.5}Sr_{0.5}CoO_{3-d}. 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. The rich detail that 3D imaging reveals about this three-phase boundary in a yttrium stabilized zirconia anode of a solid-oxide fuel cell. 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.

IV. FUEL CELL ELECTROCHEMISTRY

In the basic fuel cell, the electrodes provide a means of contact between reactants that are continuously supplied to the electrolyte. The fuel (hydrogen) is supplied to a catalyst-coated anode, and the oxidant (oxygen, either pure or atmospheric) is supplied to a catalyst-coated cathode. It should be noted that other fuels, notably carbon monoxide, methane, and methanol, can theoretically be oxidized in some fuel cells, but the hydrogen oxidation reaction generally predominates. This is the primary reason for the importance of fuel cells in the hydrogen economy. The catalyst at the electrodes enables relatively low temperature oxidation of hydrogen and reduction of oxygen which releases ions to flow through the electrolyte and produce water at one of the electrodes; which one depends on the chemistry of the electrolyte. The operating temperature range of a fuel cell is determined by the range in which the catalysts are effective and in which the electrolyte is mechanically durable and conductive of ions. The passage of these ions sets up an electric potential difference between the electrodes which can drive a current through a load, thus

completing the circuit. As with any direct conversion device, the amount of electric energy produced by a fuel cell is, in idealized terms, a function of the Gibbs free energy released by the reaction taking place

$$\Delta G = \Delta H - T\Delta S: (1)$$

This relationship can be used to define the theoretical upper limit of a fuel cell's efficiency, and algebra with thermodynamic relations reveals that this theoretical maximum efficiency is directly proportional to the electric potential setup by the catalyzed reaction

$$\eta_{th} < -nFE/\Delta H = 1 - (T\Delta S/H): (2)$$

For a hydrogen/oxygen fuel cell with reactants at standard conditions (of 1 atm and 25 C), the ideal potential is 1.23 V. Further calculus with the Gibbs free energy equation and other fundamental relations of thermodynamics reveals that this ideal potential actually drops with increasing reactant temperature (3) and rises with increasing reactant pressure (4)

$$(\partial E_o/\partial T)_P = \Delta S/nF: (3)$$

$$(\partial E_o/\partial P)_T = -\Delta V/nF: (4)$$

Integrating the Gibbs free energy equation with boundary conditions relevant to a hydrogen/oxygen fuel cell results in the fuel cell Nernst equation

$$E = E_o + (RT/2F)\ln[PH_2/PH_2O] + (RT/2F)\ln[(PO_2)^{1/2}]: (5)$$

The Nernst equation yields the theoretical limit of cell voltage and thus the highest efficiency that laws of thermodynamics will allow for a fuel cell with a given reactant pressure and temperature. Of course, the thermodynamically ideal efficiency cannot be achieved in a practical fuel cell, as the cell voltage achievable is reduced by the losses affecting the performance of any direct conversion device. These losses increase (and the cell voltage thus decreases) as current density (current flowing per unit cell area) increases. Different loss mechanisms predominate in different regimes of current density. At lower current densities, cell voltage is decreased by the rate limiting effects of oxidation/reduction kinetics, which are known as activation losses. As current density increases, ohmic resistance to the flow of ions through the electrolyte begins to drive down cell voltage due to what are known as ohmic losses. Then, at the highest current densities, fluid flow resistance will lead to starvation at reaction sites, thus forcing cell voltage down even more rapidly due to concentration losses. It is worth noting that these losses all tend to become less pronounced, and achievable cell voltage thus increases, as operating temperature increases. Most of the engineering research in fuel cell technologies, particularly in the realm of nanoengineering, is focused on finding ways to mitigate the effect of these losses and produce fuel cells that approach idealized efficiency limits over a useful operating life. Nanotechnology is yielding dividends in the fabrication of durable electrodes that enable very high contact area per unit and thus offer decreased effective current density, as well as in the development of electrode and electrolyte materials with low ohmic resistance. The combination of thermodynamic limitations and the effects of losses results in a general principle for fuel cells: Cell voltage, and thus efficiency,

decreases with increasing current density but generally tends to increase with operating temperature and pressure. One implication of this principle is that designers of automotive fuel cells, for whom volume and weight are just as or more important than fuel efficiency, will tend to design compact fuel cells that operate at high current density, while designers of stationary power plants may choose larger, heavier, but lower current density fuel cells that offer higher fuel efficiency. Another implication of this principle is that fuel cell efficiency increases as power demand falls off from the maximum power output (i.e., from the design current density) of the cell. This is in contrast to heat engines involving rotating or reciprocating machinery, in which case efficiency markedly decreases as power demand falls off from the level associated with the optimal design speed of the engine. (This is one reason why automobile internal combustion power trains have multispeed transmissions.) However, as the compressors and pumps generally used to feed reactants to the fuel cell themselves fall off in efficiency if demand significantly varies from their design speed, the net efficiency of a complete fuel cell power plant often remains nearly constant as power demand increases up to the design-rated value.

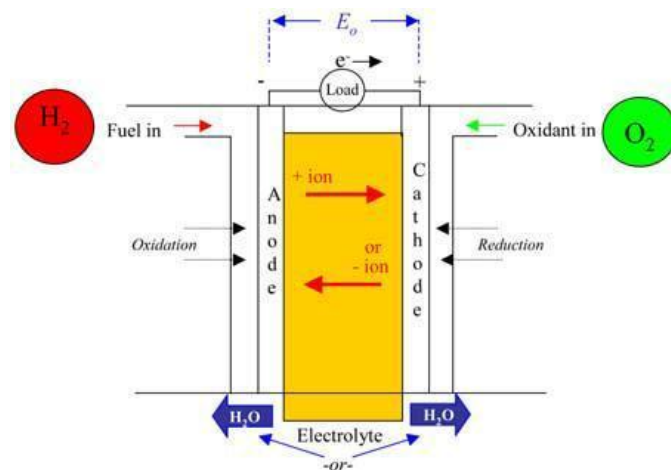


Fig.2: Individual fuel cell. Each fuel cell creates electric potential across its electrodes that is a function of pressure and temperature of reactants fed and of losses inherent in the electrode/electrolyte combination selected. Individual cells are wired in series and parallel to provide the voltage and current required of the power plant output.

V. FUEL CELL POWER PLANT ENGINEERING

The basic components of a complete fuel cell electric power plant are identified. Individual fuel cells are connected in series and parallel to yield what is known as a fuel cell stack that produces the current and voltage required. The other components of the power plant, known as the balance of plant, function to feed reactants to the stack, to remove water, waste heat, and other reaction products from the stack, and to condition the electric power output. All of these components have inefficiencies resulting in more waste heat and require net energy input that acts as a parasitic loss on the net fuel cell

power output. As the output of a fuel cell is dc electricity, it must be passed through an inverter to yield the ac electricity used in most power grids. Inefficiencies in this inverter also produce waste heat that must be removed. Oxygen is fed to the stack from either the atmosphere or a reservoir of pure oxygen with either high storage pressure or a compressor (with its own parasitic power requirements) driving the flow. The more challenging engineering problem is the efficient provision of hydrogen. Hydrogen cannot be mined nor is it readily available from the atmosphere. It must be provided from one of two processes: 1) electrolysis or 2) reforming. Depending on the application, the components for these processes may or may not be integrated in the plant with the fuel cell stack.

A. Electrolysis

An electrolyzer is basically a fuel cell driven in reverse, with water (liquid or vapour) fed to catalyst-coated electrodes and dc electricity driving ions through an electrolyte to produce pure hydrogen and oxygen. An electrolyzer and a fuel cell can be combined into what is known as a regenerative fuel cell system, which in certain applications can offer an energy storage system with weight advantages over batteries. It is through electrolysis that non fossil-fuel electricity sources, such as hydro, solar, and nuclear, can be used to produce hydrogen as a transportation fuel with no emission of carbon into the atmosphere. However, electrolysis can itself be a relatively inefficient (roughly 50%–70%, give or take) use of electricity, and (when compared to natural gas) hydrogen is relatively expensive to compress and pipe over long distances. Thus, electrolysis units are rarely found useful as part of a fuel cell-fed electric utility grid.

B. Reforming

The more economically practical and energy efficient means of hydrogen provision is from hydrocarbon fuels via a process known as reforming. This is the process by which the aerospace industry currently makes hydrogen for rocket propellant and by which German industry made hydrogen to buoy Zeppelins during the First World War. In a fuel cell power plant system, this process takes place in a unit known as the fuel processor or reformer. A reformer cracks hydrogen from a hydrocarbon fuel and produces a gas known as reformat, rich in hydrogen but also containing carbon dioxide (CO₂) and carbon monoxide (CO). Processes to accomplish this include steam reforming (6), an endothermic process in which the vaporized hydrocarbon and steam react in the presence of a nickel catalyst, and partial oxidation (7), an exothermic process in which the hydrocarbon is oxidized without combustion in the presence of a platinum catalyst

e.g., for methane: $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$ (6)

e.g., for methane: $\text{CH}_4 + (1/2)\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2$ (7)

These two processes are often combined into a process known as autothermal reforming, which operates at temperatures ranging from 600 C to 900 C and is endothermic, thus requiring some burning of the hydrocarbon fuel to provide the

net energy input. The reformat produced at this step in these processes is rich in CO. While CO₂ is generally inert in a fuel cell, CO is a poison to most fuel cell catalysts. Different catalyst/electrolyte combinations have varying degrees of tolerance to it. CO clean up can be accomplished in a fuel processor by cooling the reformat to encourage the water gas shift reaction (8), in which CO and water exothermically combine to produce CO₂ and hydrogen, and then warming it back up to encourage preferential oxidation (9) of CO into CO₂ on a platinum catalyst bed

$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$:

(8) $\text{CO} + (1/2)\text{O}_2 \rightleftharpoons \text{CO}_2$: (9)

Also, virtually no fuel cell catalyst can tolerate sulphur in the fuel stream. Thus, the fuel processor must remove the sulphur content common to fossil fuels. This is normally done by reacting the vaporized hydrocarbon with hydrogen on a zinc catalyst bed near the input of the fuel processor. Note that the need to desulphurize crude oil via the same catalyzed reaction has resulted in an industrial demand for hydrogen that has, in turn, motivated the construction of hydrogen pipeline networks to service clusters of refineries and petrochemical plants. There are two paramount engineering limitations relevant to reformer design. First, as it is a relatively high-temperature energy-consuming unit, there can be significant warm up delays on start up (on the order of minutes at least). Also, for the same reasons, sudden step changes in demand for reformat can force incomplete reactions in the unit, leading to deposition of elemental carbon. This phenomenon, known as coking, can clog the catalyst beds and significantly degrade the fuel processor's performance. Second, the size, number of reaction stages, and parasitic energy needs of the fuel processor are directly related to the purity of hydrogen required in the reformat and to the heaviness and cleanliness of the hydrocarbon fuel. Thus, a fuel processor that is only required to convert a pure, light hydrocarbon to a relatively carbon monoxide-rich (or dirty) reformat can be small, low temperature, and integrated into the fuel cell stack; whereas, a reformer which must convert heavy, dirty marine fuel oil into relatively clean reformat must run very hot and is often ten times the size of the fuel cell stack it feeds. It is worth noting here that some hydrocarbons, most notably methanol, can be directly oxidized in certain types of fuel cells without the reforming step, albeit at relatively low efficiency (often less than 20% at current densities of interest). Along with the cartridge fuel cells and metal-air batteries, such as direct methanol fuel cells (DMFC) are being developed in competition with lithium-ion batteries for powering small electronic devices.

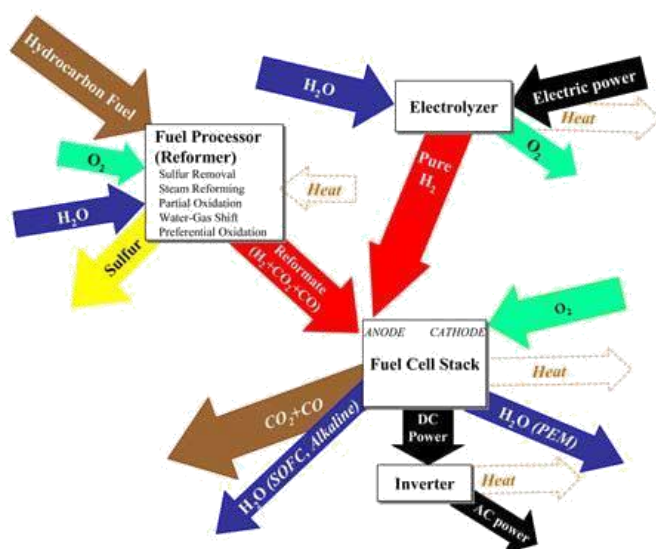


Fig.3: Fuel cell power plant components. Complete fuel cell power plant system includes equipment for hydrogen production, reactant and water management, and electric power conditioning.

VI. FUTURE ASPECT

Of all the alternative fuels available, perhaps none has captured the imagination for possibilities as a future vehicle energy source than hydrogen. A big part of that excitement is that hydrogen is a potentially emissions-free renewable fuel that can be produced not from foreign-sourced petroleum, but from domestic resources right here at home. Although not yet widely used as a vehicle or transportation fuel, an increase in research and development by both government and industry is working toward successful, and eventually commonplace, use of clean, economical, and safe production of hydrogen production as well as the greater availability of hydrogen fuel cell vehicles. Much is known about hydrogen as an element. In fact, it is the simplest and most abundant element found in the entire universe so it is little wonder that its use as a renewable fuel came under consideration. When hydrogen is at Earth-surface pressures and temperatures, it is a colourless, odourless gas. However, due to its elemental properties, hydrogen is almost never found on its own in nature, but is instead bonded with other elements, such as oxygen. Despite it being so commonplace, you may be surprised to learn that very little hydrogen gas is found in the Earth's atmosphere. Instead, enormous quantities of hydrogen is found in water, as well as methane and other hydrocarbons, plus other organic matter. But for all the hydrogen that can be found in these compounds, producing hydrogen from them has proven challenging. In fact, efficiently producing hydrogen from nature's compounds is the greatest hurdle for using hydrogen as a future renewable energy source. About 95% of hydrogen produced in the U.S. today is through the use of steam reforming of methane or natural gas. So where does it all go? It is somewhat ironic to learn that nearly all of the 9 million tons of hydrogen produced every year goes into the refining

process for petroleum, along with some amounts also being used for treating metals, producing fertilizers, and even in the processing foods. Hydrogen has had other uses throughout history, including its use in space flight since the 1950s. But these uses are not the only ones for hydrogen, as you already know. Hydrogen also can be used to provide fuel for fuel cells and internal combustion engines, the result being the capability to power zero or nearly zero emissions vehicles. That potential is key to the major research and development efforts underway that are all aimed at making hydrogen fuel cell vehicles cost effective and practical for widespread use among consumers. Hydrogen can even be blended with other fuels to make new energy sources. For example, it can be blended with natural gas to create methane, a transportation fuel that can be used in natural gas vehicles to substantially decrease the amount of nitrogen oxides that are emitted.

On the Threshold as an Alternative Fuel
The Energy Policy Act of 1992 defines hydrogen as an alternative fuel. As stated earlier, hydrogen's clean-burning properties make it a very attractive candidate for transportation fuels. Coupled with its capability of being produced domestically and the potential for high efficiency with fuel cell vehicles and it is easy to see why hydrogen is garnering considerable attention. A fuel cell vehicle is estimated to be about two to three times more efficient than a gasoline engine one. The energy that can be captured from one gallon of gasoline is equal to about 2.2 pounds (1 kilogram) of hydrogen gas. Research on fuel cells is primarily directed at ensuring that fuel cell vehicles are able to store enough fuel onboard to have a driving range in the same ballpark as conventional vehicles. Some hydrogen storage technologies are available and undergoing more research and demonstration. How might this be accomplished? Some of the technologies being developed include compressing gaseous hydrogen in high-pressure tanks at up to 10,000 pounds per square inch and cooling liquid hydrogen cryogenically to 423°F (-253°C) in insulated tanks. Still other storage technologies are being developed, including bonding hydrogen chemically with other substances.

VII. ADVANTAGES

1. **Readily Available** : Hydrogen is a great source of energy for a number of reasons, the biggest one being that it is so readily available. While it may take some work to access, there is no element in the universe as abundant as hydrogen.
2. **No Harmful Emissions** : Another advantage to using hydrogen energy is that when burned, it leaves almost no harmful byproducts. In fact, when used in NASA's spaceships, the burned hydrogen gas leaves behind clean drinking water for the astronauts.
3. **Environment Friendly** : Hydrogen is also non-toxic, which makes it a rarity among fuel sources. Nuclear energy, coal, and gasoline are all either toxic or found in hazardous environments. This makes

hydrogen ideal for use in a number of ways other fuel sources can't compete against

4. **Used as Fuel in Rockets** : Hydrogen energy is also very powerful and very efficient. It's powerful enough to propel spaceships and safer than using any other similar product to accomplish such an energy-intensive duty. In fact, hydrogen is three times as powerful as gasoline and similar fossil fuels, meaning it takes less of it to accomplish more.
5. **Fuel Efficient** : Hydrogen energy is very efficient fuel source than traditional sources of energy and produces more energy per pound of fuel. This clearly means that a car loaded with hydrogen fuel will go much farther than the one using same amount of traditional source of energy.
6. **Renewable** : Unlike non-renewable sources of energy which can't be produced again and again as they are limited; hydrogen energy can be produced on demand. Hydrogen is available in plenty. All we need is fossil fuels to break the water molecules to separate it from oxygen.

VIII. DISADVANTAGES

1. **Expensive** : Hydrogen gas also requires a lot of work to free it from other elements. If it were simple and easy to isolate everyone would be using it. It's already being used to power some hybrid cars, but at the moment it is not a viable source of fuel for everyone. That's simply because it's expensive and time-consuming to produce. That means until technology advances enough to simplify and ease the process; hydrogen energy will continue to be too expensive for most people.
2. **Storage** : Hydrogen is also hard to move around. Whereas oil can be sent through pipelines, and coal can be carried in the back of dump trucks, super-light hydrogen is hard to transport in a reasonable fashion. It is very expensive to move anything more than small amounts of it, making it impractical for most functions.
3. **Not Easy to Replace Existing Infrastructure** : As expensive as hydrogen is to produce and transport, it becomes even more expensive when you consider trying to use it to replace gasoline. There is no existing infrastructure in place to accommodate hydrogen as a fuel source for the average motorist. Gas stations and cars themselves would all have to be refitted at an astronomical cost to taxpayers and governments. It seems insane to even suggest that current fuel sources be replaced when what is already in place is working so well.
4. **Highly Flammable** : Hydrogen in itself is a very powerful source of fuel. We all know the effects of

hydrogen bomb that was dropped on Hiroshima and Nagasaki in Japan. It's highly inflammable and always in news for the potential risks associated with it.

5. **Dependency on Fossil Fuels** : Though hydrogen energy is renewable and its environmental impacts are minimal, we still need other non-renewable sources like coal, oil and natural gas to separate it from oxygen. We may reduce our dependency on fossil fuels by using hydrogen but in turn we are actually using them to produce hydrogen fuel.

IX. CONCLUSION

Fuel cells are still a few years away from commercialization on a large scale. It is very difficult to tell which fuel and which technology will be predominant in the future. There are some problems and issues regarding the production and storage of hydrogen. If these can be solved then hydrogen which is present in large amount in nature can become the predominant fuel in the future. Take a long-term, conservative perspective on hydrogen. While hydrogen might ultimately prove to be a viable and environmentally desirable alternative fuel post-2035, it is currently getting funding and policy attention that is vastly disproportionate to both its probability of success and likely environmental benefits. Hydrogen should be viewed as a long-term, high-risk R&D effort, requiring at least three major scientific breakthroughs (fuel cell membranes, storage, and renewable hydrogen generation) before it is practical or desirable. It is worth continuing hydrogen R&D, but at least twenty years premature to be investing substantial funds in deploying vehicles or infrastructure. Also, hydrogen is no alternative to government regulations; indeed, for hydrogen and fuel cell vehicles to become commercially successful, the government will have to intervene in the vehicle marketplace far more than it has ever done in the past.

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