Briefing on the state of the art of Hydrogen Technology (prepared by R.Chahine/Hydrogen Research Institute, UQTR)

Vision & Transition: A sustainable energy system using electricity and hydrogen as carriers and providing safe, reliable and secure energy supply. This vision is built on meeting two expectations: 1- that on the supply side hydrogen can be produced cleanly and economically from primary energy sources; and 2- that on the demand side hydrogen applications, like fuel cells for transportation, can effectively compete with the alternatives. Unlike other energy systems, both expectations should be met; one will not work without the other and there are major challenges that must be overcome before they become a reality. The transition to the hydrogen economy will not be simple or straightforward, its course will be dictated on one hand by our ability to overcome the major economical and technical hurdles spread across the whole spectrum of the hydrogen economy namely production, storage & distribution and use; and on the other hand by advancements in competing technologies that are not hydrogen dependent.

Challenges of the hydrogen economy: In a recent exhaustive report[1] published by National Academy of engineering and emphasizing hydrogen-fuelled transportation, the four most fundamental technological and economic challenges were resumed as follows:

1. *"To develop and introduce cost-effective, durable, safe, and environmentally desirable fuel cell systems and hydrogen storage systems*. Current fuel cell lifetimes are much too short and fuel cell costs are at least an order of magnitude too high. An on-board vehicular hydrogen storage system that has an energy density approaching that of gasoline systems has not been developed. Thus, the resulting range of vehicles with existing hydrogen storage systems is much too short.
2. *To develop the infrastructure to provide hydrogen for the light-duty-vehicle user*. Hydrogen is currently produced in large quantities at reasonable costs for industrial purposes. At a future, mature stage of development, hydrogen (H_2) can be produced and used in fuel cell vehicles at reasonable cost. The challenge, with today's industrial hydrogen as well as tomorrow's hydrogen, is the high cost of distributing H_2 to dispersed locations. This challenge is especially severe during the early years of a transition, when demand is even more dispersed. But the transition is difficult to imagine in detail. It requires many technological innovations related to the development of small-scale production units. Also, non-technical factors such as financing, siting, security, environmental impact, and the perceived safety of hydrogen pipelines and dispensing systems will play a significant role. All of these hurdles must be overcome before there can be widespread use. An initial stage during which hydrogen is produced at small scale near the small user seems likely. In this

[1] The Hydrogen Economy: Opportunities, costs, barriers, and R&D Needs (2004); *National Research Council and National Academy of Engineering of the National Academies,* National Academic Press, USA. Available at http://www.nap.edu/catalog/10922.html.

case, production costs for small production units must be sharply reduced, which may be possible with expanded research.

3. *To reduce sharply the costs of hydrogen production from renewable energy sources, over a time frame of decades.* Tremendous progress has been made in reducing the cost of making electricity from renewable energy sources. But making hydrogen from renewable energy through the intermediate step of making electricity, a premium energy source, requires further breakthroughs in order to be competitive. Basically, these technology pathways for hydrogen production make electricity, which is converted to hydrogen, which is later converted by a fuel cell back to electricity. These steps add costs and energy losses that are particularly significant when the hydrogen competes as a commodity transportation fuel suggesting that most current approaches—except possibly that of wind energy—need to be redirected. The required cost reductions can be achieved only by targeted fundamental and exploratory research on hydrogen production by photobiological, photochemical, and thin-film solar processes.
4. *To capture and store ("sequester") the carbon dioxide by-product of hydrogen production from coal.* Coal is a massive energy resource that has the potential for producing cost-competitive hydrogen. However, coal processing generates large amounts of CO_2. In order to reduce CO_2 emissions from coal processing in a carbon-constrained future, massive amounts of CO_2 would have to be captured and safely and reliably sequestered for hundreds of years. Key to the commercialization of a large-scale, coal-based hydrogen production option (and also for natural-gas-based options) is achieving broad public acceptance, along with additional technical development, for CO_2 sequestration".

State of the art of the hydrogen Technologies: Several exhaustive reports dealing with different aspects of the hydrogen economy were published in the last couple of years in USA, Japan and the European Community. These reports arriving at similar conclusions served as a basis for establishing major national hydrogen programs in these countries where hydrogen and fuel cells are considered to be core technologies for the 21st century important for economic prosperity. A summary of the state of the art of hydrogen technologies detailed in such reports[2] was recently published in Physics Today[3], relevant excerpts are reproduced here with some edititing to shorten text:

---

[2] US Department of Energy, Office of Basic Energy Sciences, *Basic Research Needs for the Hydrogen Economy*, US DOE, Washington, DC (2004), available at http://www.sc.doe. gov/bes/hydrogen.pdf; Basic Energy Sciences Advisory Committee, *Basic Research Needs to Assure a Secure Energy Future*, US DOE, Washington, DC (2003), available at http://www.sc.doe.gov/bes/reports/files/SEF_rpt.pdf; Committee on Alternatives and Strategies for Future Hydrogen Production and Use, *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs*, National Research Council, National Academies Press, Washington, DC (2004), available at http://www.nap.edu/catalog/10922.html.

[3] George W. Crabtree, Mildred S. Dresselhaus, and Michelle V. Buchanan, The Hydrogen Economy, Physics Today, December 2004. Available at http://www.physicstoday.org/pt/vol-57/iss-12/p39.html

Hydrogen as energy carrier: Hydrogen does not occur in nature as the fuel H_2. Rather, it occurs in chemical compounds like water or hydrocarbons that must be chemically transformed to yield H_2. Hydrogen, like electricity, is a carrier of energy, and like electricity, it must be produced from a natural resource. At present, most of the world's hydrogen is produced from natural gas by a process called steam reforming. However, producing hydrogen from fossil fuels would rob the hydrogen economy of much of its raison d'être: Steam reforming does not reduce the use of fossil fuels but rather shifts them from end use to an earlier production step; and it still releases carbon to the environment in the form of CO_2. Thus, to achieve the benefits of the hydrogen economy, we must ultimately produce hydrogen from non−fossil resources, such as water, using a renewable energy source.

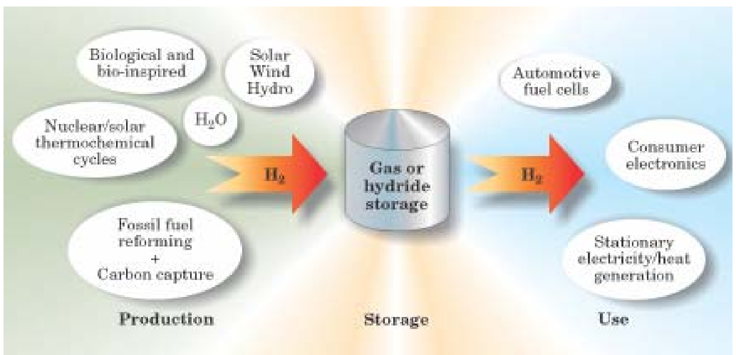

Figure 1. The hydrogen economy as a network of primary energy sources linked to multiple end uses through hydrogen as an energy carrier. Hydrogen adds flexibility to energy production and use by linking naturally with fossil, nuclear, renewable, and electrical energy forms: Any of those energy sources can be used to make hydrogen.

Figure 1 depicts the hydrogen economy as a network composed of three functional steps: production, storage, and use. There are basic technical means to achieve each of these steps, but none of them can yet compete with fossil fuels in cost, performance, or reliability. Even when using the cheapest production method—steam reforming of methane—hydrogen is still four times the cost of gasoline for the equivalent amount of energy. And production from methane does not reduce fossil fuel use or CO_2 emission. Hydrogen can be stored in pressurized gas containers or as a liquid in cryogenic containers, but not in densities that would allow for practical applications—driving a car up to 500 kilometers on a single tank, for example. Hydrogen can be converted to electricity in fuel cells, but the production cost of prototype fuel cells remains high: $3000 per kilowatt of power produced for prototype fuel cells (mass production could reduce this cost by a factor of 10 or more), compared with $30 per kilowatt for gasoline engines.

The gap between the present state of the art in hydrogen production, storage, and use and that needed for a competitive hydrogen economy is too wide to bridge in incremental advances. It will take fundamental breakthroughs of the kind that come only from basic research.

Beyond reforming: Almost all of the hydrogen currently produced is by reforming natural gas. The challenge is to find inexpensive and efficient routes to create hydrogen in sufficient quantities from non−fossil natural resources. The most promising route is splitting water, which is a natural carrier of hydrogen. It takes energy to split the water molecule and release hydrogen, but that energy is later recovered during oxidation to produce water. To eliminate fossil fuels from this cycle, the energy to split water must come from non−carbon sources, such as the electron−hole pairs excited in a semiconductor by solar radiation, the heat from a nuclear reactor or solar collector, or an electric voltage generated by renewable sources such as hydropower or wind.

The direct solar conversion of sunlight to H_2 is one of the most fascinating developments in water splitting. Established technology splits water in two steps: conversion of solar radiation to electricity in photovoltaic cells followed by electrolysis of water in a separate cell. The two processes, however, can be combined in a single nanoscale process: Photon absorption creates a local electron−hole pair that electrochemically splits a neighboring water molecule. The efficiency of this integrated photochemical process can be much higher, in principle, than the two sequential processes. The technical challenge is finding robust semiconductor materials that satisfy the competing requirements of nature.

Water can be split in thermochemical cycles operating at elevated temperatures to facilitate the reaction kinetics. Heat sources include solar collectors operating up to 3000°C or nuclear reactors designed to operate between 500°C and 900°C. More than 100 types of chemical cycles have been proposed. At high temperatures, thermochemical cycles must deal with the tradeoff between favorable reaction kinetics and aggressive chemical corrosion of containment vessels. Separating the reaction products at high temperature is a second challenge: Unseparated mixtures of gases recombine if allowed to cool. But identifying effective membrane materials that selectively pass hydrogen, oxygen, water, hydrogen sulfate, or hydrogen iodide, for example, at high temperature remains a problem. Dramatic improvements in catalysis could lower the operating temperature of thermochemical cycles, and thus reduce the need for high−temperature materials, without losing efficiency.

Bio−inspired processes offer stunning opportunities to approach the hydrogen production problem anew. The natural mechanisms for producing hydrogen involve elaborate protein structures that have only recently been partially solved. …The hope is that researchers can capitalize on nature's efficient manufacturing processes by fully understanding molecular structures and functions and then imitating them using artificial materials.

Storing hydrogen: Storing hydrogen in a high−energy−density form that flexibly links its production and eventual use is a key element of the hydrogen economy. The traditional storage options are conceptually simple—cylinders of liquid and high−pressure gas. Industrial facilities and laboratories are already accustomed to handling hydrogen both ways. These options are viable for the stationary consumption of hydrogen in large plants that can accommodate large weights and volumes. Storage as liquid H_2 imposes severe energy costs because up to 40% of its energy content can be lost to liquefaction.

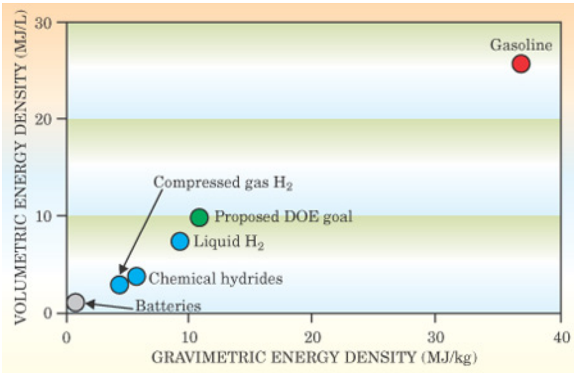

Figure 2. The energy densities of hydrogen fuels stored in various phases and materials are plotted, with the mass of the container and apparatus needed for filling and dispensing the fuel factored in. Gasoline significantly outperforms lithium−ion batteries and hydrogen in gaseous, liquid, or compound forms. The proposed DOE goal refers to the energy density that the US Department of Energy envisions as needed for viable hydrogen−powered transportation in 2015.

For transportation use, the on−board storage of hydrogen is a far more difficult challenge. Both weight and volume are at a premium, and sufficient fuel must be stored to make it practical to drive distances comparable to gas−powered cars. Figure 2 illustrates the challenge by showing the gravimetric and volumetric energy densities of fuels, including the container and apparatus needed for fuel handling. For hydrogen, that added weight is a major fraction of the total. For on−vehicle use, hydrogen need store only about half of the energy that gasoline provides because the efficiency of fuel cells can be greater by a factor of two or more than that of internal combustion engines. Even so, the energy densities of the most advanced batteries and of liquid and gaseous hydrogen pale in comparison to gasoline.

Meeting the volume restrictions in cars or trucks, for instance, requires using hydrogen stored at densities higher than its liquid density. The volume density of hydrogen stored in several compounds and in some liquid hydrocarbons is higher than the liquid or the compressed gas at 10 000 psi (700 bar).

The two challenges for on−vehicle hydrogen storage and use are capacity and cycling performance under the accessible on−board conditions of 0−100°C and 1−10 bars. To achieve high storage capacity at low weight requires strong chemical bonds between hydrogen and light−atom host materials in stable compounds, such as lithium borohydride ($LiBH_4$). But to achieve fast cycling at accessible conditions requires weak chemical bonds, fast kinetics, and short diffusion lengths, as might be found in surface adsorption. Thus, the high−capacity and fast−recycling requirements are somewhat in conflict. Many bulk hydrogen−storage compounds contain high volumetric hydrogen densities but require temperatures of 300°C or more at 1 bar to release their H_2. Compounds with low−temperature capture and release behavior have low hydrogen−mass fractions and are thus heavy to carry. (Moreover hydrogenation/dehydrogenation is energy intensive and require high capacity heat exchange systems). Hydrogen absorption on high surface area materials is a potential route to fast cycling, but up until now results show that the hydrogen uptake is very small at ambient conditions.

Hydrogen Use: A major attraction of hydrogen as a fuel is its natural compatibility with fuel cells. The higher efficiency of fuel cells—currently 60% compared to 22% for gasoline or 45% for diesel internal combustion engines—would dramatically improve the efficiency of future energy use. Coupling fuel cells to electric motors, which are more than 90% efficient, converts the chemical energy of hydrogen to mechanical work without heat as an intermediary.

Although fuel cells are more efficient, there are also good reasons for burning hydrogen in heat engines for transportation. Jet engines and internal combustion engines can be rather easily modified to run on hydrogen instead of hydrocarbons. Internal combustion engines run as much as 25% more efficiently on hydrogen compared to gasoline and produce no carbon emissions. BMW, Ford, and Mazda are road− testing cars powered by hydrogen internal combustion engines that achieve a range of 300 kilometers, and networks of hydrogen filling stations are being implemented in some areas of the US, Europe, and Japan. Such cars and filling stations could provide an early start and a transitional bridge to hydrogen fuel−cell transportation.

The versatility of fuel cells makes them workable in nearly any stationary or mobile application where electricity is useful. Europe already has a demonstration fleet of 30 fuel−cell buses running regular routes in 10 cities, and Japan is poised to offer fuel−cell cars for sale. Fuel−cell power for consumer electronics like laptop computers, cell phones, digital cameras, and audio players provide more hours of operation than batteries at the same volume and weight. Although the cost per kilowatt is high for these small units, the unit cost can soon be within an acceptable consumer range. Electronics applications may be the first to widely reach the consumer market, establish public visibility, and advance the learning curve for hydrogen technology.

A host of fundamental performance problems remain to be solved before hydrogen in fuel cells can compete with gasoline. [Technological breaktroughs are needed for simultaneously improving fuel cell performance, reliability and cost]. The heart of the fuel cell is the ionic conducting membrane that transmits protons or oxygen ions between electrodes while electrons go through an external load to do their electrical work. Each of the half reactions at work in that circuit requires catalysts interacting with electrons, ions, and gases traveling in different media. Designing nanoscale architectures for these triple percolation networks that effectively coordinate the interaction of reactants with nanostructured catalysts is a major opportunity for improving fuel−cell performance. The trick is to get intimate contact of the three phases that coexist in the cell—the incoming hydrogen or incoming oxygen gas phase, an electrolytic proton−conducting phase, and a metallic phase in which electrons flow into or from the external circuit.

A primary factor limiting proton−exchange−membrane (PEM) fuel−cell performance is the slow kinetics of the oxygen reduction reaction at the cathode. Even with the best platinum−based catalysts, the sluggish reaction reduces the voltage output of the fuel cell from the ideal 1.23 V to 0.8 V or less when practical currents are drawn. This voltage reduction is known as the oxygen overpotential. The causes of the slow kinetics, and solutions for speeding up the reaction, are hidden in the complex reaction pathways and intermediate steps of the oxygen reduction reaction. It is now becoming possible to understand this reaction at the atomic level using sophisticated surface−structure and spectroscopy tools combined with equally powerful and impressive computational quantum chemistry.

Beyond the oxygen reduction reaction, fuel cells provide many other challenges. The dominant membrane for PEM fuel cells is perfluorosulfonic acid (PFSA), a polymer built around a C−F backbone with side chains containing sulfonic acid groups (SO_3^-) (for example, Nafion). Beside its high cost, this membrane must incorporate mobile water molecules into its structure to enable proton conduction. That restricts its operating temperature to below the boiling point of water. At this low temperature—typically around 80°C— expensive catalysts like platinum are required to make the electrochemical reactions sufficiently active, but even trace amounts of carbon monoxide in the hydrogen fuel stream can poison the catalysts. A higher operating temperature would expand the range of suitable catalysts and reduce their susceptibility to poisoning. Promising research directions for alternative proton−conducting membranes that operate at 100−200°C include sulfonating C−H polymers rather than C−F polymers, and using inorganic polymer composites and acid−base polymer blends.

Solid oxide fuel cells (SOFCs) require O^-_2 transport membranes, which usually consist of perovskite materials containing specially designed defect structures that become sufficiently conductive only above 800°C. The high temperature restricts the construction materials that can be used in SOFCs and limits their use to special environments like stationary power stations where adequate thermal insulation and safety can be ensured. Finding new materials that conduct O^-_2 at lower temperatures would significantly expand the range of applications and reduce the cost of SOFCs.

Safety: The public acceptance of hydrogen depends not only on its practical and commercial appeal, but also on its record of safety in widespread use. The special flammability, buoyancy, and permeability of hydrogen present challenges to its safe use that are different from, but not necessarily more difficult than, those of other energy carriers. Researchers are exploring a variety of issues: hydrodynamics of hydrogen−air mixtures, the combustion of hydrogen in the presence of other gases, and the embrittlement of materials by exposure to hydrogen, for example. Key to public acceptance of hydrogen is the development of safety standards and practices that are widely known and routinely used—like those for self−service gasoline stations or plug−in electrical appliances. The technical and educational components of this aspect of the hydrogen economy need careful attention.

Technical progress will come in two forms. Incremental advances of present technology provide low−risk commercial entry into the hydrogen economy. Those advances include improving the yield of natural−gas reforming to lower cost and raise efficiency; improving the strength of container materials for high−pressure storage of hydrogen gas; and tuning the design of internal combustion engines to burn hydrogen. To significantly increase the energy supply and security, and to decrease carbon emission and air pollutants, however, the hydrogen economy must go well beyond incremental advances. Hydrogen must replace fossil fuels through efficient production using solar radiation, thermochemical cycles, or bio−inspired catalysts to split water. Hydrogen must be stored and released in portable solid−state media, and fuel cells that convert hydrogen to electrical power and heat must be put into widespread use. Achieving these technological milestones while satisfying the market discipline of competitive cost, performance, and reliability requires technical breakthroughs that come only from basic research.