## R &D of Energy Technologies

# ANNEX A IV-HYDROGEN ENERGY

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#### AIV-1 THE POTENTIAL FOR A HYDROGEN ENERGY ECONOMY

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#### **AIV-1.1 Introduction**

For hydrogen to become a viable energy source, numerous fundamental problems must still be solved. These problems involve all components of a hydrogen energy system: production, storage, use, and safety and distribution issues.

The first sticking point is hydrogen production. There are no natural sources of hydrogen in sufficient quantities that could be used directly as an energy supply; there is no analogue of the oil well for hydrogen. Therefore, hydrogen is best regarded as an energy carrier rather than as a new source of energy. Producing hydrogen inevitably requires another source of energy.

So why turn to hydrogen? Hydrogen carries high energy per unit mass (one kg of hydrogen has approximately the energy content of one gallon of gasoline – about 2.7 kg), potentially facilitating energy portability. In addition, pure hydrogen is a non-polluting fuel, producing only water vapor at its point of use, so that pollutants will not be dispersed throughout a hydrogen energy economy but will primarily be localized where hydrogen and other elements of the energy system are produced.

Currently, two-thirds of US oil consumption goes toward transportation energy needs, so the potential for hydrogen energy to affect US energy applications from economic and national security standpoints is driven primarily by the possibility of developing practical transportation solutions. Hydrogen-powered vehicles will use a hydrogen fuel cell or hydrogen combustion engine. Hydrogen storage must be developed to be much more efficient, and vehicle power systems must be reduced seriously in cost before hydrogen can move into transportation in a significant way. Further challenges come in the areas of safety, distribution infrastructure (e.g. refueling stations), and environmental pollution control in production of hydrogen and other elements of a hydrogen energy system.

The major drawback to a hydrogen energy economy is the inherent inefficiency in the production of hydrogen. In order to obtain hydrogen for use as a fuel, we must extract it from hydrogen-containing compounds such as hydrocarbons or water. Breaking up these compounds to release hydrogen requires energy, so there is always a net loss of energy. This is partly compensated for by the higher efficiency in end use. Furthermore, even though hydrogen fuel has a high specific energy in MJ per kilogram, at normal pressures and temperatures (typical ambient) it is a highly dilute gas and energy must be expended to compress it for transport and storage.

To assess the prospects for a hydrogen energy economy, we examine in more detail the major areas that must be addressed to make this a reality: production, storage, use, and miscellaneous issues including safety, distribution infrastructure, convenience of use, and environmental pollution. An examination of improvements that are needed in each of these areas to achieve a viable hydrogen economy is only the first step in charting a course toward hydrogen energy because the technology must achieve several performance goals at once, goals that are demanding and potentially contradictory.

The whole hydrogen energy system can, in principle, be assembled in many ways, with multiple options at each of the stages: production, storage, use, and miscellaneous. Therefore, a reliable assessment of the potential for hydrogen energy requires consideration not only of the separate system components but also of a creative combination of those components. Each differently assembled system will stack up differently in terms of economic cost, energy availability and cost, environmental pollution, safety, and potential for US energy independence.

#### AIV-1.2 Hydrogen Production

The major means of producing hydrogen fuel are reforming of fossil fuels or biological materials and electrolysis of water. Various energy sources can be employed to carry out the reforming or electrolysis, e.g. fossil fuels, solar (photovoltaic), biomass, hydroelectric, geothermal, wind, or nuclear energy. The primary fossil fuel resources are natural gas and coal. We are currently able to produce hydrogen from natural gas at prices competitive with gasoline, but US natural gas reserves are too small to contemplate this as a major source of hydrogen. Production costs from coal and electrolysis of water depend strongly on plant size. Currently, hydrogen produced from coal or electrolysis of water is not competitive with gasoline due primarily to the added costs of delivery and storage. Renewable forms of energy could be used to electrolyze water, which would be a clean method of production, if fundamental improvements in efficiency can be achieved.

Nearly all of the present worldwide production of hydrogen gas (H<sub>2</sub>) is from reforming natural gas. This production amounts to approximately 40 billion standard cubic feet per day and is used primarily to manufacture fertilizer, to remove sulfur and nitrogen from refined petroleum products, and to manufacture methanol. Secondary uses are in petroleum refineries and in manufacturing processes for chemicals, metals, and electronics, with a minor use to supply fuel cells.

The most efficient method currently used to reform natural gas is Steam Methane Reforming (SMR) in a large industrial plant (85% of total hydrogen production). The SMR process consists primarily of the highly endothermic SMR reaction (CH₄+H₂O ⊚ CO + 3H₂) followed by the Water-Gas Shift reaction (WGS: CO + H₂O ⊚ CO₂ + H₂). It is possible to achieve 89% energy efficiency in this process if the steam byproduct is also used. The cost of hydrogen produced by SMR from natural gas is currently almost competitive with

gasoline. So if there were sufficient natural gas reserves, SMR could provide hydrogen for widespread use in fuel cells today. Unfortunately, US natural gas reserves are inadequate for this need. In addition, this reforming process (as well as the other current processes in less widespread use) releases CO<sub>2</sub> to the atmosphere as a byproduct (11.8 kg CO<sub>2</sub> per kg H<sub>2</sub>). In order to address environmental pollution concerns, this CO<sub>2</sub> would have to be captured and sequestered, increasing the cost of production. Long-term prospects for a hydrogen economy would be significantly increased by the development of processes that are efficient and economically viable on a small scale, so that reforming can be distributed, minimizing the distribution and transport of hydrogen. Nonetheless, reforming natural gas is severely limited by the natural gas supply itself. "The challenge to the continued use of natural gas creates an opportunity for coal-derived hydrogen."

Among fossil fuels, US reserves of coal are by far the most promising for future energy needs. Oil and natural gas are projected to become increasingly scarce and expensive beyond 2020, and coal is our only likely alternative. While coal has the potential to provide a significant fraction of our energy needs for many years, coal combustion also produces CO<sub>2</sub>, SO<sub>2</sub>, and metals emissions in quantities that pose serious environmental concerns. These accompanying compounds must be removed and, in the case of CO<sub>2</sub>, sequestered, which requires additional energy and increases costs. On the other hand, coal gasification is a possible route to using coal for energy in a way that controls the concomitant environmental pollution, but this is a more expensive approach to hydrogen production, so the economics of the process are problematic. Finally, the resulting hydrogen contains impurities that interfere with the operation and lifetimes of some fuel cells, notably the proton-exchange-membrane, or PEM, fuel cell. Similar issues arise in consideration of hydrogen production from reforming biomass, tar, petrochemical byproducts, waste, tires, etc.

Hydrogen can also be produced using nuclear energy with thermochemical cycles. In a thermochemical cycle, there are a series of chemical reactions with the net result that high-temperature heat plus water yields hydrogen and oxygen. All other chemical reagents are internally recycled. High-temperature heat is converted to hydrogen with an efficiency of ~50%. Economic assessments indicate hydrogen costs similar to hydrogen from natural gas; however, the technology is in an early state of development. Both the thermochemical cycles and the high-temperature reactors need significant advances in high-temperature materials or the development of lower-temperature thermochemical processes. The development of improved separations membranes for the thermochemical processes could significantly improve efficiencies and lower peak temperature requirements. The high-temperature reactors use helium or molten-salt coolants.

The above discussion focuses on thermochemical means of producing hydrogen. Electrical means are also possible, as in the electrolysis of water. Renewable sources of electricity (e.g. hydroelectric, wind, solar, geothermal, nuclear fission and nuclear fusion) could thus be used for hydrogen production, and the energy inefficiency inherent in electrolysis

(hydrogen free energy / input electrical energy = approximately 75%) could be rendered relatively irrelevant if sufficiently economically viable renewable sources are available. Electrolysis is readily adaptable to a distributed hydrogen source mode if the input energy is available in appropriate distribution. Nevertheless, electricity costs currently make electrolysis too expensive for a viable hydrogen energy economy. While it has been proposed to produce hydrogen directly by photocatalysis or photo-electrochemical processes, using the energy in visible light to break up water molecules, the total fuel required for such systems, if fossil fuels are to be eliminated, would require a seven-fold increase in arable land use with all its attendant environmental consequences. So this proposal does not look promising except in limited, perhaps regionally important applications.

Yet another potential source of hydrogen is from biological processes using photosynthesis and processes such as fermentation or biophotolysis. Such processes generate more than 250 million tons of hydrogen per year in natural systems. Cost of large-scale human-controlled hydrogen production by these means is currently about two orders of magnitude too high, so their usefulness will depend strongly on future research.

#### AIV-1.3 Hydrogen Storage

Efficient and compact hydrogen storage requires both favorable thermodynamics and favorable kinetics: large quantities of hydrogen are needed (both weight % and volume % – which depends on energy considerations and chemical binding) and the hydrogen must be taken up and released sufficiently quickly and completely to be useful (kinetics). In addition to compressing hydrogen as a gas or liquid, researchers are considering ways to bind it to solids. Unfortunately, often the conditions that favor binding large numbers of hydrogen to a given atom or molecule are also those that lead to strong bonding. For example, CH4 has a nicely favorable H to C ratio, but the binding energy is very high. High binding energy means the hydrogen is hard to pull off of this molecule, so the kinetics would not be favorable. At the other extreme, liquid hydrogen does not meet the storage targets because the H-H binding is too weak and the atoms are far apart. For carbon-based storage, the maximum practical H to C ratio (about 1:1) comes with about one H2 molecule trapped in each carbon hexagon of a system like graphite.

Another consideration is molecular hydrogen storage versus atomic storage. Molecular storage involves low binding energy to the storage medium, so release can be achieved at relatively low temperatures, but such systems might also require lower than ambient temperatures to maintain the stored hydrogen. Hydride storage involves ionic bonding with binding energies in the eV range, and consequently very high temperatures are required for release of stored hydrogen.

The physics challenge involves engineering the storage molecule to bind a large number of H<sub>2</sub> molecules or multiple H atoms per storage species, while avoiding ionic bonding.

This is not likely possible at greater than 1:1 ratio for H:C in carbon-based materials, for example. It is clear that much work is required on catalysts to bring temperature and pressure requirements for storage and release into a practical range.

A very important area for further research is the role of dopants in solid-state storage materials. Dopants can play a catalytic role, changing the energetics of binding and release. They can also affect kinetics by influencing diffusion, for example, and by providing sites for dissociation and reassociation. They will change phonon properties and thereby affect transport in the materials. They may also affect the stability of the host material, allowing greater quantities of interstitial hydrogen to be taken up. They may also play other roles that are not yet understood.

One final caution relative to the fundamentals for hydrogen storage: most targets and benchmarks that have been proposed for a transition to a hydrogen economy are posed in terms of storage properties, not release properties. But release is equally important to storage for the development of practical systems. The number of fill and empty cycles a storage system can tolerate is yet another practical matter that is not well understood for current technologies.

Current hydrogen systems include pressurized tank storage for gaseous or liquid hydrogen and solid-state storage in metal hydrides and complex metal hydrides, in other molecules, and via adsorption, especially in or on nanostructured materials. High surface area and abundant pore volume in nanostructured materials make these especially attractive as potential absorption storage materials. Hydrogen can currently be stored at pressures up to 10,000 psi in tanks made of carbon-fiber-reinforced composites. But the volume is still many times greater than for gasoline with the same energy content. Hydrogen stored as a liquid at 20 K has a higher energy density but compressing it requires about 1/3 of the energy content in the fuel. The cryogenic tanks must be kept cold, and they lose hydrogen to evaporation. While these current systems do not meet the needs of a practical hydrogen energy economy, much research is going forward, with tantalizing hints of possibilities that could resolve the storage problem. Pressurized tank storage is closest to meeting practical benchmarks at present.

#### AIV-1.4 Use of Hydrogen As a Power Source

Especially for transportation applications, fuel cells are expected to be the primary system to utilize hydrogen energy in a future hydrogen economy. Current technology for hydrogen fuel cells is reasonably energy efficient, and the deployment of hybrid vehicles is developing most of the automotive power-train technologies that must couple with the fuel cell. The drawbacks associated with the fuel cell are the need for a very expensive platinum catalyst, limitations in membrane technology, and sensitivity to impurities in the input hydrogen gas.

These problems are being addressed by such approaches as combinatorial chemistry, investigation of nanoscale materials for substitute catalysts or catalytic support, and biological and biomimetic approaches in which oxygen reduction and proton production from hydrogen molecules are carried out by metalloenzymes, as is found in biological systems. Basic research at the interface of biological and physical sciences is an important direction that may help resolve some of the important problems with current fuel cells.

#### **AIV-1.5 Other Issues**

All three of the above steps, production, storage, and use, raise safety issues in the handling of hydrogen. The hydrogen system must be designed so that non-technical users are able to use it safely and with confidence – the perception of safety is just as important as the actual safety of the systems if the public is to accept hydrogen as a widespread fuel source. In addition, there are both major economic and safety issues associated with a hydrogen distribution infrastructure that is yet to be built up. Convenience of use for the hydrogen end-user is closely related to both safety and distribution. Finally, important issues will have to be resolved relative to impact on the environment. Conditions that might lead to explosions or fires or the possible harm to global climate by undue leaks of hydrogen into the atmosphere will require further research to inform standards and regulations.

Safety issues include the wide concentration range of flammability of hydrogen (4-75% volume) as compared to gasoline (1.0-7.6% volume), and the wide detonation range (18.3-59% volume vs. 1.1-3.3% for gasoline). A small spark can ignite a flammable mixture, so that high-pressure leaks can even be self-igniting due to the friction of the fluid escaping through the break. Because hydrogen is so small, it diffuses extremely easily so that imperfections that will not allow other gases to leak can breach the integrity of a hydrogen vessel. Its diffusivity allows it to incorporate into the material of its containers, especially at the surface, and cause embrittlement. Other complications come from the fact that it has no odor and can burn invisibly. Nonetheless, because it diffuses so quickly and is so buoyant, hydrogen moves up and away from the leak point if it is in the open.

Many safety issues have already been addressed in the course of the considerable experience of industry and government in producing, transporting and handling up to 9 million tons each year. However, the advent of hydrogen vehicles and vehicle refueling stations poses new challenges since many of those handling hydrogen for their cars will not have technical training or equipment.

Environmental pollution issues are complicated because they must address the full system impact, i.e. pollution from hydrogen production processes, pollution due to impurities in hydrogen use, pollution in the manufacture of production, storage, and use equipment, etc. The advantage of hydrogen is that automobiles powered by hydrogen fuel cells are expected to have negligible emissions, other than water, so pollutants will not be dispersed by the vehicles. However, if the hydrogen input to the fuel cell is not sufficiently

pure, the fuel cell may emit secondary pollutants that could have negative environmental effects. It may even emit CO<sub>2</sub>, or CO<sub>2</sub> emissions from some other part of the system process in quantities comparable to those from current vehicles.

Another issue that is insufficiently understood is the impact of significantly increased releases of hydrogen on the atmosphere. Current estimates suggest increased water vapor in the atmosphere will cool the lower stratosphere and enhance destruction of ozone at the poles. The size of this effect is highly uncertain. Furthermore, H<sub>2</sub> itself is an indirect greenhouse gas: adding H<sub>2</sub> to the atmosphere reduces the concentration of the OH radical, which is the primary methane sink. Increased H<sub>2</sub> thereby leads to more methane, a greenhouse gas. The loss of OH is also of potential concern, as OH plays a role in cleansing the atmosphere. On the positive side, the hydrogen economy may lead to reduced emissions of NOx and, in turn, reduced concentrations of tropospheric ozone.

There are huge technical barriers to developing a functioning hydrogen economy. Nevertheless, it is imperative that we address the problems of energy independence and environmental pollution associated with our present energy economy. These issues can best be addressed by a strong research agenda for the next decade or two if we are to be in a position to adopt widely a new energy source like hydrogen in the long term.

#### **AIV-1.5 The US Position**

The US government has made the Department of Energy hydrogen program a major initiative, stating as a vision "a prosperous future for the Nation where hydrogen energy and fuel cell power are clean, abundant, reliable and affordable and are an integral part in all sectors of the economy and all regions of the country."<sup>2</sup>

As an example, the Department of Energy is planning a "the FutureGen plant, a near-zero emissions coal-fed plant that will produce power and hydrogen. The anticipated \$1.0 billion budget will support the design, construction, and operation of a 275 MW prototype plant to serve as a large-scale engineering laboratory for testing new clean power, carbon capture, and coal-to-hydrogen technologies."<sup>3</sup>

#### References

- [1] Doctor, Richard D. and John C. Molburg, "Clean Hydrogen from Coal with CO<sub>2</sub> Capture and Sequestration," Chapter 6 in <u>The Hydrogen Energy Transition</u>, (Editors Daniel Sperling and James S. Cannon), Elsevier (2004).
- [2] Quoted in "Breakthrough science for a cleaner energy future", Pacific Northwest National Laboratory, 2004.
- [3] Doctor, op cit

#### AIV-2 R&D TOWARDS PROVISION OF HYDROGEN

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#### **AIV-2.1 Introduction**

One of the advantages of hydrogen as an energy carrier is that it can be produced from a wide variety of primary energy sources and different production technologies (see Figure 1). Techniques based on fossil fuels like steam reforming of natural gas, gasification of coal or partial oxidation of heavy oil are state of the art technologies and are used for decades. Beside these mature processes there are some technologies e.g. electrolysis, used only for special applications, and others, like photoelectrolysis or photobiological methods, which are object of current research activities and have to be developed for the industrial scale.

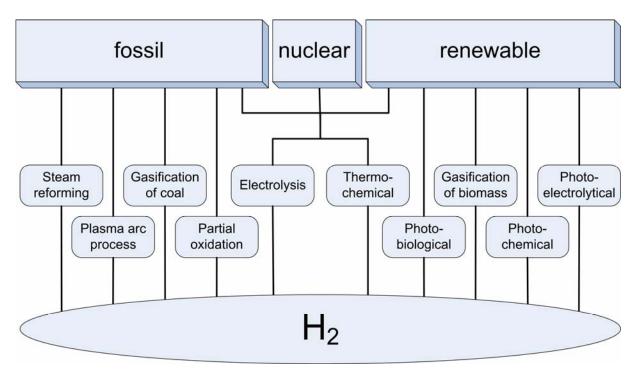


Figure 1- Hydrogen production processes

In contrast to this variety, nowadays more than 90 % of the 500 billion m³ (i.e. 5.4 EJ) hydrogen produced per year is based on fossil fuels such as petroleum, natural gas or coal. The main applications for this hydrogen by far are the production of ammonia fertilisers and the synthesis of methanol. Further usages are welding, hydrochloric acid production and metallic ore reduction. Only a small amount is used for energetic purposes e.g. for the propulsion of rockets or submarines.

For the future hydrogen energy economy huge amounts of cheap hydrogen have to be provided. Seen in an energy economic context, the amount of fossil hydrogen used for chemical processes today is only a small part of world's energy consumption of about 385 EJ

per year /OECD 02/. But in the future technologies making use of sustainable energy sources have to be deployed.

The production can be carried out either in large centralised facilities or in decentralised units, depending on the used primary energy source, the application and other factors like distribution costs. Target figures for the costs of hydrogen for transport purposes (compression and delivery to a petrol station included) are about 1.50 € per kg (i.e. 0.05 €/kWh) as given by in the Strategic Research Agenda of the European Hydrogen and Fuel Cell Technology Platform /SRA 04/ or by the U.S. Department of Energy /IPHE 02/. For conventional techniques based on non-renewable resources this may be achievable in the short term, but for the new technologies today this is a challenging objective and it has to be proven, witch of the processes can reach the target. Actually the price for gaseous hydrogen produced by natural gas in distributed plants is about 5.00 €/kg excluding taxes /DOE 03/.

#### AIV-2.2 Hydrogen generation by electrolysis

Hydrogen production by electrolysis was the most common way until the mid of the last century. Currently only a small percentage of the hydrogen is produced by electrolysis, mainly for applications requiring small quantities of high purity. Driven by electricity from renewable power sources e.g. wind or solar-power, electrolysis could be a technology for a sustainable hydrogen supply. Especially large solar thermal power units in the world's sunbelt combined with electrolysers may produce a high amount of carbondioxid-free hydrogen in the future.

In electrolysis an ion conducting electrolyte which separates the cathode (hydrogen generation) and the anode (oxygen generation) may be made of potash lye in a porous diaphragm (alkaline electrolysis), a proton conducting membrane (membrane electrolysis) or an oxygen ion conducting solid oxide (solid oxide electrolysis). Even proton exchange membrane fuel cells (PEMFC) can act like an electrolyser when they are operated reverse i.e. feed with water and a voltage is impressed on. So far only the alkaline and the membrane electrolysers are commercially available. They are offered from a hydrogen output smaller than 1 m³/h up to 500 m³/h with an efficiency factor higher than 70 %. For centralised hydrogen production by electrolysis a scale up of two orders of magnitude would be necessary.

Reducing the costs of investment and operation is the main objective in research and development of electrolysers. Elimination of exotic material on the electrodes (precious metal catalysts) and extending the lifetime by using electrodes with higher electrochemical stability are two approaches for lower capital costs. Since about two thirds of hydrogen production costs are caused by electricity /BEL 02/, improving the system efficiency has an outstanding relevance for electrolysis. E.g. alkaline electrolysers benefit from activation of the electrodes by a plasma arc process and membrane electrolysers profit by improved catalysts, especially for the oxygen electrode.

Operation cost could also lowered by substituting heat energy for electricity. As for the electrolysis of steam less electricity is needed, in high-temperature electrolysers with solid

oxide cells ("Hot Elly") the thermal energy of solar concentrator plants, nuclear reactors or geothermal heat could be used to produce hydrogen with high efficiency.

Another approach to reduce the overall efficiency of the hydrogen supply is the pressurized electrolysis. Membrane electrolysers normally are operated at a pressure of about 0.05 MPa. To reduce the energy demand for compression of hydrogen the fed water could be compressed before high pressure electrolysis at 30 bar or, in the future, at 10 MPa. Primarily for mobile applications where storage systems with a pressure level of 350 or 70 MPa are used, the total efficiency could be highly improved in this way.

Hydrogen production costs by electrolysis are strongly depending on the electricity costs. Today an electricity price of about 0.07 €/KWh results in costs of 4.00 € per kg of hydrogen /IVY 04/. But the economic efficiency of (PEM-)electrolysers could also be raised when new materials for the electrodes and cheaper membranes would be available. Further basic research is necessary especially in the fields of high-temperature electrolysis. Improvements of electrolyte materials and system components would allow large solid oxide electrolysers for central hydrogen production with high efficiency.

Because electricity is more easily transportable than hydrogen, hydrogen production by electrolysis is expedient only when there is a local or temporal oversupply of renewable energy like sun or wind. Otherwise the integration of renewable electricity into the public grid should be privileged. On the other side water electrolysis is capable for a decentralized supply of small amounts of hydrogen, e.g. at fuelling stations for vehicle fleets and especially at the beginning of a hydrogen energy economy.

#### AIV-2.3 Hydrogen from fossil energy carriers

Today the production of hydrogen from fossil fuels is the most common way, either as a basic material for the chemicals industry or as a by-product of crude oil refining. Hydrogen for energetic purposes could be produced with high efficiency and low costs devoting natural gas, oil or coal. But the techniques used are not sustainable, because they cause CO<sub>2</sub>-emissions and are based on non renewable energy sources. Nevertheless during a transition period towards a hydrogen energy economy it will be necessary to revert to these established methods for an ongoing market and to supply hydrogen by competitive costs and in large quantity ab initio.

#### AIV-2.3.1 Steam reforming

Steam reforming of natural gas is one of the most effective methods of hydrogen production. There are large steam reformers with a capacity of  $100,000 \text{ m}^3\text{/h}$  of hydrogen and an overall efficiency of 70 - 80 %. Nowadays the major part of hydrogen, about 50 %, is produced from natural gas by steam reforming. The costs are about  $0.80 \text{ €/kg H}_2$  /ANG 00/.

At the first step of the steam reforming process light hydrocarbons (e.g. natural gas) react with steam to a mixture of carbon monoxide and hydrogen. This endothermic catalytic process requires temperatures of 800 to 950 °C and a pressure of 3 to 25 MPa. In the subsequent exothermic shift reaction (CO-shift) carbon monoxide is oxidised by dint of catalysts and addition of steam to carbon dioxide and additional hydrogen is gained. With

an upstream feedstock purification and a downstream purification of the hydrogen there are totally four process steps.

The catalysts used in these processes are usually non-precious metals such as nickel or copper/zinc. Nevertheless organic sulphur contained in natural gas has to be removed (to a content < 1 ppm) to avoid the blocking of the catalytic surface.

Steam reforming of natural gas in large scale is a mature technology. Anyway there is a potential for optimisation. E.g. incorporating a CO<sub>2</sub>-adsorbent in the reformer (to remove carbon dioxide from the product stream) drives the reaction to produce additional hydrogen at lower temperatures. By this and by improved catalysts with higher reactivity the production costs for hydrogen may be reduced by 25 to 30 % /DOE 04b/.

For small scale hydrogen production there are two types of steam reformers: conventional, down-sized reformers and specially adapted reformers for combined heat and power plants with small stationary PEMFCs. The latter operates under lower pressure and temperature than conventional reformers, and beyond it is more compact. Improving the overall performance by minimising and simplification of the system are the main approaches here.

#### AIV-2.3.2 Partial oxidation

Heavy hydrocarbons cannot be broken down catalytically by means of steam reforming because solid carbon separates out above 800 °C and within a short time it would block the catalyst and the gas flow. Therefore, derivation of hydrogen from heavy, less pure liquid or solid hydrocarbons is accomplished by partial oxidation with oxygen or air. Unlike steam reforming, this process is carried out without the use of catalysts at higher temperatures between 1,300 and 1,500 °C and at a pressure of 3 to 10 MPa. After the partial oxidation process, a desulphurisation and a CO-shift are necessary before the hydrogen could be separated from carbon dioxide.

Partial oxidation of heavy fuel oil has been achieved in industrial-scale processes by Texaco and Shell. The achievable total efficiency is about 73 % and costs are about  $0.80 \, \text{e/kg H}_2 \, \text{/ANG}$  00/. The low costs are mainly due to the cheap basic material. However by this process high specific CO<sub>2</sub>-emissions are caused.

For the future the use of ceramic membrane reactors, where a simultaneous separation of oxygen from air and the partial oxidation of methane for hydrogen production is possible, promises an improvement in efficiency and costs. Even optimised systems integration may raise the overall performance of partial oxidation for some percentage points.

#### AIV-2.3.3 Gasification of coal

Coal is still an important pillar of our present-day power supply. The anticipated life of worldwide coal deposits e.g. by far surpasses that of petroleum and natural gas. Compared to natural gas, which is needed for many chemical processes, coals are quite inflexible energy carriers and their main application is the production of electricity and heat. In the context of final consumption of fossil fuels, hydrogen production of anthracite or lignite combined with a CO<sub>2</sub>-sequestration may be a way to apply these energy sources even for applications in the transporting sector.

In coal gasification a thermal decomposition of the fuel into a combustible gas takes place. In this process, air, oxygen, hydrogen, steam or a mixture of theses fluids are supplied. In allothermic gasification, heat is supplied from outside the system; in autothermic gasification, the process itself generates the necessary temperature by open flame combustion of part of the fuel.

There are several different techniques for the gasification of anthracite and lignite. All of them have in common that due to their complexity the efficiency is of about 60 % and specific carbon dioxide emissions and costs (about 1.30 €/kg H₂) are quite high.

#### AIV-2.3.4 Plasma arc process (Kvaerner process)

In a plasma arc at temperatures of 1,600 °C light hydrocarbons can be converted by electricity to hydrogen and ultra pure carbon. Due to the specific process conditions, there are practically no CO<sub>2</sub>-emissions. A pilot plant utilizing this technology produces 500 kg/h of carbon and 2,000 m³/h of hydrogen from 1,000 m³/h of natural gas and 2,100 KWh of electricity, which leads to an overall performance near 50 % /TÜV/. Even though the carbon could be used for technical purposes the economic efficiency of this process for hydrogen production has not yet been reached.

#### AIV-2.4 Hydrogen from renewable energy sources

On the account of sustainability, in the long term hydrogen must be produced from renewable energy sources. There is quite a number of techniques for the production of hydrogen without harmful emissions, especially devoid CO<sub>2</sub>-emissions. But nearly all of them today cause quite high costs and most of them still have to be developed for the use in a technical or large-scale manner.

Electrolysis driven by renewable energy may be an option for a sustainable hydrogen production when the integration of fluctuating energy e.g. wind or solar power into the public grid could not be realised due to a excess supply or high costs.

#### AIV-2.4.1 Photoelectrolysis hydrogen generation

A new developed type of electrolysis is the so called photo electrolysis. By special photovoltaic cells a sufficient voltage (higher than 1.23 V) is generated to split water directly by the UV-content of sunlight or by visible light. Because the photovoltaic cells work direct in the deionised water, this technique eliminates the costs of the conventional electrolysers and may increase the overall efficiency of solar hydrogen generation. Theoretically the efficiency for tandem junction systems is 42 %. Actual research results show a practical solar-to-hydrogen efficiency up to 12.4 % (based on LHV of H<sub>2</sub>) /DOE 04b /.

In tandem junction cells a transparent photo-anode absorbs light of the blue spectrum of sunlight and oxidizes the oxygen of water. The hydrogen production takes place at the photo-cathode, where photons of the green and red spectrum are absorbed and a sufficient photo-voltage is generated /BFE 99/.

State of the art multi-junction cells made of amorphous (a-Si), copper-indium-gallium-diselenide (CIGS) or advanced semiconductor materials like dye-sensitized titanium dioxide

(TiO<sub>2</sub>) or tungsten trioxide (WiO<sub>3</sub>) can either realize low costs or high efficiency. The main challenge is to find stable materials that split water and have a high light absorption and do not suffer from photo-corrosion or have energetically unfavourable band-edge positions. So the objectives of further development are more stable and cheaper cells with a high solar-to-hydrogen efficiency. First good results were achieved with nano-crystalline iron oxide (FeO), a low-cost semiconductor with a favourable small band gap and low environmental impact, for the photo-anode. But the production of transparent layers made of FeO has to be improved /BFE 99/.

#### AIV-2.4.2 Hydrogen from biomass

Biomass resources such as consumer waste, agriculture residues or biomass specially grown for energy use, similarly to coal could be used for hydrogen production by gasification or by pyrolysis. Due to the low energy content of biomass long transportation distances have to be avoided and the generation of hydrogen has to take place in small, decentralised plants. Thus the economy scale could only be utilised in a small range. The amount of CO<sub>2</sub> emitted by biomass processes has been absorbed by the plants in their period of growth, thus the hydrogen made of biomass is nearly CO<sub>2</sub>-free. Only the expenditures of fossil fuels within the biomass-to-hydrogen path cause some additional greenhouse gas emissions.

In gasification of biomass at temperatures of about 1,400 °C carbon hydrates and carbon are partially oxidised to carbon monoxide and hydrogen. A following shift-reaction totally oxidised with water towards carbon dioxide and further hydrogen.

There are some pilot projects of hydrogen production by gasification around the world (e.g. "Blauer Turm" in Herthen, Germany) but further developments in the field of preconditioning the biomass, ash-removal and synthesis gas cleaning (reducing the chlorine and sulphur content) are necessary for an economic operation. Even production of a uniform output utilising inhomogeneous biomass input has to be implemented.

Biomass pyrolysis produces a liquid product (bio-oil) that contains a wide spectrum of components that can be separated into valuable chemicals and fuels, including hydrogen. Researchers are currently focusing on hydrogen production by catalytic reforming of biomass pyrolysis products. Specific research areas include reforming of pyrolysis streams and development and testing of fluidized catalysts.

Another technology is the hydrogen production by fermentation of biomass by microorganisms. Here organic materials rich of carbon hydrate are decomposed in aerobic biologic processes, either on mesophilic conditions (temperatures of about 30 °C) or on thermophilic conditions (about 60 °C). The theoretical maximum hydrogen yield is four molecules hydrogen per mole of hexose sugar (e.g. glucose) i.e. approximately 0.5 m³ hydrogen gas per kilogram glucose /MAD 03/.

#### AIV-2.4.3 Photobiologic hydrogen generation

Some photosynthetic microbes produce hydrogen in their metabolic activities while using light as energy source. Cyanobacteria or algae (e.g. chlamydomonas rheinhardii) can split water molecules in hydrogen and oxygen by enzymes. This sub-process of the photosynthesis is normally used to work up carbon dioxide and produce biomass but on

special conditions pure hydrogen is released. By use of metabolic switchers (e.g. sulphur deprivation) an alternation between photosynthetic growth phase and hydrogen production phase can be enforced. For hydrogen production in a technical scale these algae cultures can be cultivated in low-cost plastic tanks. No special light conditions are necessary, in fact the microbes prefer not to intensive sunlight radiation of the temperate climate zones /MUEL 04/.

Another promising approach is the use of a separated enzyme (hydrogenase) of the algaes. Theoretically a single enzyme molecule can produce up to 9,000 molecules of hydrogen per second. Only about 60 mg of hydrogenase would be necessary to generate one cubic meter of hydrogen in one hour /MUEL 04/.

In contrast to cyanobacteria, photosynthetic bacteria need an organic nutrient solution to produce hydrogen. A research goal is to optimise the process due to the oxygen sensitivity of the enzyme systems. Therefore scientists screen natural micro-organisms and design new genetic forms which are more tolerant to oxygen. Today by purple bacteria 150 litres of hydrogen can be produced per kilogram biomass, at a total efficiency of about 70 % /ANG 00/.

Not optimized algae systems have a production rate of about 30 m<sup>3</sup> hydrogen per square meter and year (at twelve hours of radiation per day). Screening of different species, adaption by genetic mutation and optimisation of flow fields in the bioreactors will improve the system efficiency. But even research on detailed cellular processes is necessary to understand and improve hydrogen generation by photo-biological systems.

#### AIV-2.4.4 Photochemical and photocatalytical hydrogen production

In the direct photo-chemical reduction of water a sensitizer (a molecule or semiconductor) is exited by visible light and can thereafter affect the reduction of water by the delivery of electrons. Several different sensitizers with different absorption characteristics can be used simultaneously, leading to a higher hydrogen production rate. A catalyst, usually a heterogeneous noble metal catalyst (e.g. PtBi<sub>2</sub>O<sub>3</sub>RuO<sub>2</sub>) is needed to speed up the reaction.

Photocatalytical processes e.g. using Ag/AgCl layers are another promising approach for hydrogen generation by sunlight. At the photo anode (Ag/AgCl) water is oxidized into oxygen, at the photo-cathode (platinized GaInP<sub>2</sub>) water is reduced to hydrogen. The charge equalisation is realised by a salt bridge.

The main problem of all techniques is the fast aging of the materials due to the electrochemical conditions. Other research challenges are the improvement of efficiency and optimization of gas separation equipment.

#### AIV-2.4.5 Thermochemical hydrogen production

Water separates at temperatures of about 3,000 K into hydrogen and oxygen. Because it nearly impossible to control or separate a mixture of these two gases at these high temperatures, several methods are developed where the decomposition of water proceeds successively in different steps at lower temperature levels.

In thermochemical water splitting processes like the sulfur-iodine cycle, the UT-3 cycle or the SybMet process, water is decomposed into hydrogen and oxygen through combinations of

chemical reactions, and these reactions are carried out by utilising only heat to drive them. Suitable high temperature heat sources are solar thermal concentrator and central receiver systems or high temperature gas-cooled nuclear reactors.

The water splitting process takes place in different, separated process steps, where water reacts in endothermic and exothermic chemical reactions e.g. with sulphur dioxide or calcium bromide. The theoretical overall performance of these processes is reported in the range of 40 to 50 %, but for commercial applications further improvements concerning the heat-transfer and the temperature control are required. Due to the complexity of these processes and problems in separating the products at high temperature an economic operation could not be proven up to now.

#### **AIV-2.5 Conclusion**

The provision of cost competitive hydrogen in sufficient quantity and quality is the groundwork of a hydrogen energy economy. If there are no suitable technologies for economic processes without greenhouse gas emissions or other non-sustainable environmental impacts, hydrogen production will be the bottleneck of the future energy economy.

Today only procedures based on fossil fuels and electrolysis are commercially available. With improved efficiency, low costs and minimised carbon dioxide emissions these technologies have to be used at the beginning of the hydrogen energy economy. Therefore research and development on materials and processes playing an important role within these mature systems have to be strengthened in the short term.

Nevertheless only hydrogen based on renewable energy sources conforms to all demands on an sustainable energy carrier. This means research and development in all fields of hydrogen production have to be intensified so that in the future a wide variety of processes, based on different energy sources, is available and for varying basic conditions out of different methods the most suitable could be chosen.

#### References

ANG 00	J. Angloher, Th. Dreier: Techniken und Systeme zur Wasserstoffbereitstellung – Perspektiven einer Wasserstoff-Energiewirtschaft Teil 1. Wasserstoff-Initiative Bayern, 2000
BEL 02	B. Kruse, S. Grinna, C. Buch: <i>Hydrogen statu sog muligneter – Bellona rapport nr. 6</i> . Bellona Foundation, Oslo, 2001
BFE 99	Reller, A.: <i>Solarchemie   Wasserstoff – Überblicksbericht zum Forschungsprogramm</i> 1999. Schweizer Bundesamt für Energie, Bern, 1999
DOE 03	U.S. Department of Energy: Hydrogen, Fuel Cells & Infrastructure Technologies Program – Multi-Year Research, Development and Demonstration Plan. Draft June 3, 2003
DOE 04a	U.S. Department of Energy: <i>Hydrogen, Fuel Cells &amp; Infrastructure Technologies - Hydrogen Production &amp; Delivery</i> . <a href="http://www.eere.energy.gov/hydrogenandfuelcells/hydrogen/current_uses.html">http://www.eere.energy.gov/hydrogenandfuelcells/hydrogen/current_uses.html</a> , 04/10/2004

DOE 04b U.S. Department of Energy: Hydrogen, Fuel Cells & Infrastructure Technologies - Hydrogen Production & Delivery. http://www.eere.energy.gov/hydrogenandfuelcells/hydrogen/production.html, 04/10/2004 IPHE 02 International Partnership for the Hydrogen Economy, Implementation and Liaison Committee: Hydrogen Production Scoping Paper. Draft, 02/02/2004 **IVY 04** J. Ivy: Summary of Electrolytic Hydrogen Production - Milestone Completion Report. National Renewable Energy Laboratory, Battelle, 2004 MAD 03 J. Maddy, S. Cherryman, F.R. Hawkes, D.L. Hawkes, R.M. Dinsdale, A.J. Guwy, G.C. Premier, S. Cole: Hydrogen 2003 - A Sustainable Energy Supply for Wales: Towards the Hydrogen Economy. University of Glamorgan, Mid Glamorgan, 2003 MIL 01 Miller, E.; Rocheleau, R.: Photoelectrochemical Hydrogen Production. Proceedings of the 2001 DOE Hydrogen Program Review, Washington, 2001 K. Müller, Th. Happer: Biokraftstoff aus Algen - Photobiologische Wasserstofferzeugung und MUEL 04 CO2-Fixierung. VDI-Expertenforum "Entwicklungslinien der Energietechnik", Bochum, 2004 OECD 02 OECD, IEA (eds.): World Energy Outlook 2002 - Highlights. Paris, 2002 **SRA 04** European Hydrogen and Fuel Cell Technology Platform: Strategic Research Agenda. Bruxles, to be published in October 2004 TÜV TÜV Süddeutschland (ed.): *Hydrogen – a world of energy*. Munich, n.d.

# AIV-3 REPORT ON THE THERMO-CHEMICAL WATER SPLITTING (VIA THE IODINE-SULFUR CYCLE) AT THE HTTR

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"Thermo-chemical method" for hydrogen production offers a technology with which nuclear energy is transformed into hydrogen, the energy carrier. This paper briefly describes the present status of study on Iodine-Sulfur cycle, a promising thermo-chemical cycle, and, outline of the HTTR project being conducted by JAERI, which aims to develop technologies for massive hydrogen production using HTGR (High Temperature Gas Cooled Reactor).

#### AIV-3.1 Thermo-chemical water splitting cycles

Hydrogen production by direct thermal decomposition of water requires high temperature heat of a few thousand Kelvin. However, by combining high-temperature endothermic chemical reactions and low-temperature exothermic chemical reactions, in which the net chemical change resulting from the sequence of component chemical reactions is the water decomposition, it is possible, in principle, to decompose water only with the heat of lower temperature. The cycle of chemical reactions produces the free energy required for water splitting. It is called thermo-chemical method and has a possibility of large-scale carbon-free hydrogen production.

Thermo-chemical water splitting cycle was first studied by Funk, and an actual example was proposed by researchers of CEC, JRC Ispra establishment, in early 70's. Since then, a number of thermo-chemical cycles have been proposed assuming High Temperature Gas-Cooled Reactor (HTGR) as the heat source, which can supply heat with its maximum temperature of close to 1000°C. After mid-80's, activities in Europe and in North America slowed down in accordance with the slowing down of their HTGR projects. Recently, however, with the emerging interest in the "hydrogen energy system" in accordance with the progress of fuel cell technology, the thermo-chemical method attracts growing interest again.

#### AIV-3.2 Iodine-Sulfur cycle

Hundreds of cycles have been studied from the viewpoints of the feasibility of component chemical reactions in terms of conversion ratio and/or products separation, theoretical thermal efficiency of hydrogen production etc. Among them, those that utilize thermal decomposition of sulfuric acid, which are categorized as "sulfur cycles", have been considered one of the most promising cycles.

Thermal decomposition of sulfuric acid, reaction (1), proceeds in the following two steps.

Both steps are highly endothermic and proceed smoothly without side reactions and with high conversion ratio at the temperature range indicated. The endothermic characteristics match well with the temperature distribution of the heat source, HTGR. The heat of HTGR is transferred to the chemical process through the sensible heat of helium gas, the temperature of which varies, e.g. 900-400°C. These make the reaction quite suited as the high temperature endothermic reaction for thermo-chemical water splitting cycle.

Iodine-Sulfur cycle (or Sulfur-Iodine cycle, or ISPRA Mark 16 cycle) is a well-studied and promising sulfur cycles, which combines following chemical reactions with the sulfuric acid decomposition reaction.

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4$$
 (2)

$$2HI = H_2 + I_2$$
 (3)

Here, reaction (2), known as "Bunsen reaction", is the low-temperature exothermic reaction, where raw material, water, reacts with iodine and gaseous sulfur dioxide producing an aqueous solution of hydriodic acid and sulfuric acid. The acids are then separated and thermally decomposed to produce hydrogen and oxygen.

The cycle has been studied in US, Europe and Japan since 1970's, and some important breakthroughs were attained by General Atomics (GA). So far, the research has been carried out in the following fields,

- (a) study on the chemistry of each reaction section,
- (b) demonstration of the closed-cycle hydrogen production.
- (c) heat/mass balance analysis of the process flowsheet,
- (d) screening of corrosion-resistant materials.

There are two main issues concerning the chemistry of the reaction and the separation. One is how to separate the hydriodic acid and sulfuric acid produced by the Bunsen reaction. The other is how to carry out the hydrogen iodide decomposition section, where the presence of azeotrope in the vapor-liquid equilibrium of hydriodic acid makes the energy-efficient separation of HI from its aqueous solution difficult and also unfavorable reaction equilibrium limits the attainable conversion ratio of HI to a low level, ca. 20%.

As for the former problem, the researchers of GA found that the mixed acid solution produced by the Bunsen reaction separates spontaneously into two liquid phases in the presence of excess amount of iodine. The heavier phase is mainly composed of HI, I<sub>2</sub>, and H<sub>2</sub>O, and is called "HIx" solution. The main components of the lighter phase are H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O. The phenomenon (LL phase separation) offered an easy way of separating the hydriodic acid and the sulfuric acid. As for the hydrogen iodide processing, some ideas have been proposed by GA, RWTH Aachen and JAERI.

One of the specific and important characteristics of thermo-chemical cycle is that the reactants except water are cyclically used in the process. The closed-cycle continuous hydrogen production by Iodine-Sulfur process featuring the LL phase separation has been examined at JAERI. Although the chemistry of sulfuric acid decomposition section and that of hydrogen iodide decomposition section are rather straightforward in terms of reaction and separation, in the Bunsen reaction section, occurrence of side reactions forming sulfur and/or hydrogen sulfide should be suppressed while maintaining the liquid-liquid phase separation. Feasibility of the process control was demonstrated in small-scale continuous hydrogen production experiments of 1NL-H<sub>2</sub>/h and of 30NL-H<sub>2</sub>/h, as well.

Preliminary flowsheeting studies carried out at GA, RWTH Aachen, Ecole Polytechnique Montreal, CEA etc suggested that the "process thermal efficiency" in the range of 35-50% could be possible assuming intensive heat recovery. Here, the thermal efficiency is defined as the ratio of the Higher Heating Value (HHV) of hydrogen to the net energy input for the process. Precise thermodynamic data concerning the concentrated process solutions is desired for the accurate evaluation of the heat/mass balance.

Since sulfuric acid and halogen are very corrosive, selection of the structural materials is an important issue. Screening tests have been carried out using test pieces of commercially available materials at GA, JAERI etc. As for the gas phase environment of H<sub>2</sub>SO<sub>4</sub> decomposition step, some refractory alloys that have been used in conventional chemical plants showed good corrosion resistance. Also, in the gas phase environment of HI decomposition step, a Ni-Cr-Mo-Ta alloy was found to show good corrosion resistance. As for the Bunsen reaction step, glass-lining materials, Ta etc showed corrosion resistance. In the environment of HIx distillation, Ta showed excellent corrosion resistance. The severest environment is the boiling condition of concentrated sulfuric acid under high pressure (e.g. 20bar), where ceramic materials containing Si such as SiSiC, SiC, and Si<sub>3</sub>N<sub>4</sub> were the only materials that showed excellent corrosion resistance. In summary, for gas phase service, there exists little concern on the structural materials. As for the equipments used in the Bunsen reaction step, lining materials should be used. Special design consideration is required for the equipment to be used in the boiling and condensing conditions of the acids.

#### **AIV-3.3 HTTR Project**

JAERI is conducting R&D programs to develop technologies for the thermo-chemical hydrogen production using HTGR. The program covers R&D on HTGR technology, R&D on the system integration technology to connect HTGR and hydrogen production plant, and R&D on Iodine-Sulfur cycle.

R&D on HTGR technology is being carried out using the High Temperature Engineering Test Reactor (HTTR, maximum thermal output of 30 MW) that is installed at Oarai Research Establishment of JAERI. The HTTR attained the first criticality in November 1998. The full power operation was attained with reactor outlet helium temperature of 850°C in December 2001, and of 950°C in April 2004. Safety demonstration tests using the HTTR are underway to demonstrate the inherent safety of the HTGR. The tests are divided into two phases. The first phase tests, which simulate the anticipated operational occurrences without a reactor scram, include primary coolant flow reduction tests and control rod withdrawal tests at power operation. These tests are being conducted from 2002 to 2005. The second phase tests, which simulate accident conditions, will be conducted after completion of the first phase tests. The second phase tests include the loss of forced cooling, all blackout, depressurization, reactivity insertion and etc.

The objective of R&D on the system integration technology is to develop technologies for the safe and economical connection. Safety related issues such as explosion near the nuclear plant and the release of radioactive materials are the important topics in this study. It covers the safety design to prevent the combustible gas release or mitigate its effect, and the damage estimation of nuclear plant due to blast waves from explosion, the development of high

temperature isolation valve, the estimation of tritium permeation through the intermediate heat exchanger (IHX), etc. Also, control technology that utilizes steam generator has been developed in order to prevent the propagation of thermal disturbance on nuclear reactor from the chemical plant.

As for Iodine-Sulfur cycle, a pilot test is planned. In the test, test plant of about 30 Nm³-H₂/h will be developed, which is made of industrial materials and can be operated under prototypical high-pressure condition. High temperature helium gas heated by simulated electric heater will be used to drive the process. Operation of the test plant will demonstrate the technical feasibility of Iodine-Sulfur cycle, and, also, the test data will be used to verify the analytical codes to be developed.

After completion of the pilot test of Iodine-Sulfur cycle, it is planned to proceed to the demonstration test of nuclear hydrogen production using HTTR based on the technology development mentioned above.

### AIV-4 HYDROGEN PRODUCTION AND STORAGE

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#### **AIV-4.1 Introduction**

Hydrogen is considered the energy carrier of the future. It is meant to replace fossil fuels such as hydrocarbons and coal as major energy carriers for transportation purposes, and for domestic and industrial sources for thermal energy. It can be used in several ways, but its penetration into the market will depend upon the availability of low cost, reliable fuel cells. The use of hydrogen in fuel cells, such as the proton exchange membrane fuel cell (PEM), requires high purity hydrogen.

It is also possible to use hydrogen in internal combustion engines. The advantage is that some of these engines can run on other fuels (gasoline, natural gas) as well. This will ease the introduction of hydrogen into the market and the transition to a hydrogen infrastructure.

#### AIV-4.2 Hydrogen production

Since hydrogen is an energy carrier and not a source of energy, it must be synthesized by some large scale process in order to get an economic viable production. Today this is done by so called steam reforming of methane and to some degree coal, but these routes will most likely require CO<sub>2</sub> deposition in the future. Future production routes involve the use of solar energy (PV) to produce hydrogen by electrophoresis, thermal nuclear energy combined with different Hydrogen generating cycles and from gasification of biomass.

In order for any of these processes to be efficient, they will depend on development of better gas separation membranes where H<sub>2</sub> is separated from other gases such as O<sub>2</sub>, CO<sub>2</sub>, CO, etc. Further development of catalysts is needed in order get more efficient conversion into hydrogen from the different feedstock (hydrocarbons, coal, biomass). These new catalysts will be advanced nano-scale materials with multifunctional surface properties. The only way to do so is by an integrated approach, where modeling and experimental exploration go hand in hand. This requires further development of new methods in computational materials science in order to be able to predict both structural properties as well as surface properties in these porous catalysts. In connection with the surfaces, an important goal is to predict the chemical reaction kinetics. On the experimental side, further progress in electron microscopy is needed as well as more powerful neutron and synchrotron X-ray sources.

#### AIV-4.3 Hydrogen storage

Hydrogen storage is one major obstacle for the introduction of hydrogen in the transportation sector. There are three options; compressed gas, liquefied gas and hydrogen stored inside pores in solid, porous materials.

#### AIV-4.3.1 Liquefied hydrogen

Due to a high energy penalty in liquefaction, liquid hydrogen is not considered an economic viable alternative in a sustainable society. The boiling point of hydrogen is about 20 K at 1 bar. This requires use of cryogenic storage tanks. This technology is known and proven and does not required any further basic research in order to reach the market. Some major car manufacturers plan to introduce cryogenic storage tanks into their passenger cars.

#### AIV-4.3.2 Compressed gas

Compressed hydrogen gas at 700 bars at room temperature is today considered as the practical limit for a passenger car to run for 500 km without refueling. Today storage tanks made of reinforces polymers and metallic bottle necks are available commercially.

To support pressures of 700 bars and even higher, and to be able to sustain an external impact, new light weight materials need to be developed. These materials will most likely be composite materials where one particle or fiber is bonded in the matrix of the other. To fully understand and to be able to predict the properties of interphases within solids, will require the use of simulation tools on an atomic level. Simultaneously, these results must be supported by experiments with the same resolution. Various forms of electron microscopy as well as X-ray and neutron diffraction will be applied. Of particular interest will be development of 3D imaging techniques using synchrotron X-ray to study the internal structure of crystals in real space.

#### AIV-4.3.3 Hydrides

Solid state storage is either in form of hydrides or absorption in nano particles. Both materials require certain physical condition for absorption of hydrogen and another condition for the release. The desired properties for such materials are

- large storage capacity, i.e. more than 7 % hydrogen by weight
- rapid binding and release of hydrogen
- light weight

Candidates of materials have been synthesized and investigated for a number of years. Many of them are so called intermetallic with two or more different elements. Among these one finds Mg-based alloys, V-based alloys and Alanates. (NaAlH<sub>4</sub>).

A large effort has been put into trying to store large amounts of hydrogen in carbon nanotubes. However, no progress has been made. Still, carbon is an interesting matrix for storing hydrogen. If one is able to modify or control the strength of the hydrogen adsorption in other and cheaper forms of carbon, other forms like graphite can become new candidates that has the possibility of storing more than 7 % by weight of H<sub>2</sub>.

To further advance the development of these materials, the same integrated approach between modeling and advanced experiments as discusses for novel

catalysts above, is needed. In addition, further studies into the kinetics of hydrogen molecular flow in and out of these structures, which may involve nanofluidics, is important for exploring their potential for efficient, reliable and practical storage of hydrogen.

The situation is very much similar to development of super conductors. A large effort was put into finding materials with higher  $T_c$  than about 40 K. Nothing was achieved until the sudden discovery of high  $T_c$  super conductors by Bednorz and Müller, which earned them the Nobel Prize in 1987.

The future of hydrogen is truly dependent upon a multidisciplinary effort involving, physics, chemistry and materials science.

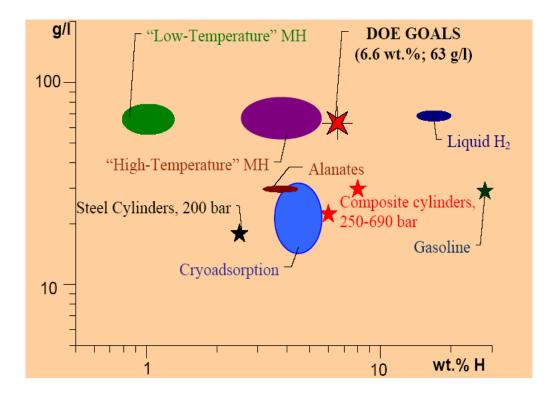


Figure 1-: Hydrogen storage weight and volume capacities. (Yartis, IFE, Norway)

# AIV-5 USE OF NATURAL GAS PIPELINES TO TRANSPORT HYDROGEN GAS

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The transport of hydrogen gas under high pressure in steel pipelines has been common practice for more than 50 years. Such hydrogen pipelines with a worldwide total length up to some 100 km are in use for instance at companies like "Chemische Werke Hüls", "Linde", "Air Products" and "Air Liquide" [HYD]. According to hitherto existing experience, natural gas steel pipelines can be used to transport hydrogen as well because:

- inside corrosion via embrittlement by hydrogen is not to be expected as long as plastic stretching due to unduly high strain can be avoided [GRA]; this is guaranteed observing the usual safety regulations of long distance gas pipelines
- hardening of steel within the area of weld does not cause an increased susceptibility for embrittlement by hydrogen
- outside corrosion on pipelines for natural gas as well as for hydrogen can be avoided by means of insulating wrapping including the application of cathodic protection against corrosion.

#### **References:**

HYD http://www.hydrogen.org/knowledge/H2-kfa

GRA Gräfen et al., CERT-Untersuchungen an Leitungsrohrstählen über eine Korrosionsgefährdung durch wasserstoffhaltige Gase bei hohen Drücken, Wertstoffe und Korrosion 39 (1988) p. 517 - 525