

GERAÇÃO TERMONUCLEAR E O VETOR HIDROGÊNIO

(Texto de Apoio)

PROFESSOR:

Prof. Dr. Adonis Marcelo Saliba-Silva – IPEN/CNEN-SP

(saliba@ipen.br)

EMENTA DO MINICURSO:

Economia do Hidrogênio. Apresentação geral de produção de hidrogênio, por meios carbogênicos e não carbogênicos. Hidrogênio Nuclear: projeto e resultados alcançados. Eletrólise e eletrolisadores de baixa temperatura. Eletrolisador de alta temperatura e ciclos termoquímicos. Armazenamento e transporte para produção centralizada. Amônia: produção centralizada e reforma da amônia para produção distribuída. Produção distribuída de hidrogênio com energias alternativas. Proposta para um módulo de produção de hidrogênio associado à produção de energia elétrica em localidades remotas.

MINICURRÍCULO DO PROFESSOR:

Graduado em Engenharia Metalúrgica pela Universidade Federal de Minas Gerais (1975), mestrado em Engenharia Metalúrgica e de Minas pela Universidade Federal de Minas Gerais (1978), mestrado em Iron and Steel Technology - University of Sheffield (1981) e doutorado em Tecnologia Nuclear pela Universidade de São Paulo (2001). Atualmente é Tecnologista Senior da Comissão Nacional de Energia Nuclear. Desenvolve e coordena o programa de Hidrogênio Não-carbogênico do IPEN/CNEN (produção de hidrogênio via fontes alternativas de energia: solar, eólica, nuclear entre outras). Professor do CPG IPEN/USP sobre Hidrogênio Não-carbogênico: Produção e Tecnologias. Desenvolve projetos e pesquisas em materiais nucleares e em fabricação de elementos combustíveis nucleares para reatores de pesquisa e também faz pesquisas eletroquímicas para avaliação de metais de alta resistência corrosiva. Desenvolve pesquisas em eletrólise aquosa para produção de hidrogênio utilizando energias renováveis.

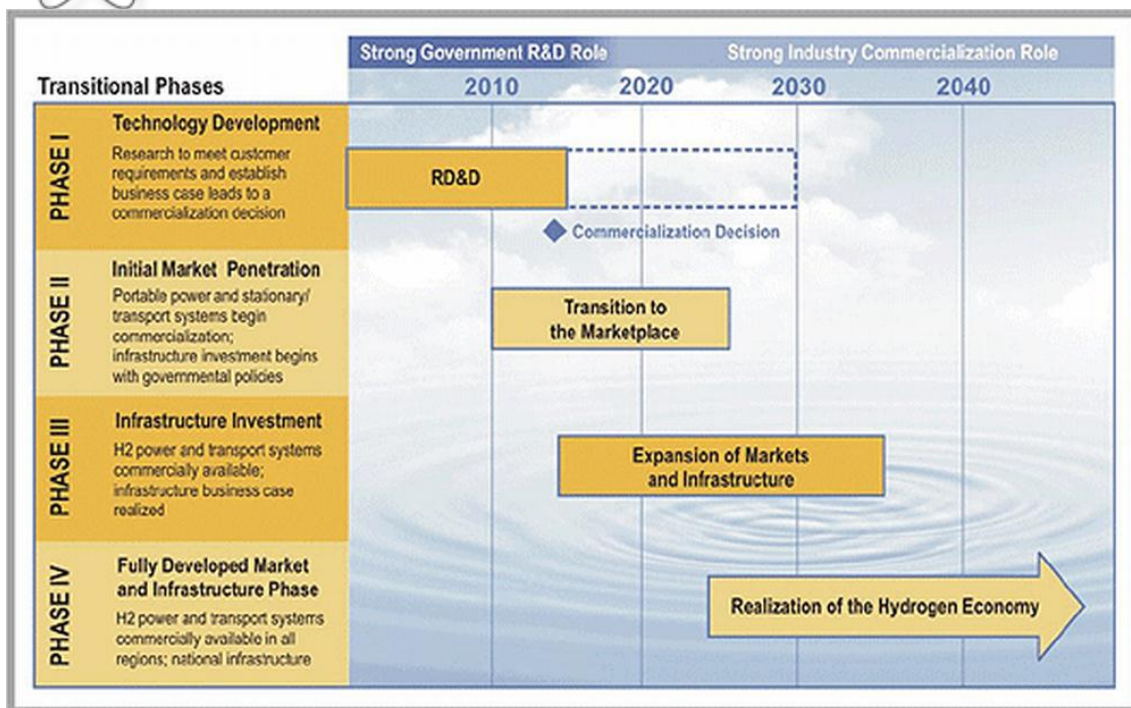
Economia do Hidrogênio

A economia do hidrogênio é proposta para resolver alguns dos efeitos negativos da utilização de combustíveis de hidrocarboneto em que o carbono é liberado para a atmosfera. O interesse atual na economia do hidrogênio foi lançada em 1970 por Lawrence W. Jones da Universidade de Michigan.

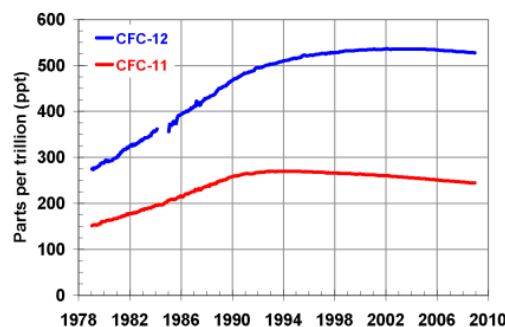
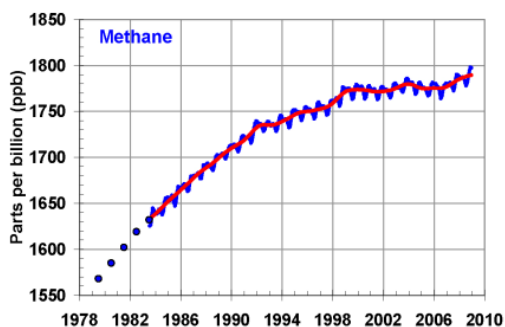
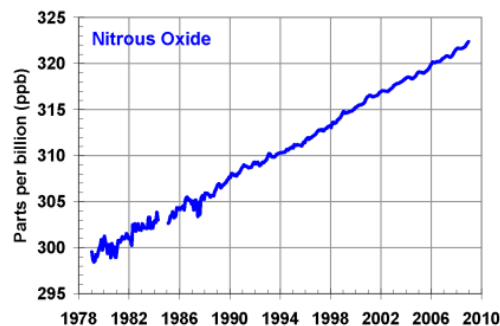
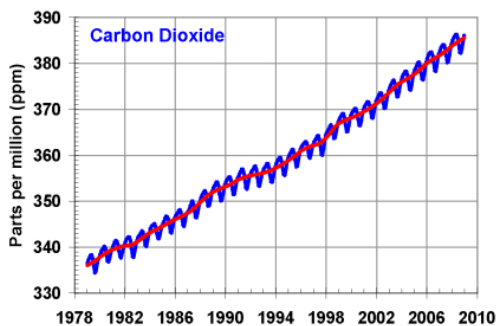
Na economia atual com base em hidrocarbonetos fósseis, o transporte é abastecido principalmente pelo petróleo. A queima de combustíveis fósseis emite dióxido de carbono e outros poluentes. O fornecimento de recursos de hidrocarbonetos economicamente utilizável em todo o mundo é relativamente limitado, e a demanda por combustíveis de hidrocarbonetos é crescente, especialmente na China, Índia e outros países em desenvolvimento.

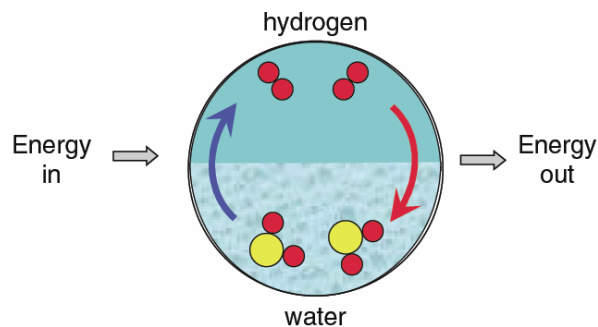
Os defensores de uma economia do hidrogênio em escala mundial afirmam que o hidrogênio pode ser uma fonte de energia mais limpa para os usuários finais, especialmente em aplicações de transporte, sem emissão de poluentes (tais como as partículas em suspensão) ou o dióxido de carbono no ponto de uso final. Ao se utilizar o hidrogênio de forma maciça, mesmo que originário de combustíveis fósseis, levaria a uma diminuição significativa de emissão de dióxido de carbono, pois se poderiam, por um lado, utilizar veículos elétricos híbridos e assim reduzir significativamente as emissões de dióxido de carbono por captura de carbono ou métodos de sequestro de carbono utilizados no local de produção do gás.

O hidrogênio tem uma alta densidade de energia por peso. Um ciclo termodinâmico para motor de combustão interna a hidrogênio é dito ter uma eficiência máxima de cerca de 38%, 8% maior do que a gasolina do motor de combustão interna. A combinação da célula a combustível e motor elétrico é de 2-3 vezes mais eficiente que um motor de combustão interna. No entanto, o custo de capital elevado de células de combustível, cerca de 5500 dólares / kW, é um dos principais obstáculos ao seu desenvolvimento. Isso significa que a célula de combustível é apenas tecnicamente, mas não é economicamente, mais eficiente que um motor de combustão interna. Outros obstáculos incluem as questões técnicas de armazenagem de hidrogênio e a exigência de pureza do hidrogênio utilizado em células a combustível. Com a tecnologia atual, uma produção de energia elétrica com célula de combustível exigiria alta pureza do hidrogênio, tão alto quanto 99.999%.

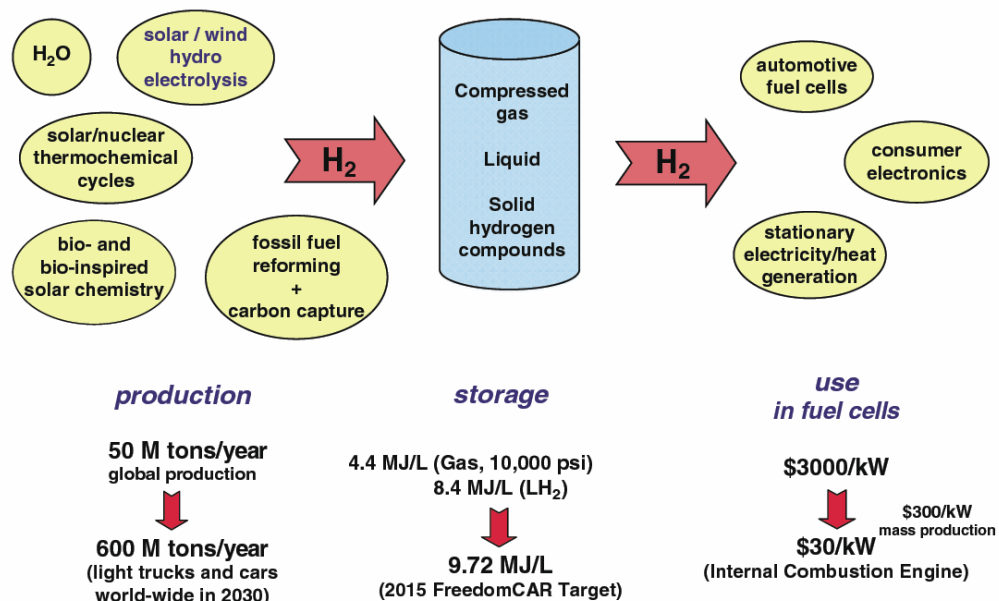


http://www.esrl.noaa.gov/gmd/aggi/aggi_2009.fig2.png





Hydrogen–water cycle. Hydrogen is a green carrier of energy; water is a green carrier of hydrogen. Hydrogen is created from water by injecting energy at the point of production from any source—photons, electrons, or heat. Water is created from hydrogen when energy is released at the point of use, by electro-oxidation to electrons and heat in fuel cells, or combustion to heat in engines or turbines. Even though the hydrogen–water cycle is closed and sustainable, the energy chain it links can be open and depletable, if, for example, fossil energy is used to split water. Sustainability is maintained if renewable energy is used to split water and the energy released is used only for work and heat.



The three links of the hydrogen energy chain: production, storage, and use in fuel cells. Each link must connect seamlessly with the others to create an effective infrastructure, and each link has fundamental challenges that must be solved, as indicated.

CRABTREE, G.W.; DRESSELHAUS, M.S. *The Hydrogen Fuel Alternative*, MRS Bulletin – vol. 33, April 2008 – <http://www.mrs.org/bulletin> - p. 421-428

Pesquisas do Governo dos EUA para implementação da Produção de H₂ na Economia do Hidrogênio

<http://hydrogen.energy.gov/production.html>

Hydrogen can be produced from diverse domestic feedstocks using a variety of process technologies. Hydrogen-containing compounds such as fossil fuels, biomass or even water can be a source of hydrogen. Thermochemical processes can be used to produce hydrogen from biomass and from fossil fuels such as coal, natural gas and petroleum. Power generated from sunlight, wind and nuclear sources can be used to produce hydrogen electrolytically. Sunlight alone can also drive photolytic production of hydrogen from water, using advanced photoelectrochemical and photobiological processes.

This DOE Hydrogen Program activity is focused on advancing cost-effective, efficient production of hydrogen from renewable, fossil and nuclear energy resources.

Hydrogen from Natural Gas

The Offices of [Energy Efficiency and Renewable Energy \(EERE\)](#) and [Fossil Energy \(FE\)](#) are working to reduce the cost of producing hydrogen via steam methane reforming. EERE is focused on distributed hydrogen production from natural gas and bio-derived liquid feedstocks and FE is focused on sub-centralized and centralized hydrogen production. Although hydrogen from natural gas is certainly a viable near-term option, it is not viewed by DOE as a long-term solution because it does not help solve the green house gas (GHG) or energy security issues.

Hydrogen from Coal

Research sponsored by the [Office of Fossil Energy](#) is focused on advancing the technologies needed to produce hydrogen from coal-derived synthesis gas and to build and operate a zero emissions, high-efficiency co-production power plant that will produce hydrogen from coal along with electricity. FE is also investigating carbon sequestration technologies, in associated programs, as an option for managing and stabilizing greenhouse gas emissions from coal-fired plants.



Hydrogen from Nuclear Power

Research sponsored by the [Office of Nuclear Energy \(NE\)](#) is focused on developing the commercial-scale production of hydrogen using heat from a nuclear energy system. Key research areas include high-temperature thermochemical cycles, high-temperature electrolysis, and reactor/process interface issues.

Hydrogen from Renewable Resources

Research sponsored by [EERE](#) is focused on developing advanced technologies for producing hydrogen from domestic renewable energy resources that minimize environmental impacts. Key research areas include electrolysis, thermochemical conversion of biomass, photolytic and fermentative micro-organism systems, photoelectrochemical systems, and high-temperature chemical cycle water splitting.



Produção por Reforma de Gás Natural

(http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural_gas.html)

Natural Gas Reforming

Although today most hydrogen is produced from fossil materials, such as natural gas at this oil refinery, the Program is exploring a variety of ways to produce hydrogen from renewable resources.

Distributed natural gas reforming is an important pathway for near-term hydrogen production during the transition to a hydrogen economy.

How Does It Work?

Natural gas contains methane (CH₄) that can be used to produce hydrogen via thermal processes, such as steam-methane reformation and partial oxidation.



- **Steam-Methane Reforming**

About 95% of the hydrogen produced today in the United States is made via steam-methane reforming, a process in which high-temperature steam (700°C–1000°C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar

pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming is endothermic—that is, heat must be supplied to the process for the reaction to proceed.

Subsequently, in what is called the "water-gas shift reaction," the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. In a final process step called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

Steam-Reforming Reactions

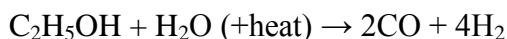
Methane:



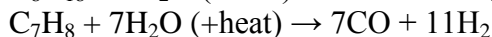
Propane:



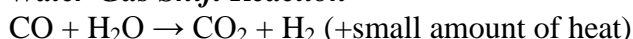
Ethanol:



Gasoline (using iso-octane and toluene as example compounds from the hundred or more compounds present in gasoline):



Water-Gas Shift Reaction



- **Partial Oxidation**

In partial oxidation, the methane and other hydrocarbons in natural gas are reacted with a limited amount of oxygen (typically, from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. With less than the stoichiometric amount of oxygen available for the reaction, the reaction products contain primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of carbon dioxide and other compounds. Subsequently, in a water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and more hydrogen.

Partial oxidation is an exothermic process—it gives off heat. The process is, typically, much faster than steam reforming and requires a smaller reactor vessel. As can be seen from the chemical reactions of partial oxidation (below), this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

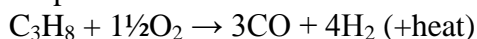


Partial Oxidation Reactions

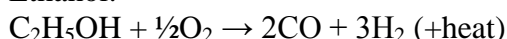
Methane:



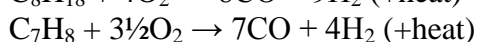
Propane:



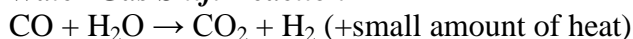
Ethanol:



Gasoline (using iso-octane and toluene as example compounds from the hundred or more compounds present in gasoline):



Water-Gas Shift Reaction



Why Is This Technology Being Considered for the Hydrogen Economy?

- **Advanced technology and infrastructure (most advanced of all production pathways).**

Natural gas reforming technology is advancing rapidly, and a natural gas pipeline delivery infrastructure already exists. Today, 95% of the hydrogen produced in the U.S. is made via natural gas reforming in large central plants. (The hydrogen produced is used predominantly for petroleum refining and ammonia production for fertilizer).

- **Greenhouse gas emissions are lower than gasoline-powered internal-combustion engine (ICE) vehicles.**

Producing hydrogen from natural gas does result in some greenhouse gas emissions. When compared to ICE vehicles using gasoline, however, fuel cell vehicles using hydrogen produced from natural gas reduce greenhouse gas emissions by 60%.

It Is Important to Note...

- Current estimates indicate that using natural gas to produce hydrogen during the transition period to a hydrogen economy would increase overall U.S. natural gas consumption by less than 5%.
- DOE is not funding research activities for large-scale central production of hydrogen from natural gas. DOE efforts are focused on distributed natural gas reforming for the transition period only. Large-scale hydrogen production from natural gas reforming is a mature technology, and natural gas resources in the United States are limited—15% of the natural gas we use is imported. Producing



large amounts of hydrogen from natural gas in the long term would only trade U.S. dependence on imported oil for U.S. dependence on imported natural gas.

Research Focuses on Overcoming Challenges

Although the technology for distributed natural gas reforming is advancing rapidly, several challenges remain. Capital equipment costs, as well as operation and maintenance costs, must be reduced, and process energy efficiency must be improved in order to meet hydrogen cost targets.

In order for hydrogen to be successful in the market place, it must be cost-competitive with the available alternatives. In the light-duty vehicle transportation market, this means that hydrogen needs to be available untaxed at \$2–\$3/gge (gasoline gallon equivalent). This would result in hydrogen fuel cell vehicles having the same cost to the consumer on a cost-per-mile-driven basis as a comparable conventional internal-combustion engine or hybrid vehicle.

Key research areas:

- Intensifying the process (combining steps into fewer operations)
- Developing better designs to lower equipment manufacturing and maintenance costs
- Improving process efficiency by using better catalysts and better heat integration.



Produção de Hidrogênio - Tecnologias

J.D. Holladay et al./Catalysis Today 139 (2009) 244–260

Table 6
Technology summary table

Technology	Feed stock	Efficiency	Maturity
Steam reforming	Hydrocarbons	70–85% ^a	Commercial
Partial oxidation	Hydrocarbons	60–75% ^a	Commercial
Autothermal reforming	Hydrocarbons	60–75% ^a	Near term
Plasma reforming	Hydrocarbons	9–85% ^b	Long term
Aqueous phase reforming	Carbohydrates	35–55% ^a	Med. term
Ammonia reforming	Ammonia	NA	Near term
Biomass gasification	Biomass	35–50% ^a	Commercial
Photolysis	Sunlight + water	0.5% ^c	Long term
Dark fermentation	Biomass	60–80% ^d	Long term
Photo fermentation	Biomass + sunlight	0.1% ^e	Long term
Microbial electrolysis cells	Biomass + electricity	78% ^f	Long term
Alkaline electrolyzer	H ₂ O + electricity	50–60% ^g	Commercial
PEM electrolyzer	H ₂ O + electricity	55–70% ^g	Near term
Solid oxide electrolysis cells	H ₂ O + electricity + heat	40–60% ^h	Med. Term
Thermochemical water splitting	H ₂ O + heat	NA	Long term
Photoelectrochemical water splitting	H ₂ O + sunlight	12.4% ⁱ	Long term

Produção de H₂ por Eletrólise Ácida

Proton exchange membrane electrolyzer. PEM electrolyzers build upon the recent advances in PEM fuel cell technology . PEM-based electrolyzers typically use Pt black, iridium, ruthenium, and rhodium for electrode catalysts and a Nafion membrane which not only separates the electrodes, but acts as a gas separator . In PEM electrolyzers water is introduced at the anode where it is split into protons and oxygen . The protons travel through the membrane to the cathode, where they are recombined into hydrogen . The O₂ gas remains behind with the unreacted water. There is no need for a separations unit. Depending on the purity requirements a drier may be used to remove residual water after a gas/liquid separations unit. PEM electrolyzers have low ionic resistances and therefore high currents of >1600 mA cm⁻² can be achieved while maintaining high efficiencies of 55–70%

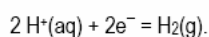
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WATER ELECTROLYSIS: PROTON REDUCTION AND WATER OXIDATION

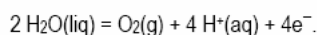
Electrolysis is a process for breaking water (H₂O) into its constituent elements (hydrogen, H₂, and oxygen, O₂) by supplying electrical energy. The advantage of this process is that it supplies a very clean hydrogen fuel that is free from carbon and sulfur impurities. The disadvantage is that the process is expensive, relative to steam reforming of natural gas, because of the cost of the electrical energy needed to drive the process.

Chemically, the electrolysis of water is simply the reverse of the electricity-generating reaction that occurs in a fuel cell. Physically, an electrolyzer is designed very much like a fuel cell, with two electrodes immersed in a common aqueous electrolyte solution. The reaction can be thought of as occurring in two "half-cells" separated by a gas-impermeable electrolyte membrane (the figure provides a schematic drawing of the electrolysis process).

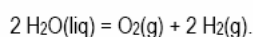
In the cathode half-cell, hydrogen ions (protons) are reduced to hydrogen:



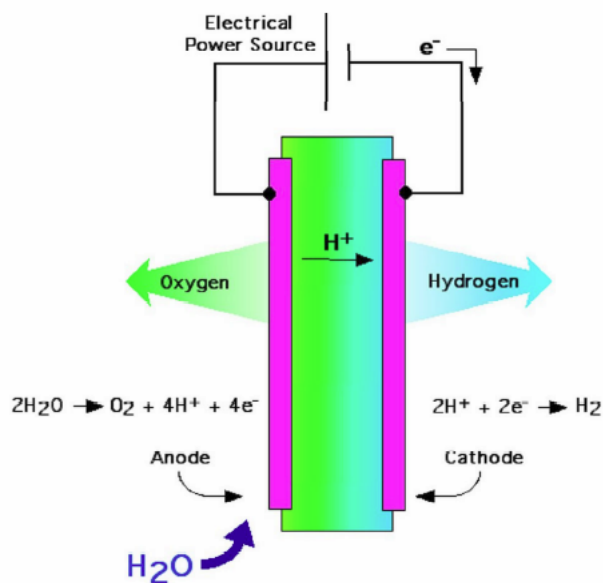
On the anode side, water is oxidized to oxygen and protons:



By multiplying the first half-reaction by two and adding the two half-reactions together, we obtain the overall reaction:



Because water is a very stable molecule relative to oxygen and hydrogen, this reaction requires input of energy. In principle, the reaction can be driven by an applied voltage of 1.23 V, which translates to a free energy input of 237 kJ/mole of hydrogen. In practice, somewhat larger driving voltages (1.55–1.65 V) are used because of slow kinetics in the two half-cells. The energy efficiency of the cell can be calculated simply as the theoretical voltage (1.23 V) divided by the applied voltage; for example, a cell operating at 1.60 V would have an efficiency of $1.23/1.60 \times 100\% = 77\%$. The process of oxidizing water in the oxygen-evolving half-cell is mechanistically and kinetically more complex than the hydrogen-evolving process because it requires four electrons and proceeds through a series of distinct oxidation intermediates. In an uncatalyzed reaction, some of these intermediate electron transfer steps require more energy than others, and some are slower than others. As a consequence, extra voltage is needed to drive the cell, primarily at the oxygen-evolving electrode, and efficiency is reduced. An ideal catalyst for water oxidation would equalize the energy required at each step in addition to equalizing the rates of each electron transfer, thus maximizing efficiency. The water oxidation complex that supports oxygen evolution in photosynthesis is one catalyst that comes close to meeting this ideal and provides a tantalizing model for building catalysts for electrolyzer anodes and fuel cell cathodes.



Basic Research Needs for the Hydrogen Economy (DOE/Argonne), 2003 at
<http://www.sc.doe.gov/bes/hydrogen.pdf>

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3.2.1.1. Alkaline electrolyzer. Alkaline electrolyzers are typically composed of electrodes, a microporous separator and an aqueous alkaline electrolyte of approximately 30 wt% KOH or NaOH [20,159]. In alkaline electrolyzers nickel with a catalytic coating, such as platinum, is the most common cathode material. For the anode, nickel or copper metals coated with metal oxides, such as manganese, tungsten or ruthenium, are used. The liquid electrolyte is not consumed in the reaction, but must be replenished over time because of other system losses primarily during hydrogen recovery. In an alkaline cell the water is introduced in the cathode where it is decomposed into hydrogen and OH⁻ [127]. The OH⁻ travels through the electrolytic material to the anode where O₂ is formed. The hydrogen is left in the alkaline solution [127]. The hydrogen is then separated from the water in a gas liquid separations unit outside of the electrolyser [127]. The typical current density is 100–300 mA cm⁻² and alkaline electrolyzers typically achieve efficiencies 50–60% based on the lower heating value of hydrogen [159]. The overall reactions at the anode and cathode are:

Anode:



Cathode:



Overall:

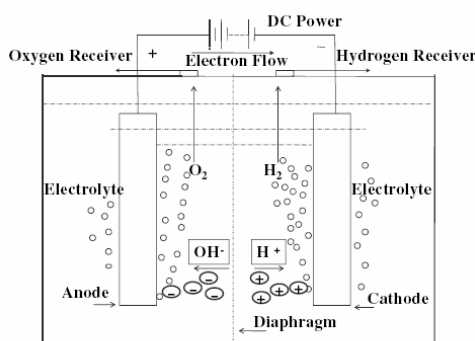
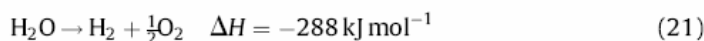


Fig. 2. A schematic illustration of a basic water electrolysis system.

Recent progress in alkaline water electrolysis for hydrogen production and applications

Kai Zeng¹, Dongke Zhang*

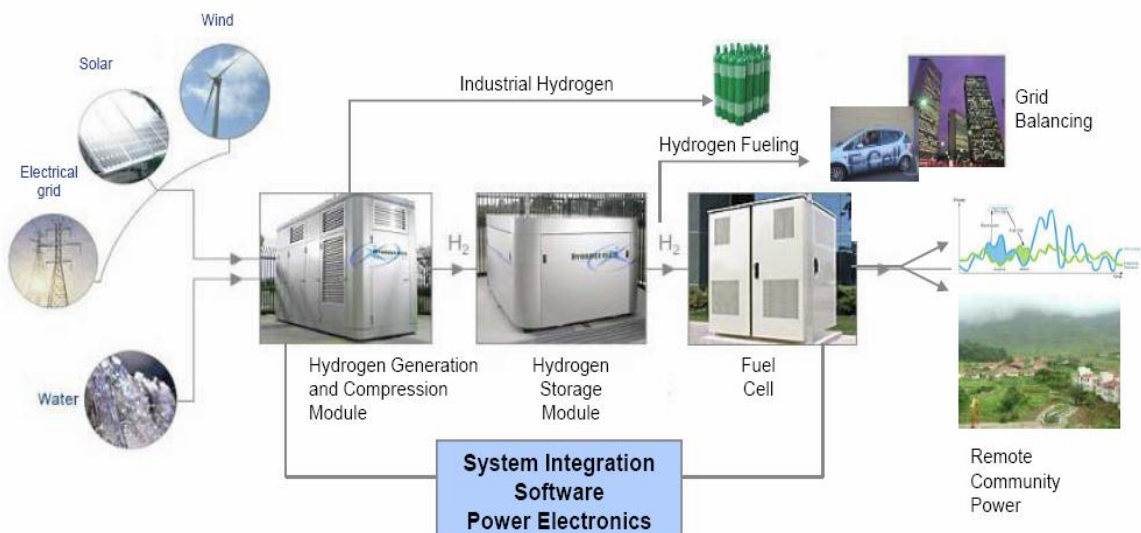
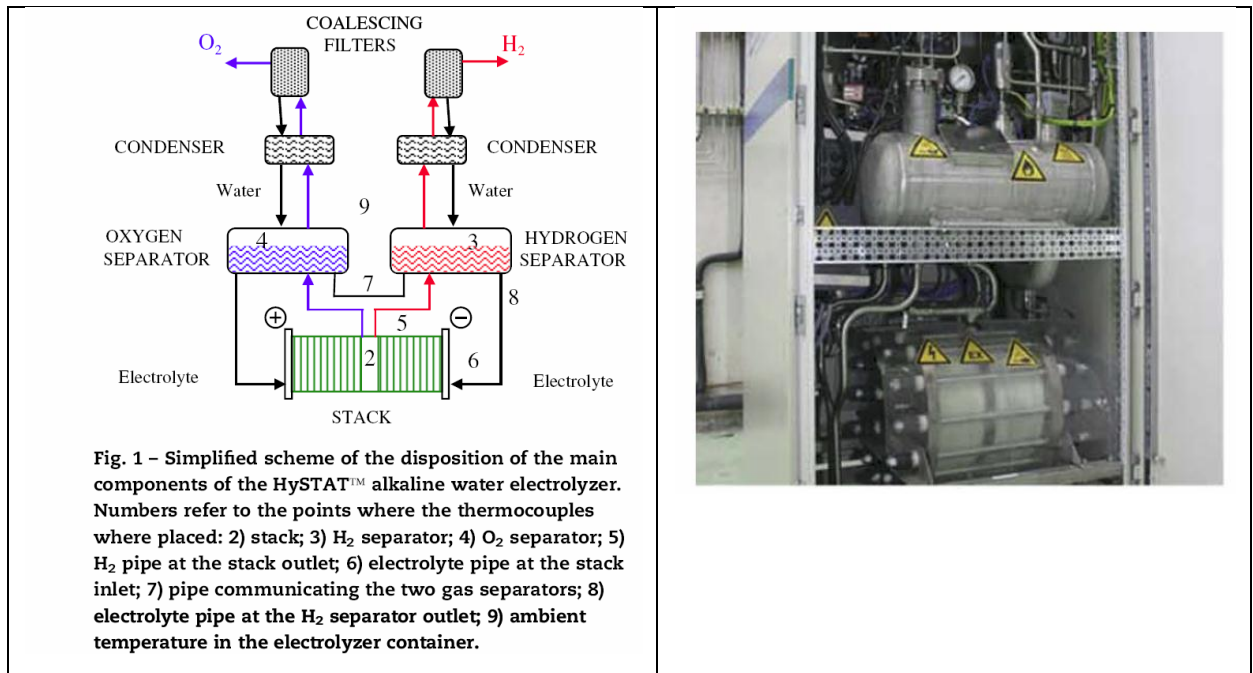
Progress in Energy and Combustion Science 36 (2010) 307–326



Esquema de um eletrolizador moderno tipo HySTAT

[DIEGUEZ et al. , Int. J. Hydrogen Energy, 33 (2008) 7338 – 7354]

Commercial alkaline water electrolyzer (HySTAT from Hydrogenics) designed for a rated hydrogen production of 1 Nm³ H₂/h at an overall power consumption of 4.90 kWh/Nm³ H₂





Eletrólise a Membrana de Óxido Sólido (SOEC)

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3.2.1.3. *Solid oxide electrolysis cells.* Solid oxide electrolysis cells (SOEC) are essentially solid oxide fuel cells operating in reverse. These systems replace part of the electrical energy required to split water with thermal energy, as can be seen in Fig. 8 [174]. The higher temperatures increase the electrolyzer efficiency by decreasing the anode and cathode overpotentials which cause power loss in electrolysis [174,175]. For example, an increase in temperature from 375 to 1050 K reduces the combined thermal

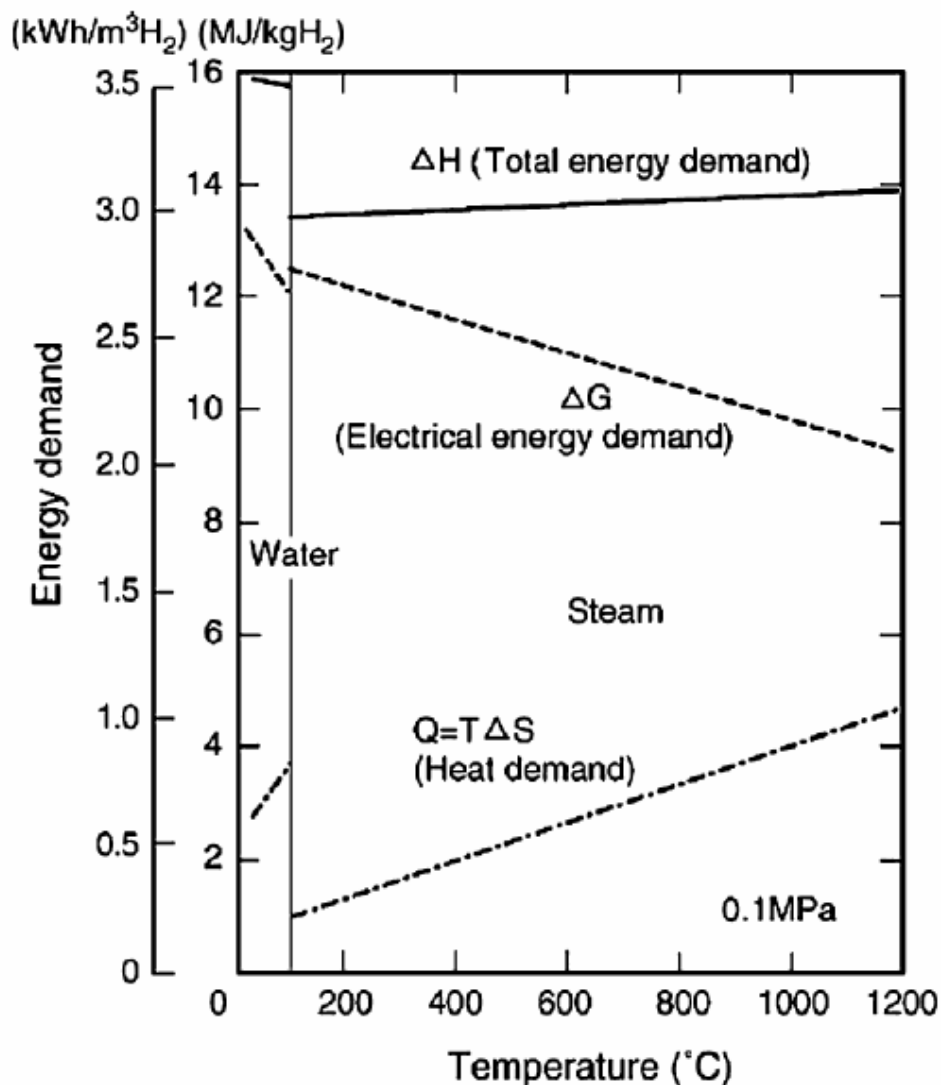


Fig. 8. Energy demand for water and steam electrolysis (Copyright Elsevier [174]).

and electrical energy requirements by close to 35% [175]. A SOEC operates similar to the alkaline system in that an oxygen ion travels through the electrolyte leaving the hydrogen in unreacted steam stream [127]. The reactions are shown in Eqs. (17)–(19).

Other advantages for high temperature electrolysis with a solid oxide based electrolyzer include: the use of a solid electrolyte which, unlike KOH for alkaline systems, is non-corrosive and it does not experience any liquid and flow distribution problems [165,174]. Of course the high temperature operation requires the use of costly materials and fabrication methods in addition to a heat source [165]. The materials are similar to those being developed for solid oxide fuel cells (SOFC), yttria stabilized zirconia (YSZ) electrolyte, nickel containing YSZ anode, and metal doped lanthanum metal oxides [165,174], and have the same problems with seals which are being investigated.

High temperature electrolysis efficiency is dependent on the temperature and the thermal source. The efficiency as a function of electrical input alone can be very high with efficiencies 85–90% being reported [127]. However, when the thermal source is included the efficiencies can drop significantly. For example, SOEC operating from advanced high temperature nuclear reactors may be able to achieve up to 60% efficiency. In addition to using conventional combustion or nuclear energy to produce the high temperature source, solar energy is under development and may result in higher efficiencies [173–181].

Combining SOEC with a SOFC for co-generation of hydrogen and electricity has been proposed [182]. In this hybrid system a SOFC and SOEC are manifolded into the same stack and fed the same fuel, such as natural gas. Hydrogen is then produced by the SOEC and electricity is produced by the SOFC. Proof-of-concept short stacks have been demonstrated with efficiencies of up to 69% [182]. However, the fuel utilization is still relatively low at approximately 40% and coking is a serious issue in addition to the other challenges faced by SOEC [182].

At Savannah River National Laboratory, a single cell electrolyzer has been built and operated for 100 h. Testing of a multi-cell electrolyzer is planned for this year. Westinghouse are also investigating the electrolyzer and decomposition reactor.

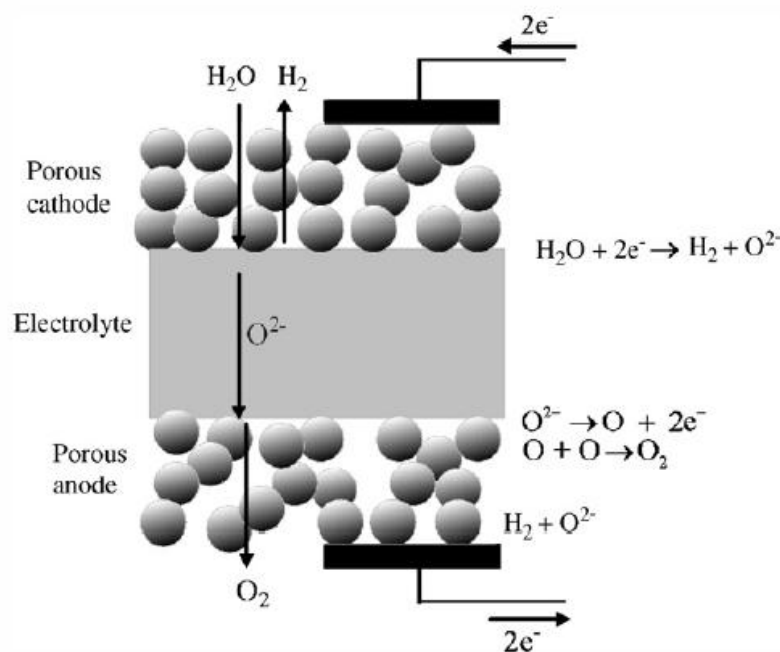


Fig. 1 – Schematics of SOEC hydrogen production.

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 33 (2008) 2337– 2354

Review

Technological development of hydrogen production by solid oxide electrolyzer cell (SOEC)

Meng Ni, Michael K.H. Leung*, Dennis Y.C. Leung

Table 1 – Reported ionic conductivity of different doped zirconia materials at typical temperatures

Material	Conductivity (S/cm)	Temperature (K)	Remarks
8YSZ	0.13	1273	Prepared by spay drying of nitrate precursor solution
10.5YSZ	0.034	1073	Thin film prepared by aerosol-assisted metal-organic chemical vapour deposition (AAMOCVD)
10YSZ	4.52×10^{-6}	673	300 nm-thick film was prepared by atomic laser deposition (ALD)
9.5YSZ	0.057	1173	Fifteen to 25µm-thick film prepared by magnetic pulse compaction of tapes cast of nanopowders
8YSZ	0.083	1173	Spark Plasma Sintering at 1573K and at pressure 70Mpa
CaO–ZrO ₂ with 12.5 mol% CaO	0.055	1273	Nil
La ₂ O ₃ –ZrO ₂ with 5 mol% La ₂ O ₃	0.0044	1273	Nil
MgO–ZrO ₂ with 13.7 mol% MgO	0.098	1273	Prepared by conventional ceramic processing involving wet mixing, pressing, sintering and machining
Sc ₂ O ₃ –ZrO ₂ with 9–11 mol% Sc ₂ O ₃	0.28–0.34	1273	Prepared by sintering of coprecipitated powders
Sc ₂ O ₃ –ZrO ₂ with 6 mol% Sc ₂ O ₃	0.18	1273	The sintered film was treated by hot isostatic pressing (HIP) to improve the mechanical strength

Ciclos Termoquímicos

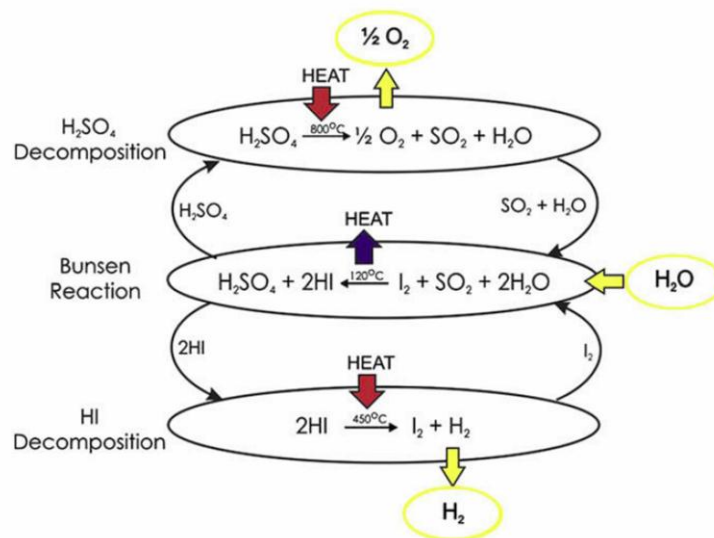
R. Elder, R. Allen / *Progress in Nuclear Energy* 51 (2009) 500–525

Thermochemical water splitting is the conversion of water into hydrogen and oxygen using a series of chemical reactions. All chemical intermediates are recycled internally within the process so that water is the only raw material and hydrogen and oxygen are the only products. The concept of thermochemical production of hydrogen from water was first studied thermodynamically in the 1960s.

Sulphur-Iodine Cycle

The Sulphur Iodine (SI) cycle, or GA process, involves three separate sections. The first is the Bunsen section, where water is reacted with iodine and sulphur dioxide in an exothermic reaction, at around 120°C, to form sulphuric and hydriodic acids. At certain reactant concentrations, involving an excess of iodine, a phase separation occurs between the two acid products leading to a H₂SO₄ phase principally devoid of HI and vice versa. In the second section, sulphuric acid is decomposed in an endothermic 2-stage reaction first to SO₃ and then to SO₂. The first stage occurs at a temperature of 400–500°C, whereas the second stage occurs at 800°C in the presence of a solid catalyst. The third section involves the decomposition of hydriodic acid to form hydrogen and iodine. This is a slightly endothermic reaction and can be conducted in the liquid or gas phase.

The SI cycle was first investigated by General Atomic (GA) in the 1970s, however, energy prices and economics put a stop to ongoing research. In the late 1990s GA restarted investigating thermochemical cycles, and, finding that the SI cycle had the highest predicted efficiency and the greatest potential for further improvement, they selected it for further research. It has since been developed in Japan, Korea and Europe as well as the USA. Current predicted efficiencies are in the 35–45% range.



The Sulphur Iodine cycle.

The European Union Framework 6 funded HYTHEC (Hydrogen from Thermochemical cycles) project investigated ways to improve the process efficiency. Through the US DoE and French-CEA I-NERI (International Nuclear Energy Research Initiative) agreement, an integrated lab scale (ILS) experiment of the SI cycle is being developed. The Bunsen section, developed by

CEA, and the H₂SO₄ section, developed by Sandia National Laboratory, have both been shipped to GA, where the HI section was developed. Bench scale experiments of the SI cycle performed at the Japan Atomic Energy Agency (JAEA) demonstrated a stable production of hydrogen and further pilot-scale tests are underway.

The Hybrid Sulphur cycle

The Hybrid Sulphur (HyS) cycle, or Westinghouse cycle, is a combination of electrolysis and thermochemical processes. It consists of two main steps, the electrolysis of water and sulphur dioxide at around 87°C to give hydrogen and sulphuric acid, followed by the decomposition of sulphuric acid first to sulphur trioxide and steam and then further to sulphur dioxide and oxygen. The sulphuric acid decomposition stage is in common with the Sulphur Iodine cycle. It occurs at around 800°C so a high temperature heat source such as an advanced nuclear reactor is needed. Having sulphur dioxide present in the electrolyzer reduces the required electrode potential

for water splitting from a theoretical value of 1.23–0.17 V, therefore reducing the amount of energy required significantly compared to traditional electrolysis. Optimization of the flowsheet suggested that an efficiency of 47% (LHV, 55% using HHV) is possible using a decomposition temperature and pressure of around 930°C and 10 bar. Another recent flowsheet optimisation estimates the value to be 49.4% (HHV). The cost of hydrogen production of nuclear hydrogen production plant is estimated to be \$1.64/kg for a baseline case. There is much scope for further improvements in efficiency by reducing the electrode potential and investigating structural materials stable at the high temperatures involved.

The European Union Framework 7 funded HyCycleS project, which started in January 2008, will investigate high temperature materials and catalysts as well as the H₂SO₄ decomposition reactor and product separator.

The hybrid copper chloride cycle

The hybrid copper chloride cycle is being developed at Argonne National Laboratory in the USA. It has the advantage that the highest temperature step operates at only 550°C, some 300°C lower than the HyS and SI cycles. The cycle comprises three thermal reactions, in which

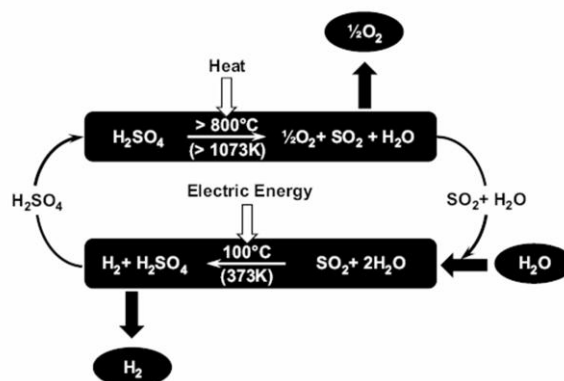


Fig. 1 – Hybrid sulfur (HyS) cycle.

Hybrid sulfur flowsheets using PEM electrolysis and a bayonet decomposition reactor

Maximilian B. Gorenssek*, William A. Summers



hydrogen, oxygen and HCl are generated, and an electrochemical step in which CuCl forms CuCl_2 and metallic Cu. The idealized efficiency is estimated to be 42% (LHV, about 49% using HHV), however, there are significant gaps in the thermodynamic knowledge and on the optimum operation of the HCl and O_2 generation reactions, and significant development work is required. Produção Nuclear de Hidrogênio

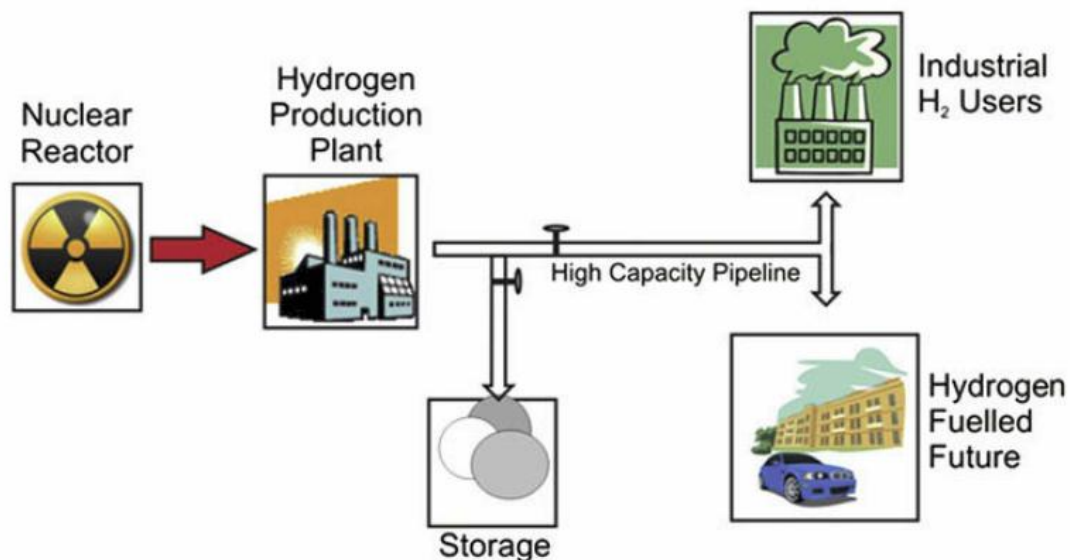


Reator HTTR (JAERI – Japão) dedicado a produção de H_2

Nuclear heat for hydrogen production: Coupling a very high/high temperature reactor to a hydrogen production plant

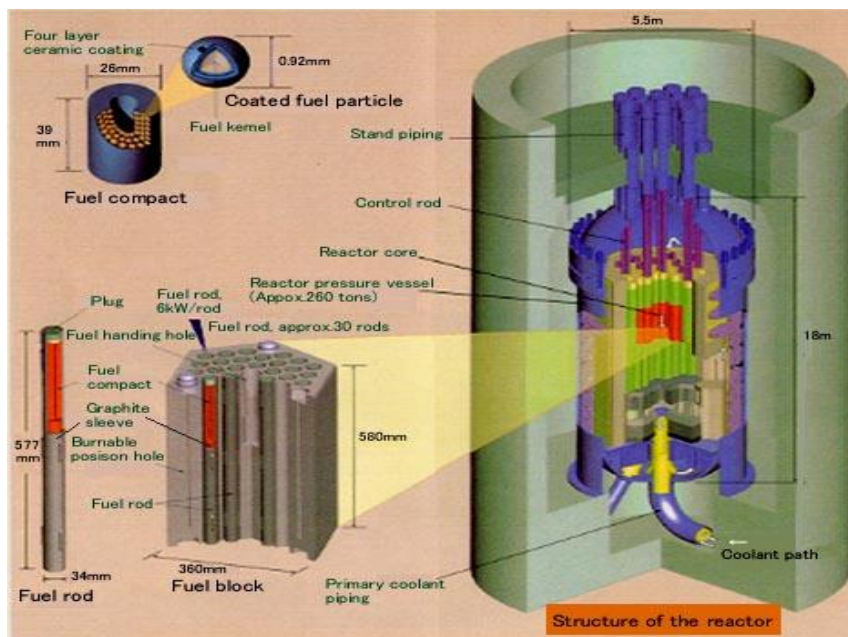
Rachael Elder*, Ray Allen

Hydrogen has been dubbed the fuel of the future. As fossil fuel reserves become depleted and greenhouse gas emissions are reduced inline with the Kyoto protocol, alternative energy sources and vectors, such as hydrogen, must be developed. Hydrogen produced from water splitting, as opposed to from hydrocarbons, has the potential to be a carbon neutral energy solution. There are several methods to extract hydrogen from water, three leading candidates being high temperature electrolysis, the SI thermochemical cycle and the HyS hybrid thermochemical cycle. All three of these processes involve a section requiring very high temperatures. The Very High Temperature Reactor (VHTR), a gas cooled Generation IV reactor, is ideally suited for providing this high temperature heat. Nuclear hydrogen production is being investigated around the world. The four leading consortiums are the Japan Atomic Energy Agency (JAEA), PBMR/Westinghouse, GA, and AREVA NP/CEA/EDF.



Schematic of nuclear hydrogen future

A nuclear hydrogen plant involves four key pieces of equipment: the VHTR, the hydrogen production plant (HPP), the intermediate heat exchanger (IHX) and the power conversion system (PCS). The choice of all four items varies dramatically between programmes. Both pebble bed and prismatic fuel block VHTRs are being developed, which can be directly or indirectly coupled to a HPP and PCS placed either in series or parallel. Either a Rankine steam cycle or a Brayton gas turbine cycle can be employed in the PCS.



Reatores Nucleares

Generation IV reactors identified for development.

Type	Reactor	Acronym	Outlet temperature (°C)
Thermal	Very high temperature reactor	VHTR	>1000
	Supercritical water reactor	SCWR	550
	Molten salt reactor	MSR	700
Fast	Gas cooled fast reactor	GFR	850
	Sodium cooled fast reactor	SFR	550
	Lead cooled fast reactor	LFR	550 up to 800

Generation IV reactors are a new generation of nuclear reactors designed to broaden the opportunities for nuclear energy. They will be inherently safer than previous generations, highly economical, proliferation resistant and will produce minimal waste. Their development is currently underway around the world and it is predicted that by 2030 the first will be in operation. In the interim, Generation III+ reactors will be built, offering improved economics over the current generation for near term deployment.

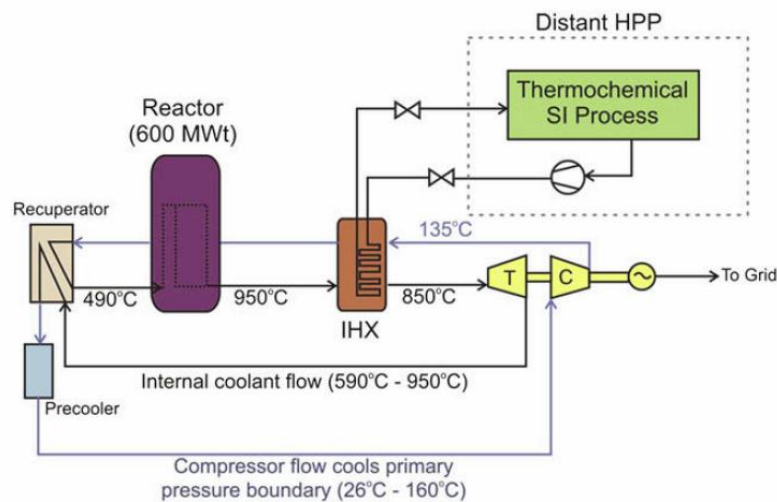


Reactor	Location	Power (MWt)	He temp. in/out (°C)	Core	Operation years
Dragon	UK	20	350/750	Cylindrical	1965–1975
Peach Bottom	USA	115	377/750	Cylindrical	1967–1974
AVR	Germany	46	270/950	Pebble bed	1968–1988
Fort St Vrain	USA	842	400/775	Hexagonal	1976–1989
THTR	Germany	750	270/750	Pebble bed	1985–1989
HTTR	Japan	30	395/950	Hexagonal	1998
HTR-10	China	10	250–300/ 700–950	Pebble bed	2000
PBMR	SA	500	350/950	Pebble bed	In development
ANTARES	France	600	400/850	Hexagonal	In development
GT-MHR	USA/Russia	550–600	490/950	Hexagonal	In development
HTR-PM	China	450	250/750	Pebble bed	In development
GTHTR300	Japan	600	589/850	Hexagonal	In development

Nuclear heat has great potential for coupling to a hydrogen production plant (HPP) utilising HTE, the HyS cycle or the SI cycle. Referring back to [Table 1](#), there are two types of nuclear technology which can achieve the high temperatures required: the VHTR and the GFR. A great deal of research is being carried out around the world on VHTRs, whereas the GFR has received less interest to date. The VHTR is a high temperature gas cooled reactor (HTGR) which operates at outlet temperatures of 750 °C and higher.

Nuclear hydrogen programmes.

Company	JAEA	GA	PBMR/Westinghouse	AREVA NP
Country	Japan	USA	SA/USA	France
Reactor	GTHTR300	MHR-GT	PBMR	ANTARES
Power	600	550–600	500	600
PCS	Brayton	Brayton	Rankine	Rankine
HPP	SI	HTE/SI	HyS/HTE	HTE/SI
Cycle configuration	Direct PCS, series indirect HPP	Direct PCS, parallel indirect HPP	Indirect, series HPP and PCS	Indirect, parallel HPP and PCS
IHX	Helical coil S&T	Single-stage PCHE	Two stage PCHE	PCS: helical coil S&T Process: PCHE or fin plate



Process scheme for the GTHR300C

Produção Centralizada ou Distribuída?

Central, semi-central, and distributed production facilities are expected to play a role in the evolution and long-term use of hydrogen as an energy carrier. The different resources and processes used to produce hydrogen may be suitable to one or more of these scales of production.

Distributed Production

Hydrogen can be produced in small units where it is needed, such as vehicle refueling stations, in a manner known as "distributed production." Distributed production may be the most viable approach for introducing hydrogen in the near term in part because the initial demand for hydrogen will be low. Two distributed hydrogen production technologies that may offer potential for development and commercialization during the transition to a hydrogen economy are 1) reforming natural gas or liquid fuels, including renewable liquids, such as ethanol and bio-oil, and 2) small-scale water electrolysis.

Centralized Production

Large central hydrogen production facilities (750,000 kg/day) that take advantage of economies of scale will be needed in the long term to meet the expected large hydrogen demand. Compared with distributed production, centralized production will require more capital investment as well as a substantial hydrogen transport and delivery infrastructure.

Semi-Central Production

Intermediate-size hydrogen production facilities (5,000–50,000 kg/day) located in close proximity (25–100 miles) to the point of use may play an important role



in the transition to a hydrogen economy and in the long-term use of hydrogen as an energy carrier. These facilities can provide not only a level of economy of scale but also minimize hydrogen transport costs and infrastructure.

DOE and others are analyzing the options and trade-offs for hydrogen production and delivery during the transition to a hydrogen economy. Options other than distributed production may also play a role. For example, large hydrogen production facilities currently exist in or near petroleum refineries because they use hydrogen in petroleum processing. It might be possible to take a small fraction of this hydrogen and transport it to nearby refueling stations during the transition. Learn more about [hydrogen delivery](#).

Armazenamento e Transporte de Hidrogênio

(CRABTREE, G.W.; DRESSELHAUS, M.S. *The Hydrogen Fuel Alternative*, MRS Bulletin – vol. 33, April 2008 – <http://www.mrs.org/bulletin> - p. 421-428)

Effective storage and delivery of hydrogen — produced from diverse sources and intended for diverse uses — are key elements of the hydrogen economy. Flexible use of hydrogen as a carrier of energy requires a means to store excess product for later use, to transport stored hydrogen from the point of production to the point of use, and to charge and discharge hydrogen conveniently from the storage container according to need. In addition to interfacing production with use, hydrogen storage provides a load-leveling mechanism for the cyclic renewable energy production from wind and solar sources.

Hydrogen as a compressed gas, even at the highest practical pressure of 10,000 psi 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 700 atm 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.

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

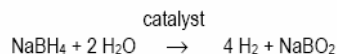
unbonded orbitals that promote reactivity with hydrogen. The second promising development for hydrogen storage materials is the growing ability of density functional theory to numerically simulate material behavior....A recent study examined 300 candidate compounds for their structures, hydrogen storage 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. Potential candidates are hydrides with light elements from the first and second rows of the periodic table, to maximize the mass percentage of hydrogen

Table I: Hydrogen Storage Capacity of Amine Borohydrides NH_nBH_n.		
Reaction	Wt % H₂	T (°C)
NH ₄ BH ₄ ⇒ NH ₃ BH ₃ + H ₂	6.1	<25
NH ₃ BH ₃ ⇒ NH ₂ BH ₂ + H ₂	6.5	<120
NH ₂ BH ₂ ⇒ NHBH + H ₂	6.9	~155
NHBH ⇒ BN + H ₂	7.3	>500

USING SODIUM BOROHYDRIDE FOR ONBOARD HYDROGEN STORAGE

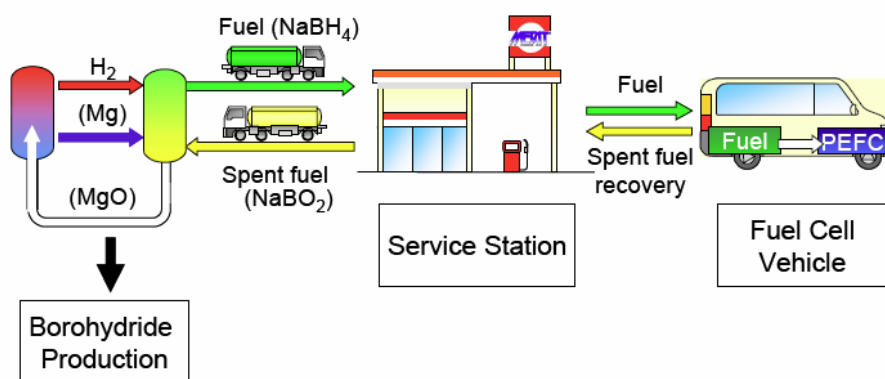
Sodium borohydride (NaBH_4) is a rich source of hydrogen being developed by Millennium Cell under the trade name "Hydrogen On Demand." The chemical reaction in which hydrogen is formed is as follows:



Sodium borohydride is derived from borax, a nontoxic compound used in laundry detergents. The hydrogen storage density of NaBH_4 is high. A 30 wt% NaBH_4 fuel (30 wt% NaBH_4 , 3 wt% NaOH , and 67 wt% H_2O) has a theoretical hydrogen content of 6.6 wt% — equal to about 66 g H_2/L , compared with 70 g H_2/L for liquid hydrogen and 23 g H_2/L for compressed hydrogen (at 5,000 psi).

The supply chain for onboard hydrogen storage and use of NaBH_4 is shown in the diagram. The NaBH_4 fuel is delivered to a service station following production. The fuel is processed onboard a vehicle by means of a catalyzed reaction with water to generate the hydrogen needed to power a fuel cell. The spent fuel (containing NaBO_2) is recovered from the vehicle and shipped from the service station to a central reprocessing facility, where it is reprocessed back to NaBH_4 . Schemes for spent fuel regeneration have been demonstrated and are believed to be feasible.

Hydrogen storage materials can be divided into those that are recharged with hydrogen onboard a vehicle and those that must be removed from the vehicle for recharging or reprocessing. Total hydrogen fuel costs — including costs for hydrogen production, transportation of hydrogen or storage materials, and reprocessing — will be among the many factors that will determine the method selected for delivering hydrogen to the fuel cell onboard a vehicle.



Ammonia

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 $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, the temperature for decomposition to MgCl_2 and NH_3 is 150°C . The ammine salt $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ 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.



Figure 3. Pellets of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, a carrier for ammonia. The pellets hold NH_3 at nearly its density in liquid ammonia, but at a vapor pressure of only 2 mbar; there is no significant release of ammonia to the environment and the pellets can be handled safely. The pellets are charged at room temperature and release ammonia above $\sim 100^\circ\text{C}$. After Reference 31.

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.

Electrolysis as a potential solution for remote areas

The hydrogen production by the combination of electrolysis, using either PEM electrolyzer or alkaline one, becomes feasible in remote areas not well covered by the grid. A suggested solution, mainly for remote areas of rain forest, would be the usage of solar energy to produce hydrogen by an electrolyzer inside a barge with solar panels and small wind turbines, floating in the rivers of the rain forest producing hydrogen during the day by solar/wind and by night using only wind. The H₂ could be pressurized and stored in tanks located bellow the barges in contact with river water. The barges could also distribute the gas to the villages in the route travel. The barge being in the middle of the rivers would avoid the shade of trees crowns and also eventual animals which would tread over the solar panels if they were on the ground. The supplied hydrogen would be employed to get power using fuel cells. In this way, this schema would be complete, extracting energy from the nature and giving the required electricity to remote areas without producing harmful impact in the nature.

In general, we could say that an area of around 100 m² of photovoltaic panel over a barge, could supply roughly around 15 kg of H₂/day by electrolyzers (either by membrane or alkaline type), consuming an average of 5-6 kWh to produce 1 Nm³ H₂. The energy contained in 15 kg of H₂ converted by fuel cell, would give around 250 kWh/day of electric energy ready to be used by any remote village (200 houses, with average consumption of 40 kWh/day). As normal barges may reach easier big dimensions such as having horizontal area of 4000m² or more, then the photovoltaic system could reach 40-50 times more energy from proportionally installed solar panels. Nevertheless, this solution could be much better depending on the new upcoming technologies promising great increase in solar energy capture. Barges could be planned as *The Science Barge* developed by Groundwork Hudson Valley in New York having small solar panels and eolic turbines using this system to produce H₂.



General view of The Science Barge



Detailed view of The Science Barge, showing the solar panels and small eolic turbines.

The Science Barge is a project of Groundwork Hudson Valley in NY (14)

Saliba-Silva et al., Water Electrolysis for Hydrogen Production in Brazilian Perspective, THE 8th LATIN-AMERICAN CONGRESS ON ELECTRICITY GENERATION AND TRANSMISSION - CLAGTEE 2009, Ubatuba, 2009