INTERNATIONAL PROGRAMS

T. Nejat Veziroglu
Clean Energy Research Institute, University of Miami, Coral Gables, FL 33124, USA

Tokio Ohta
Frontier, Information and Learning Organization, 4-8-15 Inamuragasaki, Kamakura 2480024, Japan


Contents

1. Hydrogen Production.
   1.1 Hydrogen from Fossil Fuels
   1.2 Electrolysis
   1.3 Thermochemical Methods
   1.4 Other Methods
2. Hydrogen Storage and Transport.
   2.1 Stationary Storage Systems
   2.2 Mobile Storage Systems
   2.3 Physico-Chemical Storage Systems
   2.4 Hydrogen Transport and Distribution
   3.1 Combustion Systems
   3.2 Fuel Cells
   3.3 Hydride Applications
   3.4 Other Applications
4. Transition to Hydrogen Economy.
   4.1 Demonstration Projects
   4.2 Economics
   4.3 Safety
   4.4 Standards
5. International Centre for Hydrogen Energy Technologies.
   5.1 Mission
   5.2 Linkage with Industry
   5.3 Partnerships
5.4. Pilot Projects
5.5. Demonstration Projects
5.6. Research and Educational Activities
5.7. Database Project
Glossary
Bibliography
Biographical Sketches

Summary

Since the Hydrogen Energy System or Hydrogen Economy was formally proposed at the international forum provided by The Hydrogen Economy Miami Energy (THEME) conference, March 1974, there has been growing research and development work covering all aspects of the proposed new system. In this article, the recent research and development activities will be considered. It is convenient to divide them into four sections, viz., Hydrogen Production, Hydrogen Storage and Transport, Hydrogen Utilization and Transition to Hydrogen Economy.

1. Hydrogen Production

Today, for most applications (other than for food processing), hydrogen is produced from fossil fuels, since such production yields the cheapest hydrogen. For food processing, e.g., hydrogeneration of vegetable oils, hydrogen is produced by electrolysis of water, since in such applications pure hydrogen is needed and hydrogen produced from fossil fuels is contaminated with carbon and hydrocarbons. Of course, for electrolysis of water, first electricity must be generated. In order to by-pass the electricity generation step, thermo-chemical methods of hydrogen production are being considered. Accordingly, it would be useful to divide hydrogen production into four sub-sections as follows: Hydrogen from Fossil Fuels, Electrolysis, Thermochemical Methods and Other Methods.

1.1 Hydrogen from Fossil Fuels

Since CO₂ emission is the main cause of global warming and the ensuing climate change, there is intensive research to reduce CO₂ emissions in hydrogen production from fossil fuels. E. E. Shpilrain et al. (Russia) cited four methods of hydrogen production from methane, viz., (1) steam catalytic conversion; (2) steam-oxygen catalytic conversion; (3) thermal pyrolysis by a regenerative gas heater, and (4) plasma-chemical pyrolysis. They concluded that the thermal pyrolysis method exhausted the least CO₂ to the atmosphere, while the steam catalytic method was the most efficient of the four methods.

Another important problem in fossil fuel hydrogen production is the hydrogen sulfide impurities found in some fossil fuels. A. Z. Bagautdinov et al. (Russia) has considered this problem. They found out that the plasma chemical technology permits the hydrogen to be obtained from the hydrogen sulfide with low energy consumption, particularly from the hydrogen sulfide contained in natural gas. M. Malecka-Grycz et al. (Poland) studied hydrogen generation in the water-gas shift (WGS) reaction over
sulfided catalysts. They concluded that an application of sulfided, molybdenum loaded oxides and zeolites for the WGS reaction or as a double-function catalysts (WGS+Hydrodesulfurization) would provide the efficient ways for hydrogen generation from sulfur-rich fossil fuels.

J.-i. Hayashi (Japan) studied the rapid steam reforming of volatiles from flash coal pyrolysis over simultaneously formed char as catalyst for coal gasification, including hydrogen production. Their findings indicate that (1) rapid reforming of volatiles from coal pyrolysis is indispensible for gasification with efficiencies higher than 95%, and (2) Fe species highly dispersed on char surface are formed from ion-exchanged Fe in Yallourn brown coal and are responsible for catalytic steam reforming of tar exceeding its half conversion; they also enhance the carbon conversion by promoting char gasification in a time period less than 2.4s.

N. Z. Muradov (USA) investigated CO₂ free production of hydrogen by catalytic pyrolysis (CP) of hydrocarbon fuels for transportation. It was demonstrated that the gas mixtures with hydrogen concentration in the range of 50-90 v.% and with no CO/CO₂ present could be produced from gasoline using metal and carbon catalysts at 750⁰C. The optimization of the system and use of more efficient catalysts could potentially increase hydrogen concentration in the effluent gas. Thus, the hydrogen-rich gas produced by CP process could effectively be used in ICE vehicles and in combination with all types of fuel cells.

1.2 Electrolysis

Electrolysis of water for hydrogen production has been commercialized for a long time. However, research and development work is continuing in order to bring cost down by improving the conversion efficiency and by substituting cheaper materials to replace those which are expensive. N. V. Krstajic and M. M. Jaksic (Yugoslavia) have shown that some intermetallics could replace more expensive materials in electrodes. Especially MoNi₃ was a very good one. It has exhibited the same activity as platinized Pt, Tiney-Ni, Raney-Ni, and WPT₃ (and/or HfPd₃, ZrIr₃). In addition, it has exceeded even Pt in stability and activity.

L.A. Avaca et al. (Brazil) have investigated the electrode materials for water electrolysis. In the case of high area Ni and Ni-Co coatings, it was possible to demonstrate that on an area effect is responsible for the enhanced activity observed for the hydrogen evolution reaction, and that when the proper corrections for electrochemical area are made, the activities become equivalent to that for smooth Ni electrodes. However, the energetic gain in an electrolysis cell was one of the lowest values yet reported in the literature. On the other hand, Ni-Fe alloys also presented elevated activity.

E. B. Castro and C. A. Gervasi (Argentina) studies electrodes with electrodeposited cobalt oxides for alkaline water electrolysis. They experimented with two sets of electrodes prepared by anodic deposition from Co(NO₃)₂ aqueous solutions: Electrodes (I), Co-oxides electrodepoited by potentiostatic polarization and Electrodes (II) prepared by potentiodynamic electrodeposition on Ni substrates. The O₂ evolution reaction (OER) process seemed to take place by similar mechanisms on both types of
electrodeposits. It has been shown that both types of electrodes lowered the overvoltage related to OER.

M. Yamaguchi et al. (Japan) have been working for the development of high efficiency, large electrode area (2500 cm²) electrolyser under the Japanese WE-NET Programme. Their experimental electrolyser assembly was composed of iridium dioxide, platinum black and perfluorocarbon sulfonic acid membrane. The electrolyzer registered 1.54V of cell voltage, 99.4% of current efficiency and 95.5% of energy efficiency for a current density of 1A/cm² at atmospheric pressure.

Since wind electricity has become commercially feasible in many parts of the world with moderate to strong wind velocities, some researchers have been studying electrolyser for hydrogen production using wind generated electricity. F. Menzl et al. (Germany) investigated a 20 kW windmill powered alkaline electrolyser. They conducted a series of static and dynamic experiments, which confirmed that it would be feasible to develop a stand-alone wind hydrogen generation system.

1.3 Thermochemical Methods

Thermochemical cycles or methods are being considered for hydrogen production using heat, without the intermediary energy carrier of electricity. Heat sources being considered are mainly nuclear and solar. In the case of nuclear electricity generation, conversion efficiency is about 30%. It is hoped that the conversion efficiency for hydrogen production might be higher if a thermochemical method could be developed for hydrogen production using nuclear heat. K. Yoshida et al. (Japan) have been working on such a thermochemical method named UT-3. They developed a simulation program for hydrogen production from nuclear heat. The conversion efficiency calculated was 57.4%, which is quite remarkable. It almost doubles the useful energy obtainable from a nuclear reactor. Y. Tadokoro et al. (Japan) investigated an adiabatic UT-3 thermochemical hydrogen production process for an industrial scale plant. They have conceptually designed a commercial size advanced UT-3 thermochemical hydrogen production plant in order to assess the final hydrogen production cost. The results obtained show the possibility of an adiabatic UT-3 process thermal efficiency of more than 45%. They proposed that the heat needed would come from a High Temperature Gas Reactor (HGR). The efficiency they calculated is some 10% less than the efficiency given in the first study; however, it is still about 50% above the nuclear electricity conversion efficiency obtainable nowadays.

A. Steinfeld and A. Reller (Switzerland) studied solar thermochemical production of hydrogen using metal oxide redox systems. Two-step solar thermochemical cycles for the production of hydrogen and other fluid fuels have been considered. In these cycles, the first step was based on the thermal, electrothermal or carbothermal reduction of metal oxides such as Fe₃O₄, ZnO, TiO₂, SiO₂ and Al₂O₃. As reduction products, metals such as Fe and Zn, metal nitrides such as AlN, TiN, Si₃N₄, metal carbides such as Al₄C₃, TiC, SiC or CaC₂, or lower valance metal oxides such as FeO and TiO₂ could be generated. The results were promising with respect to two features: the experimental studies conducted in the solar furnace demonstrate the technical feasibility of the
relevant processes, and – as surplus – interesting chemical commodities such as metals or metal compounds were obtained.

M. Sturzenegger et al. (Switzerland) studied a new thermochemical cycle to produce solar hydrogen using manganese oxide. The results of the efficiency and chemical assessment indicated that the proposed cycle has the potential to supply hydrogen from water as efficiently as a combination of solar electricity generation with water electrolysis. They reported a maximum exergy efficiency of 74%.

H. Romero-Paredes et al. (Mexico) have investigated a solar reactor for hydrogen production using thermochemical and hybrid cycles. They described the application of a fluidized bed solar reactor in the endothermic step of a thermoelectrochemical cycle for hydrogen production using the zinc sulphate cycle (Zinc Huam cycle). It was shown that the decomposition step in the reactors was highly feasible, and demonstrated the possibility of this kind of reaction for hydrogen production.

1.4 Other Methods

One novel method of hydrogen production is the so-called photoelectrochemical method, which combines photovoltaics and electrolysis in one cell. X. Gao et al. (USA) modified photovoltaic tandem cells, consisting of a gallium indium phosphide (GaInP2) homojunction grown epitaxially on a gallium arsenide (GaAs) homojunction with a GaAs tunnel diode interconnect with an additional top p layer of GaInP2. These cells were used as electrodes to photoelectrochemically decompose water into hydrogen and oxygen in KOH electrolyte solutions. The hydrogen reaction was catalyzed at the semiconductor surface with a photoelectrochemically deposited thin layer of platinum and ruthenium. They obtained a light-to-hydrogen conversion efficiency of 6%. R. K. Karn and O. N. Srivastava (India) developed a photoelectrode system of TiO2–VO2. The rate of hydrogen production under photoelectrolysis was found to be 6 \( \text{L} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \) for the TiO2 and 13 \( \text{L} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \) for the TiO2–VO2 photoelectrode.

S.V. Tambwekar et al. (India) tried (CdS-ZnS)-TiO2 supported systems for photocatalytic activity to produce H2 from H2S (CdS-ZnS)-TiO2(D)/MgO system gave the maximum hydrogen production rate. This catalyst could sustain the reaction for a longer duration due to the formation of thiosulfate cycle.

R. Aiello et al. (USA) investigated production of hydrogen from chemical hydrides via hydrolysis with steam. The objective of this work was to develop a method of producing H2 for use in hand-portable fuel cells eliminating the bulkiness and high pressures associated with storage tanks. They considered the hydrides of NaBH4 and LiAlH4. The rate of the hydrolysis reaction of NaBH4 was slower than that of LiAlH4. Both reactions produced nearly 100% of the theoretical yield of hydrogen as long as excess steam was added. The pH of the condensed, unreacted steam was nearly neutral, which would allow it to be recycled back to the reactor.

There has been a lot of interest in hydrogen production by bacteria, since it does not require any mechanical and/or electrical system. R. Bagai and D. Madamwar (India) studied a combination of cells of Phormidium valderianum, Halobacterium halobium
and Escherichia coli to produce hydrogen. It was found that an immobilized system was far more stable than the free cells and produced hydrogen continuously over 60 days, under on/off light (6 h) and dark (18 h) cycles. The optimal conditions for maximal production of hydrogen were standardized. A Singh et al. (India) used reverse micelles for the enhanced rate of photoproduction of hydrogen using the coupled system of Halobacterium halobium and chloroplasts organelles. The coupled system immobilized in reverse micelles formed by sodium lauryl sulfate and carbon tetrachloride yielded maximum rate of H₂ evolution. The optimum temperature for such hydrogen production was 40°C using light of 520-570 nm wavelength and 100 lux intensity.

H. Zu et al. (Japan) investigated hydrogen production from the wastewater of a tofu factory by using anoxygenic phototrophic bacterium Rhodobacter sphaeroides immobilized in agar gels. The maximum rate of hydrogen production observed from the wastewater was 2.1 l h⁻¹ m⁻² gel. The hydrogen production lasted up to 50 h. The yield of hydrogen was 1.9 ml/ml wastewater or 0.24 ml/mg carbohydrates contained in the wastewater. E. Nakada et al. (Japan) considered photosynthetic bacterial hydrogen production combined with a fuel cell. An 11 liter volume photobioreactor was directly connected to a polymer electrolyte fuel cell. Evolved gas did not contain any inhibitory gas for the fuel cell and could be directly supplied. Total volume of the evolved hydrogen gas was 140 l/m² under illumination (107 W/m²) for 100 h. The output power of the fuel cell was 1 W. The conversion efficiency of light to electricity reached 1.9%.

S. Ikeda et al. discovered that simultaneous H₂ and O₂ evolution can be achieved by just stirring the powder of a p-type semiconductor such as CuO₂, CuMO₂ (M = Al, Ge, Ga) NiO, Co₃O₄ and Fe₃O₄ in pure water at room temperatures. Frictional rubbing of the stirring rod onto the bottom of the glass vessel is needed. This method is called the mechano-catalytic water-splitting. T. Ohta has proposed the FEC-model, which is based on the frictional electricity, for this phenomenon, but the final has not been established yet.

2. Hydrogen Storage and Transport

It is convenient to divide this section into four, viz., Stationary Storage Systems, Mobile Storage Systems, Physico-Chemical Storage Systems, and Hydrogen Transport and Distribution.

2.1. Stationary Storage Systems

Seasonal energy storage is one of the important problems of energy management. Because of its high energy density, and because of its high conversion efficiency to and from electricity, hydrogen is being extensively considered for seasonal energy storage. E. Newson et al. (Switzerland) studied seasonal storage of hydrogen in stationary systems with liquid organic hydrides. They considered a methylcyclohexane-toluene-hydrogen (MTH) system, in which low cost summer electricity was used for water electrolysis to yield hydrogen for hydrogenation of toluene. Dehydrogenation in winter gave hydrogen for heat and power generation by fuel cells with an estimated overall
electrical efficiency of 41%. G.W.H. Scherer et al. (Switzerland) conducted an economic analysis of the same system. Based on numerical modeling of the individual plants, simulations of several design alternatives of the MTH system, were performed for 1000 GWh of stored summer electricity and 80MW output. The overall efficiencies $\eta_{\text{tot}}$ and the economic results of these simulations were $\eta_{\text{tot}}=0.40$ and 0.26 $$/kWh or the MtH-SOFC system alternative, $\eta_{\text{tot}}=0.33$ and 0.30 $$/kWh for the MTH-MCFC, and $\eta_{\text{tot}}=0.25$ and 0.36 $$/kWh for the MTH-system with gas and steam turbines.

S. R. Vosen and J. O. Keller (USA) investigated hybrid energy storage systems for stand-alone electric power systems. The results showed that (1) the cost of electric energy storage using a neural-net type of control system (intelligent, feed-forward control) for a hybrid battery-hydrogen storage configuration was 48% of the cost of a hydrogen-only option, and (2) a neural net-type control algorithm could result in a cost saving of storage components of 30% over a simple state of charge algorithm.

S. Fang et al. (China/Canada) considered the application of mathematical models to the calculation of selected hydrogen storage properties of AB2-type alloys. Two mathematical models have been applied to AB2-type hydrogen-absorbing alloys. The first model was for the calculation of hydride formation enthalpy and the second model allowed the calculation of P-C-T curves. The pertinent physical parameters for these intermetallic compounds and their hydrides could be estimated from THE model. From the second model, the relationship between the hysteresis factor (RT ln $P_u/P_d$) and temperature, hydrogen concentration and slope factor of the plateau region for the P-C-T curves has been obtained.

B. K. Singh et al. (India) investigated the synthesis, characterization and hydrogenation behavior of hydrogen storage material: $\text{Fe}_{0.8}\text{Zr}_{0.2}\text{Ti}_{1.3}$. The structural and microstructural characteristics of the as-synthesized hydrogen storage material $\text{Fe}_{0.8}\text{Zr}_{0.2}\text{Ti}_{1.3}$ revealed that the alloy is multiphasic. The storage capacity for this material was found to ~ 1.20 wt.% at 200°C and the desorption kinetics were found to be two times higher than the native material $\text{FeTi}_{1.3}$.

S.Y. Kim and B. H. Kang (South Korea) carried out thermal design analysis of a liquid hydrogen vessel. The analysis showed that the vapor-cooled heat stations could enhance substantially the performance of the vessel for cryogenic fluids with high $C_p/h_{fg}$ where $C_p$ is the specific heat and $H_{fg}$ the latent heat of vaporization, such as LH2 and liquid helium (LHe).
Bibliography


©Encyclopedia of Life Support Systems (EOLSS)


**Biographical Sketches**

**T. Nejat Veziroglu:** born 24 January 1924, in Istanbul, Turkey; has received A.C.G.I. Degree in Mechanical Engineering from the City and Guilds Institute of London, B.Sc. Degree in Mechanical Engineering from the University of London, D.I.C. in Advanced Studies from the Imperial College of London, and Ph.D. Degree in Heat Transfer from the University of London; has served as the Chairman of the Department of Mechanical Engineering, University of Miami (1971-75) as the Associate Dean of Engineering Research, University of Miami (1975-79), and is presently the Director of the Clean Energy Research Institute, University of Miami; has published some 300 scientific reports and papers, edited 200 volumes of proceedings, and is the Editor-in-Chief of the monthly scientific journal, the International Journal of Hydrogen Energy; and is the Founding President of the International Association for Hydrogen Energy.

**Tokio OHTA:** born 3 November 1925, in Japan; has received his education from the Department of Physics, University of Kyoto with Ph.D. degree in Solid State Physics; has taught at the University of Kyoto, Portland State University of Oregon, U.S.A., and the University of Tokyo; served as the Dean of Faculty of Engineering, Yokohama National University (1985-88), as the President of Yokohama National University (1988 - 94); has been appointed to the Superintendent of the International Network University (1999 - 2004); has been appointed as the Committee Staff of Science and Technology to the Prime Minister (1974 - 94); has been appointed as the Committee Staff of the Minister of International Trade send Industry (1794 - 99); has been conferred to the next highest order of His Majesty, the Emperor of Japan and was bestowed the Sacred Treasure Prize with silver and gold medal (April, 2001); has published some 170 papers and 60 books on the solid state physics and the energy systems; has been elected to the Vice President of International Association for Hydrogen Energy, and he is the Founding Past President of the Hydrogen Energy Systems Society of Japan.