HYDROGEN ENERGY RESEARCH PROGRAMS IN JAPAN

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Abstract--Under the "Sunshine Program" for energy development, Japan has undertaken a broad-based research program on hydrogen as a major carrier. This activity covers all the major aspects of the proposition, namely, hydrogen production, storage, transmission and usage as well as economic implications of the hydrogen energy carrier system. The work is distributed over several Government laboratories, universities and technical institutes, and industrial establishments. The progress achieved in various directions during the four year period 1974--78 is reviewed in the present article.

INTRODUCTION

WITH VERY little domestic resources of any kind of fuel material (coal, oil, natural gas and nuclear fuels), Japan is placed in the unenviable position of having to meet nearly 85 % of her fuel requirements by imports at heavy cost. Of this, oil imported mainly from the Middle East (a very sensitive area in international politics) constitutes over 80% as it is the principal energy medium used in its industrial and transportation sectors. Japan's energy-demand has grown to enormous proportions during the past 15-20 yrs, mainly because of the phenomenal growth of her industry, which in turn became necessary for sustaining her economic growth and securing a reasonable standard of living for her people. If the present trend continues, Japan's dependence on imported fuels may soar to over 430 million tons of oil-equivalent by the end of 1985. Japan is not behind other industrialized countries in recognizing the implications of depletion of the earth's fossil fuel reserves and consequent rise in their price. Indeed, the Government of Japan has reacted timely to the developing crisis of energy resources and has launched, in 1974 an ambitious program of development of alternative energy sources and energy systems to substitute for petroleum. This is the famous "Sunshine Project", which aims at the development of four major alternative energy sources, namely, solar energy, geothermal energy, coal gasification and liquefaction, and hydrogen energy. The role of hydrogen energy in the scheme is that of an energy carrier, complementary to electricity which fills, at the most, barely 20 % of the total energy consumption. The remaining 80 % is provided by fluid fuels (petroleum and natural gas). This is the general pattern of distribution in all the developed countries and it cannot be changed significantly in favour of electricity nor would it be economically desirable to do so, because in many applications the present use of petroleum cannot be switched to electricity (e.g. aircraft fueling) in the foreseeable future.

Japan's scientists share the view widely canvassed in other advanced countries that hydrogen is the most ideal candidate fuel to substitute for petroleum, as it can he produced in virtually unlimited quantities from the inexhaustible water resources of the planet by the application of almost any form of primary energy, is directly usable in the existing appliances (IC engines, gas-turbines, burners and combustors) now used with petroleum and natural gas without major modifications, and causes practically no pollution of the air when combusted, as water is practically the only product of its combustion.

The broad program of Japan's R & D activities on hydrogen energy covers all aspects of the problem, such as production-technology, storage, distribution, utilization, economics and safety considerations. These activities are liberally funded by the Government at the level of nearly 540 million *yen per annum* and are coordinated and supervised by the Agency for Industrial Science and Technology (AIST) under the Ministry of International Trade and Industry (MITI). The implementation of the component projects is entrusted to Government research laboratories as well as to private industrial establishments. In consultation with the implementing organization, AIST has drawn up

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TABLE 1. Elements of the Sunshine Project and phasing of objectives

a phased program of advancement and accomplishment on the various projects up to the end of this century. This is shown in Table 1, from which it is seen that in almost all areas it is targeted to reach an advanced state of development by 2000. The highlights of the progress made during the first three years (1974-77) are reviewed in the following sections.

PRODUCTION OF HYDROGEN

Japan's R & D programs on hydrogen production relate to the development of two main processes for the decomposition of water by the application of external energy, namely electrolysis and high temperature thermochemical reaction cycles. Both of these will utilize the heat generated in nuclear reactors, the latter directly as such and the former after conversion to direct current electricity, and will thus be potentially independent of supplies of coal, oil and other fossil fuels.

Water electrolysis will be a primary means to obtain hydrogen through utilization of the off-peak excess electric power expected to be available in the future due to enlarged difference of power demands during peak and off-periods caused by decreasing load rate as well as to cope with the difficulty in adjusting the power generation in a short period for such facilities as nuclear and superthermal power plants. However, the overall efficiency of conversion of the primary thermal energy into hydrogen by water electrolysis is limited by the poor efficiency of conversion of heat into electrical energy. Attention has therefore been directed in recent years to find ways of utilizing thermal energy directly to decompose water into its elements. Direct, single-step, pyrolysis of water is impractical as appreciable dissociation will occur only at very high temperatures exceeding 2500°C. The same net result can be achieved at much lower, but still high, temperatures (800-1000°C) attainable in High Temperature Gas-cooled (Nuclear) Reactors (HTGR), by reacting the water with chemical reagents which can be regenerated in subsequent chemical reaction steps and re-cycled. The overall efficiency of such "thermochemical water-splitting cycles" (TWSC) for the conversion of the primary thermal energy input into hydrogen combustion energy is expected to be about 50 % even after taking various operational energy losses and penalties into consideration. Furthermore, TWSC systems offer greater scope for expansion to very large scale production of hydrogen and the capital investment in an optimum cycle plant is also expected to be much less than for an advanced type of water electrolysis plant. It is no wonder, therefore, that there is intense research activity in the U.S.A., Europe (particularly West Germany and Italy) and Japan to discover the most efficient TWSC. Japanese scientists have made significant advances in this area.

Work in Japan on both electrolytic and thermochemical processes for large-scale hydrogen production is reviewed below.

WATER ELECTROLYSIS

Conventional alkaline water electrolysis

Research and development work on high temperature and high pressure alkaline water electrolysis is distributed mainly between the Government Industrial Research Institute at Osaka (GIRIO) and a consortium of public and private industrial laboratories (Showa Denko K.K., Hitachi Shipbuilding and Engineering Co. Ltd., Mitsubishi Research Institute and Yuasa Battery Co. Ltd.). The aim of the combined effort is to increase the operating current-density and energy efficiency of the Allis-Chalmers filter-press type of electrolyser, under the chosen cell conditions of 120°C and 20 kg/cm², Efforts have been directed particularly towards development and/or improvement of separator materials, electrode materials and cell construction, which will ensure long-lasting efficient perform. ance under these conditions. The group of industrial research laboratories mentioned above is committed to develop by 1980 a highly efficient and compact filter-press type of water electrolyser with a production capacity of 20 $Nm³$ and operating at 120°C and 20 kg/cm².

GIRIO and Yuasa Battery Co. have found that PTFE membranes impregnated with potassium titanate, prepared by hydrothermal treatment of $TiO₂$ -impregnated-PTFE membranes in KOH solution to be very durable and satisfactory as cell-diaphragm material. It is claimed that the diaphragm thus produced has a large pore-size $(1-2)\mu$ and lower electrical resistance than DuPont's Fybex, which is PTFE directly impregnated with potassium titanate.

In regard to electrode materials, Showa Denko has developed a Raney nickel catalyst electrode

which operates efficiently at very low cell voltages, e.g. 1.6 V at 20 A/cm² and 70°C, while Mitsubishi favours 17 -mesh nickel plated wire-mesh for "best results". GIRIO is experimenting with some new metal alloys and surface treatments of electrodes, the details of which are not disclosed.

The electrical resistance due to gas bubbles in the electrolyte is often relatively large in high current density operation. This aspect is under detailed study in the development of improved porous nickel electrodes and cell design at the GIRIO and Mitsubishi laboratories.

The Hitachi group has developed a computer program for analysing the dynamic characteristics of the water electrolyser. By dividing the electrolysis plant into its component units, namely, the electrolysis cell, liquid-gas separator, connecting pipes, heat exchanger and piping, the computer program was so arranged that the dynamic characteristics of each component unit could be obtained. The computer program has provided very useful for the optimization of plant design and safety characteristics.

Solid polymer electrolyte electrolysis

The use of perfluorosulphonic acid membrane (Nation, Dupont) as an acidic electrolyte both for hydrogen-oxygen fuel cell and, in the reverse mode, for water electrolyser is largely a development of General Electric of the U.S.A. Although high coulombic efficiencies ($\sim 85\%$ at 100°C) are achieved by using this solid polymer electrolyte, commercialization of SPE for large scale operation is hampered by the necessity to use noble metals (Pt, Ir) as electrocatalysts, because of the high acidic character of the wet electrolyte. The use of thin films of these metals, directly coated on the two sides of the membrane, is the usual expedient adopted to reduce the cost. The Japanese contribution to this effort is the special plating method at GIRIO, by the use of which the noble metal loading can be reduced to under 1 mg/cm². Typically, a GIRIO $[Pt/Nafion, H, O l]qd./Pt-Ir]$ electrolysis cell at 100 $^{\circ}$ C operated at about 1.7 V for a current density of 200 mA/cm². Though the high first cost of SPE cell may be an inhibiting factor to its being developed for large scale operation in the immediate future, it is an ideal outfit for small homesteads for storage of electrical output from windmills, solar photocells and the like. It has the great advantage of being readily reversible to operate as an efficient fuel cell, generating electricity on the intake of hydrogen and oxygen produced by it in the electrolysis mode.

THERMOCHEMICAL PROCESSES

A number of thermochemical reaction cycles for hydrogen production are under study and evaluation of commercial feasibility at the Government Industrial Research Institute, Osaka, (GIRIO) and several industrial research establishments in Japan, with Government fund-support. The status of these studies is reviewed below:

GIRIO is investigating a new iron-bromide cycle:

$$
3\text{FeBr}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{ HBr} + \text{H}_2
$$
 (1)

$$
\text{Fe}_3\text{O}_4 + 8\,\text{HBr} \rightarrow 3\,\text{FeBr}_2 + 4\,\text{H}_2\text{O} + \text{Br}_2 \tag{2}
$$

$$
H_2O + Br_2 \rightarrow 2 HBr + \frac{1}{2} O_2,\tag{3}
$$

which is claimed to have less technical problems than the analogous iron-chlorine cycle, and the following ammonia-iodine cycles:

(a) Copper-ammonia-iodine cycle:

$$
2\text{CuI} + 2\text{NH}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO} + 2\text{NH}_4\text{I}
$$
 (1)

$$
2CuO + I2 \rightarrow 2CuI + O2
$$
 (2)

$$
2NH_4I \rightarrow 2NH_3 + I_2 + H_2. \tag{3}
$$

(b) Barium-ammonia-iodine cycle:

$$
\text{BaI}_2 + 2NH_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{BaCO}_3 + 2NH_4\text{I}
$$
 (1)

$$
\text{BaCO}_3 + \text{I}_2 \rightarrow \text{BaI}_2 + \text{CO}_2 + \frac{1}{2}\text{O}_2 \tag{2}
$$

$$
2NH_4I \rightarrow 2NH_3 + I_2 + H_2. \tag{3}
$$

(c) Arsenic-ammonia-iodine cycle:

$$
As_2O_3 + 2I_2 + 6NH_3 + 5H_2O \rightarrow 2(NH_4)H_2AsO_4 + 4NH_4I
$$
 (1)

$$
2(NH_4)H_2AsO_4 \to As_2O_3 + 2NH_3 + O_2 + 3H_2O
$$
 (2)

$$
4NH4I \rightarrow 4NH3 + 2I2 + 2H2.
$$
 (3)

The common and key reaction of these cycles is the decomposition of ammonium iodide, which proceeds by a two-step mechanism:

$$
2NH_4I \rightarrow 2NH_3 + 2HI
$$

$$
2\mathbf{H}\mathbf{I} \rightarrow \mathbf{H}_2 + \mathbf{I}_2.
$$

The second step is rate-limiting. 13-25% decomposition of NH₄I to NH₃, H₂ and I₂ has been reported in the temperature range 600-900°C. At higher temperatures, undesirable decomposition of ammonia also occurs. The decomposition of NH_AI occurs in a more facile manner in the presence of nickel thus:

$$
2NH_4I + Ni \rightarrow 2NH_3 + H_2 + Nil_2
$$

$$
Nil_2 \rightarrow Ni + I_2.
$$

These two reactions proceed easily at 430 and 700°C, respectively, and the decomposition of ammonium iodide is pushed to 80 % without undesirable side-reactions. The most attractive feature of these cycles is their requirement of relatively moderate temperatures, which cam be attained in solar furnaces and conventional nuclear reactors. However, unsolved technical problems exist in each of the above cycles, such as the relative slowness of the second reaction and separation of reaction products in the copper-ammonia-iodine cycle, undesirable side-reactions accompanying the second step of the barium-ammonia-iodine cycle, and loss of some ammonia in the second step of the arsenic-ammonia-iodine cycle. Unless these problems are solved, the construction of a complete closed cycle with any of the cycles will not be possible.

The National Chemical Laboratory for Industry (NCLI) in Tokyo, has investigated an iodine system cycle and a sulphur cycle with results as summarized below:

The iodine based cycle consists of the following reaction steps:

$$
6CaO + 6I_2 \frac{100 \text{ °C}}{\text{in aq. solution}} Ca(IO_3)_2 + 5CaI_2(aq.) \tag{1}
$$

$$
Ca(IO3)2 \xrightarrow{500-800°C} CaO + I2 + 221O2
$$
 (2)

$$
\sim 5CaI_7 + 5H_7O \xrightarrow{500-700\degree C} 5CaO + 10HI
$$
 (3)

$$
10\,\text{H I} \xrightarrow{300-700\,^{\circ}\text{C}} 5\,\text{H},\,+\,5\,\text{I},\tag{4}
$$

In (1), CaI₂ solution (50–60 wt %) is obtained along with a solid precipitate of Ca(IO₃), by addition of excess iodine. In (2), Ca(IO₃)₂ produces Ca₅(IO₆)₂ at 550°C, but decomposes to give O₂, I₂ and CuO at 800°C. Although (3) is expected to be difficult because of the large positive value of the free energy change (19 kcal at 727 \degree C), CaI, powder can actually be hydrolysed fairly fast in a stream of nitrogen containing water vapour at 300-700°C. Further, this reaction can be promoted by the addition of CaCl₂ to the system. The decomposition of HI (4) occurs to the extent of 28 % at 650°C; which corresponds to thermodynamic equilibrium condition at this temperature.

An overall thermal efficiency of $22-34\%$ at $70-80\%$ heat recovery is claimed for this cycle on the basis of process flow-sheet analysis.

In a later modification of the above cycle, MgO is substituted for CaO. The advantages claimed in favour of MgO are lower temperature requirements for (2) and (3) and faster reaction rates.

The sulphur-cycle, studied by NCLI, which is very similar to the Westinghouse hybrid cycle; comprises the following reaction steps:

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$$
3SO_2 + 2H_2O \xrightarrow{150^{\circ}C} 2H_2SO_4 + S
$$

$$
3S + 2H_2O \xrightarrow{450\degree C} 2H_2S + SO_2
$$

$$
2H_2S \xrightarrow{750^{\circ}C} 2H_2 + 2S
$$

$$
2H_2SO_4 \xrightarrow{850^{\circ}C} 2H_2O + 2SO_2 + O_2
$$

$$
SO_2 + 2H_2O + I_2 \xrightarrow{\text{Electrolysis}} H_2SO_4 + 2HI
$$

$$
2\text{H1} \xrightarrow{25^\circ \text{C}} \text{H}_2 + \text{I}_2
$$

$$
H_2SO_4 \xrightarrow{.850\degree C} H_2O + SO_2 + \frac{1}{2}O_2.
$$

For A(3), MoS₂ and WS₂ supported on alumina were examined for their catalytic activity and stability in the temperature range 600-800°C and were found to be stable up to 750°C. A Vycor glass membrane was used successfully for the separation of H_2 from H_2S in the same step. For the decomposition of H₂SO₄, ferric oxide (Fe₂O₃) was found to be the most promising catalyst. The electrolysis call for the reaction B(1) was divided by a cation exchange membrane to separate the $H₂SO₄$ produced at the anode and the HI produced at the cathode. The performance characteristics of the cell are now under study.

Feasibility studies of thermochemical cycles has been one of the most active areas of the hydrogen energy research in Japan. Hitachi scientists are engaged in detailed feasibility studies on several new thermochemical water-splitting cycles grouped under Cu-Cl and $\text{Na}_2\text{CO}_3\text{-}1_2$ systems. Typical new cycles in these two groups are as follows:

(a) *Cu-Cl family*

$$
2Cu + 2NH4Cl-400-600°C 2CuCl + 2NH3 + H2
$$
 (1)

$$
2CuCl + 2NH3 + H2O \xrightarrow{50-80°C} Cu2O + 2NH4Cl
$$
 (2)

$$
2Cu_2O + 2H_2SO_4 \xrightarrow{50-100\degree C} 2Cu + 2CuSO_4 + 2H_2O
$$
 (3)

$$
2CuSO4 \xrightarrow{750-850^{\circ}C} 2CuO + 2SO3
$$
\n(4)

$$
2CuO \xrightarrow{850-950^{\circ}C} Cu_2O + \frac{1}{2}O,
$$
 (5)

$$
2SO_3 + 2H_2O \xrightarrow{120-300\degree C} 2H_2SO_4. \tag{6}
$$

(b) $\text{Na}_2\text{CO}_3\text{-}1_2$ *family* Basic cycle (typical):

$$
2NHAI \xrightarrow{400-500\degree C} 2NH3 + I2 + H3
$$
 (1)

$$
2\text{NaI} + 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{25\text{°C}} \text{Na}_2\text{CO}_3 + 2\text{NH}_4\text{I}
$$
 (2)

$$
Na_2CO_3 + I_2 \xrightarrow{600-700\degree C} 2NaI + CO + \frac{1}{2}O_2. \tag{3}
$$

Modified cycle:

$$
2\text{NaI} + 2\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} \xrightarrow{400-460\degree\text{C}} 2\text{NaHCO}_3 + 2\text{NH}_4\text{I}
$$
 (1')

$$
2NaHCO3 \xrightarrow{200-300\degree C} Na2CO3 + CO2 + H2O
$$
 (2)

$$
2NH_4I + Ni \frac{400-500\degree C}{4} NiI_2 + 2NH_3 + H_2
$$
 (3')

$$
\text{Nil}_2 \xrightarrow{700-800\degree\text{C}} \text{Ni} + \text{I}_2. \tag{4}
$$

Reaction (1) of the basic cycle is conducted through the intermediary of Ni as in $(3')$ and $(4')$, (2) is conducted in two steps with intermediate formation of NaHCO₃, as in (1') and (2') of the modified cycle.

The yields of each unit reaction of the cycles were determined experimentally and it was found that all the reactions could proceed without much difficulty. Especially, the reactions of the modified $Na₂CO₃-I₂$ cycle proceed most easily.

The overall thermal efficiencies of these cycles were estimated on the basis of enthalpy changes of the individual reactions, energies consumed for separation of products from reactants and energy conserved through recovery of waste heat. The thermal efficiency of the $Na₂CO₃-I₂$ cycle is highest among these cycles with an expectation of $\geq 30\%$ thermal efficiency in practical plants. The individual reactions of this cycle are therefore being studied in detail in order to arrive at the optimum reaction conditions.

Turning to work in University research laboratories in this area, Professor Yoshida of the University of Tokyo has experimented with the following cycle, designated UT-2:

$$
CaBr2(s) + H2O(g) \xrightarrow{700-750\degree C} CaO(s) + 2HBr(g)
$$
 (1)

$$
\text{CaO(s)} + \text{Br}_2(g) \xrightarrow{450-500\degree C} \text{CaBr}_2(s) + \frac{1}{2}\text{O}_2(g) \tag{2}
$$

$$
\text{Fe}_3\text{O}_4(\text{s}) + 8\text{HBr}(\text{g}) \xrightarrow{120-140\degree\text{C}} \text{FeBr}_3(\text{s}) + 2\text{FeBr}_3(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \tag{3}
$$

$$
2\mathrm{FeBr}_3(s) \xrightarrow{200-300\degree C} 2\mathrm{FeBr}_3(s) + \mathrm{Br}_2(g) \tag{4}
$$

$$
3FeBr_2(s) + 4H_2O(g) \xrightarrow{550-650^{\circ}C} Fe_3O_4(s) + 6HBr(g) + H_2(g),
$$
 (5)

and also a modified version of this cycle, in which (3) and (4) are combined into a single reaction thus:

Fe₃O₄(s) + 8HBr(g)
$$
\xrightarrow{200-300\degree C}
$$
 3FeBr₂(s) + 4H₂O(g) + Br₂.

Experimentally, the process is carried out in two fixed bed reactors, one initially charged with $CaBr₂$ and other initially charged with FeBr₂, and subjected separately to the series (1) and (2) and (3), (4) and (5). An overall thermal efficiency of nearly 37% is claimed for this process, based on flow-sheet analysis.

Professor T. Ohta and his group at the Yokohama National University have been investigating the following cycle (designated as Yokohama Mark 5/Mark 6):

$$
2FeSO_4 + I_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2HI
$$
 (1)

$$
2\mathbf{H}\mathbf{I} = \mathbf{H}_2 + \mathbf{I}_2 \tag{2}
$$

$$
Fe_2(SO_4)_3 + H_2O = 2FeSO_4 + H_2SO_4 + \frac{1}{2}O_2,
$$
 (3)

where (1) is photochemical, (2) is electrochemical in Mark 5 and thermochemical in Mark 6, and (3) is electrochemical. As the electricity required in the electrochemical processes (2) and (3) , reactantcirculation, heliostating and other mechanical operations is also obtained by employing a solar thermoelectric device, this schedule envisages total utilization of radiant solar energy. One of the main problem areas in this scheme is the separation of H_2 from undissociated HI in (2). This is being attempted by employing thermal diffusion columns. The conditions of separation are being studied.

Computer simulation of thermochemical cycles. Mitsubishi Heavy Industries Ltd. has undertaken the development of interactive computer simulation systems to assist in the evaluation of the feasibilities of various thermochemical cycles by computing the mass and heat balance, process thermal efficiency and other important conceptual characteristics of the processes. In carrying out the ealcula, tions, the information on the construction of the process and the operating conditions of unit opera $+$ tions are used as input data, and mass and heat balance, recycling rate of materials and process thermal efficiency are obtained as output data. The simulator enables trial calculations to he made of complicated chemical processes involving multi-stage reaction sequences. The greatest feature of this system is that it adopts an interactive system employing a character display device and a plotting device to draw the process flow diagrams automatically from the results of computation.

The simulation technique was applied to the iron-chlorine cycle and the following modified (iron--copper-chlorine) cycle was evolved as more advantageous than the basic cycle in respect of operation and overall thermal efficiency:

$$
3FeCl2 + 4H2O - 600°C, Fe3O4 + 6HCl + H2
$$
 (1)

$$
Fe3O4 + 8HCl + aq. \xrightarrow{100\degree C} 2FeCl3 + FeCl2 + 4H2O + aq.
$$
 (2)

$$
2\text{FeCl}_3 + 2\text{CuCl} + \text{aq.} \xrightarrow{100\degree\text{C}} 2\text{FeCl}_2 + 2\text{CuCl}_2 + \text{aq.} \tag{3}
$$

$$
2CuCl \xrightarrow{550\degree C} 2CuCl + Cl_2 \tag{4}
$$

$$
H_2O(g) + Cl_2(g) \xrightarrow{800\degree C} 2HCl(g) + \frac{1}{2}O_2.
$$
 (5)

Mitsubishi scientists have determined and experimentally verified the optimum operating conditions for each of the above reactions and arrived at a workable process flow-sheet. A thermal efficiency of 32% is indicated for a molar ratio of 2:1 for $H₂O$: Cl, for the reverse Deacon reaction (5).

NEW INNOVATIVE METHODS FOR HYDROGEN PRODUCTION

Direct thermal decomposition of water

The Electrotechnical Laboratory, Tokyo, has revived interest in the direct thermal decomposition of water at temperatures exceeding 2000 K proposed to be provided by solar energy concentrators (heliostat-paraboloid reflector systems). The innovation introduced to shift the reaction equilibrium continuously towards decomposition is the use of a diaphragm, selectively permeable to hydrogen and oxygen, to separate these products continually from the water vapour mixture. The feasibility of achieving a reasonable rate of decomposition by this method is being examined in the laboratory, using a 13 KW Xenon arc-image furnace, which can have a radiation flux of 1.5 kW/cm², and a number of refractory metals and ceramics are being tested for use as separation membrane.

Photo-electrolysis of water with semiconductor electrodes

The discovery by Fujishima and Honda of Tokyo University in 1969/70 that a crystal of n-type (TiO2) placed in aqueous electrolyte and illuminated with ultra-violet light could cause decomposition of water through the agency of the photo-generated holes and electrons has aroused worldwide interest to develop this principle into a viable means of utilizing solar energy for the production of hydrogen from water. Apart from the research continued in Professor Honda's laboratory to find electrode materials which can exhibit photoelectrolytic activity under visible light illumination, work on similar lines is also being pursued at the research laboratories of Sanyo Electric Co. Ltd, Osaka, and in the electrochemical research laboratories of the Osaka University. The main problem area in the development of a practical solar photoelectrolytic device to produce hydrogen from water is to find photoanode materials which are photoactive in the visible region and are at the same time chemically stable (resist photoanode corrosion) in the electrolyte. The Sanyo group has fabricated an experimental *n*-TiO₂/p-GaP cell for which an energy conversion efficiency of 1.5% has been reckoned for hydrogen production.

STORAGE AND TRANSPORTATION OF HYDROGEN

Under the Sunshine Project, work on this aspect is concentrated mainly on the study of selected metal hydrides which afford a convenient means of reversible hydrogen storage, suitable for stationary and mobile applications.

While the National Chemical Laboratory for Industry at Tokyo is investigating the hydrideforming characteristics of magnesium-nickel and zirconium-manganese alloys, the Government

Industrial Research Institute at Osaka is engaged in similar studies on titanium-based alloys (TiFe and TiCo) and the inter-metallic compounds of unseparated rare earth metals (Misch-metal) with nickel.

The maximum hydrogen content of the Zr-Mn hydride corresponds to the formula $ZrMn_2H_{3,3}$ (i.e. about 1.6 wt $\frac{6}{2}$). It has a dissociation pressure of 1 atmosphere at around 150°C and partial molar enthalpy of $8-10$ kcal/mol H₂.

Compared with the more widely used Ti-Fe alloy, the TiCo is more easily "activated" to absorb hydrogen and is less sensitive to impurities in hydrogen, but the latter has a lower dissociation pressure and requires a higher temperature for de-hydriding. The dissociation pressure of TiCo can be increased by the addition of small quantities of a third metal, Fe or Mn, to form the ternary alloys TiCo_{1 - x}Fe_x and TiCo_{1 - x}Mn_x (x = 0.05-0.5).

"Mischmetal" (Mm) is the mixture of metals obtained directly from the rare-earth and is considerably cheaper than the individual pure rare-earth metals (e.g. Lanthanum, La). The alloy $MmNi₅$ forms a hydride MmNi_sH₆ with almost the same hydrogen content (1.4 wt %) as LaNi_sH₆, but the former has too high a dissociation pressure, about 28 atm at 20°C compared with 4 atm for the later. This disadvantage of the $MmNi₃$ alloy could be rectified by partial replacement of Ni by Co. The most suitable composition, MmNi_{2.5}Co_{2.5}, forms a hydride with 1.2 wt% H₂, dissociation pressure of 7 atm at 20 $^{\circ}$ C and heat of formation of 8.4 kcal/mol H₂.

UTILIZATION OF HYDROGEN FOR ENERGY-PRODUCTION

Fuel cells

GIRIO and Electrotechnical Laboratory, Tokyo, are both engaged in research on the fabrication of hydrogen fuel cells based on ion-conducting solid electrolytes. While GIRIO is experimenting with phosphotungstic acid, H₃(PW₁₂O₄₀) 29H₂O, possessing a specific conductivity of 6 x 10⁻² mho cm⁻¹ at room temperature as a very promising solid electrolyte, Electro-Technical Laboratory (ETL) is working on zirconia-based solid electrolyte fuel cells which will operate in the temperature range 600-800°C. The later work has advanced to the stage of developing the technology for the production of zirconia fuel cells and fuel-cell stacks. ETL has successfully deployed mathematical modeling and simulation techniques to optimize the performance of individual fuel cells, fuel-cell stacks and power plants. An experimental stack of zirconia cells fabricated by ETL generates 4.4 W electrical power, 4.78 V of open circuit terminal voltage, and 4.24 A of short circuited currents under working conditions.

The economics and commercial viability of fuel cells plants for large scale centralised, distributed and mobile power generation systems are being actively studied by the Japan Electrical Manufacturers' Association.

HYDROGEN AS AUTOMOBILE ENGINE FUEL

The main thrust of research effort in this area in Japan is provided by Professor Furuhama and his group at the Musashi Institute of Technology. To them goes the credit of having adventurously participated in a 2800 km auto-rally along the west coast of U.S.A. in August 1975 with a regular passenger car (Datsun, 1.4 l) fueled with hydrogen from a liquid hydrogen container. That was a bold venture on a foreign soil, considering the fact that it was largely a students' effort and the car entered the rally without sufficient field trials. Even so, the results with regard to engine performance, fuel economy and exhaust emission were quite satisfactory. This initial success appears to have encouraged Professor Furuhama and his school to expand and diversify their research in the broad area of hydrogen fueling of spark ignited internal combustion engines. Their present efforts are in the direction of developing an appropriate design of IC engine to accomodate the ignition characteristics of hydrogen. This appears to be more meaningful than trying to modify existing gasoline fueled auto-engines to run on hydrogen, because the ignition characteristics of the two fuels are so very different.

Japan Automobile Research Institute Inc. is engaged in a techno-economic evaluation study of the merits of hydrogen-fueling of automobile engine and of the problems associated with this proposition, such as on-board storage, fuel-injection alternatives, gasoline-hydrogen mixing as a transitional measure etc. No results of this study are yet available.

The Japan Society of Industrial Machinery Manufacturers has conducted studies on hydrogenpowered gas turbine engines, using what is described as a regenerative combination of the Rankine and Aphodid cycles. The study, which includes the use of hydrogen in MHD power generators, confirms the feasibility and technical merits of hydrogen gas turbine power plants.

The Society of Aerospace Companies Inc. has conducted'some preliminary studies on conceptual design of hydrogen-fueled airplanes with respect to performance, economy, configuration, fuel tank, fuel system and engines and have proposed $\mathbb{R} \& \mathbb{D}$ programs for the practical realization of hydrogenfueled commercial aircraft.

HYDROGEN BURNERS

The Government Industrial Research Institute at Osaka has made a comparative study of the combustion characteristics of hydrogen and conventional liquid and gaseous fuels, particularly with respect to NO_z emission, flash-back and safety-hazards and burner-design for hydrogen combustion. The study has revealed that NO_z levels in $H₂$ -combustion could be drastically reduced by premixing the hydrogen with air; the luminosity of \hat{H}_2 flames could be markedly increased by addition of C_2-C_4 hydrocarbons; and hydrogen could be advantageously mixed with petroleum oils in industrial oil-burners with suitable modification of the burners and the fuel feed technique.

GIRIO is also studying various arrangements and catalysts for the tlameless catalytic combustion of hydrogen which will have useful application in space heating systems and domestic cooking ranges.

CONCLUSION

The foregoing review provides an indication of the broad spread of research activities undertaken in Japan for the evolution of a national hydrogen energy system. The emphasis, naturally, is on the development of commercially viable, economical methods of production of hydrogen on a very large scale, without the use of fossil fuels. Government research laboratories, universities, technical institutions and the research wings of major industrial establishments of Japan are active partners in this gigantic national effort. While most of the research schemes are sponsored and funded by the Ministry of International Trade and Industry under the "Sunshine Program", substantial financial assistance for the work undertaken in universities and technical institutions is provided by the Ministry of Education. Many of these schemes are expected to climax or enter a decisive phase in 1980, the year in which Japan will host the Third World Hydrogen Energy Conference.

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