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INDIA'S HYDROGEN ENERGY PROGRAM—A STATUS REPORT

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Abstract—Hydrogen energy research in India started in 1976 on the initiative of the Government of India and covers almost all areas of technical relevance to the deployment of hydrogen as an energy vector. Specifically, these include its production from water by electrolysis, photoelectrolysis, photo-catalysis and biophotolysis, its storage as liquid hydrogen and metal hydrides, its consumptive use as engine fuel and thermal fuel and nonconsumptive application in metal hydrides-based chemical heat pumps. All this research is sponsored and supported by the Government of India. The genesis of hydrogen energy research in India and its growth during the first 10 years have already been reviewed at the VI-WHEC (Vienna, 1986). The present review is an update of the previous report

HISTORICAL BACKGROUND

India's interest in the use of hydrogen as an energy vector started in 1976 as part of the strategy to meet the challenges of the oil crisis which posed a serious threat to the country's development plans. The deliberations of the First World Hydrogen Conference held in Miami in 1976 reached the ears of the Indian planners through diplomatic channels. Convinced of the merits of hydrogen as a fuel, the Government of India set up a special Task Force in July 1976, under the Department of Science and Technology (DST), to initiate an action plan for the development and phased implementation of hydrogen energy programs in the country. This author had the unique privilege and honour to head this Task Force as its Chairman. A number of research projects on hydrogen energy were sponsored by the DST in universities, higher technical institutes and national research laboratories. These included hydrogen production through a variety of processes, storage through metal hydrides and usage as IC engine fuel.

Hydrogen energy received a fresh boost in 1983 when it found a place in the DST's documentation of 'Thrust Areas in Engineering Sciences' [1], identified by an expert panel of specialist engineers and scientists. The citation, reproduced in Fig. 1, recognizes 'hydrogen as a fuel of great potential and likely to be the only source of energy available to man in years to come'.

Subsequently, when the Department of Non-conventional Energy Sources (DNES) was established under the Ministry of Energy, hydrogen energy came under the purview of this department. Soon, a Technical Advisory Committee on Hydrogen Energy (TACHE) was constituted, with this author as its first Chairman for a year. At its first meeting held in December 1983, a concrete plan of hydrogen energy-related research and development programs was drawn up, in specific terms for the first time, for phased implementation during the 15-year period 1985–2000. This meeting constituted an important milestone in the organization of hydrogen energy R and D efforts in India as it laid the foundation for a coordinated and systematic approach to attain specified technical goals within specified time frames. The salient points and main recommendations have been summarized by Hinds [2]. The overall action plan, estimated to cost $70 million, was divided into three phases:

(1) Development of new processes and new techniques and processes through research.

(2) Utilization of current on-hand technologies for semi-commercial scale production.

(3) Commercialization of matured technologies and evolution of market penetration technologies for optimal benefit.

An important recommendation of the committee was that hydrogen energy research should be 'institutionalized' through the establishment of a *Hydrogen Energy Centre* dedicated exclusively to the invention and development of hydrogen energy technologies suited to this country.

The development plans and the advances made in various sponsored research projects on hydrogen energy were reviewed and discussed at a three-day National Workshop on Hydrogen Energy, held under the auspices of DNES at IIT, Delhi, in July 1985. It was attended by scientists, engineers and technologists invited from all parts of the country. The deliberations of the Workshop covered a wide range of hydrogen energy topics including production, storage, transportation, combustion and utilization. The highlights of the Workshop were: (1) the frank and forthright admission by the head of the DNES (who inaugurated the proceedings) of the widening gap between the country's oil resource and demand in spite of intensified exploration exercises and fresh finds of off-shore wells and his assurance of the Indian Government's commitment to support hydrogen energy research and (2) the recommendations of the

THRUST AREAS

IN

ENGINEERING SCIENCES

The working group was of the considered opinion that hydrogen as a fuel has great potential and indeed it is likely to be the only source of energy available to man in years to come. Consequently, the group felt that considerable research and development activities be immediately generated in the area of hydrogen generation, hydrogen storage and hydrogen utilization. Among these, the first priority be given to develop techniques for efficient and cheap generation of hydrogen. The present approaches for generation of hydrogen are :

Electrolysis of water.

Interception of the process of photosynthesis.

Photoelectrolysis of water using semiconductor electrolyte.

The working group recommends that all the three approaches be pursued.

Government of India

Department of Science & Technology

New Delhi- 110016

December 1983

Fig. 1. Hydrogen energy—a "thrust area" in engineering sciences [1].

panel of experts for intensified research and development efforts in almost all areas of hydrogen energy technology. The need to educate the public on the manifold merits of hydrogen as a universal clean fuel was also emphasized. A brief report on the Workshop and the texts of the lectures given have been published [3, 4].

The next major exercise in reviewing the progress in hydrogen energy research in India was the two-day National Workshop and Review Meeting on Hydrogen Energy held at the Banaras Hindu University, Varanasi, at the end of January 1988, again under the auspices of the DNES. It was mostly a repetition of the 1985 Delhi Workshop with not much additional progress to show as Government fund support for hydrogen research had weakened considerably during the past three years because of a major shift of priorities to short term projects of direct and immediate relevance to the country's needs.

DETAILS OF R&D PROGRAMS

India's contribution to hydrogen energy research during the past 12 years comprises a large number of Government-sponsored projects in the areas of hydrogen production from water, storage through liquefaction and metal hydride formation and utilization as fuel in internal combustion engines. These have already been reviewed [5]. The titles indicating the aims of the research programs and the names of the implementing institutions are listed below.

A. Hydrogen production

1. *Water-electrolysis:* design, development and fabrication of advanced bipolar type of industrial size electrolysis plant (Bhabha Atomic Research Centre, Bombay).

2. *Photoelectrochemical cells:* quest for stable, high efficiency semiconductor anode materials (Indian Institute of Technology, Madras; Banaras Hindu University, Varanasi; University of Madras, Madras).

3. *Photo-biological processes* with selective water-splitting micro-organisms (Bose Institute, Calcutta; Banaras Hindu University, Varanasi).

B. Hydrogen storage

1. (a) *Liquefaction* advanced techniques (Indian Space Research Organization, ISRO, Trivandrum; National Physical Laboratory, New Delhi; Indian Institute of Technology, Kharagpur).

   (b) *LH_2 storage and transportation* (ISRO, Trivandrum).

2. *Metal hydrides* (Indian Institute of Technology, Madras and Kanpur; Banaras Hindu University, Varanasi).

C. Utilization

1. (a) *As IC engine fuel* (I.I.T. Madras and Delhi, BHU, Varanasi).

   (b) *Flame combustion* burners for domestic and industrial applications (I.I.T. Delhi).

SOME HIGHLIGHTS OF HYDROGEN ENERGY RESEARCH IN INDIA

The highlights of the work carried out in India on some of the topics listed above, i.e. those in which significant contributions have been reported, are presented in the following sections.

HYDROGEN PRODUCTION

Photoelectrochemical decomposition of water

The well known work of Fujishima and Honda on the photoelectrolytic production of hydrogen from water, first reported in 1969 [6], stimulated world-wide interest as it held out interesting prospects of converting solar energy directly into chemical fuels. It is well-known that the successful application of this technique for hydrogen production depends critically on finding suitable semiconductor electrode materials (especially for the anode) which will combine the electronic characteristics necessary for high photoconversion efficiency with long term material stability.

In India, research in this area was initiated by this author at the Indian Institute of Technology, Madras, in 1976. Using a simple liquid-junction Schottky-barrier cell of the type described by Fujishima and Honda [7], the photoanodic behaviour of a number of II–VI and III–V compound semiconductors (binary and ternary oxides, sulphides, selenides and phosphides) were examined for their suitability as anodic materials in the photoelectrolysis of water. It was found that ferric oxide (Fe_2O_3), doped with TiO_2 up to 1% manifested the best combination of electronic characteristics (with an ideal band-gap width 2.2 eV), good materials stability and a flat-band potential that required ony a small back-up voltage (about 0.5 V) to trigger photoelectrolysis. These studies were first reported by this author at the Third WHEC in 1980 [8].

Apart from the search for new photoanodic materials with the desired combination of properties, efforts are also on in some laboratories to improve the photoanodic performance of TiO_2 by suitable surface and structural modifications. It may be recalled that the rutile phase of titanic oxide figured prominently in the pioneering work of Fujishima and Honda. It has the important advantage of outstanding corrosion resistance and relative ease of production in large sheets by simple surface-oxidation of Ti metal sheets either by controlled thermal odixation in air [9] or by electrochemical oxidation or anodizing. Turning to work in India in this direction, investigations currently in progress in Prof. O. N. Strivastava's laboratory at the Banaras Hindu University suggests that significant improvements in the photoanodic performance of TiO_2 can be induced in two ways:

(a) Surface activation by doping the TiO_2 surface with photoactive catalysts, like indium oxide (In_2O_3) on the surface of TiO_2.

(b) Structural modification by 'alloying' or 'complexing' with other oxides or chalcogenides with a view to reducing the band-gap of TiO_2.

In the former method [10], titanium metal sheets were 'anodized' to produce a surface layer of TiO_2 and indium metal was electrodeposited on it. Heating the indium coated sheets in oxygen atmosphere at 500°C for an hour formed clusters of In_2O_3 on top of the TiO_2 surface. This treatment produced a two-fold improvement in the photoelectrochemical characteristics of TiO_2 as seen from the current–voltage curves and H_2/O_2 evolution curves shown in Figs 2 and 3.

It should be noted, however, surface doping with In_2O_3 cannot and does not alter the spectral photo response of TiO_2 (because of no change in the band-gap) and it still requires an applied bias 0.4 V for photoelectrolysis. Improvements in these characteristics (band-gap and flat band potential) would require changes in the energy band structure of the host material.

Some recent studies have shown that the large band gap of TiO_2 (3 eV) could be shrunk by doping it with oxides of other metals (e.g. with VO_2, Phillips *et al.* [11].

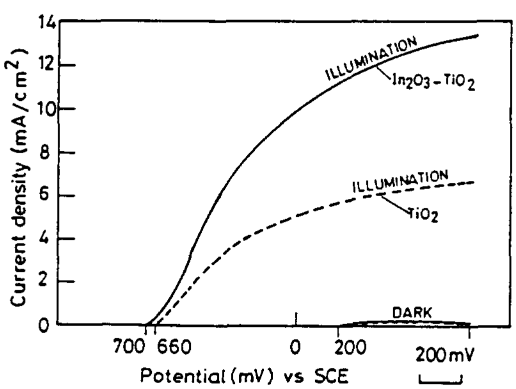

Fig. 2. *C–V* plots for TiO_2 and In_2O_3–TiO_2 under 1000 W Xe–Hg lamp illumination [10].

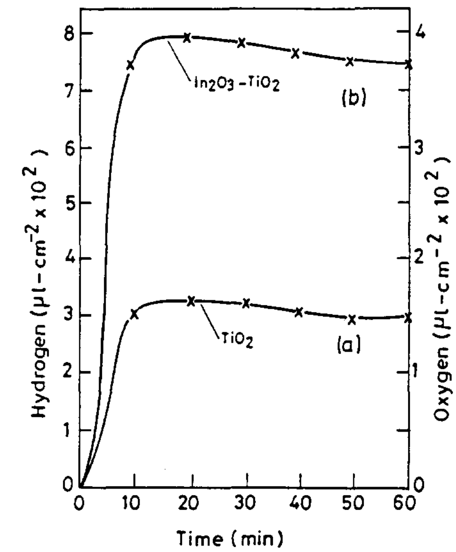

Fig. 3. H_2/O_2 evolution vs time under Xe–Hg lamp illumination with 500 mV applied bias [10].

However, since this is achieved by lowering the conduction band, the flat band becomes more positive than in virgin TiO_2, thereby increasing the external bias voltage required to induce photoelectrolysis. The better plan would be to raise the valence band edge through anion substitution. Pursuing this idea, Prof. Srivastava and his co-workers (personal communication) have synthesized a TiO_2–TiS_2 'alloy' by controlled oxidation of TiS_2 crystals followed by a reduction course in hydrogen. Preliminary trial experiments with the new material indicate that, as expected, the TiO_2–TiS_2 electrode gives wider spectral coverage and PEC response than plain rutile. Detailed studies of the material are in progress. It is also proposed to synthesize and evaluate the PEC behaviour of analogous mixed lattice materials like TiO_2–$TiSe_2$.

While offering better spectral coverage, anion substituted TiO_2 photoelectrodes would still require a bias voltage to induce hydrogen evolution.

An alternative to the conventional photoelectrolytic cell with fixed semiconductor electrodes is the 'semiconductor particulate' system in which the photolysis of water occurs in aqueous suspensions of s.c. particles under the influence of light of appropriate energy. Particulate systems possess a number of advantages over electrode systems, which are conducive to enhanced photocatalytic action. At the University of Madras, Department of Energy, Prof. P. Maruthamuthu has initiated studies on the photo-decompostion of water in suspensions of doped WO_3 particles in the presence of sacrificial agents like oxalic acid, H_2S, SO^2, $S_2O_3^{2-}$, MV^{2+} [12–15]. The results obtained so far encourage the confidence that an effective hydrogen photoproduction process can be based on s.c. particulate systems.

Biosynthetic methods

During the past few years scientists of the Faculty of Botany of Banaras Hindu University (Professors H. D. Kumar [16] and A. K. Kashyap [17], and their colleagues) have performed extensive studies on the photobiological route to hydrogen production, i.e. biophotolysis of water, with the help of photosynthetic bacteria. Understandably, their studies focused on cyanobacteria (blue green algae)—their isolation, characterization and assessment of their growth potential under varied culturing conditions and optimization of the hydrogen generating activity of selected strains of the micro-organisms through environmental and metabolical regulation. As the hydrogen liberating power of a bacterial organism is directly related to its nitrogenase activity, this activity was estimated in selected strains of cyanobacteria. On the basis of nitrogenase activity, strong nitrogen-fixers, like *Anabaena*, *Nostoc*, *Scytonema*, *Aulosira* and *Chlorogloeopsis* spp., were selected for study of hydrogen production metabolisms. Hydrogen uptake capacities, as indicated by their acetylene reducing activity in the presence of added hydrogen, confirmed the presence of active uptake hydrogenase enzyme in the heterocystous algae. Hydrogen evolution activity in all the isolated streams has been evaluated under aerobic conditions.

HYDROGEN STORAGE

Metal hydrides

Most of the work carried out in India on metal hydrides for hydrogen storage applications has already been reviewed [5]. Continuing their work on rare earth penta-nickelides (RNi_5), with focus on producing materials of this class with manageable (near atmospheric) plateau pressure, optimal reversible hydrogen storage capacity, fast absorption–desorption characteristics and optimum benefit/cost relation, Prof. Srivastava and his group at Banaras University [18] have synthesized a new Mischmetal–Ni–Al alloy of the composition $Mm'\ Ni_{4.5}\ Al_{0.5}$, where Mm′ denotes a typical Indian Mischmetal modified by the addition of La (10%) and Nd (5–10%) to bring down the plateau pressure to the desired level. This alloy hydrogenates to $Mm'Ni_{4.5}\ Al_{0.5}\ H_{5-6.5}$ and is said to possess the desired characteristics for mobile hydrogen storage. It has been field-tested in a small 100 cc motor-bike, as reported by Hinus [19]. On-board carriage of the alloy with sufficient hydrogen for a 40–50 km run without undue weight penalty and the mechanics of quick recharging are but two of the major engineering problems that remain to be solved.

Liquid hydrogen

Work on the production and cryogenic storage of liquid hydrogen is in progress at the Indian Space Research Organization (in large quantity for space rocket propulsion) and at the National Physical Laboratory, New Delhi, and the Indian Institute of Technology, Kharagpur (in small quantity for research application). There is nothing new to add to what has already been reported [5].

HYDROGEN UTILIZATION

1. *Combustive applications*

The studies carried out at the IITs at Madras and New Delhi and at BHU, Varanasi, on problems related to the use of hydrogen as I.C. engine fuel and thermal fuel, have already been reviewed [5]. IIT Delhi and BHU have plans to fit standard Indian-made light vehicles with hydrogen fueling systems for field-testing and demonstration purposes.

2. *Heat pump applications*

Metal hydride actuated heat pumps (MHHP) and heat transformers (MHHT) have attracted considerable attention during the past few years because of their high potential for energy conservation and the operational advantages they offer over other forms of chemical heat pumps. As an essential part of the design exercise, detailed thermodynamic analyses with different pairs of metal hydrides are being carried out by various research groups. These analyses vary in approach and content according to the design-goals set by the investigators.

In India, research aimed at the design and development of MHHP and MHHT systems for refrigeration and energy upgradation has been in progress for the past few years in the Refrigeration and Air-conditioning Laboratory at IIT Madras. The author is associated with this work. The thermodynamic analyses of MHHP and MHHT [20] included the evaluation of exergetic efficiency besides the Coefficient of Performance. The inter-related parameters and performance-indices have been presented in the form of nomograms which would greatly facilitate the selection of suitable alloy pairs for specific applications and the prediction of performance characteristics.

Next, we considered hybrid systems linking the MHHT thermally with the Vapour Compression Heat Pump (VCHP), a concept which we first introduced in 1984 [21]. Thermodynamic analysis revealed [22] important gains of hybridization such as higher overall COP and enhanced temperature boosting compared to the single-stage, or even cascaded, 'pure' VCHP systems. These hybrids will be particularly useful in applications which require both cooling and heating as, for example, in the pasteurization of milk and food preservation industries.

Finally, we have performed the thermodynamic analysis of two-stage MHHT with two pairs of metal hydrides as an alternative to the MHHT–VCHP hybrid. The results [23] reveal that temperature lifts of the order of 100–150°C can be achieved with most of the 12 alloy-pair combinations considered.

We have now undertaken a research project, sponsored by the India Government, for the design and development of experimental MHHP and MHHT and hybrid systems for energy upgradation. The project envisages the study of a wide range of metal hydride compositions and, hopefully, will culminate in the optimal design, fabrication and experimental testing out of prototype MHHP, MHHT and their hybrids with vapour compression heat pumps and refrigeration systems.

CONCLUDING REMARKS

It is saddening to conclude this report on a somewhat despondent note. During the past 2 or 3 years there has been a sharp decline in hydrogen energy research activity in India, mainly because of truncation of Government fund support. This is due, firstly, to diversion of funds to higher priority needs such as defence, security, natural calamities like droughts and floods, etc., and, secondly, to a slackening of interest in hydrogen as an oil-substitute. The recent discoveries of offshore oil and gas resources have raised hopes of abundance in oil even beyond the next 20 or 30 years. However, it would be advisable to proceed more prudently on these illusory hopes by first conducting realistic analyses of the country's resource-demand balance in the context of the projected plans to step up the pace of industrialization and also in the light of the inevitable growth of urbanization. It is also necessary to consider the environmental impact on doubling or trebling of petrofuel combustion during the next 2 or 3 decades. Already, near lethal conditions prevail in most of our metropolitan down-town areas. The consequences of further increase in oil combustion in our city roads are too frightening even to contemplate.

It is also relevant to consider the potential role that hydrogen alone can play in the massive utilization of solar energy as a source of power [24] and as a means of energy-storage and load-levelling in nuclear power plants.

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