CULTURAL DEVELOPMENT AND THE KEY TECHNOLOGIES OF HYDROGEN ENERGY SYSTEMS - AN INTRODUCTORY REVIEW FOR THE BEGINNERS

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Keywords: key events for energy systems, hydrogen energy system, hydrogen system civilization, combustion, fuel cell, thermochemical, water splitting system (WSS), thermoelectric WSS, photoelectrochemical WSS, triboelectric WSS, sonolysis, quantum dot super lattice, built-in field, energy band structure, oxide semiconductor, hopping conduction, hydrogen storage system, metalhydride, liquid hydrogen, nanomaterials

Contents

Summary

From the history of energy systems (energy sources, energy carriers, energy storage, energy transport, energy utilization, environmental effects, adapted materials, and the transitional key events), the inevitable trend from C (carbon) to H (hydrogen) in the fuel-systems is specified, which is called the hydrogen energy systems (HES). Technological development, the present stage, and the tasks for fuel cell, electrolysis, chemical feedstock, and other important subjects, are discussed. Water splitting system (W.S.) by the renewable energies is an important subject.

It is noticed that the latest frontiers of electrolysis have two types, one is the involved electrolysis (in situ electrolysis), and another is the combined electrolysis. Quantum dot

super lattice, energy band structure with the built-in field at the interface, and selection of the oxide semiconductors are the key for thermoelectric W.S., photochemical W.S., and tribolysis, respectively. Recent approaches to the hydrogen storage, which is due to the metalhydride-system, the liquefied hydrogen-system, and the nanomaterial-system, are reviewed.

In addition, the system of civilization synthesized by scientific research-culture, the technological civilization of energy conversion, and the chemical economy that are cultivated and carried by hydrogen are studied.

Hydrogen society is emerging now.
The leading subjects will be as follows;

(i) Hydrogen utilization methods with the higher additional values. Examples are: (i) More active usage of hydrogen-protein for the artificial nutritious food and (ii) Hydrogen application for the medical equipments (micro power generator, actuator of robot, heat pump, medical industries, et al.).

(ii) Methane-hydrogen complex. The importance of methane in fuel systems will increase relative to petroleum, from now on. Nevertheless, the cry for reduction of CO_2 will become pressing, so that the mixed city-gas will spread, which may be supplied to the on-site power stations.

(iii) Hydrogen vehicles. If the DOE's target is cleared, the hydrogen cars will be more and more popularized. The feasibility of hydrogen-fueled airplane has been studied for long time, and this type of plane will be realized in the future.

(iv) The technological development for HES will lead to effective methods for energy-usage, energy saving consciousness, school and life-long-education for clean energy. Consequently, sense of the sustainable development for the domestic, district, national, and global societies will be improved.

(v) Energy resources. As for the renewable energy resources, solar cell and wind-power generations must be increased. The capacity of solar cell generation was 1.81 x 10^6 kW (as of the end of 2003), and that of wind-power generation was 39.43 x 10^6 kW (as of the end of 2003).

There exist ca. 15000 times solar energy compared to that consumed by humankind a year, and the great expenses for the development must be considered as a part of the compensations for the various and huge losses by global warming.

Endeavors to the achievement of these subjects will construct *the hydrogen-system civilization* defined in this chapter.

1. Introduction

The development of civilization is, in general, due to information, energy, and materials. Accordingly the history of energy systems consists of the intellectual key events, energy resources, energy carriers, and the materials characterized by the energy. The chronological table for the key events is shown in Table 1.

After the primitive age, the main energy has always been biomass and the fossil fuels, which are classified into three phases: solid (fire wood, charcoal, coal, and coke), liquid (petroleum), and gas (natural gas, petroleum gas). The noticeable key events for the transitions are enumerated in the following.

(1) *From firewood to coal*: (i) Large needs of charcoal for iron manufacturing. (ii) Establishment of iron manufacturing by coke (1750). (iii) Depletion of forests in England, which was the environmental problem for the first time. (iv) Coal served iron manufacturing and the manufactured iron-boiler needed coal, so that the both proliferated in harmony the use of coal. They brought about the industrial revolution.

(2) *From coal to oil*: (i) Liberation from the heavy labor for coal mining. (ii) Efficiency from batch-system to pipeline-network. (iii) Introduction of automatic combustion and no necessity for big chimney. (iv) No smog (dusty smoke, NO_x, SO_x, CO_x, and carbon dust), which was the second environmental problem. (v) Discovery of the big oil field (e.g., Ghawar, 1948). (vi) Chemical feed-stock of the various synthetic materials (e.g., plastics, fiber, vinyl, vinylon, acetate, rubber, fertilizer). The carbon C from oil has been utilized as synthesized materials, which developed the oil civilization. Such utilization system as for oil is realized for coal too, but it is not as easy as for oil. (vii) Invention and the improvement of internal combustion engines (ICE). (viii) Electric power generation was spurred, and aluminum was spread as a new structural material. (iv) Uneven distribution of oil fields and the limited quantity of oil reserve. (vii) Unreasonable price fixing in some cases. (viii) Great amounts of CO_2 emission.

(3) *From oil to natural gas*: (i) Evener distribution of natural gas fields and the larger reserve quantity. (ii) Storage and transportation by the improved cryogenic methods (liquefaction and the equipments). (iii) Less CO_2 emission.

(4) *Entrance of the hydrogen energy systems (HES)*: Although the fossil fuel utilization has been the motive power for the global economical growth up to now, the global warming by green house effect of the emitted CO_2 has become the inevitable obstacle to be surmounted. Otherwise the decarburization trend has been realized in the history of energy (Figure1), and the utilization trend for fossil fuels shows definitely the hydrogen rich fuels (Figure 2).

HES are defined as the systems, in which hydrogen manufactured by WSS with use of the renewable energy resources is applied to the energy carrier and also to the chemical feed-stock.

Key events for the transition to HES are (i) success of the effective proton exchange membrane fuel cell (PEMFC) which may replace ICE, (ii) hydrogen applications to fuel cell and to rocket propellant thoroughly investigated by taking advantage of NASA's space project, (iii) hydrogen application studied as the chemical feed-stock such as the ammonia synthesis which was the great success for the alternative of the natural resource (e.g., Chile saltpeter), and (iv) Kyoto protocol for the global reduction of CO_2 emission.

Year	**Key-event**	**Energy resources**	**Energy career**	**Structural materials**
	Primitive Utilization of fire age	Biomass	Firewood	Wood
	Invention of the single machines (lever, wheel, pulley)	Human & Charcoal Animal power		
1300	First organized coal-mining	Coal	Coal	Iron
1750	Iron-manufacturing by coke	(A.Darby) (in addition)	Coke	Stone
1785	First industrial evolution	Gasoline	Ceramics	
1867	Practical electric power generation		(in addition)	Stone
	(E. Siemens)		(in addition)	
1870	Invention of steam engine (J. Watt)			
1877	4-cycle Internal combustion engine(N. Otto)			
1882	First hydropower electric generation			
1885	Gasoline engine (G. Daimler, C. Benz)			
1893	Diesel engine (R. Diesel)			
1900	Discovery of sea floor oil field			
	(Caspian sea)			
1942	Experimental nuclear plant (E. Fermi)			
1948	Discovery of Ghawar oil field	Petroleum	Oil	Aluminum
1960	OPEC was organized	Methane	Gas	Plastics
1962-72	NASA's Apollo project	(in addition)	Electric	(in addition)
	(liquid hydrogen engine, fuel cell)		power	
1964	First LNG transport for long distance (Algeria-France)	(in addition)		
1979	Accident of the three miles island's nuclear plant			
1986	Accident of the Chernobyl's nuclear plant			
1991	Gulf war			
2005	Kyoto protocol for CO_2-reduction, Development of PEMFC			

	driven car			
Oil+Coal+Gas = 86%; Nuclear = 7%; Non-commercial = 7%; (as of 2000)				

Table 1: Key events for the transition of energy systems

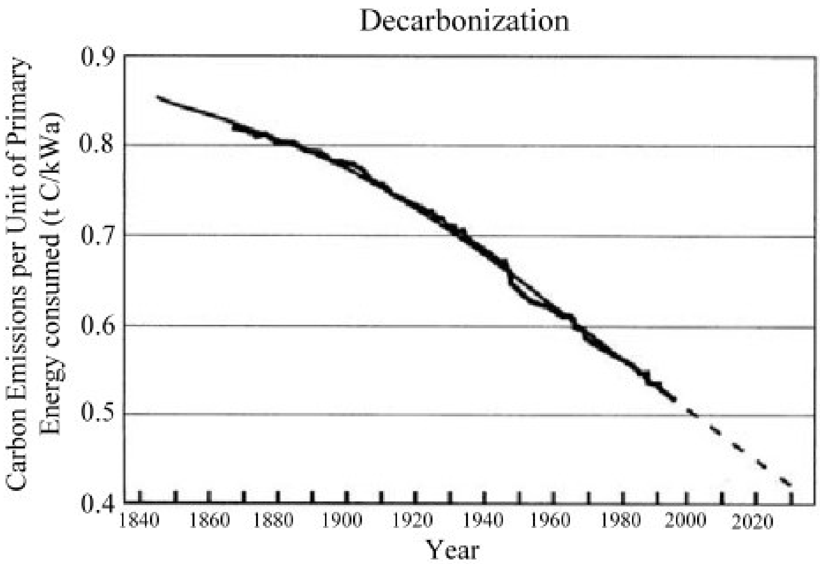

Figure 1: Decarburization trend in the energy consumed to date

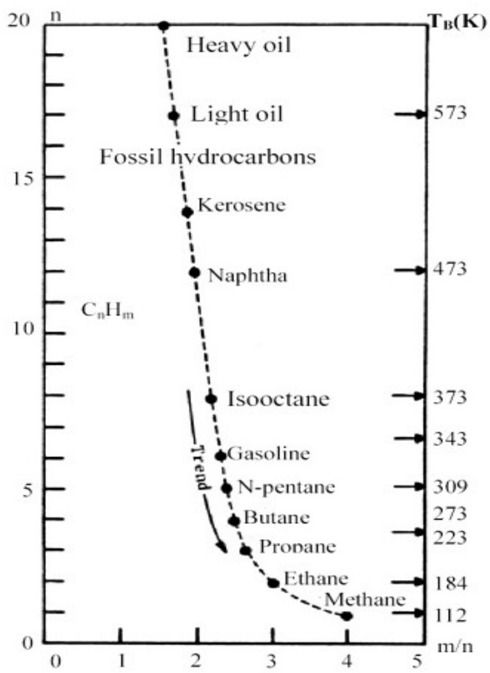

Figure 2: Utilization trend of fossil fuel (C_nH_m) as plotted n vs. m/n and the boiling temperature T_B (K)

2. Formation of Hydrogen Energy Systems

The merits of HES can be expressed by the following 5 *E*s: (i) *Ecological* (manufactured from water and returns to water), (ii) *Economical* (if the disaster damage caused by the global warming is estimated economically, the equivalent cost is avoided by HES), (iii) *Efficient* (energy conversion is most efficient among all fuels), (iv) *Emerging* (the ace of leading subjects for the next Kondratyiev cycle), (v) *Energetic* (maximum chemical wattage).

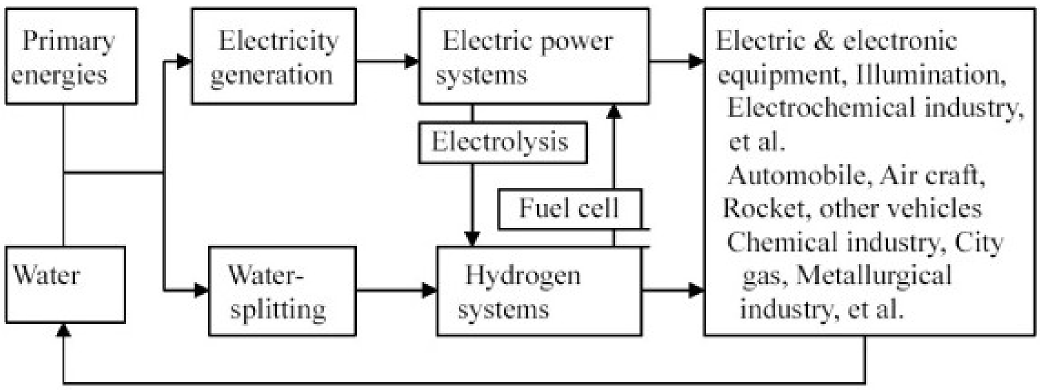

Figure 3: Hydrogen energy systems as cooperated with the electric power systems

Definition of *Hydrogen Systems Civilization*: The civilization synthesized by scientific culture, the technological civilization of energy conversion, and the civilization of chemical economics which are cultivated and carried by hydrogen.

1.	1776	H. Cavendish: Discovery of the "combustible air" - hydrogen (Zinc +dilute sulfuric acid)
2.	1777	K. W. Scheele: Discovery of oxygen
3.	1784	Cavendish confirmed that "combustible air" reacts with oxygen to generate water. Hearing this News, Lavoisier named "combustible air" Hydrogen.
4.	1787	A. L. Lavoisier: Discovery of hydrogen independently of Cavendish (Steam throwing over red-hot iron)
5.	1800	W. Nicholson, A. Carlyle: Water-electrolysis with use of a voltaic cell invented by A. Volta
6.	1883	M. Faraday: Radical development of electrolysis
7.	1840	R. Grove: Invention of fuel cell
8.		J. P. Joule: Exact estimation of work equivalent of heat
9.	1866	T. Graham: Discovery of massive absorption of hydrogen in Pd
10.	1870	J. Verne: SF novel " Mysterious Island", an idea of the hydrogen fuel
11.	1885	J. J. Balmer: Discovery of "Balmer series" in hydrogen spectrum
12.	1895	C. von Linde: Liquefaction of air
13.	1900	M. Planck: Discivery of energy quantum
14.	1898	J. Dewar: Liquefaction of hydrogen
15.	1908	F. Harbor. Ammonia synthesize
16.		K. Oness: Liquefaction of helium. Discovery of superconductivity was

		followed in 1911
17.	1913	N. Bohr: Bohr model for hydrogen atom
18.	1923	BASF Co.: Industrialization of methanol
19.	1925	W. Heisenberg, E. Schroedinger: Quantum mechanical application to hydrogen atom
20.	1932	N. F. Urey: Discovery of deuterium, which is the simplest nucleus composed of one proton and one neutron. The force between them was not known until Yukawa's idea.(1934)
21.	1937	Explosion of Hindenburg airship
22.	1938	I. Rabi: Discovery of magnetic resonance
23.	1942	H. Gaffiron et al: Discovery hydrogen evolving algae by light
24.	1945	V. N. Ipatieff and G.S Momroe: Methanol synthesis (CO_2) by Cu-alumina catalysis.
25.	1947	W. E. Lamb: Experimental evidence of quantum electrodynamics found for the electron energy shift of hydrogen atom
26.	1949	H. Gest et al: Discovery of photo synthesizing bacteria
27	1952	F. Bacon: Hydrogen-oxygen fuel cell. with KOH-electrolyte
28.		First test of Hydrogen bomb in U.S.A., and in1953 by Soviets union
29.	1960	N. F. Ramsey, D. Kleppener: Invention of hydrogen Maser
30.	1956-63	Platt & Whitney Co.: Liquid hydrogen engine RL10
31.	1960 -70	GE Co., Dupon Co.: Development of solid polymer electrolyte, Nafion
32.	1960	ICI Co.: Invention of low-pressure synthesis of methanol
33.	1962-72	NASA: Appollo project (Propellant for Saturn rocket and hydrogen-oxygen fuel cell for the space ship)
34.	1964	J. Funk et al: The first investigation for the thermochemical water splitting
35.	1969	K. Honda, A. Fujishima: Discovery of photochemical water splitting C. Marchetti: Thermochemical water splitting as applied to nuclear plant
36.	1972	Brookhaven National Laboratories, S. Furuhama, W. Van Vorst, et al: Development of hydrogen fueled cars
37.	1973	D. P. Gregory: Energy transport by hydrogen, proposal of hydrogen economy
38.	1973	T. Ohta et al: Proposal and the experimental development of solar hydrogen energy systems by thermoelectric water splitting
39.	1974	T. N. Veziroglu, J. O'M. Bockris, T. Ohta, et al: Organization of International Association for Hydrogen Energy
40.	1978	T. Minota: Culture and the development of hydrogen protein
41.	1991	S. IIjima: Discovery of carbon nano-tube, which provides a promising hydrogen storage nanomaterials
42.	1997	Kyoto protocol: The reduction duty of CO_2 emission giving the spur to hydrogen energy systems
43.	1998	Marked development of the hydrogen fueled car with use of the stack of PEMFC, most of which are manufactured by Ballard Co.
44.	2005	Kyoto Protocol has come into the effect since 16th of February.

Table 2: Chronological table for the hydrogen-system civilization

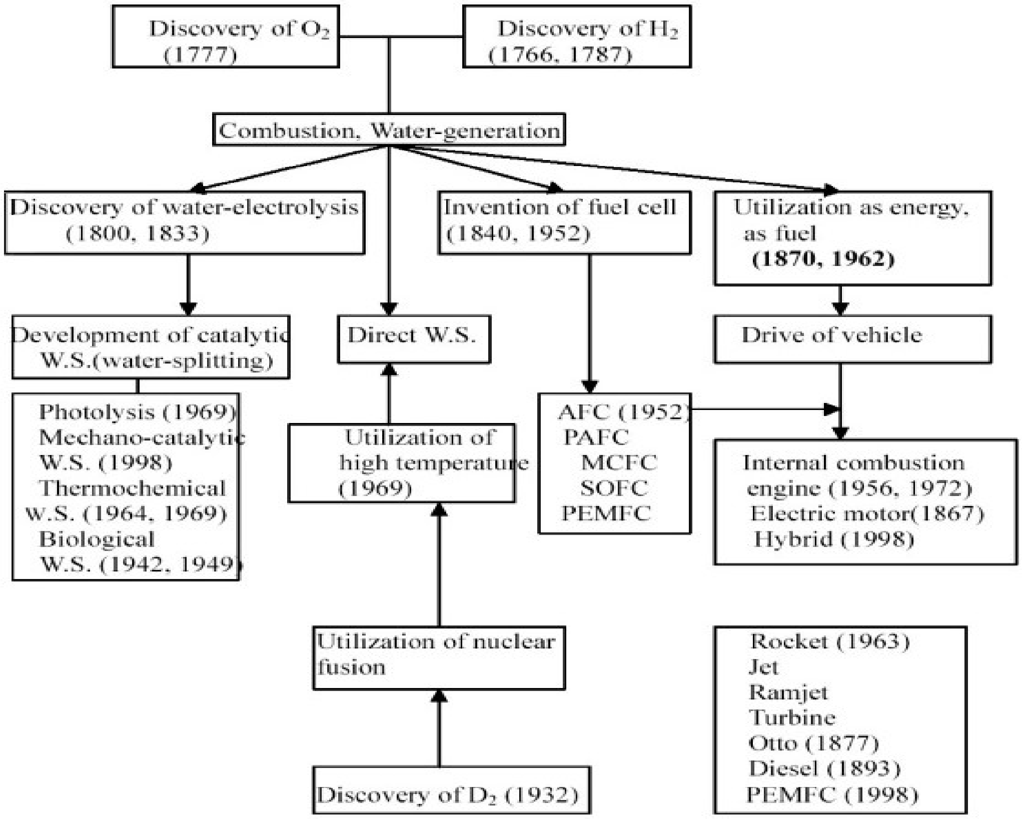

Figure 4: Technological genealogy of the energetic applications of hydrogen

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Bibliography

Besenbruch GE, McCorkle KH, Norman JH, O'keefe DR, Schuster JR, Yoshimoto M. Hydrogen production by the GA sulfur-iodine process, a progress report. In: Veziroglu TN, Fueki K, Ohta T. editors. Hydrogen Energy Progress, Oxford: Pergamon Press;1980. p159-79.

Domen K, Ikeda S, Takata T, Tanaka A, Hara M, Kondo JN. Mechano-catalytic overall water-splitting into hydrogen and oxygen on some metal oxides. In: Ohta T. editor. Energy Systems: Adaptive Complexity. Oxford: Elsevier; 2000. p159-79.

Grove W R. On a gaseous voltaic battery. Phil Nag 1842; 21:417-420.

Harada H. Isolation of hydrogen from water and/or artificial seawater by sono photo catalysis using alternating irradiation method. Int J Hydrogen Energy 2000;26:303-7.

Harman TC, Taylor PJ, Walsh MP, LaForge BE. Quantum dot superlattice thermoelectric materials and devices. Science 2002; 297:2229-32.

Hsu KF, Loo S,Guo F, Chen W, Dyck JS, Uher C, Hogan T, Polychroniadis EK, Kanatzidis MG. Cubic $AgPb_mSbTe_{2+m}$: Bulk thermoelectric materials with high figure of merit. Science 2004;303:818-21.

Ihara S. Direct thermal decomposition of water. In: Ohta T. editor Solar-hydrogen energy systems, Oxford: Pergamon Press; 1979. p59-79.

Lede T, Lapicque F, Villermaux J. Production of hydrogen by direct thermal decomposition. In: Proc. 4th World Hydrogen Energy Conference.1982; p523-32.

MacDonald DKC. Principles of Thermoelectricity: New York: John Wiley and Sons, 1964.

Maruyama S. Hydrogen storage with carbon nanotubes. Oyo Butsuri 2002;71:323-6.

Mitsui A. Biological and biochemical hydrogen production. In: Ohta T. editor. Solar-hydrogen energy systems, Oxford: Pergamon Press; 1979. p171-91.

Miura M, Kimura Y, Saito Y. Dehydrogenation and hydrogen-spillover abilities of palladium-based electrode catalyst for thermo regenerative fuel cell. In: Proc. 5th Int. Conference on New Energy Systems and Conversions. 2001; p179-84.

Nakicenovic N, John A. CO_2 reduction and removal for the next century. Energy 1991; 11/12:1347-77.

Ohta T. Hydrogen energy systems as to be applied in Japan. In: Veziroglu TN. editor. Proc. Hydrogen Economy Miami Energy Conference. 1974; p S1569-70. [*This is the opening presentation at International Hydrogen Energy Conference.*]

Ohta T. On the maximum D^+-D^+fusion rate by the implosion of cavitation bubble. Int. J Hydrogen Energy 2004; 29:1553-4.

Ohta T. On the theory of mechano-catalytic water-splitting system. Int J Hydrogen Energy 2000; 25:911-7.

Ono S, Yamaguchi M. Solar energy storage by metalhydride. In: Ohta T. editor. Solar-hydrogen energy systems, Oxford; Pergamon Press; 1979. p193-24.

Rigden J S. Hydrogen. London: Harvard University Press, 2002.

Taleyarkhan RP, Cho JS, West CD, Lahey Rt, Nigmatulin RT, Block DC. Additional evidence of nuclear emission during acoustic cavitations. Phys Rev E.2004; B36109:1-11.

Taleyarlhan RP, West CD, Cho JS, Lahey RT Jr, Nigmatulin RT, Block RR. Evidence for nuclear emission during acoustic cavitations. Science 2000; 295:1866-73.

Tanisho S. A scheme for developing the yield of hydrogen by fermentation. In: Miyake T, Matsunaga T, San Pietro. editors. Biohydrogen II, Oxford: Pergamon Press; 2001. p131-40.

Telkes M. Solar thermoelectric generator. J Appl Phys 1954; 25: 765-73.

Tsutsumida K, Kihara N, Torigoe, Matsuura K, Tsuyoshi A, Rowe DM. The fast heat recovery system for transmovable thermoelectric generator. In: Proc. 4th Int Conference on New Energy Systems and Conversions. 1999; p 327-32.

Watanabe T, Fujishima A, Honda K. Photoelectrochemical hydrogen production. In: Ohta T. editor. Solar-hydrogen energy systems, Oxford: Pergamon Press; 1979. p137-69.

Yamaguchi M, Ohta T. Water decomposition by solar thermoeleectric system. Bull. Facul. Eng. Yokohama Nat. University 1975; 24:107-14.

Biographical Sketches

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 as 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 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.

Nobuyuki KAMIYA born on 22 April, 1941 in Japan, he graduated from Department of Chemical Engineering, Tokyo Institute of Technology. Received Ph.D. degree in Applied Chemistry in 1969, he joined Yokohama National University where he has taught Chemistry and Energy Engineering. He is now professor of Department of Energy and Chemical Engineering of YNU. During his carrier, he worked with Prof. Ohta and developed water splitting hydrogen formation by photochemical, thermochemical and electrochemical hybrid systems. Recently he has been engaged in developing fuel cells, especially materials for electrodes. He has been a member of the editorial board of Hydrogen Energy System Society of Japan and a director of Electrochemical Society of Japan.