

Research and development of solar hydrogen production

— Toward the realization of ingenious photocatalysis-electrolysis hybrid system —

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It is important to carry out research strategically and in a step-by-step manner in order to put new solar energy conversion technologies into practical use and to realize a society based on renewable energy. In this paper, we clarified the meaning of “solar hydrogen,” compared various solar hydrogen production technologies, and discussed their feasibilities. Specifically, we showed the effectiveness of the “photocatalysis-electrolysis hybrid system,” which was invented by AIST, as a promising candidate technology for low cost solar hydrogen production, based on preliminary cost estimations. The scenario toward the realization of the hybrid system is also discussed.

Keywords : Solar hydrogen production, photocatalysis-electrolysis hybrid system, artificial photosynthesis, redox mediator

1 Introduction: Significance of solar energy use technology and its issues

Recently, the issues of depletion of fossil resources and global warming due to carbon gas emitted by their consumption have become apparent, and it is necessary to reduce the dependence on fossil resources as quickly as possible to respond to such issues. For the humankind to build a sustainable society and to continue growth, the early development of an innovative technology for utilizing renewable energy is essential. Among the renewable energies, solar energy is most abundant, and is the source of wind, wave, tide, and biomass power. It is possible to cover one year’s worth of the entire global energy consumption with one hour’s worth of solar energy that shines on earth, and its total amount is about 500, 5,000, and 50,000 times greater than wind, geothermal, and hydro power, respectively. However, there are two major disadvantages to solar energy: the energy density is low and it is greatly influenced by weather. Therefore, the technologies that can be used effectively are limited. While photovoltaic generation, use of solar heat, and fuel manufacturing using biomass are already put to practical use, it cannot be foreseen that extending these technologies may replace fossil resources to solve the global energy problem.

To further make use of the solar energy with low energy density, an innovative technological development which is much lower in cost and is simpler than photovoltaic generation is essential. Options of solar energy use includes “artificial photosynthesis” where the photons are directly converted to chemical energy, just as in photosynthesis in plants. While the term artificial photosynthesis sounds extremely attractive, it may lead to misunderstandings since

the definition is vague. In a wide sense, it means to wholly or partially simulate the photosynthetic mechanism of plants, and the research is done not necessarily to solve the energy problem. In a situation where energy has become an outstanding issue, it is necessary to rethink the meaning of the terms for artificial photosynthesis and its R&D scenario to quickly realize the practical use of new solar energy conversion technologies.

2 What is solar hydrogen production?

In the artificial photosynthesis technology, the term “solar hydrogen production” using photocatalysts and photoelectrodes is becoming popular. In FY 2012, research on hydrogen production from water using photocatalysts and photoelectrodes using the term “solar hydrogen” started in the Future Pioneering Project of the Ministry of Economy, Trade and Industry (METI). The solar hydrogen production focuses on the water decomposition using solar energy to achieve a clean and sustainable hydrogen society (Fig. 1). While the ultimate goal expected from the research of artificial photosynthesis and solar hydrogen production technology is solving the energy problem on a global scale, it is important to note that the latter is used with strong goal orientation. The photosynthesis mechanism is divided into the light and dark reactions. The light reaction, which is the first stage where the reductant of a high-energy state is produced as oxygen is pulled out of water, directly pushes the energy-storing chemical reaction through photons, and the decomposition of water is the basic reaction of photosynthesis. If hydrogen energy derived from solar energy using water as the source material can be manufactured in a large amount, several existing technologies can be applied to CO₂ fixing reaction that corresponds to the dark reaction.

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While there is much artificial photosynthesis research that focuses only on the organic synthesis of the dark reaction, unless it is combined with the energy-storing chemical reaction of the light reaction, it does not lead to the solution of the energy problem. The objective and direction arising from the term “artificial photosynthesis” is unclear, and much is in the realm of *Type 1 Basic Research*. To quickly move to *Type 2 Basic Research*, it is necessary to consciously use an objective-oriented term. From the above thinking process, in this paper, among the artificial photosynthesis technologies, the technology to produce hydrogen and oxygen by decomposing water, with the objective of building a sustainable society through solar energy, will be called “solar hydrogen production,” and this will be positioned as *Type 2 Basic Research*. (The system in which the two technologies for photovoltaic generation and electrolysis are simply combined may be called the solar hydrogen production in a wide sense, but it does not belong in the realm of artificial photosynthesis because it does not directly use photons for chemical reaction. Also, power generation methods using high temperature produced by gathering sunlight as well as water decomposition by thermochemical cycle are not addressed in this paper.)

Figure 2 is a technological map in which the vertical axis shows the solar energy conversion efficiency and the horizontal axis the cost or system complexity for the various solar energy conversion technologies. Photovoltaic generation, use of solar heat, and fuel production using biomass lie on the line representing practical use. While the current solar hydrogen production technologies that use photocatalysts and photoelectrodes are still far from being practically applied, it is necessary to present their future potential for practical efficiency that is overwhelmingly simpler and lower in cost compared to the system that combines photovoltaic generation and electrolysis. The application and diffusion of solar hydrogen production technology as well as the realization of future renewable

energy society that does not depend on fossil resources are not easy and are likely to take time. Therefore, it is desirable to surely and strategically engage in research while looking over the direction we must take from this point. It is necessary to discern which technology will surpass the line of practical use and arrive first at the final goal.

This paper compares various solar hydrogen production technologies and discusses their future prospects. Particularly, the main objectives are to present a scenario for practical use, efficiency, and cost performance of the “photocatalysis-electrolysis hybrid system”^{[1][2]} that the authors developed, and to compare this with other technologies to discuss whether it can stand at the starting line of *Type 2 Basic Research*.

3 Importance of the research scenario for practical use of solar hydrogen production and the cost target

3.1 Setting the long-term scenario and the appropriate interim goal

The research of artificial photosynthesis and solar hydrogen production has been influenced greatly by the price of fossil resources. The first boom occurred around the 1973 Oil Shock, but as the oil prices decreased after 1986, the research stalled rapidly. In the 1990s, the global warming issues came into focus with the accompanying increase in oil prices, and the research is attracting attention again. In the United States, the Solar Innovation Hub, a major solar hydrogen production project of the Department of Energy (DOE), started in 2010, but the interest in solar energy is falling slightly after the sharp decrease in natural gas prices due to the shale gas revolution. Although the ebb and flow of research cannot be avoided, such a situation is not desirable for the R&D of solar energy conversion that requires a long time to reach practical use. To continue long-term research, it is extremely important to set the research scenario and roadmap for

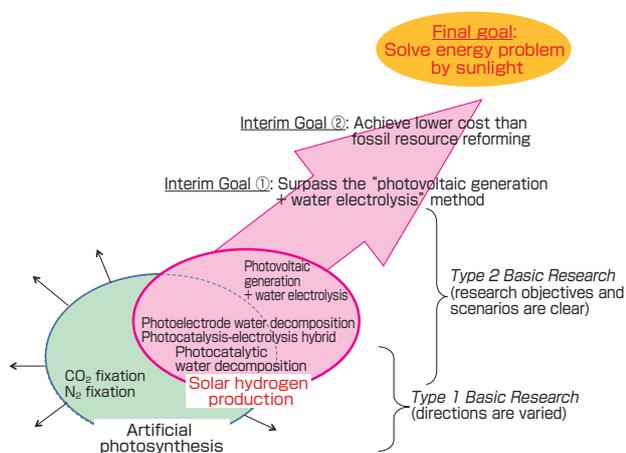


Fig. 1 Positioning of the solar hydrogen production and its interim and final goals

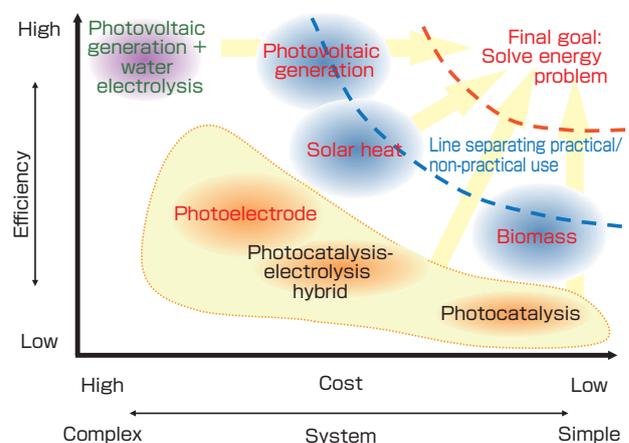


Fig. 2 Technological map of various solar energy conversion uses

practical use, the interim goals, and long-term prospects, not just the clarification of the research significance as the final goal. Also, to have as many people understand the points of this paper is the most effective way to achieve the goal and will lead to stable and continuous R&D. Since the Great East Japan Earthquake, interest in renewable energy has increased in Japan. Because the expectations are high, the achievability and speed to practical use are demanded, not simply idealistic theory.

Up to this point, the roadmaps for energy have been created by the Cool Earth Promotion Programme of the government, Science Council of Japan, Japan Society of Applied Physics, Chemical Society of Japan, and others. For example, the Dream Roadmap^[3] of the Science Council of Japan that was written after the Great East Japan Earthquake contains several keywords such as artificial photosynthesis and solar hydrogen production, and practical use is set between 2030~2040. However, when the keywords are set in too distant future, though the research significance may be recognized, it will not help promote the short to mid-term research and may even work negatively. For now, it is important to set the short to mid-term strategic scenario and the interim goals that are highly achievable. We offer the following discussion, and set two clear interim goals as shown in Fig. 1: ① to reduce the cost to lower than the hydrogen obtained by simply combining photovoltaic generation and electrolysis, and ② to reduce the cost to lower than the hydrogen from reforming of fossil resources.

3.2 Specific interim goals for the hydrogen production cost

The roadmap (2010) for hydrogen production in the fuel cell and hydrogen technology development^[4] of the New Energy and Industrial Technology Development Organization (NEDO) describes the interim goal for cost. For the cost of off-site hydrogen production, low carbon is achieved using renewable energy in 2020 at the same cost (30 yen/Nm³) as the steam reforming of natural gas, and aims for lower cost in 2030. On the other hand, for the cost of large-scale photovoltaic generation, the prospect for 2030 in the Report of the Committee for Investigation of Cost and Others^[5] of the Energy and Environment Council of the government is 9.9~26.4 yen/kWh. In the NEDO roadmap for photovoltaic generation (PV2030+, 2009),^[6] the power generation cost goal for 2020 is 14 yen/kWh and for 2030 is 7 yen/kWh. Calculating the cost of combining the photovoltaic generation and large-scale solid polymer electrolytic device based on the report of the Central Research Institute of Electric Power Industry,^[7] the cost of hydrogen production will be over 35 yen/Nm³ even if the power generation goal of 7 yen/kWh is achieved.

The two interim goals that we presented are greatly affected by the costs of photovoltaic generation and fossil resources,

but the cost of hydrogen production is calculated to be less than 35~65 yen/Nm³ in the Interim Goal ① and 30 yen/Nm³ in the Interim Goal ②. In the future, to achieve these cost goals and to achieve a clean hydrogen society using renewable energy, early development of an innovative technology unseen before is mandatory. Even if something is an ideal technology, if there are a number of very difficult issues to overcome, it is necessary to consider that time is needed for realization.

4 Comparison of various solar hydrogen production technologies using semiconductors

4.1 Principle of water decomposition by semiconductors

The first process in using sunlight is the absorption of photons by photoabsorptive materials. In the research for solar hydrogen production in artificial photosynthesis, the photoabsorptive materials are roughly divided into semiconductors and dyes. Currently, the former is much more advanced than the latter. The researches for solar hydrogen production technology using semiconductors have been conducted throughout the world and can be historically divided into two streams: photocatalysts and photoelectrodes. The principles of the two methods are shown in Fig. 3. The water decomposition by TiO₂ photoelectrode was invented in Japan,^[8] and the concept of the photocatalytic water decomposition was established later. When the light is absorbed by a semiconductor, electrons are generated in the conduction band and holes in the valence band, and these are used in the reduction and oxidation reaction of water, respectively. While the principle of light absorption and charge separation are the same as in the solar cell, the overall concept is closer to fuel production using biomass in the point that the solar energy is directly converted to chemical energy or hydrogen for long-term storage.

Figure 4 shows the various water decomposition technologies by photocatalysts and electrolysis, and their potential map. In the water decomposition of photocatalysts, the potential of the conduction band is limited to being more negative than the redox potential of hydrogen ($E^\circ(\text{H}^+/\text{H}_2) = 0 \text{ V}$), and the valence band potential is more positive than the potential when oxygen is produced from water ($E^\circ(\text{O}_2/\text{H}_2\text{O}) = +1.23 \text{ V}$). Also, in the case of photoelectrodes, they use external bias (external power), as shown in Fig. 3. By using external bias, there are advantages that there will be loose limitation to the level of semiconductors used in photoelectrodes, charge separation is promoted, and hydrogen and oxygen can be separately produced. In the example of the n-type semiconductor in Fig. 3, the potential of the necessary external bias is the difference between the minimum potential of the conduction band and H^+/H_2 potential in theory, and the voltage can be lower than the ordinary electrolysis of water. On the other hand, there are advantages of having a short charge transfer distance and simplification,

since the reaction is completed for each semiconductor particle in the photocatalyst.

4.1.1 Diversification and progress of the photocatalyst system

Currently, the photocatalyst and photoelectrode systems are diversified and progressing in various forms as shown in Table 1. The photocatalyst system can be roughly categorized into conventional photocatalyst (single-step photoexcitation type), double-step photoexcited photocatalyst using the redox mediator (Z-scheme type), and the photocatalysis-electrolysis hybrid system. A redox mediator is a substance that transfers the electron while undergoing the cycle of oxidation and reduction. The reaction of double-step photoexcitation is similar to photosynthesis in plants, and is called the Z-scheme reaction that describes the zigzag processes where the electrons are photoexcited twice using the redox mediators. In the photocatalysis-electrolysis hybrid system, external bias is used as in Fig. 4, but since the needed bias is equal to

the potential difference between redox potential of the redox mediator and the hydrogen in theory, the voltage can be lower than the ordinary electrolysis of water. The Japanese research is advanced in all areas of the photocatalyst system. Under certain conditions (such as 10 % solar energy conversion efficiency), the conventional and Z-scheme photocatalysts are estimated to achieve hydrogen production costs at 30 yen/Nm³ or less,^[9] but there are several issues that must be overcome for practical use, as shown in Table 1 and chapter 5.

4.1.2 Diversification and progress of the photoelectrode system

The photoelectrode system is categorized into n-type semiconductors, p-type semiconductors, p+n type semiconductors, and pn bonding films. The combination of the n- and p-type semiconductors can conduct water decomposition without external bias. However, when hydrogen is generated by the p-type semiconductor, cocatalyst for the hydrogen production with low overvoltage such as Pt

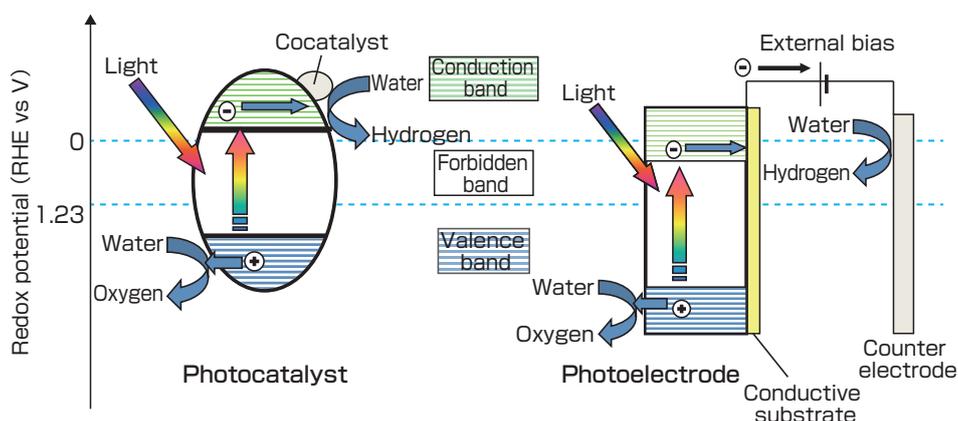


Fig. 3 Principle of water electrolysis by photoelectrode and photocatalyst using semiconductor

When light is absorbed by the semiconductor, electrons are produced in the conduction band and holes in the valence band, and these products are used in the reduction and oxidation reactions of water, respectively. The diagram of a photoelectrode is an example of an n-type semiconductor. The electrons from the conduction band move to the counter electrode and are used for hydrogen production.

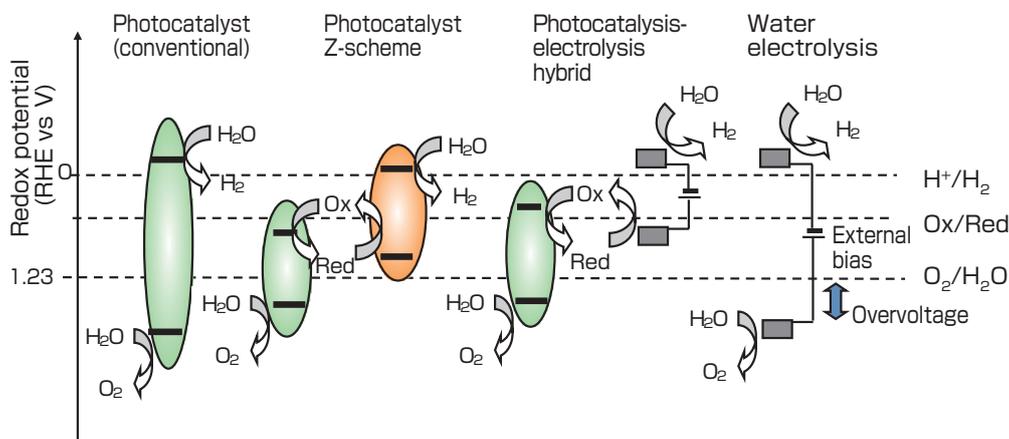


Fig. 4 Various hydrogen production technologies from water and their potential map
Ox and Red are the oxidants and reductants of the redox mediator.

Table 1. Comparison of various solar hydrogen production technologies using semiconductor

	Advantage	Disadvantage	
Photocatalyst system	Conventional photocatalyst (single-step photoexcitation)	<ul style="list-style-type: none"> Simplest External bias not necessary 	<ul style="list-style-type: none"> Efficiency is currently low Mixed production of hydrogen and oxygen Hydrogen production cocatalyst needed for large area Potential limitation of semiconductor is strict Hydrogen accumulation at large area
	Double-step photoexcitation photocatalyst (Z-scheme type)	<ul style="list-style-type: none"> More variety compared to single-step photoexcitation External bias not necessary In theory, gas separation and production are possible 	<ul style="list-style-type: none"> Efficiency is currently low Activity declines when gas separation Hydrogen production cocatalyst needed for large area Hydrogen accumulation at large area
	Photocatalysis-electrolysis hybrid system	<ul style="list-style-type: none"> Few potential limitation of semiconductor Hydrogen accumulation is easy Efficiency is currently high 	<ul style="list-style-type: none"> External bias necessary
Photoelectrode system	n-type semiconductor	<ul style="list-style-type: none"> Hydrogen accumulation at counter electrode is easy Many oxidants, preparation is easy 	<ul style="list-style-type: none"> External bias necessary
	p-type semiconductor	<ul style="list-style-type: none"> Efficiency is high at current state 	<ul style="list-style-type: none"> External bias necessary Hydrogen production cocatalyst needed for large area Hydrogen accumulation at large area Same material as solar cell, high cost
	p-type + n-type semiconductor	<ul style="list-style-type: none"> External bias not necessary 	<ul style="list-style-type: none"> Hydrogen production cocatalyst needed for large area Hydrogen accumulation at large area
	pn bonded film (without bias)	<ul style="list-style-type: none"> External bias or wire not necessary Diffusion length of charge is short 	<ul style="list-style-type: none"> Hydrogen production cocatalyst needed for large area Hydrogen accumulation at large area

is necessary over a large area, and the development of a non-precious metal for hydrogen production cocatalyst becomes extremely important. Also, a hydrogen-accumulating hood is necessary for a large area. The p-type semiconductor photoelectrode has higher efficiency at the moment compared to the n-type, but with the condition of film-forming using the same material and method as the solar cell, the cost becomes extremely high, and it is difficult to achieve the hydrogen production cost of 40 yen/Nm³ or less with the extension of this technology^[9] (in the DOE calculation, the multiple bonding film of the SIGS compound semiconductor is used). For the n-type semiconductor electrode, while the clear cost estimate is not published, it can be assumed that lower cost can be achieved compared to the p-type semiconductor photoelectrode since the method and hydrogen accumulation are simple and the precious metal is used only at the counter electrode. It is therefore studied throughout the world, mainly in Europe. The authors have reported the solar energy conversion efficiency of 1.35 % [external bias considered; applied bias photon-to-current efficiency (ABPE)] which was the highest value achieved in the n-type oxidant semiconductor photoelectrode.^[10]

4.2 Which method should be prioritized?

If there is infinite time for R&D, hydrogen production using the simplest conventional photocatalyst will probably have the lowest cost. However, considering the practical use in the near future, for example, 2030, the speed and the scale of barriers to realization must be considered, not just the future cost of hydrogen production. As shown in Fig. 2, current solar energy conversion efficiency, system cost, and complexity are in trade-off relationships with most of the technologies. Similar trends can be seen for the solar hydrogen production technology in Table 1. Although it is

difficult to compare technologies with differing advantages and disadvantages, a certain level of research concentration is necessary to accelerate the practical use. The authors considered both the hydrogen production cost and barriers to realization, and have engaged in research thinking that the originally developed photocatalysis-electrolysis hybrid system may emerge as one of the priority methods. In the following chapters, we explain the principle, background of development, current progress, reasons for prioritization considering the advantages and disadvantages, cost estimate, and research scenario toward practical use for the photocatalysis-electrolysis hybrid system.

5 Principles and advantages of the photocatalysis-electrolysis hybrid system

5.1 Limitation of photocatalytic water decomposition using visible light

The authors have engaged in the research of photocatalytic water decomposition by single-step photoexcitation for over 25 years. The complete decomposition of water by ultraviolet light (steady production of H₂ and O₂ in stoichiometric proportion) has been realized in much photocatalysis, but was difficult using visible light. Since we were studying dye-sensitized solar cells using redox mediators at the same time, we shifted our viewpoint and attempted the complete decomposition of water using two types of photocatalysts and redox mediators by simulating the Z-scheme reaction as in the double-step photoexcitation seen in plant photosynthesis. As a result, we succeeded in the complete decomposition reaction of the Z-scheme type by combining the Fe³⁺/Fe²⁺ redox, photocatalyst, and ion photoreaction with use of ultraviolet light in 1997.^[11] Moreover, in 2001, we succeeded in the photocatalytic water decomposition with visible light

only, for the first time in the world.^[12]

This was a system that used the Pt-SrTiO₃ (Cr-doped) photocatalyst in the hydrogen production side, Pt-WO₃ photocatalyst in the oxygen production side, and IO₃⁻/I⁻ as the redox mediator. This system was interesting academically as an artificial photosynthesis model, and later there were reports from a few groups on improved photocatalysts. However, the apparent quantum efficiency (QE)^{Term 1} was about 6 % and the solar energy conversion efficiency (η_{sun})^{Term 2} remained at around 0.1 %. Particularly, as shown in Fig. 4, the suitable semiconductor materials were extremely limited due to the problem of potential limitation of the conducting band, and it was difficult to raise the efficiency of the photocatalyst on the hydrogen production side.

5.2 Invention of the photocatalysis-electrolysis hybrid system

In the water decomposition reaction by photocatalyst, there are several major hurdles toward practical use, not just the low efficiency. They include the fact that hydrogen and oxygen are produced as detonating gas, a transparent hydrogen accumulating cover that has large area without gas leaks is necessary, a large amount of precious metal cocatalyst is necessary to enhance the performance of hydrogen production rate, and others. Unless these issues are resolved, practical use is difficult even if a high performing photocatalyst is discovered. Therefore, the authors considered a future image of a system that was highly practical.

We came across a paper for a pilot plant for low-voltage electrolytic hydrogen production by Fe²⁺ ion.^[13] In this paper, the objective was to recover energy from H₂S as hydrogen rather than incinerating the H₂S gas emitted from the petrochemical plant. When the H₂S is bubbled through the pool containing Fe³⁺ ions, sulfur and Fe²⁺ are produced, and sulfur is removed by filtration. Since the redox potential (E°) of Fe³⁺/Fe²⁺ is +0.77 V, the electrolytic voltage can be kept at 1 V or less when the hydrogen is produced by oxidizing the Fe²⁺ to Fe³⁺ (Fig. 4). In ordinary water electrolysis, a total of about 1.6~2.0 V is necessary because the overvoltage of oxygen production is large, in addition to the theoretical electrolytic voltage (1.23 V). The majority of the hydrogen production cost by general electrolysis is the electricity cost, and if a large amount of Fe²⁺ is present, the hydrogen production cost can be reduced greatly by reducing the electrolytic voltage.

The authors took some ideas as clues from the above, and devised a “photocatalysis-electrolysis hybrid system” that produces Fe²⁺ from Fe³⁺ while producing oxygen by oxidizing water by photocatalysts, as seen in Fig. 5, and then combining it with hydrogen-producing low-voltage electrolysis.^{[11][2]} In electrolysis, the Fe²⁺ is regenerated to Fe³⁺ to produce hydrogen. The overall reaction equations are shown at the

bottom of Fig. 5. In the conventional photocatalysis, there are limitations of the conduction band potential and valence band potential as described earlier, but in this hybrid system, the potential restriction of the semiconductor is loosened, and several visible light responsive materials can be used. Moreover, since hydrogen is not produced at the surface of the photocatalyst, there is no need to depend on a precious metal cocatalyst, and hydrogen trapping is very simple. Various ion pairs can be used for the redox mediator. If the redox mediator with redox potential close to 0 V (RHE) can be used, the electrolytic voltage becomes close to zero, and the theoretical marginal efficiency of the photocatalyst of this redox reaction becomes equivalent to the conventional, single-step photoexcitation photocatalyst. The reaction of the redox mediator itself has the same function as the storage battery. As it can be seen, the “photocatalysis-electrolysis hybrid system” is a breakthrough system that solves almost all the issues of conventional photocatalysis reaction by replacing the photocatalysis reaction on the hydrogen production side of the Z-scheme reaction with electrolysis.

Although the concept of external bias used in the photocatalysis-electrolysis hybrid system may be difficult to understand, we would like to emphasize that it is not mere energy loss. Most of the energy supplied by external bias is converted into hydrogen. If the ordinary water electrolysis is done at 1.23 V, the conversion of energy from electric power to hydrogen is 100 % efficient, that is, the energy loss is of overvoltage only. Since the overvoltage of Fe³⁺/Fe²⁺ is smaller than O₂/H₂O, it becomes small as energy loss. It is an important point that to keep the external bias at 1.23 V or less means that the apparent electrolytic efficiency can be 100 % or higher using light energy.

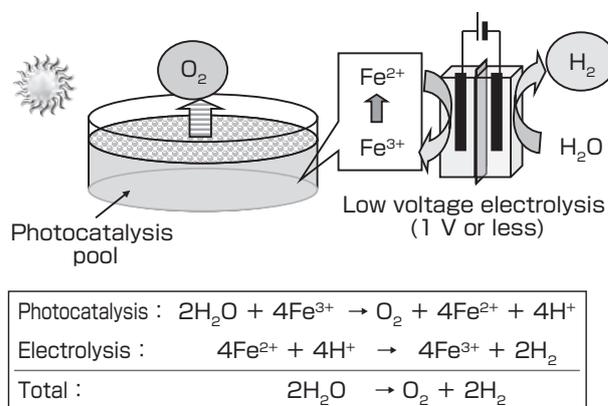


Fig. 5 Photocatalysis-electrolysis hybrid system using redox mediator

The photocatalysis pool is made of plastic bag. It consists of film formed with photocatalyst powder and electrolytic aqueous solution containing the redox mediator.

6 Technological issues in the photocatalysis-electrolysis hybrid system

6.1 Improvement of redox reactions

The elemental technologies needed for the practical use of photocatalysis-electrolysis hybrid system are shown in Fig. 6. The elemental technology development is wide ranging from the design of electrolysis device to the overall system, besides the development of the photocatalyst and the redox mediator. For the realization of the photocatalysis-electrolysis hybrid system, particularly the development of the photocatalyst with high performance redox reactions is the most important and the most difficult elemental technology development. The present status of development of this photocatalyst for redox reaction will be explained.

In the iron redox reaction, because the Fe^{3+} ion must preferentially adhere to the photocatalyst surface and receive the electron smoothly for the Fe^{3+} reduction reaction to progress with high efficiency, the reaction activity is likely to be greatly affected by the condition of the Fe^{3+} ion. Therefore, the authors studied the oxygen production reaction from various iron salt aqueous solutions using the TiO_2 powder that is a representative oxygen producing photocatalyst.^[14] As a result, it was found that the oxygen production activity of perchlorate was more than 10 times higher than conventionally used sulfates. The apparent QE of TiO_2 photocatalyst at optimal conditions was 55 % (365 nm). This is the highest value for QE at ultraviolet wavelength within sunlight in the reversible redox reaction. To be able to achieve such high QE with a simple photocatalyst is highly significant in considering the future possibility of the reaction.

Next, the visible light responsive WO_3 photocatalysts was investigated for the counter anion effect of the iron salt, and the result showed that the oxygen production activity was highest when perchlorate was used. In the perchlorate

iron solution, water preferentially coordinates with iron ion while perchlorate ion is difficult to coordinate, but the sulfate ion strongly coordinates with the iron ion. The difference of coordination of water and anion against the iron ion is thought to affect the activity. Also, when surface treatment was done against the WO_3 powder using aqueous solution containing various metal salts, it was shown that the WO_3 photocatalyst that was surface treated with cesium salt solution showed extremely high oxygen production activity.^[2] The QE at 420 nm reached 27 %, and this was the highest value in the visible light range. It is thought that there is a mechanism by which ion exchange sites are newly formed on the WO_3 surface by cesium treatment and that the adherence and reaction of Fe^{3+} and H_3O^+ are facilitated. When the solar energy conversion efficiency (η_{sun}) is calculated whereby the energy of sunlight is converted to the chemical energy of Fe^{2+} ion, it reaches 0.35 %. This value surpasses the value for switchgrass (0.2 %), a plant known as the hopeful source of biofuel. BiVO_4 is another semiconductor that can absorb longer wavelengths than WO_3 , and light up to 520 nm can be used.

The research of redox mediators other than iron ion is extremely important, and several redox mediators have been developed recently. They include IO_3^-/I^- ($E^\circ = +1.086$ V), $\text{VO}_2^+/\text{VO}^{2+}$ ($E^\circ = +1.00$ V),^[15] and I_3^-/I^- ($E^\circ = +0.545$ V).^[16] There is an advantage that the voltage necessary for electrolysis decreases as the E° approaches zero. At this moment, however, the iron redox mediator is considered optimal from the perspectives of photocatalytic activity, cost, stability, nontoxicity, and others.

6.2 Evaluation of the theoretical limit of solar energy conversion efficiency

To discuss the possibility of the practical use of the photocatalysis-electrolysis hybrid system, we conducted the estimation of the theoretical limit of solar energy conversion efficiency ($\eta_{\text{sun}}^{\text{m}}$). Figure 7 shows the photoabsorption

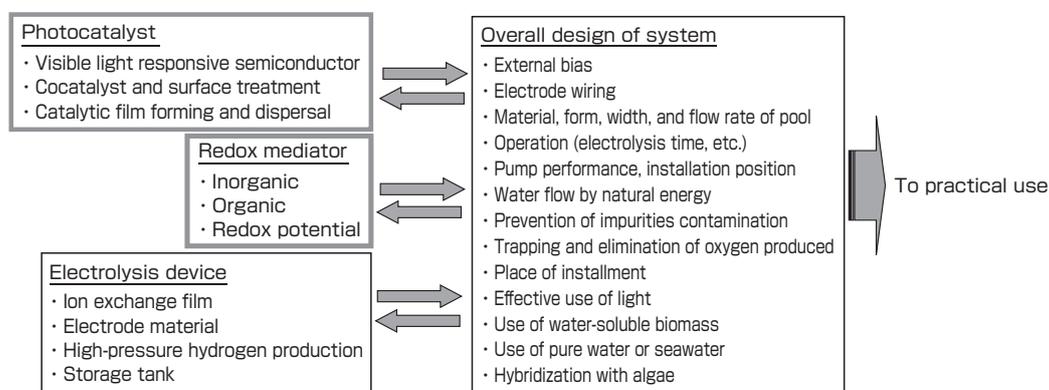


Fig. 6 Elemental technology development and scenario for achieving practical use of the photocatalysis-electrolysis hybrid system

The photocatalyst and redox mediators in the thick-lined boxes are issues that must be studied predominantly for major breakthroughs.

wavelength threshold (L_{\max} , nm) of the semiconductor and η_{sun}^m when QE is assumed to be 100 %, based on the solar spectrum data for AM-1.5 total solar irradiation as designated by JIS-C-8911. For photoabsorption rate, light with shorter wavelength than L_{\max} is assumed to have 100 % absorption (no loss by light reflection or permeation). The energy (eV) of one photon necessary for the potential difference (V) of a reaction is calculated by “ $1240/L_{\max}$.” The values for V and eV can be considered equivalent. As examples, the theoretical limits η_{sun}^m of photocatalysis reactions when the iron redox is used and when an ideal redox mediator where the redox level is 0 V are shown. Theoretically, the long wavelength light of up to 2,700 nm and 1,000 nm, respectively, can be used, but it is not realistic to set the loss (U_{loss}) from reaction overvoltage to zero. For the estimate of U_{loss} , the electrolytic voltage of 1.6 V or less (corresponds to 0.37 V or less in U_{loss}) has been achieved in the hydrolysis method so far. In photosynthesis, it is notable that the potential difference of individual redox mediators in various electron transfer processes is about 0.2 V. If iron and ideal redox mediators are used with minimum U_{loss} value (0.4 V as for two electron transfer processes), the photocatalytic reactions can be used up to 1,440 nm and 760 nm, respectively, and their η_{sun}^m will be maximum 24 % and 30 %, respectively. As such η_{sun}^m is much larger in theory than the actual η_{sun} obtained, the experimental values are likely to increase in the future.

For the current semiconductor material, η_{sun}^m is about 2.4 % when the reduction of the iron redox mediator is conducted at QE = 100 % as all light up to 480 nm are entirely absorbed as in the WO_3 photocatalyst. If all light from 520 nm to 600 nm can be used for this reaction as in BiVO_4 or Fe_2O_3 , it can be seen that the values from 3.6 % to 6.2 % can be

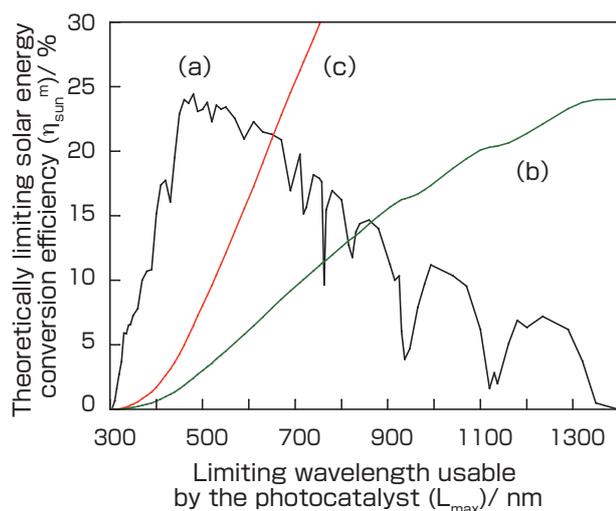


Fig. 7 Theoretically limiting solar energy conversion efficiency (η_{sun}^m) for the redox reaction of photocatalyst
 In the case where the quantum efficiency and photoabsorption efficiency up to the limiting wavelength that can be used by photocatalyst is 100 %; (a) Sunlight spectrum, (b) iron ion redox reaction, and (c) $E^\circ = 0$ redox reaction.

achieved. The relationship of L_{\max} and η_{sun}^m when QE is used as the variable using the iron redox mediator is shown in Fig. 8. It can be seen that η_{sun}^m of 3 % can be achieved if the QE is set at about 80 % using light up to 520 nm. The major characteristic of photocatalysis is that the reaction is complete with one particle, so that mixing and layering of several photocatalysts are easy. In cases where different semiconductors are layered in the photoelectrode, matching of the conduction band and the valence band is necessary, but this does not have to be considered in photocatalysts. This means, the whole performance can be increased by concurrently conducting the research to improve the QE in each photocatalyst and then combining them.

6.3 Practical evaluation of the solar energy conversion efficiency

Next, the solar energy conversion efficiency (η_{sun}) that was actually obtained will be discussed. The result up to now is that the η_{sun} of the powder photocatalysis reached about 0.35 %, as mentioned earlier. While this value seems to be very small compared to photovoltaic generation, it is at the level surpassing the efficiency of plants such as the switchgrass. For example, in the case of bioethanol production using biomass energy, the η_{sun} is about 0.8 % and algae that has the highest performance is about 3 %. Although these values are one digit less than the values for photovoltaic generation, it is important to note that it has been put to practical use in some countries and regions. Bioethanol has the major advantage unavailable in photovoltaic generation that the energy can be stored. As it can be seen, economic feasibility can be maintained sufficiently depending on the conditions and cost even if the η_{sun} is small. The concept of photocatalytic water

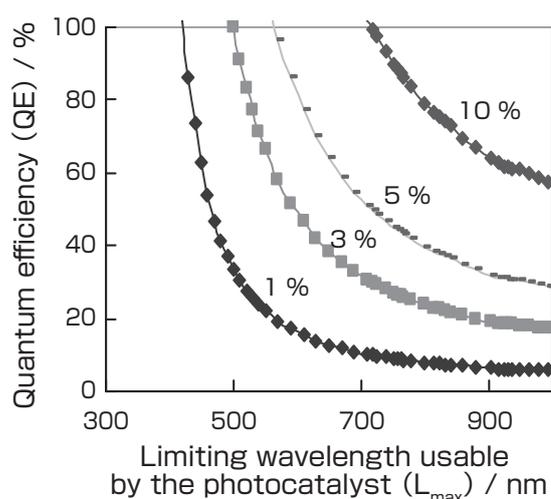


Fig. 8 Quantum efficiency (QE) of the iron ion redox reaction of photocatalyst ($E^\circ = +0.77$ V) and the theoretically limiting solar energy conversion efficiency (η_{sun}^m)
 In the case where the photoabsorption efficiency up to the limiting wavelength that can be used by the photocatalyst is 100 %

electrolysis is closer to biomass energy than photovoltaic generation in the sense that the solar energy can be stored directly as chemical energy, and to surpass the η_{sun} of biomass use is a major milestone.

The solar energy conversion efficiency by current photocatalysts is much lower than that of algae, but the increase of efficiency of the light reaction of biomass must be achieved by genetic recombination, and there is a limit to how much artificial manipulation can be done. On the other hand, the efficiency of photocatalysts can be increased dramatically by finding the materials and devising preparation methods. Moreover, unlike biomass ethanol, the photocatalytic energy conversion storage does not require the processes of harvesting, grinding, glycosylation, or fermentation. It also has the advantage that it will not wither, does not require care of cultivation, and can be used in deserts or on the sea. The photocatalytic reaction using redox is an ultimate artificial photosynthesis system that can take place in a simple, uncovered pool. By comparison with biomass use, if it can achieve 3 % or more as its η_{sun} goal, it can sufficiently compete with photovoltaic generation.

7 Cost estimation of the photocatalysis-electrolysis hybrid system and the possibility of its practical use

Ultimately, in the discussion of practical use, it is necessary to estimate the cost of the whole system and compare the costs of hydrogen production. For the photocatalysis-electrolysis hybrid system, we must see whether the hydrogen production is possible at lower cost than the system that combines photovoltaic generation and water electrolysis in the Interim Goal ①, and whether the cost will be 30 yen/Nm³ or less that is the goal of the Interim Goal ② and NEDO. For the solid polymer film electrolysis used in the cost estimation,

the report of the Central Research Institute of Electric Power Industry was used as a reference.^[7] For the photocatalysis pool and land price, the DOE report was used.^[9]

As the water electrolysis device to be compared, a large-scale solid polymer hydrolysis device (32,000 Nm³/h) is assumed. For the electricity cost, the least expensive power during the time zone is selected, and 8 yen/kWh (corresponds to nighttime electricity rate) at 40 % operation is assumed. For the photocatalysis-electrolysis hybrid system, iron ion redox is used with solar energy conversion efficiency (η_{sun}) of the photocatalyst at 3 %. Other assumptions are: the photocatalyst cost is twice that of WO₃, the photocatalyst pool is made of polyethylene, depreciation of 10 years, Fe²⁺ is produced during the day and electrolysis is done during the night (10 h). The results and the example of the assumptions are shown in Fig. 9. The area of the photocatalyst pool needed for the above production of hydrogen is 3 km². The photocatalysts pool cost is 268 yen/m², and it is the same level as the DOE report (about 300 yen/m²). The premium price over the costs related to the photocatalysts pool (facility, pump, cost of labor, land cost, management fee, interest, etc.) is about 3 yen/Nm³. If the electrolysis voltage of the electrolyte solution containing Fe²⁺ is set at 0.8 V, the cost of electric power can be reduced to half, and the cost merit of this part is extremely high compared to the usual electrolysis. From the above assumption, the hydrogen production cost of the photocatalysis-electrolysis hybrid system was estimated to be about 25 yen/Nm³. Under the same conditions, the hydrogen production cost by the usual large-scale water electrolysis using power at 8 yen/kWh would be about 41 yen/Nm³. As mentioned in chapter 3, the power cost by photovoltaic generation is currently around 40 yen/kWh, and even if 7 yen/kWh (the development goal for 2030) is achieved, the hydrogen production cost will be over 35 yen/Nm³. As a result of the above calculation, it was shown that for the Interim Goal ①, the photocatalysis-electrolysis hybrid

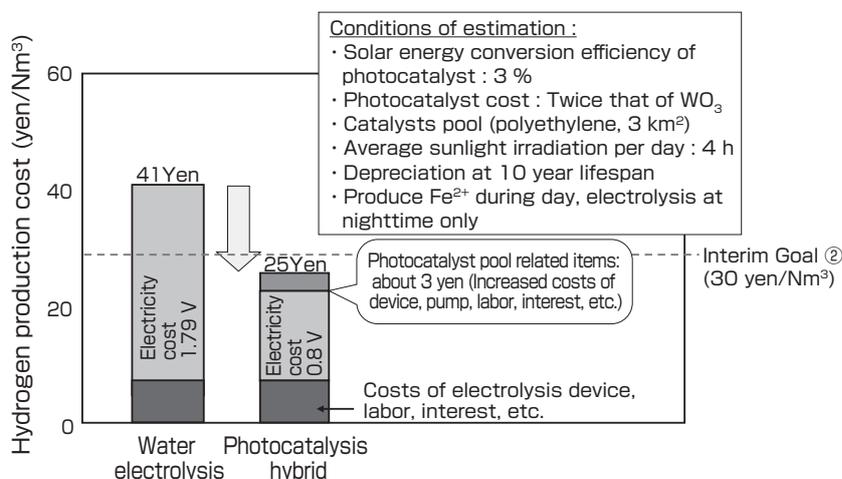


Fig. 9 Detailed cost estimation of the photocatalysis-electrolysis hybrid system

Common conditions: solid polymer type electrolysis (32,000 Nm³/h), electricity cost 8 yen/kWh, and 40 % operation rate

system is capable of producing hydrogen at lower cost than the system that simply combines the photovoltaic generation and water electrolysis. Moreover, possibilities were shown of lowering the cost of hydrogen production through the photocatalysis-electrolysis hybrid system using any kind of electric power including photovoltaic generation. Also, it can be said that 30 yen/Nm³ or less of the Interim Goal ② can be achieved depending on the conditions. This is the basic data of the cost estimation.

In practice, it is necessary to additionally consider the factors of cost increase and decrease based on this calculation. The cost increase factors include, for example, electricity charges, land cost, and cost of measures against natural disasters such as typhoons. If the electricity charges are set at 1.5 times higher or 12 yen/kWh with the aforementioned assumption, the electrolysis system hybridized with photocatalysts and the usual electrolysis without hybridization will be 33 yen/Nm³ and 58 yen/Nm³ respectively. The cost decrease factors include the development of an excellent redox mediator with redox potential closer to zero than iron ion as well as improved solar energy conversion efficiency of the photocatalyst. Since the theoretical limit is about 24 % and 30 % for the iron ion and an ideal redox mediator as explained above, the increase in performance of the photocatalyst in the future is possible, and the area of the photocatalyst pool can be reduced. Also, if the electrolyte power can be brought close to zero using the ideal redox mediator, the hydrogen production cost will be nearly 14 yen/Nm³. Considering both the cost estimation results and the low barrier to realization (possibility of realization and time), it can be concluded that there is significance in concentrating on this system.

8 Scenario toward practical use

8.1 Social roadmap

In the photocatalyst research of the Future Pioneering Project of METI, the goal values for the efficiency of solar energy contributing to hydrogen production were set as 1 %, 3 %, 7 %, and 10 % for FY 2014, 2016, 2019, and 2021, respectively. Recently, in the Innovation Plan for Environmental Energy Technology that includes the schedule of technological development up to 2050 as measures against global warming issued by the Council for Science, Technology and Innovation, the addition of artificial photosynthesis and solar hydrogen is being deliberated, and the above goal values are followed. While there is vagueness in the definition of the numerical goals, they should serve as an approximate time frame for the scenario toward practical use of solar energy conversion efficiency. Following the NEDO's hydrogen production roadmap for the hydrogen production cost, the Interim Goal ① is to be achieved before 2020, and 30 yen/Nm³ or less of the Interim Goal ② will be pursued by 2030.

8.2 Future research prospect of solar hydrogen production

The hydrogen production by sunlight using the photocatalyst (and photoelectrode) was developed mainly in the chemistry field, and was studied as part of artificial photosynthesis. However, in the future, the authors think that the term "solar hydrogen production" should be used preferentially as a keyword to allow hybridization of different fields to accelerate the practical use. As mentioned in chapter 2, solar hydrogen production is a term that clearly indicates the objective-oriented *Type 2 Basic Research*. Also, there is a school of thought which considers that external bias should not be used in artificial photosynthesis, but in solar hydrogen production, it is thought that it should be actively employed. Whether the photocatalysis-electrolysis hybrid system can be put to practical use depends heavily on the total system design including the external bias as shown in Fig. 6, as well as the improvement of the performance of photocatalytic reaction. There are very few researchers in this field, and the application to practical use is expected to accelerate if the hybridization of different fields (new participation from different fields and developments within different fields) progresses. The "photovoltaic generation + water electrolysis" in the Interim Goal ① is not a rival, but should be considered one of the partners with whom we should hybridize.

The photocatalysis-electrolysis hybrid system is similar to the concept of the hybrid automobile. It is natural that the vehicle price increases if the gasoline engine, motor, and batteries are simply all installed in an automobile, and it may not necessarily improve the actual fuel consumption. The fuel consumption is reduced only when all elemental technologies are optimized and work complementarily. The hydrogen production cost of the photocatalysis-electrolysis hybrid system corresponds to fuel consumption. Even if the initial investment of the whole system is high, we may see the prospect for practical use by decreasing the hydrogen production cost or by increasing the additional value. In the initial phase of this research, new development in photocatalyst materials such as semiconductors and cocatalysts is extremely important. The authors are working on a high-speed automatic screening technology for material development.^[17] There are countless numbers of metal compositions for semiconductors and combinations of cocatalysts and redox mediators, and searching by human hand is limited. By using a high-speed automatic screening technology, it may be possible to quickly find some unexpected, novel material candidates. As a ripple effect of this research, the research for photocatalytic reaction in the redox mediator can be directly applied to the research of oxygen-producing photocatalyst of Z-scheme reaction. Also, research for fuel cells using Fe²⁺ ion and redox flow batteries is being done, and if it becomes possible to produce large amounts of redox mediators with high reductive capacity

using solar energy, it will be possible to convert the stored energy into electric power rather than hydrogen.

8.3 Practical introductory scenario

Concurrently with the search for materials in the early phase of this research, it is necessary to conduct small verification tests for the whole system to extract and solve problems. The material development for photocatalysts will progress mainly at universities and research institutes, and the companies can utilize their potentials for designing the device and electrolysis. Therefore, collaboration of industry-academia-government is important. The authors plan to conduct small-scale verification experiments for an integrated system in the future.

Since the photocatalytic pool functions as a large storage battery, the important characteristics is that it is highly compatible with renewable energies with high fluctuation such as wind generation as well as photovoltaic generation. Accompanying the wide introduction of renewable energy, the storage of its output variation is necessary. As the technology to store a large amount of electric power at lower cost than ordinary batteries, the hydrogen production by electrolysis is being studied for the excess power of renewable energy such as wind and photovoltaic generation. Depending on the location, this electrolysis device can be combined with photocatalysts and redox reactions. If the daytime and nighttime electrolysis can be combined, the facility operation rate will increase and the hydrogen production cost can be reduced further. Large-scale smoothing of power load at short and long cycles can be achieved. The hurdle in using the excess power is low for the initial introductory verification, and the full verification research of the hybrid system for such excess power electrolysis and photocatalysts will be the first step toward practical use.

Terminologies

- Term 1. Apparent quantum efficiency (QE): percentage of the number of photons used in a reaction against the number of incident photons at a certain wavelength.
- Term 2. Solar energy conversion efficiency (η_{sun}): percentage of energy extracted against the incident solar energy. In case of iron ion, it is the percentage of energy stored in the reaction in which Fe^{3+} is reduced to Fe^{2+} by decomposing water into oxygen. In the case of agricultural crops, it is the percentage of stored energy calculated from the annual amount of dried crop harvested against the annual total solar energy. Since η_{sun} is determined by several factors such as photoabsorption wavelength range, photoabsorption efficiency, QE, and percentage of photon energy stored in a substance, it becomes smaller than the value of QE.

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Discussions with Reviewers

1 Overall

Question and comment (Yasuo Hasegawa, AIST; Hiroshi Yanagishita, Research Institute for Innovation in Sustainable Chemistry, AIST; Hiroshi Tateishi, AIST)

This paper sets as its main topics the R&D goal and scenario that are important in promoting the long-term R&D for the practical use of solar hydrogen production. It also describes the process by which the results of the basic research are expanded into various projects, and therefore, we believe it is appropriate as a paper to be published in *Synthesiology*. In general, the flow of R&D takes the course in which the scenario for practical use can be drawn only after what is considered to be *Type 2 Basic Research* is achieved. However, in this particular research, the scenario for practical use is drawn at the basic research phase. Please emphasize the necessity and importance of doing so.

Answer (Kazuhiro Sayama)

The point that you indicate is certainly the point that I wish to convey the most in this paper. There is a long history of solar hydrogen production technology development, and while this applies generally to the development of energy technology that requires a long time before it is put to practical use, the progression and direction of basic research is greatly affected by the fluctuations in energy prices and changes in energy policies, and I think those are the major barriers in promoting the R&D. To effectively promote the practical use of R&D that requires a long period of time, I think a long-term R&D plan that clearly states the development goal, milestones, and the scenario toward practical use is particularly important. These points were explained in detail in chapters 1 and 2.

2 Scenario and time axis

Question and comment (Hiroshi Tateishi)

In general, the usual course to promote the introduction of new energy technology and to achieve practical use is to start the verification research at introduction even at high cost, by combining the subject with large added value and other R&Ds, and to attempt cost reduction through concurrent basic research. In the scenario of chapter 7, can you describe this development clearly considering a time axis if possible?

Answer (Kazuhiro Sayama)

As you indicated, the overall flow along a time axis of the research for solar hydrogen production toward practical use was added in the first paragraph of chapter 7. In the photocatalyst research of the Future Pioneering Project of METI, the goal value of 10 % by FY 2021 was set as the efficiency with which solar energy should contribute to hydrogen production. This goal is followed in the Innovation Plan for Environmental Energy Technology of the Council for Science, Technology and Innovation. For the hydrogen production cost, if the NEDO's hydrogen production roadmap is followed, the Interim Goal ① should be achieved before 2020, and 30 yen/Nm³ or less of the Interim Goal ② will be sought by 2030.

3 Goal setting, scenario, and the synthesis and integration of elemental technologies

Question and comment (Hiroshi Tateishi)

Please describe more clearly the "specific scenario, research procedure, and process of synthesis and integration of the elemental technologies including the goal setting and social value" that is part of the purposes of publishing *Synthesiology*. Also, please make sure that researchers of different research fields can easily understand how *Type 1 Basic Research* conducted by you leads to *Type 2 Basic Research* and *Product Realization Research*.

Answer (Kazuhiro Sayama)

To ensure that the researchers of other fields, not just those of this field, would understand, I explained the process from *Type 1 Basic Research* to *Type 2 Basic Research*, and to the final goal of solving the energy problem.

4 "Artificial photosynthesis"

Question and comment (Hiroshi Yanagishita)

This paper mainly discusses the technological development for efficiently producing solar hydrogen. On the other hand, the term "artificial photosynthesis" is used in general, including the solar hydrogen production technology as described in this paper, and there are government R&D projects with this name. Is "artificial photosynthesis" a process for producing organic material using sunlight as in the photosynthesis in plants?

Answer (Kazuhiro Sayama)

"Artificial photosynthesis" that the general public thinks of is

the process of synthesizing organic material from CO₂, and it may be unnatural to include the technology of producing hydrogen by water decomposition using sunlight as “artificial photosynthesis.” On the other hand, in the roadmap of the Innovation Plan for Environmental Energy Technology of the Council for Science, Technology and Innovation, artificial photosynthesis and hydrogen production by sunlight are included in the category for “recovery, storage, and use of carbon dioxide,” and it has always been discussed as part of CO₂ use.

The photosynthesis mechanism is divided into the light reaction where water is decomposed and the dark reaction where CO₂ is fixed. To solve the energy problem it is necessary to simulate the former, but in general, attention is paid to the latter. There is no term that clearly expresses the importance of the reaction that simulates the former light reaction, and we needed a new term. Therefore, in this paper, we decided to use the term “solar hydrogen production,” which is now being recognized little by little, and provided detailed explanation.

Considering the background of the historical progress of the field and the principles, I think “solar hydrogen production” should be positioned within “artificial photosynthesis” (Fig. 1). In the wide-ranging field of artificial photosynthesis, the research of hydrogen production by sunlight has been rapidly progressing, and the author believes that it can eventually achieve practical use. In this paper, we defined “solar hydrogen production” as a term that expresses the objective-oriented *Type 2 Basic Research* to realize a sustainable society by creating hydrogen from solar energy and water.

On the other hand, in the future, I think there may be problems if we continue to position “solar hydrogen production” within “artificial photosynthesis.” For example, the term “artificial photosynthesis” is strongly linked to the chemistry field and *Type 1 Basic Research*, and this may be a hurdle for the development in diverse fields (particularly physics, engineering, and corporate participation) that are essential in achieving the practical use of the “solar hydrogen production” technology. I think we should widely use the term “solar hydrogen production” as a keyword to express the shift from *Type 1 Basic Research* to *Type 2 Basic Research*.

5 Time frame for achieving practical use

Question and comment (Hiroshi Yanagishita)

There are still several issues that must be cleared before achieving the practical use of technology for solar hydrogen, and I

think it is often considered as a technology for the distant future. What perspective do you have on the time frame for achieving practical use?

Answer (Kazuhiro Sayama)

As it could not have been imagined 20 years ago that photovoltaic generation would rapidly spread to homes as today, I think “solar hydrogen” will also diffuse dramatically through some technological breakthrough, as long as the principles and assumptions are appropriate and the scenario is clear. As explained in chapter 7, I think the verification research using excess electric power is the first step.

6 Future strategic development and system of the R&D

Question and comment (Hiroshi Tateishi)

I think this paper assumes a hydrogen society centering on fuel cells. For use of fuel cells, the stationary type and automobile type are assumed, and the current mainstream is fossil fuel reformulation for the former and pure hydrogen for the latter. On the other hand, the powerful sales point in the current society for photovoltaic power generation is that electric output can be obtained directly. To store solar energy by converting it into an energy mediator such as hydrogen is effective in stabilizing output temporally and spatially, but new issues are generated at the same time. How can hydrogen be stored – in high pressure, in hydrogen storing substance, or as liquefied hydrogen? How will it be transported?

Also, when actually constructing a system proposed in this paper, are you going to put it in cities or some desert or field? I think there may be different technological issues depending on the location.

It is necessary to concurrently engage in the energy system design, and I think you should discuss this with the researchers of systems in the course of future strategic development of R&D.

Answer (Kazuhiro Sayama)

The primary motivation of our research up to this point is to realize conversion and storage for solar energy. If we can produce a large amount of hydrogen from sun and water, we will be very happy just with that, and since there are many researchers who will think about how to use hydrogen, I think the research will progress rapidly.

On the other hand, I recognize that for practical use, energy system design is another side of the coin. In the future, I would like to get the systems researchers involved in the discussion to achieve the practical use of solar hydrogen production.