Basic Science and Understandings for Production and Distribution of Hydrogen

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1. Introduction

In Japan, at present, the science and technology master plan is being revised. This master plan determines the direction of the scientific and technological research for the coming 5 years. In the preliminary version of the document of the master plan, it is pointed out, as expected, that we have to put forward the research on hydrogen fuel cells, which is the key technology in order to realize the “hydrogen society”.

In the middle of June this year, Toyota and Honda obtained authorization of hydrogen vehicles from the authority, which means they can start mass production of hydrogen fuel cell vehicles in Japan. In other words, until now they had to obtain authorization of a hydrogen vehicle on a one by one basis, but from now this kind of procedure is no longer necessary. TV news has stated Japan is ready to go into the hydrogen society.

When explained on TV, the hydrogen fuel cell vehicle (FCV) usually comes with a message like: "there is no emission of toxic substances", or, “it emits only pure water ". Most of the general public normally believes hydrogen FCV is the ideal car of the future.

What is the real outlook for the hydrogen FCV? Is it really ideal in the future? Does it have technical advantages with respect to environmental aspects? Does it have any superior points in economical aspects?

In this paper, the prospect of the future of hydrogen FCVs is described on the basis of basic sciences with regard to how to make hydrogen and how to deliver hydrogen along with some discussion on the future problems to be solved before hydrogen FCVs really become common in actual use.

2. The basic sciences of hydrogen fuel cells: promises and difficulties

Some technical barriers must be overcome if hydrogen fuel cells are to be used in the automobile businesses. Such a situation is schematically express in figure 1.

The first thing we have to overcome is the reduction of production cost. Currently, the price is said to be about 200,000,000 yen (ca. $ 2 million), but it is necessary to reduce the price to less than about 3,000,000 yen. (ca. $ 30,000). It is very common for any industrial product in the early stage of production, that the price is very high and drops after mass production is started. However, a key component that will determine the cost reduction in hydrogen fuel cells after mass production begins is the catalyst. The catalyst is used to oxidize hydrogen
with the help of air to generate electricity. Currently, the catalyst is made of platinum, which is also very common in most oxidation processes in chemical industries. If it is inevitable to use platinum as the catalyst, there will be large supply problems. Approximately, 30 grams of platinum are needed to build one hydrogen FCV. Even if the weight of the platinum can be reduced to some 10 grams or so, it is necessary to have more than 600 tons of platinum to build 60 million cars in the world. Average production of platinum per year is about 200 tons. While there are sufficient platinum resources, the cost will go up very sharply if hydrogen FCVs are mass-produced.

![Barriers to Diffusion of FC Cars](image)

Figure 1. Barriers for cost reduction of hydrogen FCVs

The supply problems of platinum indicate that we have to develop oxidation catalyst with elements other than platinum or within platinum family, such as palladium or rhodium. Let us consider the role of catalyst in the fuel cell.

The chemical reaction used in the fuel cell is rather simple. It is a typical oxidation reaction.

\[ 2H_2 + O_2 \rightarrow 2H_2O \quad \text{(eq.1)} \]

Platinum is one of most effective catalysts for an oxidation reaction. The temperature of the reaction is as low as 80°C, and this temperature is far below the optimum temperature for oxidation. Chemists have long been trying to find out effective catalysts for oxidation without using platinum for many chemical processes.

Another drawback related to temperature is the poisoning of the catalyst. Carbon monoxide is known as a substance to cause catalyst poisoning in oxidation process. It is, therefore, necessary to purify hydrogen up to 99.9%, if it is to be used for fuel cell operated below 100°C. The problem of CO contamination is very serious, because in the early stages hydrogen will be produced by partial oxidation process of natural gas, and the contamination of hydrogen with small amount of CO cannot be avoided.

\[ CH_4 + 1/2O_2 \rightarrow 2H_2 + CO \quad \text{eq.(2)} \]

In order to produce polymer electrolyte type fuel cells (PEFC) with reasonable costs, the
development of catalyst is the most important factor and the possibilities are still unknown.

3. Basic science for hydrogen supply problem
3.1 Criteria to realize hydrogen society

Even when hydrogen FCVs become available, the hydrogen society will still not be realized. Unless the development of the infrastructure for the hydrogen supply is completed, hydrogen FCVs cannot be used.

It is necessary to jump over various obstacles to reach the hydrogen society. The situation is schematically expressed in figure 2.

![Barriers to Hydrogen Supply](image)

**Figure 2.** Barriers to be overcome for hydrogen supply

The most important point is that hydrogen is not primary energy. We need some other energy to produce hydrogen, though so many possible ways to produce hydrogen exist. As already described, the easiest way to produce hydrogen is from methane (natural gas) from the view point of production cost, although it is inevitable to remove CO from the reaction gas for the use of PEFC.

Hydrogen FCVs the advantage of emitting only water during operation, but the production process of hydrogen from methane (natural gas) accompanies the emission of CO₂. If the CO₂ emission of the fuel preparation process is low enough, then the environmental advantage still exists.
Figure 3. Well to Wheel CO2 emission for various type of automobiles

As shown in figure 3, the CO2 emission for hydrogen FCV is not the best according to the data comparing the overall emission of CO2 for several types of vehicle.

The hydrogen FCV does not emit any carbon dioxide while running, but emissions in hydrogen production can be considerable and could exceed the emissions by several hybrid type vehicles, such as the first and second generation of Prius. The Prius is a hybrid car, which was introduced in Japanese market in 1997 by TOYOTA and it is equipped with both a gasoline engine and an electric motor. The Prius uses gasoline for fuel but the overall efficiency is very high.

US EPA recently announced the ratings of fuel economy of all motor vehicles sold in USA. The table 1 shows the top 5 vehicles with the fuel economy for city and highway mode.

Table 1. Fuel economy top five for vehicles sold in the USA in 2006.

<table>
<thead>
<tr>
<th>Name of Car</th>
<th>City/Hwy mpg</th>
<th>City/Hwy km/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Honda Insight (manual)</td>
<td>60/66 mpg</td>
<td>25/28 km/L</td>
</tr>
<tr>
<td>2. Toyota Prius (automatic)</td>
<td>60/51 mpg</td>
<td>25/21 km/L</td>
</tr>
<tr>
<td>3. Volkswagen Golf TDI (manual)</td>
<td>37/44 mpg</td>
<td>16/19 km/L</td>
</tr>
<tr>
<td>4. Volkswagen Jetta TDI (manual)</td>
<td>36/41 mpg</td>
<td>15/17 km/L</td>
</tr>
<tr>
<td>5. Ford Escape Hybrid FWD</td>
<td>36/31 mpg</td>
<td>15/13 km/L</td>
</tr>
</tbody>
</table>

The overwhelming victory goes to the top two cars, which are both hybrid vehicles. A SUV by Ford is ranked in the 5th place, which is a hybrid as well. The fuel economy of the Golf and Prius can be compared because the weight of both vehicles is not so different. Diesel for highway mode is high and almost comparable with that of hybrid, but the difference in city mode is noteworthy.
It is meaningful to compare the efficiency of vehicles in terms of energy efficiency. The data provided by TOYOTA is shown in figure 4. This graph compares so called “well to wheel efficiency” for an ordinary gasoline automobile, old and new hybrid vehicles, a hydrogen FCV and a hydrogen FCV in the future. The current model of Prius shows 32% efficiency, whereas that of current hydrogen FCV has 29%, though efficiency of the vehicle itself is about 50%, which is high enough to compare with the 37% for the hybrid vehicle. The reason for rather low value in “well to wheel” efficiency is ascribed to the low value of fuel efficiency. Fuel efficiency here refers to the process of obtaining hydrogen from natural gas. If the hydrogen FCV will become competitive in efficiency, it will be necessary to increase fuel efficiency by up to 70%.

3.2 Renewable electric energy and hydrogen production

In order to solve the global warming problem, it is necessary to enhance the use of the renewable energy. Many kinds of renewable energy must be considered. Most promising form of energy is electricity and hydrogen can be produced by the electrolysis of water.

\[2 \text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2\]

A wide range of scenarios is proposed but the most promising one is wind turbines or photovoltaic cells. These two share the drawback of dependency on the weather. The best strategy is to get connection to a commercial power grid. It is sometimes impossible to do so because of the location or because of the policy of the electric power corporation. In these cases, it is necessary to store electricity when the conditions are suitable and use electricity in other situations. However, it is very difficult to store electricity.

For the load leveling purpose, pumped hydropower generation or large scale battery systems such as Na-S secondary battery are currently used. Low cost systems such as lead batteries are not high enough performance, in terms of durability.

Electrolysis of water seems one of several ways to utilize renewable energy. But there is one problem: low efficiency of the electrolysis process. As an industrial process, iron
electrodes are commonly used for electrolysis. In the process using metal electrodes other than platinum accompanies so called over-voltage for electrolysis. Only 1.23V is enough to decompose H₂O molecule, but if iron electrodes are used it is necessary to apply more than 2.2V. The efficiency of electrolysis process, therefore, becomes almost 50%, which is rather low.

The conclusion of the possibility of the combination of renewable energy and hydrogen is uncertain. If electricity generated by renewable energy can be used as it is, energy efficiency is higher but it is necessary to invent an appropriate method to store electricity. It is still uncertain whether a new way of the electricity storage can be developed or not. It seems the price of energy will be one important factor to determine the situation. If the price of energy goes up then the storage of electricity meets the target of cost reduction. In Japan, we already have many pumped hydropower stations, but most of them are not in operation due to high operation cost.

3.3 Other method of hydrogen production

There is a way to produce hydrogen without using electricity from renewable energy. This involves solar heat energy with solar heat collectors equipped with many mirrors, which are controlled to reflect solar light to one spot. In order to produce hydrogen, it is necessary to operate two kinds of loops of chemical reactions in different temperatures.

Figure 5. Thermal decomposition of water by using Solar furnace or HTGR

The principle of this process was invented by General Atomics Inc. and is composed of the following three chemical reactions.

\[ 2\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2 \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4 \] eq.3 (Bunsen reaction)

\[ 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \] eq.4 (Decomposition of hydrogen iodide)

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 1/2\text{O}_2 \] eq.5 (Decomposition of sulfuric acid)

Iodine and sulfur dioxide are used in the first reaction. The reaction temperature for decomposition of sulfuric acid is 900 °C and that for hydrogen iodide is 400 °C. With the solar
heat, it may be difficult to control two kinds of temperatures in a stable state.

There is one more possibility to operate this reaction without using fossil fuels: a high temperature gas cooled reactor utilizing atomic energy.

Biomass is a rather special kind of renewable energy, because it can be transformed into several forms of energy. Biomass can be converted into hydrogen as shown by the equation 6.

\[
\text{CH}_2\text{O} + \text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \text{eq.6}
\]

This reaction is also a kind of oxidation reaction. It is therefore very difficult to produce hydrogen without any contamination of CO.

If carbon such as coal or other form is to be obtained as raw materials, hydrogen can be produced from reaction to produce “the water gas” by equation 7.

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \quad \text{eq. 7}
\]

Because this is an endothermic reaction, it requires heat. Heat can be obtained by burning CO after separation from the product gas.

In the steel industry, coke ovens are used to manufacture coke (consisting of approximately pure C) from coal composed of CH₂ (on average). Huge volumes of hydrogen are produced as a byproduct in this process, but it is left unused or used for the production of ammonia. As already described, the reason of the low value of hydrogen by this process is due to the impurity of CO, which has a poisonous effect on the catalysts in fuel cells.

4. The basic science of the hydrogen storage

The hydrogen FCV must carry at least 5 kg of hydrogen to realize hundreds kilometers of cruising range. In the standard condition, 5 kg of hydrogen occupies the volume of 56m³. If available volume for fuel tank is limited to 70 liters in automobiles, it is necessary to store hydrogen with the pressure of 80,000 kPa (800 atm.). It was believed the maximum pressure for high pressure gas storage will be limited up to 350 atm, but recent advancement in the technology made it possible to increase the pressure to 700 atm, which is almost enough to be used as the way of storage of hydrogen.

Several other methods to store hydrogen were examined and tested, including liquid hydrogen, metal hydrides and organic compounds containing hydrogen. Conclusions obtained so far are not promising. Liquid hydrogen has difficulties because of low temperature (\(-253^\circ\text{C}\)), and metal hydrides have difficulties concerning required temperatures to decompose and supply hydrogen to fuel cells. Naphthalene reacts with three moles of hydrogen to form decahydronaphthalene (decalin). Decalin can be decomposed back to naphthalene by emitting 3 moles of hydrogen. It is therefore possible to store hydrogen in the form of organic compounds. This process will be useful to transport hydrogen from the production site to the place of consumption.

5. Conclusions.
Hydrogen energy is still a future technology. Many technical hurdles must be jumped before we arrive at the so-called hydrogen society.

As for the fuel cells with polymer electrolyte, the development of the catalyst is the largest problem to be overcome. The development of catalysts without using the platinum family and with strong endurance against CO contaminated hydrogen is necessary. It is difficult to predict the possibility of success in the preparation of such a catalyst.

How do we make hydrogen? This is the second most serious problem to be solved. The easiest method of production of hydrogen is from natural gas, but the “well to wheel” energy efficiency for this process has limitations, because the production process requires energy for decomposition of methane molecules.

Hydrogen has the advantage of no emissions of CO₂, which is becoming a common expectation from the society in general. It is therefore necessary to develop an effective method to produce hydrogen using renewable energy or atomic energy. Electrolysis of water has the disadvantage of low efficiency. If enough electricity can be obtained by means of renewable energy, it will be smart to use electricity as it is with the invention of electricity storage devices.

It seems water decomposition by heat has more realistic possibilities. Heat can be obtained by solar furnaces or atomic reactors.

The hydrogen storage is also quite a difficult problem to be solved. If the a high-pressure container up to 700 atm becomes available, it will not necessary to use other technologies.

In conclusion, it is difficult to suppose that the hydrogen FCV will be the most common automobiles in any country by the year 2030, which is the year when peak petroleum production is expected to occur. Until that time, electric vehicles can be used for city commuters and hybrid type vehicles are suitable for suburban transportation.