

# R&D Policies of KUCEL-MERIT Group on The Sodium Borohydride Hydrogen Energy Systems

## Preface

A fuel cell using gaseous hydrogen as a fuel for the anode and air as a source of oxygen for the cathode is called a Polymer Electrolyte Membrane Fuel Cell or a Proton Exchange Membrane Fuel Cell (either way abbreviated to PEMFC), which has been eagerly developed as a propulsion source of a car.

It has been a long time since hydrogen started to get attention as a clean energy source, but there are few applications in which hydrogen is actually used as an energy source. The one and only successful application is the nickel-metal hydride secondary battery, which utilized the charging and discharging property of a proton ( $H^+$ ) ( $H^+ = H^0 + e^-$ ;  $H^0$  refers to a monatomic hydrogen and is called as a **protium**). This reaction occurs when a proton in alkaline solution goes between the crystalline lattice of an alloy structure. However, this battery has little role in world energy supply chain or preserving the environment.

PEMFC is coming to be the first full-scale application of hydrogen utilized as the direct energy source. However, it is not well known that there are a lot of obstacles to be solved before it can really be applied to automobiles. The most important issue is a hydrogen storage/supply system. Even if all other related issues were solved, as long as this issue remains, the commercial realization of PEMFC vehicles will not happen for a while, at least ten years.

Here, KUCEL/MERIT will introduce the research and development of a new hydrogen storage/supply system for PEMFC as detailed as possible. In this new system, sodium or potassium borohydride complex compounds are used as hydrogen storage materials. There are so many kinds of borohydrides, and all of them are not newly found materials, but have been known for a long time as hydrogen reduction materials.

## [1 ] Conventional Hydrogen Storage and Supply Systems

Various kinds of materials such as compressed hydrogen, liquefied hydrogen, metal hydrides, methanol, dimethyl ether, decalin, gasoline, and cyclohexane have been the objects of development as hydrogen storage/supply systems for PEMFC in various ways. Among them, systems using organic compound as a source of hydrogen have gathered a lot of attention because they have advantages of being able to use the existing infrastructure of current fuel for automobiles. Especially, the methanol system has been eagerly developed as the size reduction of an industrially established steam-reforming system to be suitable for a car. However, it is considered to be difficult for the practical use because of the following reasons:

(1) Severe disturbance factors: The hydrogen supply for a small-sized mobile device of extremely severe disturbance factors (load fluctuation, surrounding temperatures, and starting activation) is totally different from

that of a large-sized mass production plant where high purity hydrogen can be produced under automatically controlled manners.

- (2) Poor load responses of the steam reformer: Temperature conditions, speed and amount of hydrogen required will continuously change, and high responses for these changes are not expected.
- (3) Necessity of supplementary hydrogen storage: Because the reformer is not expected to respond to the high load, it is necessary to install a supplementary hydrogen storage system. At present, a metal hydride container is installed for this purpose, but there are also some issues such as the poor hydrogen capacity and the weight penalty.
- (4) Necessity of a heat source for metal hydrides: Metal hydride needs a heat source for hydrogen release, and unreasonable heat quantity is demanded because of the low thermal conductivity of the metal hydride particle bed. Furthermore, because of the poor hydrogen capacity of the metal hydride, the available hydrogen content is less than 1 % by a weight of a container. Because of these substantial issues, using metal hydride in any part of the system will decrease the availability of the system.

As explained above, there are little advantages of using hydrogen reformed from methanol for PEMFC. Furthermore, if no measure is taken against carbon dioxide generated during the reforming process, the question remains; is it really clean energy? Here, we will not discuss the energy efficiency of "Well-to-Wheel," which refers to all the stages from producing methanol to driving a fuel cell car.

It is difficult to evaluate the systems utilizing organic based fuels other than methanol because few experimental evaluations have been published, but it is easy to imagine that these systems will have the same issues as those of methanol systems.

The development of hydrogen storage/supply systems started with compressed hydrogen and is now returning to the same system after various trials of other materials. This is due to the following advantages of this system over the dangerous situations that might be caused by the puncture of high-pressure vessels:

- (1) High response: Automated control of hydrogen pressure is possible and level of pressure does not depend so much on the temperature. Therefore, high response is expected without being affected by the surrounding conditions. It is also easy to adjust to the load changes and operating conditions.
- (2) Possibility of raising pressure levels: Right now 200 atm is the regulation of the high-pressure containers in Japan. Safety regulation will be amended and it will make hydrogen storage at higher pressures possible. From the engineering perspective, it is possible to make a duplicated-layer container with the enough pressure-tolerability. There is a high possibility that a compressed hydrogen system will remain as one of the choices of hydrogen storage/supply systems until the last stage of the development.

In any case, what should be the source of hydrogen is the biggest issue. Storing/supplying hydrogen and

producing hydrogen are on a different level. Conventional systems to produce hydrogen are water electrolysis and steam reforming of methanol or natural gas, but it is impossible to produce enough amount of hydrogen required for the “new energy era” by these methods at present. In order for hydrogen to be wide-spread as a new fuel, the total cost of production and distribution of hydrogen to the final users has to be low enough to be competitive of those of petroleum based fuels, and there will be a long way to go.

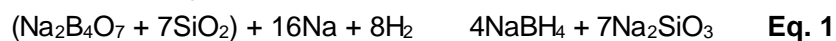
Judging from present status of hydrogen, there is little likelihood of PEMFC vehicles being popularized in this decade. In the present situation the kind of hydrogen storage/supply system to be used has not been determined, and there is no definite process to produce enough amount of hydrogen with low enough cost, it would be premature to talk about the popularization of the PEMFC vehicles.

From this point of view, it is not too much to say that the key to promote the diffusion of PEMFC vehicles is the system of the hydrogen fuel production.

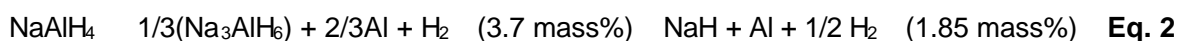
## [2 ] New materials for hydrogen storage

### (2-1) Borohydride complex compounds

Boron and sodium or potassium can form a borohydride complex compound with high hydrogen content. There are many kinds of such compounds, and their various data are introduced in a variety of handbooks of inorganic and inorganic metal complex compounds. Many of them have been limitedly used as hydrogen reducing agents, but sometimes experimentally used as hydrogen generating agents for compressed hydrogen. KUCEL/MERIT is conducting research and development of sodium borohydride ( $\text{NaBH}_4$ ) and potassium borohydride ( $\text{KBH}_4$ ) as hydrogen storage and supply materials, since they have simpler structures and are relatively easier to obtain among borohydride complex compounds. There is an established system to produce these borohydride complex compounds, but the cost is currently high and they are distributed with the price around 6,000 to 12,000 yen/kg. **Eq. 1** is the basic production process of sodium borohydrides.



On the other hand, a study of an aluminum-hydride complex compound ( $\text{NaAlH}_4$ ), one of the materials called alanate, as a hydrogen storage material has been carried out by the study group centered around University of Hawaii and the Sandia National Laboratory. Alanate can consist of 7.4 mass% of hydrogen in total, and considering its reversibility after reaction, hydrogen is generated by the following two phases of a thermal decomposition reaction:

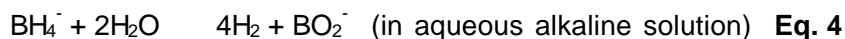
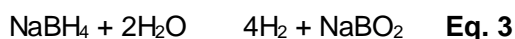


As shown in the **Eq. 2**, the maximum quantity of hydrogen reversibly usable provided by these 2-step reactions, which occur at different levels of temperatures, is 5.55 mass%. The research group is conducting the research and development of the reclaiming process of bringing the material back to alanate after the hydrogen generation of the second phase.

### The hydrogen generating reaction

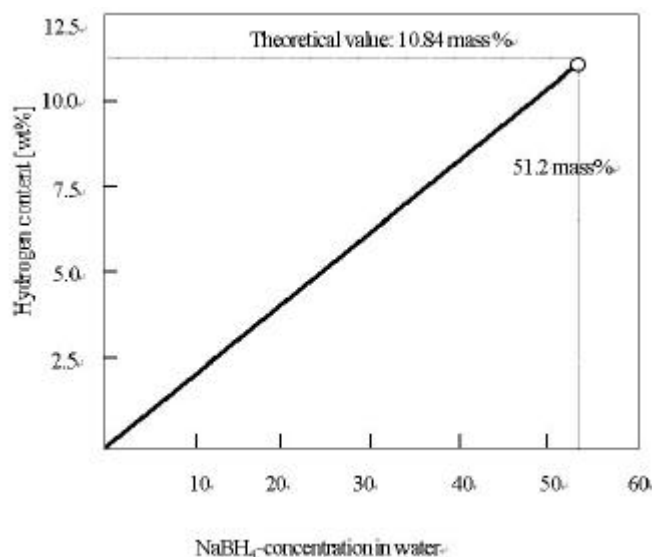
The reasons KUCEL/MERIT is concentrating on borohydride complex compounds are the system of hydrogen generation and the quantity of hydrogen generated. In short, in the reaction of these materials and water, water becomes another source of hydrogen through hydrolysis, and the quantity of hydrogen provided by these reactions is more than that of NaBH<sub>4</sub> or KBH<sub>4</sub>.

For example, the reaction of NaBH<sub>4</sub> is shown in **Eq. 3** but since these kinds of borohydride complex compounds exist as complex ions such as BH<sub>4</sub><sup>-</sup>, **Eq. 4** is more realistic as the hydrogen generation reaction.



### The quantity of hydrogen generation

The quantity of hydrogen generated by this hydrolysis is stoichiometrically 100%, independent on the reaction velocity and temperature conditions. **Figure 1** shows the amount of hydrogen generated in the 10 wt.% sodium hydroxide solution as a function of concentration of NaBH<sub>4</sub>. As shown in the figure, the maximum quantity of generated hydrogen is 10.8 mass% at the NaBH<sub>4</sub> concentration of 51.2 mass%, but in an actual condition, the continuous changes in quantity of water used for hydrolysis have to be considered, because the physicochemical properties of alkaline solution such as solubility, density, and viscosity changes widely during the reaction.



**Fig. 1** The quantity of hydrogen generation as a function of concentration of NaBH<sub>4</sub>

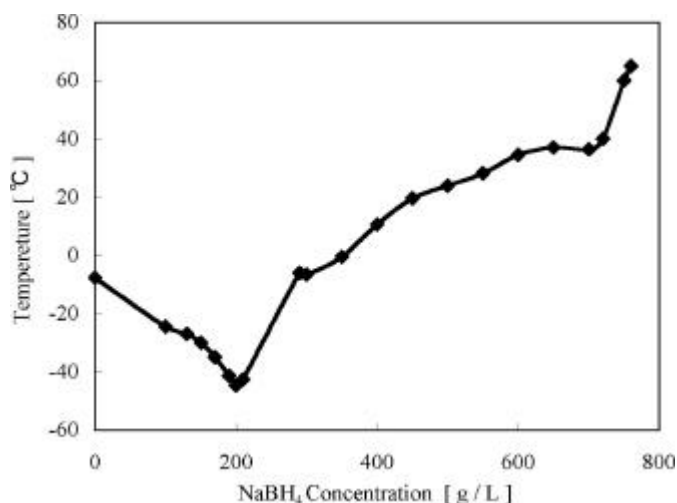
## (2-2) Stabilizing borohydride complex compounds

In contrast to alanate ( $\text{NaAlH}_4$ ), which generates hydrogen in a furious reaction if it has contact with moisture, the reactions with water or moisture of many kinds of borohydride complex compounds are relatively gentle. However, for the long-term storage of aqueous solutions of these complex compounds in stable state as hydrogen storage materials, they are usually stored in solid powder state isolated from moisture, or dissolved in alkaline solution. In the latter method, it is effective to dissolve them in dilute alkaline solution such as  $\text{NaOH}$  or  $\text{KOH}$ , and store hydrogen as a borohydride complex ion, or  $\text{BH}_4^-$ .

KUCEL/MERIT is collecting the experimental data of stability of  $\text{BH}_4^-$  complex ions in alkaline solutions as a function of (1) concentration of alkaline solution, (2) concentration of borohydride complex compounds, (3) temperature changes, (4) mechanical shocks, and (5) exposure to sunlight, etc., and are trying to build a database. At present, in any condition, a slight hydrogen generation is observed in long-term storage, and avoiding this hydrogen generation is the one of the current development tasks.

## (2-3) Physicochemical properties of borohydride complex compound solutions

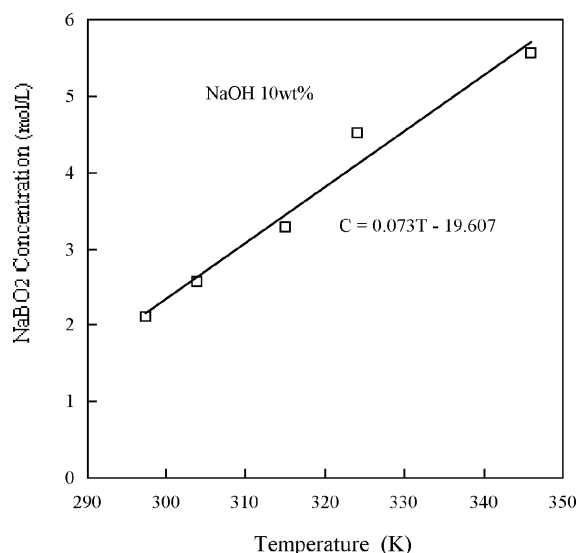
Among the physicochemical properties of the alkaline solution of borohydride complex compounds, solubility of  $\text{NaBH}_4$  in the certain concentration of alkaline solution obtained from the actual observation is shown in **Fig. 2** as a function of concentration of  $\text{NaBH}_4$  and temperature. As shown in the figure, solubility limits of  $\text{NaBH}_4$  in 10 wt. %  $\text{NaOH}$  solution is in the domain of less than  $-30^\circ\text{C}$ ; the solution does not form any crystalline precipitate at wide range of temperature conditions.



**Fig. 2 Solubility of  $\text{NaBH}_4$**

During hydrogen generation, the concentration of  $\text{BO}_2^-$  increases in place of  $\text{BH}_4^-$ , and as soon as it goes over its solubility limits, it starts to form crystalline  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ . For this reason, it is important to analyze the

physicochemical properties of  $\text{BO}_2^-$  in alkaline solution and of its crystalline precipitate as the form of  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ .  $\text{BO}_2^-$  is more liable to form precipitate than  $\text{BH}_4^-$ , and as the formation of the precipitate, it takes four molecules of water; the formation of crystalline precipitate decreases the water content of solution, and it results in the higher concentration of the alkaline solution. The solubility of  $\text{NaBO}_2$  in water obtained from actual experimentation is shown in **Fig. 3** as a function of temperature.



**Fig. 3 Solubility of  $\text{NaBO}_2$  in water as a function of temperature**

As described later, when utilizing borohydride complex compounds as a hydrogen supply system, it is important to take enough measures against the formation of crystalline materials as the concentration of alkaline solution and temperature changes.

### [3 ] Hydrogen generating system

In order to generate hydrogen from borohydride complex ion ( $\text{BH}_4^-$ ) stabilized in alkaline solution, some kind of catalyst is needed. The reaction is hydrolysis on the solid-liquid surface, but the hydrogen generated in this reaction is gaseous. In another word, this reaction is the conversion of hydrogen from anion state (protide) to gaseous state (dimolecular), and its change in volume is numerous. Gaseous hydrogen generated momentarily causes the sudden expansion in volume and a sub- to super-sonic type of shock wave.

Here, we will omit the detailed description on the effect of shock-wave phenomena, but the stability of the powder-state catalyst and its substrate is important to be tolerable against this shock wave. From these reasons, the structure of the catalyst bed is one of the important technical issues when using borohydride complex compound as a hydrogen generation material.

#### (3-1) Catalyst for conventional hydrogen generation systems

It has been discovered that precious metals used as catalysts for conventional systems barely function for borohydride complex compounds. Fe-Cu based catalysts used for steam reforming of methanol also do not function for borohydride complex compounds. This is due to the reaction mechanism illustrated as  $\text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{BO}_2^-$ . In short, as the form of borohydride complex ion,  $\text{BH}_4^-$ , hydrogen exists as the form of anion, and conventional catalysts do not function for this type of ionic compound. This anion state of hydrogen is called **protide**.

### (3-2) Catalyst for hydrogen generation for borohydride complex ions

It has been discovered that Ni or Co, or Raney-Ni or Raney-Co exhibits excellent catalytic functions for borohydride complex compounds. Also F- $\text{Mg}_2\text{NiH}_4$ , a kind of fluorinated metal hydride that KUCCEL/MERIT developed in 1991, exhibits much higher catalytic function where  $\text{MgF}_2$  generated during the fluorination process at the extreme surface is estimated to disproportionate  $\text{Mg}_2\text{NiH}_4$  and to provide NiH<sub>4</sub>-enriched surface.

### (3-3) Hydrogen generating kinetics

This catalytic hydrogen generation occurs at ambient temperature and pressure. Raising the temperature level can improve the rate of hydrogen generation, but pressure does not affect much. The kinetics of hydrogen generation by various catalysts is illustrated in Fig. 4. Figure 5 is the comparison by  $\text{Mg}_2\text{NiH}_4$  and F- $\text{Mg}_2\text{NiH}_4$ .

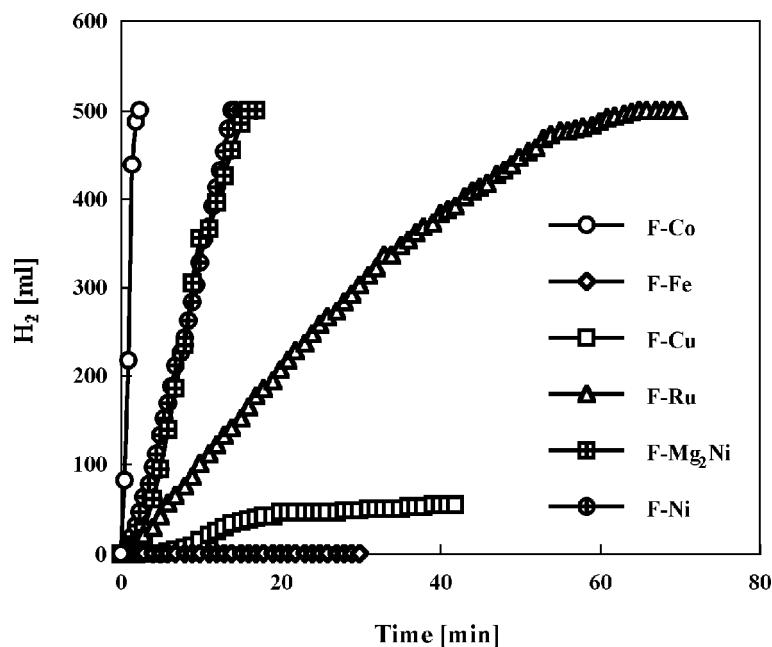
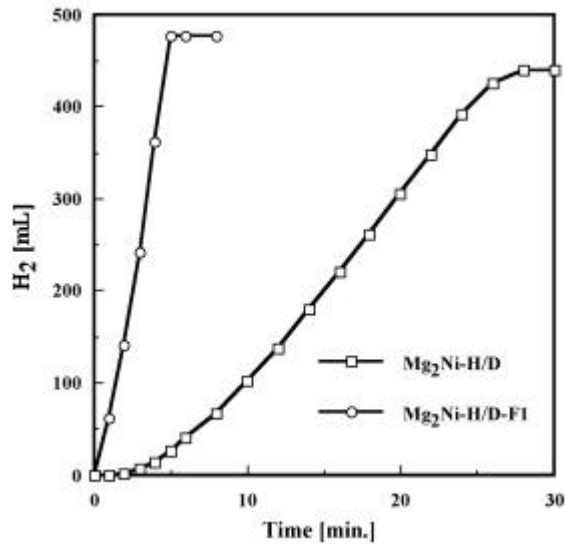


Fig. 4 Hydrogen generating kinetics by various catalysts

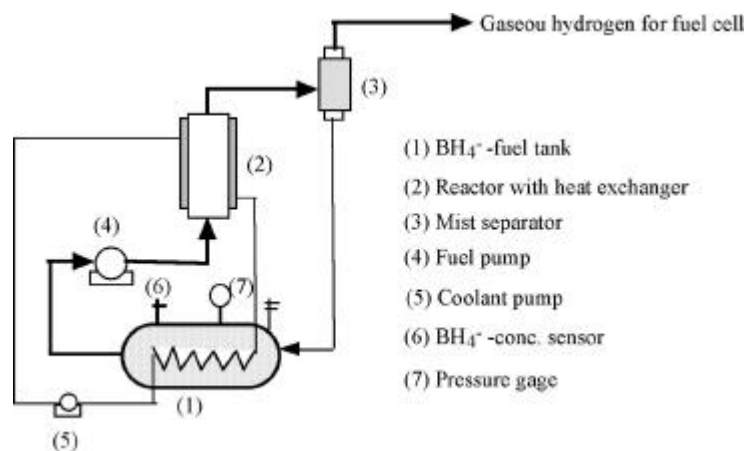


**Fig. 5 Hydrogen generating kinetics by Mg<sub>2</sub>NiH<sub>4</sub> and F-Mg<sub>2</sub>NiH<sub>4</sub>**

[4 ] Hydrogen generation device

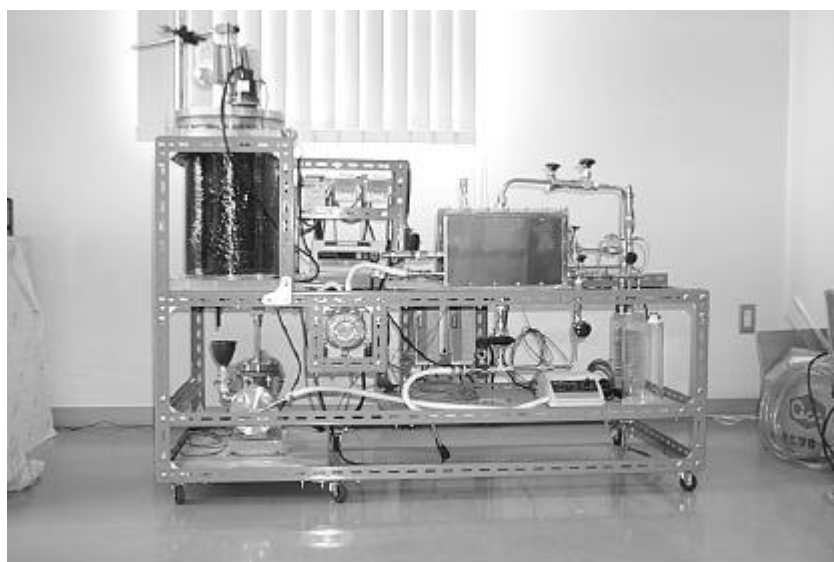
The main component of the engineering device for generating hydrogen from borohydride solution is a catalytic reactor. Because the gaseous hydrogen generated in this reactor entrains moisture and mist of NaOH, an alkaline-mist separator has to be installed. This hydrogen generating process is an exothermic reaction (**-300 kJ/H<sub>2</sub>-mol**), and this enthalpy change should be treated in order to stabilize the rate of hydrogen generation. Some contrivance has to be made against the formation of crystalline NaBO<sub>2</sub> · 4H<sub>2</sub>O and the change of the concentration of the alkaline solution during the hydrogen generation.

**Figure 6** is the schematic illustration of the device, and the experimental hydrogen generation and supply system for PEMFC is shown in **Fig. 7**. The maximum hydrogen supply required for 50 kW – 75kW sized PEMFC is expected to be 1.5 g/s – 2.0 g/s, and this device is experimentally proven to have capability to supply enough hydrogen at required speed by optimizing the catalyst and the operation condition of the reactor.



**Fig. 6 Schematic illustration of the hydrogen generating device**





**Fig. 7 Experimental model of the hydrogen generation / supply system for PEMFC**

[5 ] Production and recovery of  $\text{NaBH}_4$

The material obtained by evaporating the used solution after generating hydrogen is a crystalline-state mixture of sodium metaborate and sodium hydroxide.

KUCEL/MERIT conducted the research and development of the recovery process of sodium borohydride from the mixture of sodium metaborate and sodium hydroxide as a contracted project by New Energy and Industrial Technology Development Organization (NEDO) with Prof. Chiaki Iwata of Osaka Prefecture University, Sekisui Chemical Co., Ltd., Nippei Toyama Co., and Toyoda Automatic Looms Ltd. in the fiscal year 2000.

The four selected processes were (1) an electrochemical process patented in the U.S. for S. Ammendolla of Millennium Cell Co., (2) an electrochemical process that utilizes the protium inducing function of palladium membranes patented in Japan for Prof. Iwakura, (3) a chemical process that utilizes the protium inducing function of metal hydrides, and (4) a chemical process that utilizes the anion state of hydrogen, protide, as a hydrogen donor.

In order to produce sodium borohydride from sodium metaborate, the change of Gibbs Function has to be converted to a negative value in the basic thermodynamic relation of  $G = H + T S$ . Even if the theoretical change of Gibbs Function is a negative value, it has to be taken into consideration that  $\text{BH}_4^-$  in the sodium borohydride is instantly converted to  $\text{BO}_2^-$  in the aqueous solution.

For these reasons, in the electrochemical methods of (1) and (2), it has been proven that sodium borohydride will not be produced because it cannot avoid the reaction of  $\text{BH}_4^- \rightarrow \text{BO}_2^-$ .

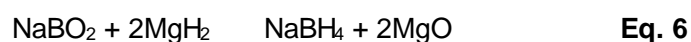
On the other hand, in the method of (3), it can bring the changes of Gibbs Function to negative values at certain temperatures, and it has been experimentally proven that sodium borohydride can be produced at

temperature levels of over 200 °C with certain yields. In the method of (4), we applied the ball milling method, which has been gathering attention for making metal hydrides in a sub-nano state, as a mechano-chemical process, and tried to utilize alkaline-metal based hydrides such as LiH, NaH, CaH<sub>2</sub>, MgH<sub>2</sub>, as a hydrogen donor. Among these materials, fluorinated MgH<sub>2</sub> denoted as F-MgH<sub>2</sub> has been experimentally proven possible to produce sodium borohydride with the extremely high yield. In addition, the mechano-chemical method with NaOH co-existing with sodium metaborate can improve the yield even more. The simplified reactions are shown in **Eq. 5** and **Eq. 6**.

(a) Production of sodium metaborate from borax:



(b) Production of sodium borohydride from sodium metaborate:



As explained above, the process of reclaiming the used solution mixture of sodium metaborate and sodium hydroxide to sodium borohydride is developed. To improve the practical applicability of this process, the process of regeneration and reuse of the hydride used for a hydrogen donor in this process has to be developed in view of the cost-effectiveness.

In the mechano-chemical method, minimizing the amount of energy consumption for the process is the next development task. Furthermore, without solving the issue of what should be the source of hydrogen for the hydrogen donor, it is difficult to expect these kinds of new hydrogen generation/supply systems to be in practical use and put into the wide-spread applications. The final target of KUCEL/MERIT is the direct use of a proton abundantly existing in an electrolyte solution as a hydrogen donor; the same mechanism as the nickel-metal hydride secondary battery. Expecting the goal not to be too far away, the research and development has been conducted as the major scheme of the laboratory.

## Afterword

In this report, the development of a new hydrogen generating system that utilizes sodium borohydride as a hydrogen storage material and is targeting its supply to PEMFC is introduced. This hydrogen generating system is the new process that has been targeted to the production and recovery of sodium borohydride from the mixture of sodium metaborate and sodium hydroxide. In order for this system to be utilized, it is necessary to solve the issue of what should be the source of hydrogen for the hydrogen donor.

To decrease the discharge of carbon dioxide and the level of environmental deterioration, it is necessary to build the hydrogen energy system and to promote its wide-spread uses, because the conventional use of fossil fuels centered around petroleum involves the discharge of carbon dioxide by its combustion and even by its

steam-reforming.

Our country has the long history of positive achievements in the development of new energy technology compared to other countries, and now is the time to concentrate on the concrete targets to use its achieved intellectual resources. KUCEL/MERIT is conducting the research and development of the new energy system concentrating on borohydride complex compounds to be hydrogen storage and supply system as the center for the "H-GenTech Alliance®", the collaborative research and development group consists of four universities and 12 entities. The aim of this alliance is the collaboration of university-based research results and entities' abilities to put them into industrial technologies. We hope this collaborative research and development leads the establishment of the new energy infrastructure started from Japan.

#### Acknowledgements

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