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Protide compounds in hydrogen storage systems

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Abstract

Based on three chemical states of hydrogen: protide (H^-), protium (H^0) and proton (H^+), a triangular hydrogen energy system was proposed. The transfers among protide, protium and proton attracted our attention. We experimentally proved that $NaBH_4$ as a protide carrier can release its energy through a fuel cell (borohydride fuel cell) directly or generate hydrogen gas for polymer electrolyte membrane fuel cell application. The used fuel (*meta*-borate) can be reverted to $NaBH_4$ through a reaction with a saline hydride (MgH_2).

Keywords: Protide compound; $NaBH_4$; Saline hydride; Hydrogen energy system; Fuel cell; Fuel recovery

1. Introduction

It is known that the hydrogen bonding can be classified into following three types:

1.1. Loss of the valence electron

The 1s valence electron is lost to give the hydrogen ion H^+, which is merely the proton. The proton usually exists in liquid, seldom in condensed phases that is invariably associated with other atoms or molecules. Tetrafluoroethylene–perfluorovinyl ether sulfonic acid copolymer (Nafion) is one of the few exceptions.

1.2. Formation of an electron-pair bond

The majority of hydrogen compounds contains an electron-pair bond, such as H_2, most of reversible metal hydrides, and carbon hydrogen compounds. The diatomic hydrogen of the gaseous hydrogen and mono-atomic hydrogen in most reversible metal hydrides are referred to as H^0 for simplicity.

1.3. Acquisition of an electron

The hydrogen atom can acquire an electron, attaining the $1s^2$ structure of He, to form the hydride ion H^-, which is also named 'protide'. This ion essentially exists as saline hydrides like NaH, MgH_2 or some complex compounds like $NaBH_4$, $NaAlH_4$.

Borohydrides and saline hydrides are well-known reducing agents. They often have quite specific uses in organic and inorganic chemistry, where they may also be the sources of H^- rather than simple reductants. They also have attracted attention as a hydrogen storage medium or a fuel for the fuel cell due to their high hydrogen contents and high electric potential in electrochemistry. Fig. 1 shows the electrochemical capacity densities of hydrogen stored by different methods. Borohydrides show higher gravimetric capacities than metal hydrides and higher volumetric capacities than compressed and liquefied hydrogen. Borohydrides show higher electrode potentials and reactivities than gaseous hydrogen [1]. They are suitable for use as a fuel for fuel cells in portable, mobile and vehicle applications. Borohydrides that are stable in dry air, are easily handled like common chemicals compared with other hydrogen storage methods. The hydrogen generation by the borohydride hydrolysis can operate under ambient conditions. They are very promising portable and mobile hydrogen sources for polymer electrolyte membrane fuel cells (PEMFCs). In this paper, we propose a triangular hydrogen energy system based on sodium

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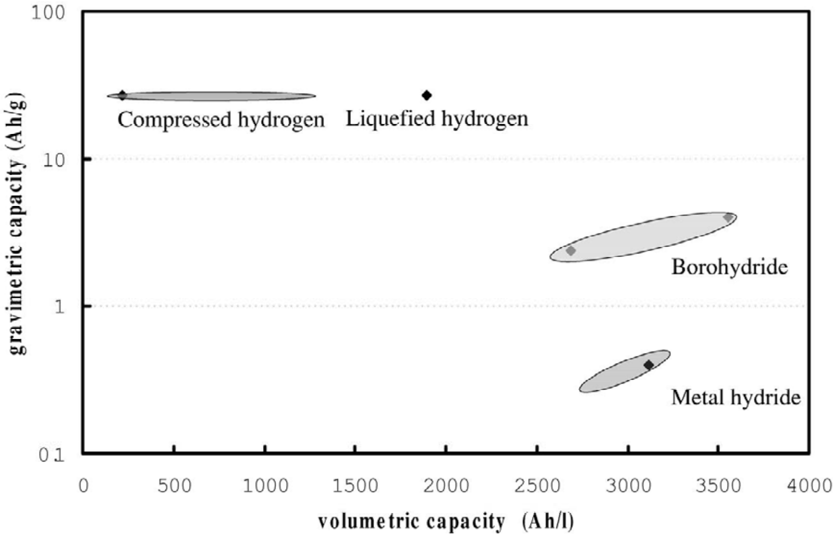

Fig. 1. Capacity comparison when hydrogen was stored in different ways.

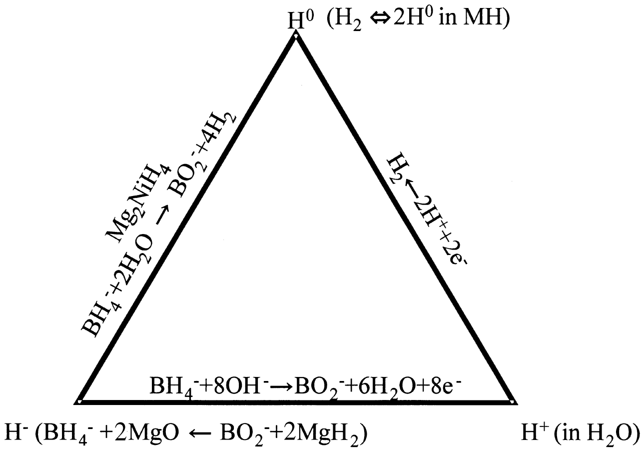

Fig. 2. Example of the triangular hydrogen energy system.

borohydride consisting of H^+, H^0 and H^- as shown in Fig. 2, which differs from the linear hydrogen energy system between H^+ and H^0.

2. Characteristics and properties of protide compounds

Protide usually exists in solid compounds or complex ions. The protide in saline hydrides behaves like halogens with a similar effective radius (2.08 Å) and crystal structures. The tetrahedral borohydride ion (BH_4^-) or aluminohydride ion (AlH_4^-) were considered to arise by the Lewis acid behavior of BH_3 or AlH_3 toward a protide, but each H was found to be equivalent [2,3]. They are usually classified as complex compounds. The hydrogen contents of protide compounds are usually higher than those of reversible hydrides as illustrated in Table 1.

Saline hydrides do not easily release their hydrogen by thermo-decomposition due to their strong ionic bonding. Unlike in saline hydrides, the stability of the protide in complex compounds depends on the electron donor. For example, although borohydride and aluminohydride have a similar molecule structure, their thermal dissociation properties are different. Dymova et al. experimentally determined the dissociation reaction of $NaAlH_4$ [4] as follows:

Table 1
Comparison of protide compounds with metal hydrides on hydrogen content

	Metal hydride					Chemical hydride			
	AB_5H_6	AB_2H_4	ABH_2	A_2BH_4	Protide compound				
					AH_x	M^IBH_4	M^IAlH_4	$M^{II}BH_4$	$M^{II}AlH_4$
Typical hydride	$LaNi_5H_6$	$ZrMn_2H_{3.46}$	$TiFeH_{1.9}$	Mg_2NiH_4	MgH_2	$LiBH_4$ $NaBH_4$	$NaAlH_4$	$Mg(BH_4)_2$	$Mg(AlH_4)_2$
Hydrogen content (wt.%)	1.4	1.7	1.8	3.6	7.6	18.4 10.6	7.4	15.1	10.2

$$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2\uparrow \leftrightarrow NaH + Al + 1.5H_2\uparrow \quad (1)$$

Their results proved that the protide (H^-) in $NaAlH_4$ partially transformed into hydrogen gas (H^0). The hydrolysis reaction of $NaAlH_4$ is an explosive reaction, which is not suitable for hydrogen generation. Unlike $NaAlH_4$, $NaBH_4$ cannot reversibly be associated and dissociated under moderate conditions, but its hydrolysis is of interest in hydrogen generation because it is a catalytic reaction whose rate is controllable. It can generate 10.8 wt.% of hydrogen based on the following hydrolysis reaction

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2 \quad (2)$$

With respect to the high potential of borohydrides, they are also a promising fuel for fuel cells as several patents have pointed out [5–8]. Some investigations on the electrochemical oxidation mechanisms of borohydride have been reported [9–11]. For example,

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- - \leftarrow 1.24\ \text{V (vs. SHE)} \quad (3)$$

The protide in borohydrides can also transform into hydrogen gas (H^0) by a hydrolysis reaction and then transform into H^+ by an electrochemical reaction.

Borohydride transforms into *meta*-borate after release of its hydrogen. The formed borate can be recovered by a chemical reduction. For example, sodium borohydride can be formed by a reaction of $NaBO_2$ with calcium hydride [12]

$$2CaH_2 + NaBO_2 = NaBH_4 + 2CaO \quad (4)$$

3. Triangular hydrogen system

Compared with the linear hydrogen system based on H^+ and H^0, the triangular hydrogen system based on H^+, H^0 and H^-, can offer a high power output by the fuel cell. As an example, we studied the possibility of using $NaBH_4$ as the medium in the triangle hydrogen energy system. Fig. 3 shows the proposed hydrogen system that concludes following processes:

(1) Electrochemical oxidation of borohydride through a fuel cell to generate power

$$NaBH_4 + 2O_2 = NaBO_2 + 2H_2O \quad (5)$$

For some applications, borohydride can be reformed into hydrogen gas by the hydrolysis reaction. The produced hydrogen supplies to PEMFCs to generate electricity through the following reactions

$$\left.\begin{aligned} NaBH_4 + 2H_2O &= NaBO_2 + 4H_2 \\ 4H_2 + 2O_2 &= 4H_2O \end{aligned}\right\} \quad (6)$$

The reverse process includes the following reactions.

(2) Electrolysis of water

$$2H_2O = O_2 + 2H_2 \quad (7)$$

(3) Fuel recovery

$$2H_2 + 2Mg + NaBO_2 = NaBH_4 + 2MgO \quad (8)$$

or

$$\left.\begin{aligned} 2H_2 + 2Mg &= 2MgH_2 \\ 2MgH_2 + NaBO_2 &= NaBH_4 + 2MgO \end{aligned}\right\} \quad (9)$$

In this hydrogen energy system, many investigations on

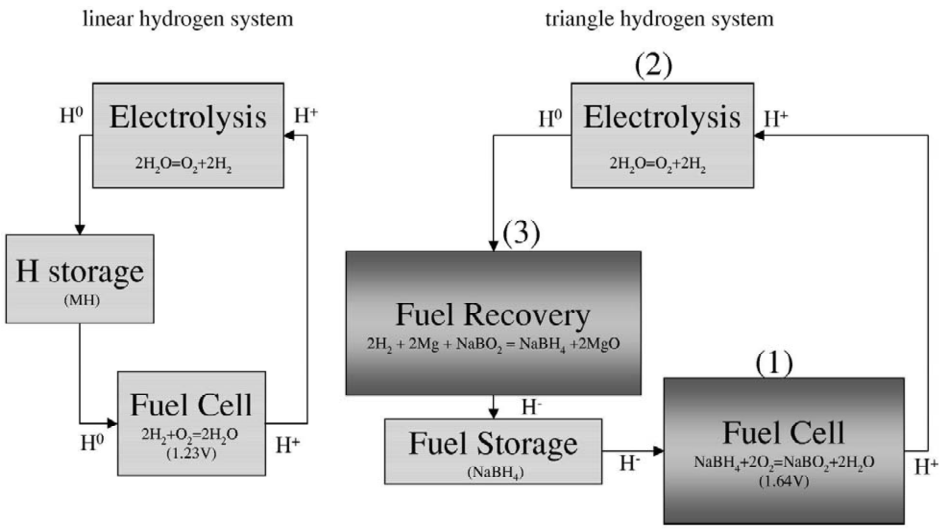

Fig. 3. Comparison of the linear and triangle hydrogen energy system.

PEMFCs, hydrogen production through the electrolysis of water have been reported. In this presentation, we focused our attentions on the fuel cell using borohydride as the fuel directly, hydrogen generation from borohydride and fuel recovery.

3.1. Fuel cell using borohydride as the fuel

Our aim on fuel cell development is to develop low cost fuel cells using borohydrides that have higher electrochemical reactivity than hydrogen gas. For simplicity, this kind of fuel cell is named borohydride fuel cell (BFC). In principle, BFC works in an alkaline environment so that catalytic agents are not limited to noble metals. Low cost Ni-based catalysts for anode and cathode could be expected to show good performances like alkaline fuel cells (AFCs). The Ni-coated steels can be used to make bipolar plates so that their manufacturing cost can be decreased greatly by using a cold press forming technique. Because the fuel is an aqueous solution that can act as a cooling medium, the cooling plates that are included in the stack of PEMFCs, are not necessary any more. Based on these considerations, we constructed fuel cells using fluorinated AB_2 (F-AB_2) as the anode catalyst, Pt–C as the cathode catalyst and Nafion membrane as the electrolyte.

The fuel was an alkaline borohydride solution containing 10 wt.% $NaBH_4$ and 20 wt.% NaOH (containing 2.1 wt.% H_2). The bipolar plates were made of stainless steel. The flow field area of the plates was 70% of the electrode area (20×30 mm). The stack consisting of ten cells demonstrated a good performance like PEMFCs (shown in Fig. 4).

3.2. Hydrogen generation

Hydrogen can been stored as a pure substance as a liquid or compressed gas (say >300 atm.) and in materials such as a number of chemical hydrides, metal hydrides, nanotubes and carbon fibers. Protide compounds are chemical hydrides. Early in the 1950s, Schleshinger et al. [13] suggested using sodium borohydride to generate hydrogen under ambient conditions. Their results showed sodium borohydride solution released 90% of the stoichiometric amount of hydrogen. In our investigation, alkaline borohydride solution in a certain concentration range (<20 wt.%) can release almost 100% of the stoichiometric hydrogen within 15 min when using Raney Ni as the catalyst (see Fig. 5). A prototype of the hydrogen generator has been produced. It produced 90% of the stoichiometric amount of hydrogen at a rate of 10 l/min at room temperature as shown in Fig. 6.

3.3. Fuel recovery

In the triangular hydrogen energy system, fuel recovery is the most difficult issue. In the linear hydrogen system, only hydrogen reacts with oxygen during energy conversion. For example, hydrogen gas from metal hydrides can be used to run a PEMFC to produce water. The hydrogen gas can be produced by the electrolysis of water, and then reacted with alloys to form metal hydrides. In the triangular hydrogen system, when protide compounds generate hydrogen gas to supply PEMFCs by a thermal decomposition, the process will be the same as that in linear hydrogen energy system. However, when protide compounds release their hydrogen by the hydrolysis or are electrochemically oxidized directly, the protide has not only a relation with oxygen but also a relation with its donor. The donor will react with oxygen when the protide is oxidized. Therefore, the fuel recovery must include processes of not only the hydrogen cycling but also the donor cycling. For example, protide in borohydride (BH_4^-) runs a fuel cell to produce *meta*-borate and water. Protide in saline hydrides can be formed by reacting alkali or alkali-earth metal with hydro-

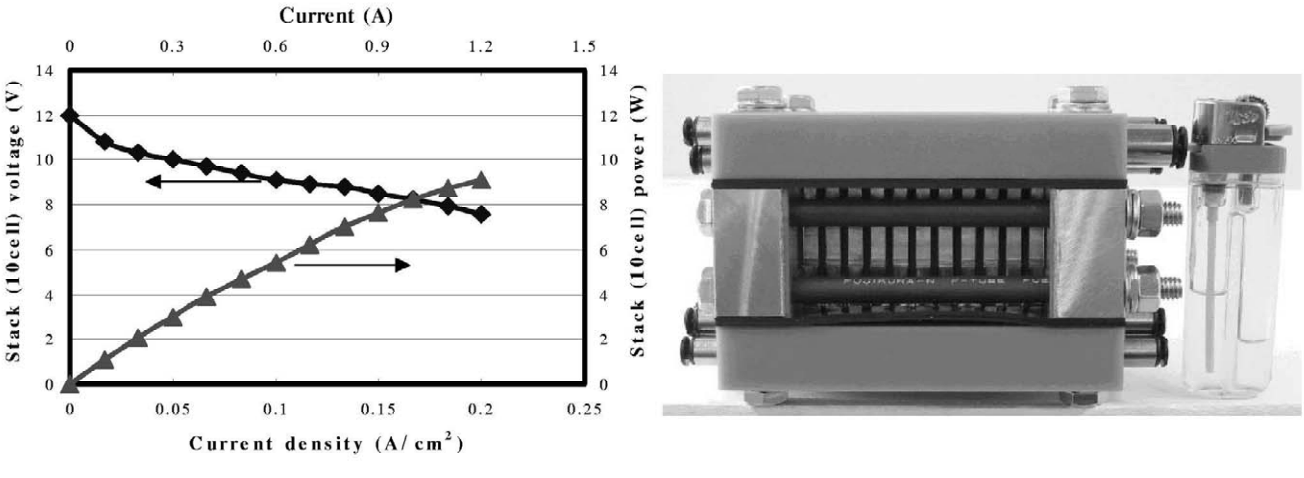

Fig. 4. Fuel cell using borohydride as a fuel and its performance. Anode: 200 mg/cm^2 flourinated AB_2 alloy, 10 wt.% $NaBH_4$–20 wt.%NaOH at flow-rate of 186 ml/min. Cathode: 2 mg/cm^2 Pt-black, atmosphere at flow-rate of 200 ml/min.

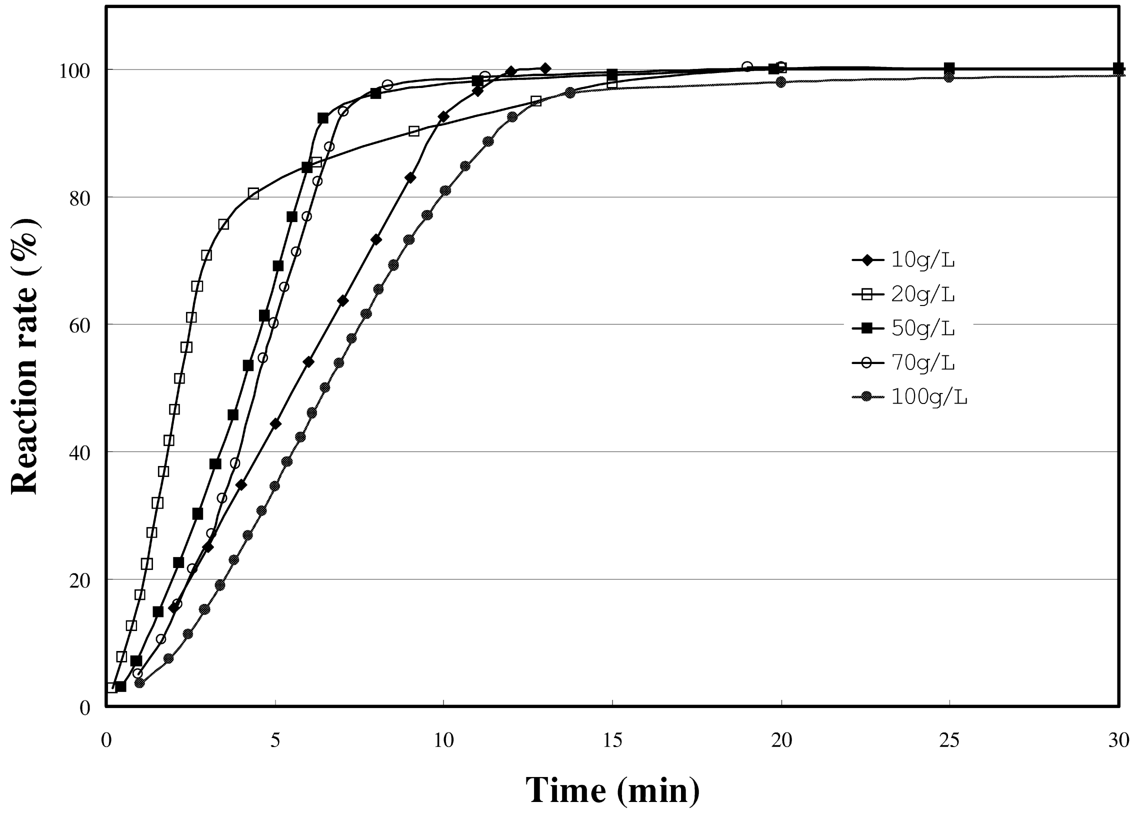

Fig. 5. Evolution of hydrogen from sodium borohydride solution at a concentration of 10–100 g/l at room temperature.

gen gas produced by the electrolysis of water. The borohydride can be obtained by a reaction of saline hydride with *meta*-borate through reaction (8) as shown in Fig. 7. The reaction was conducted with a planetary ball mill at room temperature. Thermodynamics calculation proves that this reaction is feasible (reaction $\Delta G^0 = -269.7$ kJ/mol). Even though the $NaBH_4$ conversion rate showed a deviation from its theoretical value, almost 100% of $NaBH_4$ conversion rate was achieved when an excessive amount of MgH_2 (1.25 times more than stoichiometric

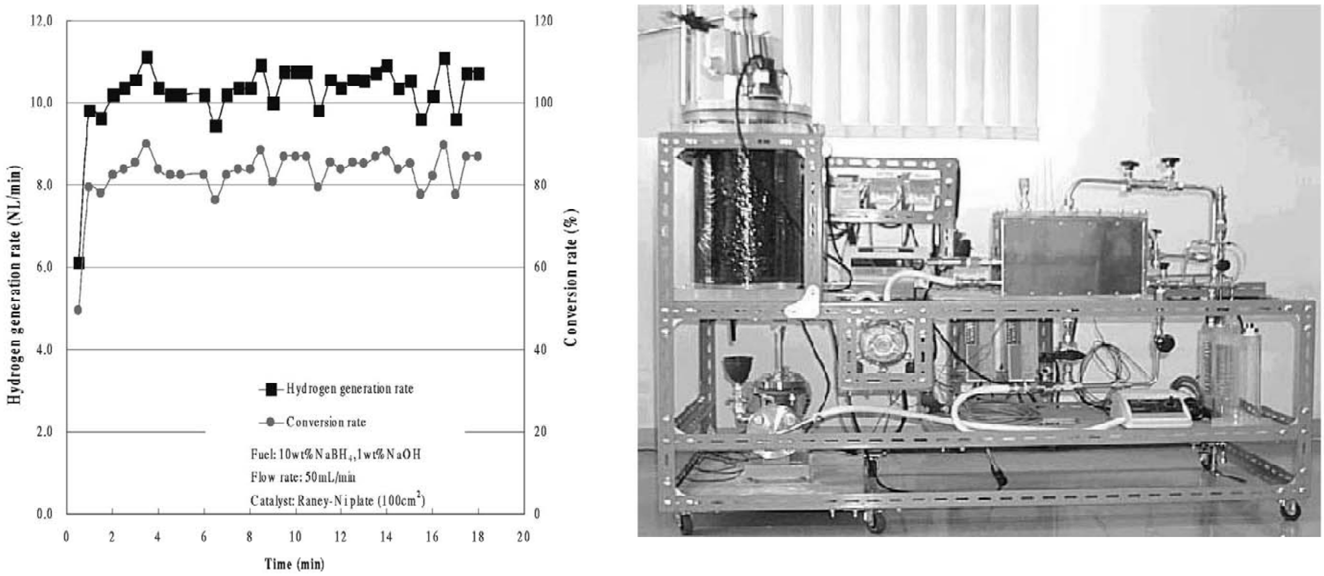

Fig. 6. Prototype of a hydrogen generator and its performance.

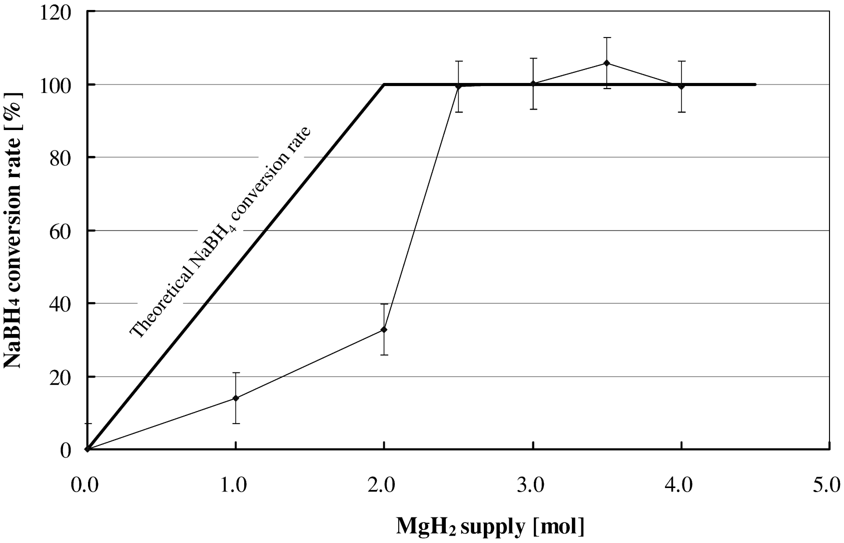

Fig. 7. $NaBH_4$ formation by ball milling based on the reaction $2MgH_2 + NaBO_2 = NaBH_4 + 2MgO$.

amount) was added. The pure $NaBH_4$ powders can be obtained by vaporization of ethylenediamine after extraction and filtration.

4. Conclusions

We experimentally proved that a triangular hydrogen energy system can be established by using $NaBH_4$ as the medium based on three hydrogen states: protide (H^-), protium (H^0) and proton (H^+). Borohydride fuel cell shows a good performance even without using noble metals in the anode. The used fuel ($NaBO_2$) can be recovered by a reaction with saline hydride (MgH_2).

For now the cost of borohydrides (ca. $58/kg $NaBH_4$) as a fuel is still unacceptable for large capacity fuel cells, however it is not a big problem for the small or microfuel cell. Therefore, borohydrides are potential candidates as a fuel for small and microfuel cell in portable and mobile devices.

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