Production of sodium borohydride by using dynamic behaviors of protide at the extreme surface of magnesium particles

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Abstract

An advanced process for the production of sodium borohydride ($NaBH_4$) as a hydrogen storage material was developed, which applied the dynamic hydriding and dehydriding behaviors of protide (H^-) in Mg–H system under transitional temperature conditions.

An abundant natural resource named borax ($Na_2B_4O_7 \cdot 10H_2O$) and the anhydrous sodium metaborate ($NaBO_2$) recovered from the "spent fuel" as $NaBO_2 \cdot 4H_2O$ were used as the starting material in the present process. Powder-state Mg played an important role in the transitional hydriding and dehydriding process where the gaseous hydrogen was converted to protide at the extreme surface of Mg to form $NaBH_4$ in exchange with the simultaneous transition of oxygen in $NaBO_2$ to form MgO.

In the present process, the protide as the most reactive state among the four states of hydrogen is applied for the synthesis of $NaBH_4$, which can exist in metal–hydrogen complexes, such as $NaAlH_4$ and $NaBH_4$.

The $NaBH_4$ yield was reached higher than 90% by a single batch process but was found to be largely dependent on the rate of temperature change and the particle size, i.e., the specific surface area of Mg particles.
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Keywords: Sodium borohydride; Protide; Magnesium; Surface; Hydrogen storage

1. Introduction

Hydrogen storage materials have long been searched for the storage of "*gaseous hydrogen*" where the application of hydrogen is very much limited to the source of IC engines and PEMFC. Conventional metal hydrides could not have attained H-capacity higher than 3 mass% except Mg-alloys even after three-decades of effort.

The mass-based H-capacity of materials has been used as the measure of the storage capacity. However, it should be evaluated by the weight basis of storage unit as the system in any engineering devices. From a practical viewpoint, the effective H-capacity of most materials under development today should be considered not more than 1 wt.% at maximum. If we leave from the standpoint of "gaseous hydrogen" applications, we may use another state of hydrogen of "protide", which is the state existing both as solid- and liquid states in metal–hydrogen complex ions [1,2]. The protide possesses two electrons and it is the most reactive state among the four-states of hydrogen, i.e., *molecular hydrogen* (H_2), *proton* (H^+), *protium* (H^o: monatomic hydrogen) and *protide* (H^-: hydride ion).

In this paper, sodium borohydride ($NaBH_4$, denoted SBH) as the source of protide will be reported with regard to its new production process that is based on the natural resource, borax, ($Na_2B_4O_7 \cdot 10H_2O$) and sodium metaborate ($NaBO_2 \cdot 4H_2O$) recovered as the "spent fuel".

The hydrogen content in SBH is 10.6 mass% and theoretical H-capacity generated by hydrolysis is 10.8 mass%. However, its H-capacity is greatly reduced by diluting in an aqueous alkaline solution of NaOH or KOH in order to maintain the stability without releasing H_2 gas for longer terms. The H-capacity is a function of SBH concentration and is

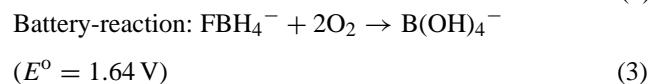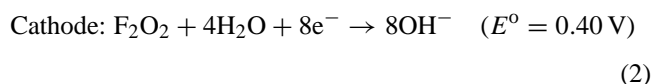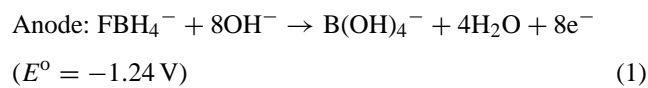restricted by the solubility limit of SBH in the alkaline solution, mostly in the 10–20 wt.% NaOH-solution. The alkaline solution that contains BH_4^- is referred to as "*borohydride*" in this paper.

Borohydride may be used not only as the source of protide in electrochemical applications for DBFC (direct borohydride fuel cell), which is based on the electrochemical characteristics given below in Eqs. (1)–(3) but also as the H_2 source for PEMFC by its catalytic hydrolysis according to Eq. (4).

2. The protide applications

2.1. Electrochemical properties and characteristics of protide [1–16]

Borohydride is transformed electrochemically to borohydroxide ion by releasing eight electrons at the surface of negative electrode (anode). The material used as the electrode can be selected from the fluorinated intermetallic compounds. The electrochemical reaction shown in Eq. (1) occurs only on the extreme surface of the fluorinated materials. It is unnecessary to apply any precious metals and materials so-called hydrogen absorbing alloys, which involve the hydrogen conversion to proton via protide.

Anode: $FBH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e^-$

$(E^o = -1.24\,V)$ (1)

Cathode: $F_2O_2 + 4H_2O + 8e^- \rightarrow 8OH^-$ $(E^o = 0.40\,V)$

(2)

Battery-reaction: $FBH_4^- + 2O_2 \rightarrow B(OH)_4^-$
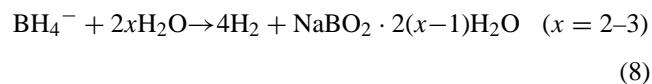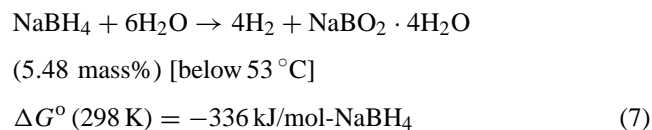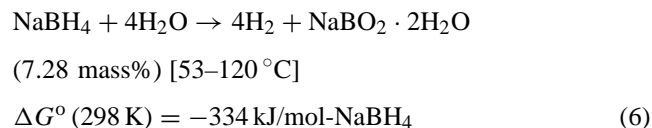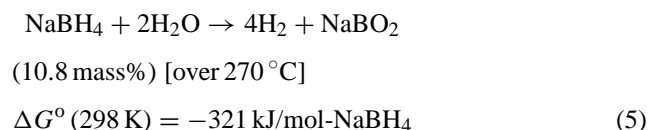
$(E^o = 1.64\,V)$ (3)

2.2. Gaseous hydrogen source for PEMFC [17–22]

Gaseous hydrogen, H_2, is generated by the catalytic hydrolysis of borohydride;

$BH_4^- + 4H_2O \rightarrow 4H_2 + B(OH)_4^-$

(in aqueous alkaline solution)   (4)
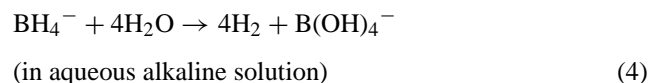
The hydrolysis is sometimes misguided by the expression listed in Eq. (5). It must be noted that SBH exists as borohydride (BH_4^-) in aqueous solutions but not as $NaBH_4$. Borohydride forms metaborate ions (BO_2^-) in the diluted aqueous solutions after releasing hydrogen, and it forms the hydrated sodium metaborates of several different states as listed in Eqs. (6) and (7) depending on the temperature levels. Eqs. (5)–(8) are only valid under the existence of stoichiometric water. The general formula is given in Eq. (8).

$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2$

(10.8 mass%) [over 270 °C]

$\Delta G^o\,(298\,K) = -321\,kJ/mol\text{-}NaBH_4$ (5)

$NaBH_4 + 4H_2O \rightarrow 4H_2 + NaBO_2 \cdot 2H_2O$

(7.28 mass%) [53–120 °C]

$\Delta G^o\,(298\,K) = -334\,kJ/mol\text{-}NaBH_4$ (6)

$NaBH_4 + 6H_2O \rightarrow 4H_2 + NaBO_2 \cdot 4H_2O$

(5.48 mass%) [below 53 °C]

$\Delta G^o\,(298\,K) = -336\,kJ/mol\text{-}NaBH_4$ (7)

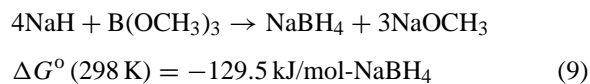$BH_4^- + 2xH_2O \rightarrow 4H_2 + NaBO_2 \cdot 2(x-1)H_2O$ $(x = 2\text{–}3)$

(8)

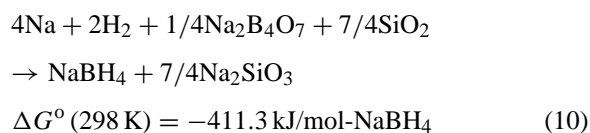## 3. Production of sodium borohydride as the hydrogen storage material [23–31]

3.1. The conventional production process

The Rohm & Haas process and the Bayer process are the two major processes commercially used today for the production of SBH. As can be seen in Eqs. (9) and (10), 4 moles of NaH or 4 moles of Na is used for producing 1 mole of $NaBH_4$. The theoretical yield of SBH is limited to 25% and accordingly, the production cost becomes rather expensive. The recovery and separation of un-reacted NaH and Na and by-products require additional processes.

(a) Rohm & Haas process [23]:

$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$

$\Delta G^o\,(298\,K) = -129.5\,kJ/mol\text{-}NaBH_4$ (9)

(b) Bayer process [24]:

$4Na + 2H_2 + 1/4Na_2B_4O_7 + 7/4SiO_2$

$\rightarrow NaBH_4 + 7/4Na_2SiO_3$

$\Delta G^o\,(298\,K) = -411.3\,kJ/mol\text{-}NaBH_4$ (10)

3.2. The advanced processes

(a) Mechano-chemical process [25,26]

In 1999, a mechano-chemical method that applies the high-speed ball-milling technique was successfully introduced to synthesize SBH by using MgH_2 as the protide donor and the oxygen acceptor in the reaction shown as Eq. (11).

However, the energy conversion efficiency was found highly restricted when mechanical force is converted to chemical energy although the SBH yield was maintained higher than 90% and even closer to 100%. In addition, it was not cost-effective to prepare MgH_2, which requires the du-

plicated hydriding/dehydriding treatments under higher temperature and pressure conditions.

$$NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO$$
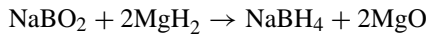
$$\Delta G^o (298\,K) = -270\,kJ/mol\text{-}NaBH_4 \tag{11}$$

(b) The dynamic hydriding/dehydriding process [27,28,31]

The SBH production can be processed by the reaction as shown in Eq. (12), where the system temperature is changed rapidly under constant H_2 pressure conditions;

$$NaBO_2 + 2H_2 + 2Mg \rightarrow NaBH_4 + 2MgO$$
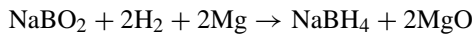
$$\Delta G^o (298\,K) = -342\,kJ/mol\text{-}NaBH_4 \tag{12}$$

Typical experimental data are shown in Fig. 1a–d for illustrating the effects of the rate of temperature change, dT/dt (°C/min) and Mg particle size (μm).

The higher the dT/dt and the smaller the particle size, the faster is the reaction rate that was measured as the percent yield of SBH. The SBH production is initiated when the system temperature reached to 500 °C and to end up near 600 °C. From this experiment, the SBH synthesis was found to proceed rapidly at the highest dT/dt rate (°C/min) and at the smallest particle size.

The SBH synthesis does not proceed effectively under isothermal conditions, particularly at the temperature levels between 500 and 600 °C that was proven by the experiments under the slower dT/dt rates as can bee seen in Fig. 1.

4. Preparation of the anhydrous sodium metaborate (NaBO$_2$) as the starting material

The following simple processes were used to prepare the anhydrous $NaBO_2$:

(a) From "Borax" as the abundant natural resource

The process that starts from borax ($Na_2B_4O_7 \cdot 10H_2O$) requires two parts of NaOH to make one part of $NaBO_2$ by an exothermal steam process as given in Eq. (13).

$$1/4Na_2B_4O_7 \cdot 10H_2O + 1/2NaOH + 5/4H_2O \rightarrow NaBO_2 \cdot 4H_2O \tag{13}$$
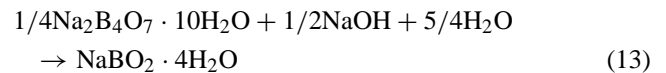
(b) From "Spent fuel" recovered after generating protide and hydrogen

The "Spent fuel" after releasing protide in the electrochemical reaction and generating gaseous hydrogen is recovered as the crystalline solution of $NaBO_2 \cdot 4H_2O$, and it is put in a simple drying process to yield anhydrous sodium metaborate ($NaBO_2$) as shown in Eq. (14);

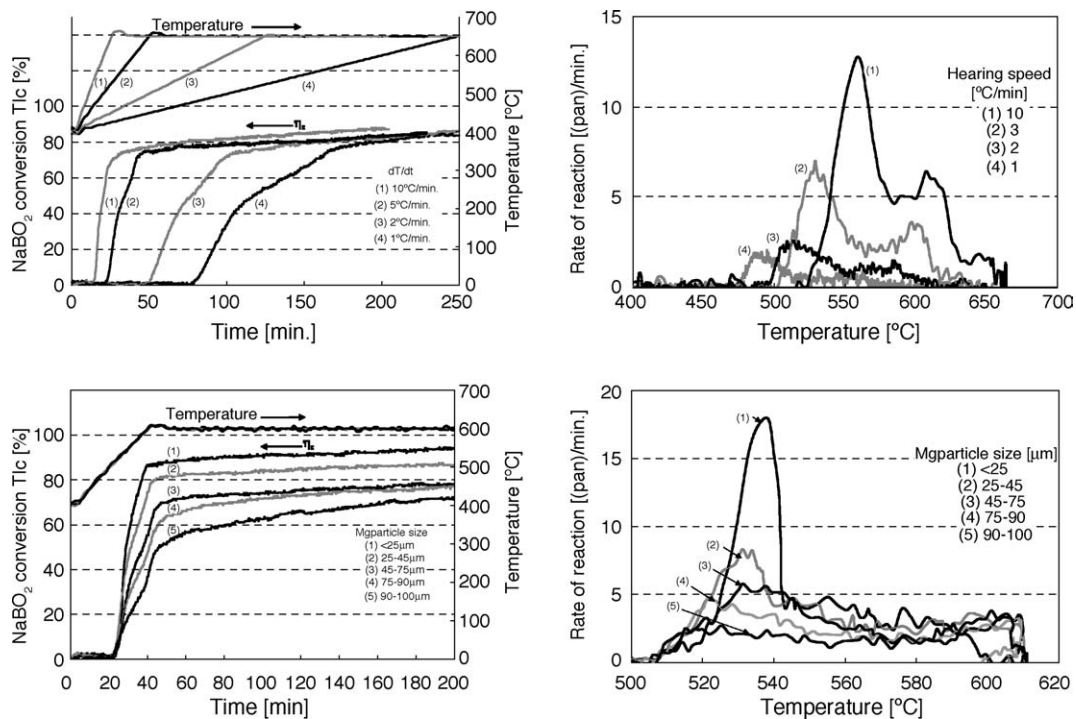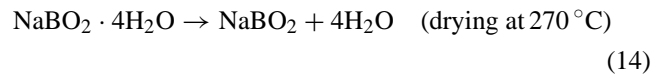$$NaBO_2 \cdot 4H_2O \rightarrow NaBO_2 + 4H_2O \quad \text{(drying at 270 °C)} \tag{14}$$

Fig. 1. (a) Effect of dT/dt (rate of temperature change) on the $NaBH_4$ conversion rate. (b) Rate of reaction at constant dT/dt as a function of time. (c) Effect of Mg particle size on the $NaBH_4$ conversion rate. (d) Rate of reaction at constant dT/dt as a function of time.
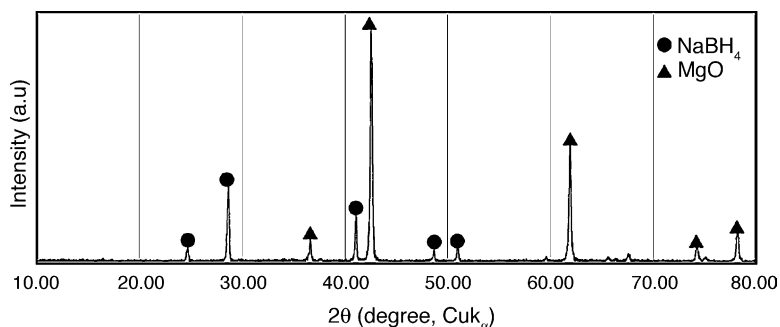
Fig. 2. XRD patterns taken after completing the dynamic H/D reaction.

5. Dynamic states of Mg–H system

5.1. Transitions from the hydriding to dehydriding regions

The thermal gradient between the initial- and the terminal points of the reaction provides the dynamic changes of Mg–H system between hydriding and dehydriding regions. At the lower temperature region, Mg–H system tends to form MgH_2 hydride at the extreme surface of Mg particles. On the contrary, it tends to dissociate hydrogen under the protide state back to the gas phase at the higher temperature region.

However, the Mg–H system is transferred dynamically from the hydriding to dehydriding regions by the rapid temperature change so as not to form hydride layer at the surface of Mg but to generate protide at the extreme surface of Mg directly from the gaseous H_2 to form $NaBH_4$. In return, oxygen is transformed to the surface of Mg particles to form MgO in exchange with the formation of $NaBH_4$.

The extreme surface of Mg is considered to function as a catalyst for converting H_2 to $2H^-$ during the dynamic temperature changes between hydriding and dehydriding regions.

5.2. Mechanism of MgO formation

No MgH_2 was formed during the dynamic thermal transition of the $NaBO_2$–H_2–Mg system and this was clearly examined by XRD, EPMA, and SEM where the materials

detected by XRD were only $NaBH_4$ and MgO. A typical XRD pattern is illustrated in Fig. 2 that was taken after completing the reaction. The formation of MgO begins with the Mg surface toward the center of particles as a function of reaction time elapsed. This is the same mechanism with the formation of MgH_2 observed under quasi-equilibrium conditions of the Mg–H system during hydriding reactions. In Fig. 3, a sectional SEM view of Mg particle after approximately 30% oxidation being reached in which a clear border between MgO and Mg phases can be observed.

From this observation, it is known that the Mg particles should be brought to the smallest size as possible for increasing the specific surface area to complete the oxidation of Mg to MgO.

The SBH yields depend on the specific surface area of Mg particles. Accordingly, the amount of Mg required for the complete reaction as indicated in Eq. (13) is determined by the particle size of Mg.

5.3. Exchange mechanism of gaseous hydrogen to protide

As MgH_2 is not formed under the transitional state of Mg–H system, the gaseous H_2 must be transformed at the extreme surface of Mg particles to the protide that is transferred instantly to the surface of $NaBO_2$ to form $NaBH_4$. The reaction mechanism at the contact surfaces between Mg and $NaBO_2$ particles is illustrated schematically in Fig. 4.

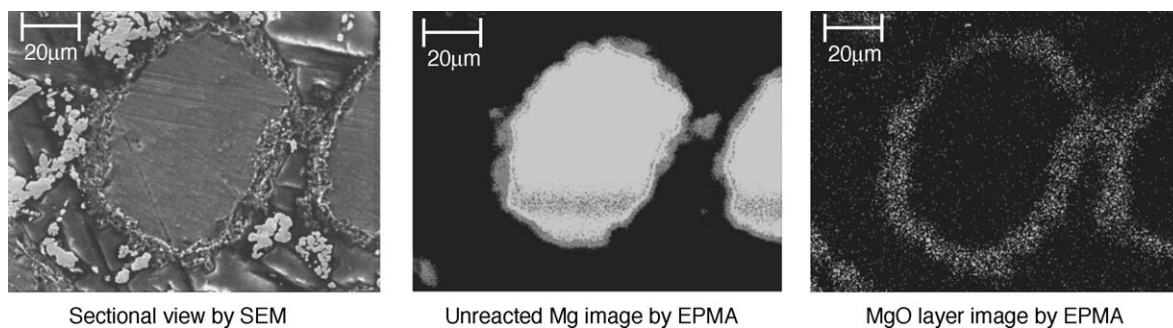Sectional view by SEM · Unreacted Mg image by EPMA · MgO layer image by EPMA

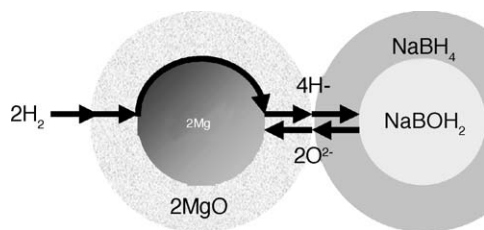Fig. 3. SEM and EPMA images of Mg particle (MgO starts from the surface).

Fig. 4. Schematic illustration of the transitional states of SBH formation.

6. Remarks

A dynamic hydriding and dehydriding process for the production of sodium borohydride as the hydrogen storage material was developed, which is based on the transitional state of hydrogen between the gaseous H_2 and protide.

The process uses Borax as the starting material and sodium metaborate as the spent fuel to synthesize the anhydrous sodium borohydride. The production cost is estimated to be 1/20 times cheaper than the conventional processes available today.

Hydrogen storage materials are the key issues for bringing PEMFC more practical. However, we must recognize that there has not been developed any hydrogen storage materials practically available today. Conventional metal hydrides in general will not be qualified for automobile applications because of their limited H-capacity and thermal requirements, and some of the hydrogen-metal complex compounds such as $NaAlH_4$ will not be employed as "On-board" or "On-site" materials because of its handling difficulties and safety issues.

The authors convince that $NaBH_4$ as the hydrogen storage material both for the large-scale storage material and the protide carrier in a wide variety of fuel cell applications with the estimated fuel cost of less than US$ 50/kW within a couple of years.

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