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# Hydrogen storage in a chemical hydride fuel system containing ammonia borane and Ni-Co/r-GO catalyst

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## Abstract

Hydrogen, one of environmentally benign energies, has attracting more and more attention. Out of many hydrogen storage systems, chemical hydrides not only have a high hydrogen storage capacity, but also produce ultrapure hydrogen in presence of adequate catalysts at room temperature. Among many chemical hydrides, ammonia borane ($NH_3BH_3$) is one of the promising candidates because its intrinsic hydrogen content is as high as 19.6 wt%. Moreover, the spent products of ammonia borane are non-flammable and rarely toxic. The chemical hydride fuel system was prepared by pulverizing ammonia borane and Ni-Co/r-GO catalysts in a high-energy ball mill. The hydrogen was produced from catalyzed hydrolysis reaction of ammonia borane composite initiated with limited amount of water. Variable parameters such as the amount of water dosage and loading of catalysts will be discussed in this study.

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*Keywords: Hydrogen; Fuel Cell; Chemical Hydride; Ammonia Borane; Reduced Graphene Oxide*

## 1. Introduction

Recently, hydrogen has gained more and more attention, as it is generally considered as one of clean energy resources. For example, water is one of the main spent products resulted from electricity generation in hydrogen-fed proton exchange membrane fuel cells (PEMFCs). However, the storage and supply of hydrogen to PEMFCs are always concerned. Chemical hydrides, one of the hydrogen storage methods, have some advantages such as a high gravimetric hydrogen storage density, a higher purity of produced hydrogen, a less energy loss and a lower operation pressure [1]. Among several chemical hydrides, ammonia borane ($NH_3BH_3$) is one of promising candidates in hydrogen storage and supply, as the intrinsic hydrogen content of ammonia borane (AB) is 19.6 wt%. Moreover, AB and its spent products are rarely toxic and stable. Furthermore, hydrogen can be generated from hydrolysis of AB at

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room temperature in presence of proper catalysts. In general, the catalysts for the hydrolysis reaction of AB can be either acids (liquid or solid) or metal catalysts [2]. Hence, the hydrolysis reaction of AB is often expressed as follows:

$$NH_3BH_3 + 2H_2O \xrightarrow{\text{catalyst}} 3H_2 + H_3BO_3 + NH_3 + \text{Heat}$$

As the higher hydrogen storage capacity of a chemical hydride fuel system is desired, a light-weighted catalyst or less water present in the reacting system is desired. In this work, a light-weighted support, i.e. graphene oxide (GO), was synthesized by using Hummers method [3] because GO has superior surface area (2630 $m^2 \cdot g^{-1}$, theoretically), electrical conductivity, mechanical strength and thermal stability [4]. The electroless deposition process (EDP) was utilized to deposit Ni and Co metal on the reduced graphene oxide (r-GO) support. Finally, Ni-Co/r-GO catalysts prepared by the electroless deposition process were employed to catalyze the hydrolysis reaction of AB.

## 2. Experimental

### *2.1. Hydrogen generation from hydrolysis reaction of $NH_3BH_3$ composite*

Experimental setup for hydrogen generation has been mentioned in our previous work [1]. Moreover, the synthesis of Ni-Co/r-GO catalysts was divided into two different procedures: (1) electrolessly-deposited simultaneously, in which Ni and Co were reduced simultaneously; and (2) electrolessly-deposited in succession, in which Ni was firstly plated as seeds for subsequent EDP of Co. The chemical fuel system made of AB/Ni-Co/r-GO catalyst composites, denoted as the solid-state AB composite, would be obtained by pulverizing appropriate weighted mixtures of AB and Ni-Co/r-GO catalyst in a high energy ball mill (Pulverisette, Fritsch GmbH, Germany) at 150 rpm for 10 min. Stainless steel balls of 5 mm in diameters were utilized as milling media. Solid-state AB composite powder after high-energy ball milling process was placed in a three-necked round bottom flask in a fume hood at 30°C. Deionized water was injected quickly by a syringe pump to the flask to initiate the hydrolysis reaction. A thermocouple was inserted in the pile of the reacting mixture to monitor reaction temperature. The generated gas was directly passed through a bottle with 0.1 N $H_2SO_4$ solution to remove any generated ammonia gas and, subsequently, through a bottle filled with silica gel particles to capture any residual moisture and ammonia gas. Finally, the instantaneous flow rate of the hydrogen gas with a high purity was recorded with a mass flow meter/controller (MFM). The water-displacement method was used to calibrate the MFM, while the conversion of AB in the presence of Ni-Co/r-GO catalysts calculated by using the MFM measurements was often compared with that measured by $^{11}B$ NMR.

### *2.2. Instrumental analyses*

Surface morphology and chemistry of the solid-state AB composites obtained after high energy ball milling at 150 rpm for 10 min were observed with the Hitachi SU-8000 scanning electron microscopy.

## 3. Results and discussion

### *3.1. Surface morphology of solid-state AB composite*

Surface morphology of the solid-state AB composite were examined with SEM. Fig. 1 displayed the SEM images of solid-state AB composites having 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously) and 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession). The particle size of the solid-state AB composites ranged from 60 to 95 μm, and the catalysts were uniformly dispersed in the solid-state AB composites after high energy ball milling treatment.

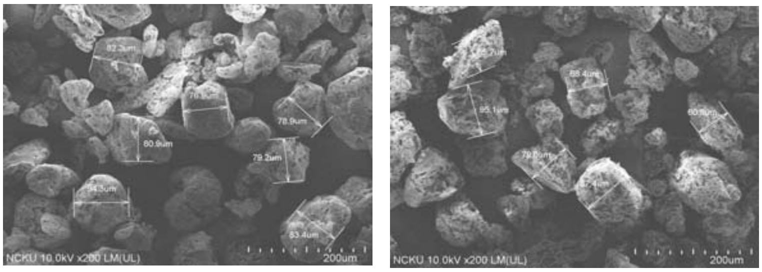

Fig. 1. SEM images of solid-state AB composites containing (a) 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously) and (b) 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession)

### *3.2. Hydrogen generation from solid-state AB composite*

Fig. 2 displayed the profiles of hydrogen evolution and reaction temperature resulted from hydrolysis of ammonia borane in presence of Ni-Co/r-GO catalysts. It is clear that temperature would increase with increasing production rates of hydrogen, since the catalytic hydrolysis of AB is exothermic. Table 1 lists the resulted conversion of ammonia borane with different dosage of water that was introduced with a fast injection rate to the three-necked round bottom flask. All water was introduced almost at once. Furthermore, almost complete evolution of hydrogen from AB in presence of both Ni-Co/r-GO catalysts could be achieved with the initial molar ratio of water to AB in feed as 5.93 and 3.97. However, the conversion of AB in presence of both Ni-Co/r-GO catalysts with an initial molar ratio of water to AB in feed as 2.02 (closed to its stoichiometric ratio) was just about 73%. It is possibly caused by the fact that some water was evaporated off with an elevated temperature in the reacting system by the exothermic heat emitted from the hydrolysis reaction of AB. Hence, the actual amount of water involved in AB hydrolysis was less than its stoichiometric ratio. Moreover, hydrogen evolution profiles from solid-state AB composites containing 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession) were smoother than that with 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously), which was advantageous on the supply of hydrogen to PEMFC in the future.

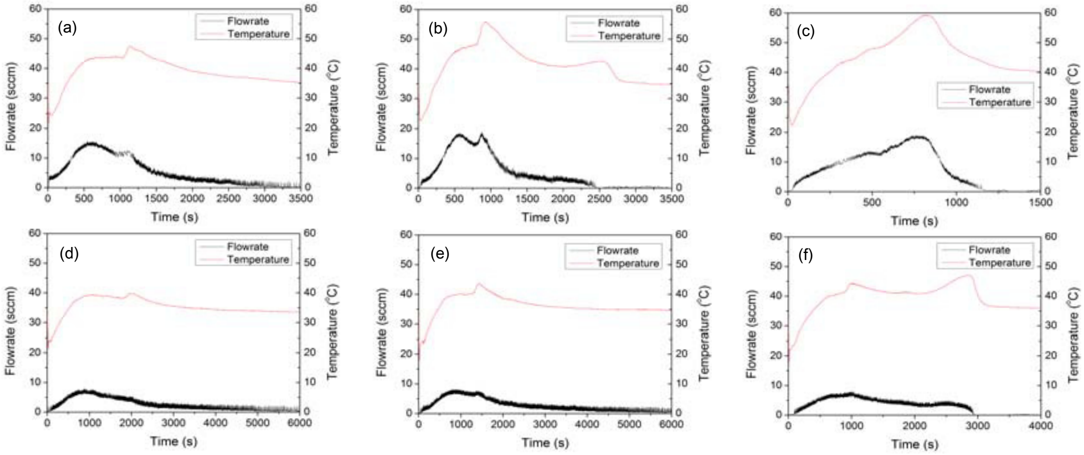

Fig. 2. Hydrogen generation profiles and temperature profiles from hydrolysis of ammonia borane in the presence of Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously and in succession) with different water dosages. With 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously): (a) $H_2O/AB = 2.02$; (b) $H_2O/AB = 3.97$; (c) $H_2O/AB = 5.93$; and with 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession) (d) $H_2O/AB = 2.02$; (e) $H_2O/AB = 3.97$; (f) $H_2O/AB = 5.93$.

Hydrogen storage capacity was calculated as the total volume of hydrogen produced divided by the total weight of the system (i.e. AB, catalyst, water) (Table 1). Interestingly, the gravimetric hydrogen storage density could reach as high as *ca.* 6.41 and 6.46 wt% in solid-state AB composites having 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously) and 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession) when water near the stoichiometric ratio was used, respectively, even though the conversion in both cases was not close to 100%. It could be attributable to water as the main reactant in hydrolysis reaction of AB. Consequently, decreasing water dosage would lead to an increase in hydrogen storage density by reducing the weight of the chemical hydride fuel system. The set goals for on-board hydrogen storage by the U.S. Department of Energy (DoE) are 6 wt% in 2010 and 9 wt% in 2015.

Table 1. Effect of the amount of water dosage to the conversion of ammonia borane (AB) estimated by MFM and hydrogen density.

| | $H_2O$/AB (mol/mol) | Deionized water (g) | Conversion by MFM (%) | $H_2$ storage capacity[a] (wt%) |
|---|---|---|---|---|
| | 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously) | | | |
| (a) | 2.02 | 0.236 | 73.2 | 6.41 |
| (b) | 3.97 | 0.463 | 100.0 | 5.81 |
| (c) | 5.93 | 0.691 | 100.0 | 4.34 |
| | 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession) | | | |
| (d) | 2.02 | 0.236 | 72.8 | 6.46 |
| (e) | 3.97 | 0.463 | 100.0 | 5.86 |
| (f) | 5.93 | 0.691 | 100.0 | 4.37 |

a The hydrogen storage capacity is calculated from the MFM-recorded volume of hydrogen

## 4. Conclusion

The solid-state AB composites possessed uniformly dispersed granules ranged from 60 to 95 μm after high-energy ball milling treatment. Complete hydrogen evolution from AB could be achieved with an initial molar ratio of water to AB in feed as 5.93 and 3.97. In contrast, the conversion of AB to hydrogen was near 73% only when the initial molar ratio of water to AB in feed was 2.02, closed to its stoichiometric ratio. In addition, the hydrogen profiles from solid-state AB composites with 3.00 wt% Ni-Co/r-GO catalysts (electrolessly-deposited in succession) were smoother than that having 5.37 wt% Ni-Co/r-GO catalysts (electrolessly-deposited simultaneously). Finally, the gravimetric density of hydrogen storage could reach as high as 6.46 wt% in solid-state AB composites with injected water near a stoichiometric ratio, which already reached the set-goal of the US DoE on-board hydrogen storage.

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