



Short communication

A composite of borohydride and super absorbent polymer for hydrogen generation

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ABSTRACT

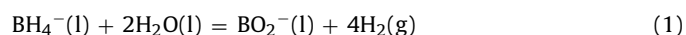
To develop a hydrogen source for underwater applications, a composite of sodium borohydride and super absorbent polymer (SAP) is prepared by ball milling sodium borohydride powder with SAP powder, and by dehydrating an alkaline borohydride gel. When sodium polyacrylate (NaPAA) is used as the SAP, the resulting composite exhibits a high rate of borohydride hydrolysis for hydrogen generation. A mechanism of hydrogen evolution from the NaBH₄–NaPAA composite is suggested based on structure analysis by X-ray diffraction and scanning electron microscopy. The effects of water and NiCl₂ content in the precursor solution on the hydrogen evolution behavior are investigated and discussed.

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1. Introduction

Until now, the choice of power sources for underwater vehicles has been limited to lead–acid and silver–zinc batteries. However, their low energy densities (~25 Wh kg⁻¹) limit travel range and the tasks that the underwater vehicles can perform. Recently, proton exchange membrane fuel cells (PEMFCs) have attracted attention to drive underwater vehicles [1]. Sodium borohydride is a convenient hydrogen source for the PEMFCs [2–4]. Borohydride hydrolysis is of interest in hydrogen generation because half of the generated hydrogen is from the borohydride and the other half is from water. This is particularly attractive for supplying hydrogen to fuel cells in underwater applications because water supply is readily available in these applications.

Theoretically, borohydride hydrolysis produces pure hydrogen, as shown in reaction (1):



However, when hydrogen bubbles evolve from an alkaline NaBH₄ solution, they carry some of the liquid to form an alkaline mist. The higher the hydrogen evolution rate, the more mist is carried. Mist accumulates on the anode, which causes the PEMFC to deteriorate. A mist separator can remove the mist, but finding sufficient space for the mist separator is difficult in an underwater vehicle, especially in an unmanned underwater vehicle (UUV).

In our previous work [5], an alkaline borohydride gel prepared using a super absorbent polymer (SAP) and NaBH₄ was suggested for borohydride hydrolysis to generate pure hydrogen. SAPs can rapidly absorb water to form hydrogels [6]. Usually, the seawater absorption capacity of a SAP is much lower than that for fresh water. According to our previous results [5], the absorption capacity of the SAP is highly dependent on the NaBH₄ concentration. The NaBH₄ content is low in the SAP gel, as illustrated in Table 1. Therefore, the energy density of an alkaline borohydride gel is not as high as that of solid sodium borohydride because water utilization by the gel is much lower than that by the solid [7,8].

Aiming to develop a hydrogen source for underwater applications, this study suggests a composite material prepared using sodium borohydride, sodium hydroxide, and sodium polyacrylate (NaPAA), which was chosen for the borohydride hydrolysis, because it may not only localize the liquid or solid substances (H₂O or borate) except hydrogen gas but also distribute the catalyst precursor solution during the borohydride hydrolysis. A hydrogen evolution mechanism is suggested based on structural analysis by powder X-ray diffraction (XRD) and morphology observation by scanning electron microscopy (SEM). The effects of water and NiCl₂ content in the precursor solution on the hydrogen evolution behavior are investigated and discussed.

2. Experimental details

The NaBH₄–NaPAA composite was made by using a ball milling method. The SAP, NaBH₄ (purity: 99%), and NaOH were placed in a 45-mL grinding bowl with 7 grinding balls of 13 mm diameter. The

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Table 1
NaBH₄ content in an alkaline borohydride gel.

	NaBH ₄ concentration					
	0	10 wt.%	15 wt.%	20 wt.%	25 wt.%	26.44 wt.%
Absorption capacity (Ref. [5])	35.41	19.89	15.04	8.22	5.22	4.19
NaBH ₄ content	0	0.48 wt.%	0.94 wt.%	2.17 wt.%	4.02 wt.%	5.09 wt.%

The alkaline borohydride solution contains 5 wt.% of NaOH. The absorption capacity is defined as the weight ratio of the absorbed alkaline NaBH₄ solution to the absorbent (SAP).

grinding bowls and balls were made of stainless steel. Ball milling was then conducted at room temperature at a motor rotation speed of 100 rpm for 30 min using a Planetary Micro Mill Pulverisette 7 (Fritsch). The NaBH₄ content in the composite was determined by the amount of hydrogen evolved from NaBH₄ hydrolysis, which was catalyzed by Ni powder (Inco Type 255).

To study the hydrogen evolution mechanism from the NaBH₄-NaPAA composite, a sample was obtained by dehydrating an alkaline NaBH₄ gel. The alkaline NaBH₄ gel was prepared by absorbing an alkaline NaBH₄ solution into a commercial NaPAA (30 mesh). To determine the appropriate dehydration temperature, differential scanning calorimetry (DSC) analysis was conducted, as shown in Fig. 1. Exothermic peaks were observed upon heating the alkaline borohydride gel to 75 °C, indicating that borohydride hydrolysis occurred. Therefore, the composite was prepared by dehydrating the gel at 40 °C under vacuum for 24 h.

Nickel is an effective catalyst for the borohydride hydrolysis. Metallic Ni can be formed through the reduction of Ni(II) by sodium borohydride [7,9]. An aqueous NiCl₂ solution was used as the catalyst precursor for the formation of metallic Ni. Hydrolysis reaction experiments were carried out in a three-necked flask (200 mL). The central neck was connected to an injector for adding the catalyst precursor solutions. The NaBH₄-NaPAA composite was initially placed at the bottom of the flask. The hydrolysis reaction was initiated by injecting the catalyst precursor solution into the flask. The volume of the generated hydrogen gas was measured by a wet gas flow meter and was converted to the value at standard temperature and pressure (STP). The flask was immersed in a water bath to stabilize the temperature at 25 °C.

The product of the borohydride hydrolysis was extracted with deionized water. The extraction solution was separated from the hydrogel by vacuum filtration. A white substance was obtained

after evaporating the extraction solution at 300 °C. The white substance was subjected to qualitative XRD analysis.

3. Results and discussion

3.1. Hydrogen evolution mechanism

Fig. 2 gives the ex situ XRD patterns of the NaBH₄-NaPAA composite before and after the borohydride hydrolysis. The NaBH₄-NaPAA composite prepared by ball milling [Fig. 2(a)] or dehydration [Fig. 2(b)] shows the existence of NaBH₄. The XRD peaks of NaBH₄ disappeared and no peak appeared for the hydrolyzed composite. The hydrolyzed composite exhibited a tendency for gelation. Fig. 3 gives the morphology of the NaBH₄-NaPAA composite prepared by dehydrating the corresponding gel. Fig. 4 shows the ex situ morphology of the NaBH₄-NaPAA composite in which 10% of the NaBH₄ has been hydrolyzed. White spots appeared in the matrix after 10% of the NaBH₄ was hydrolyzed, as shown in Fig. 4(c). Through energy dispersive analysis of X-rays (EDAX), the oxygen content in the white spot area marked in Fig. 4(c) was distinctly higher than that in the crystal area [Fig. 3(b)], as illustrated in Table 2. The oxygen in the crystal area marked in Fig. 3(b) was from NaPAA (CH₂-CH₂-COONa), because the atomic ratio of carbon to oxygen in the crystal area (C/O = 1:0.77) was close to 1:0.67 (C/O = 3:2). The XRD pattern of the substance extracted from the NaBH₄-NaPAA composite after the hydrolysis shows the presence of NaBO₂ (Fig. 5), indicating that sodium borate was formed in the composite. These results demonstrate that crystalline NaBH₄ in the composite was converted to non-crystalline (perhaps ionic) sodium borate so that no pertinent peak was detected by XRD. Further experiments are needed to identify the form of this sodium borate.

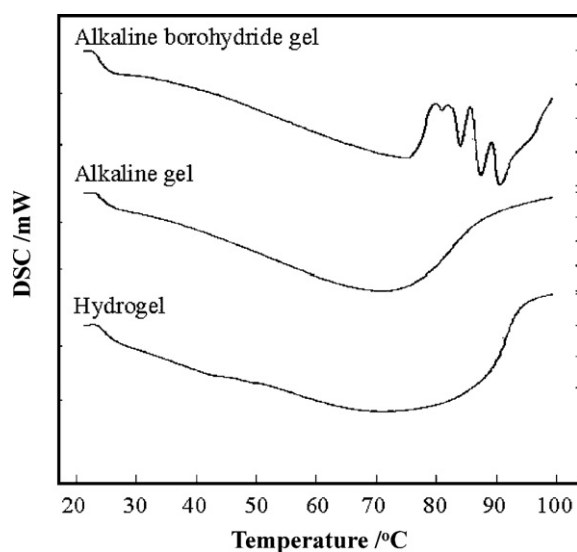


Fig. 1. Dehydration behavior of the alkaline borohydride gel measured by DSC under nitrogen.

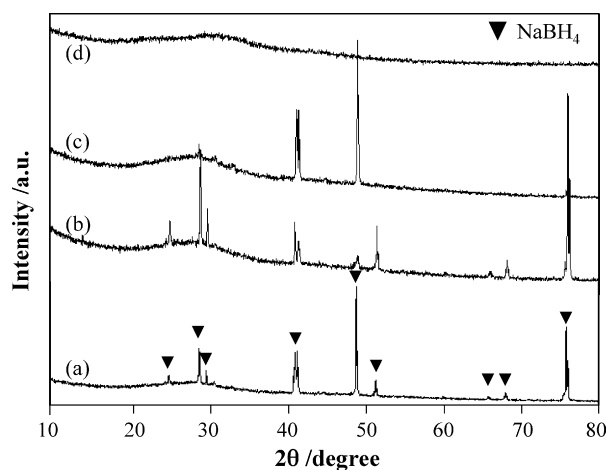


Fig. 2. XRD patterns of the NaBH₄-NaPAA composites: (a) prepared by ball milling; (b) prepared by dehydrating the corresponding alkaline borohydride gel; (c) the composite in which 10% of NaBH₄ has been hydrolyzed; and (d) the composite after releasing all of the hydrogen.

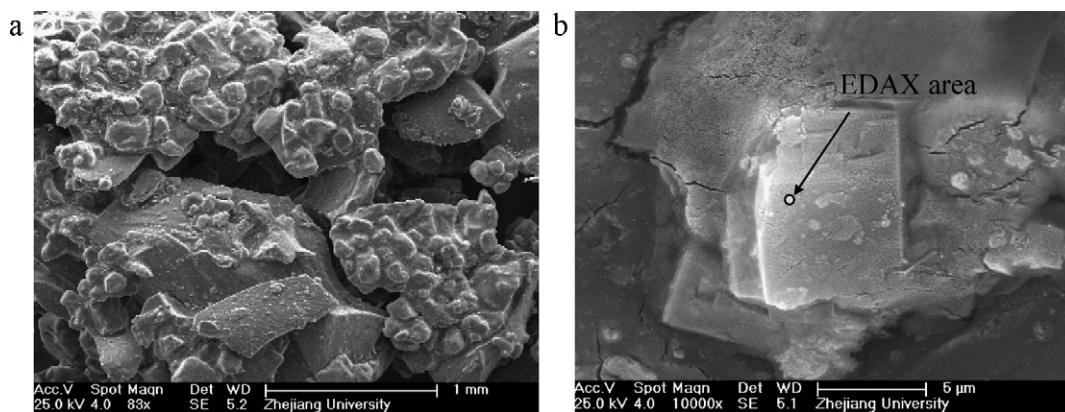


Fig. 3. Morphology of the NaBH₄-NaPAA composite.

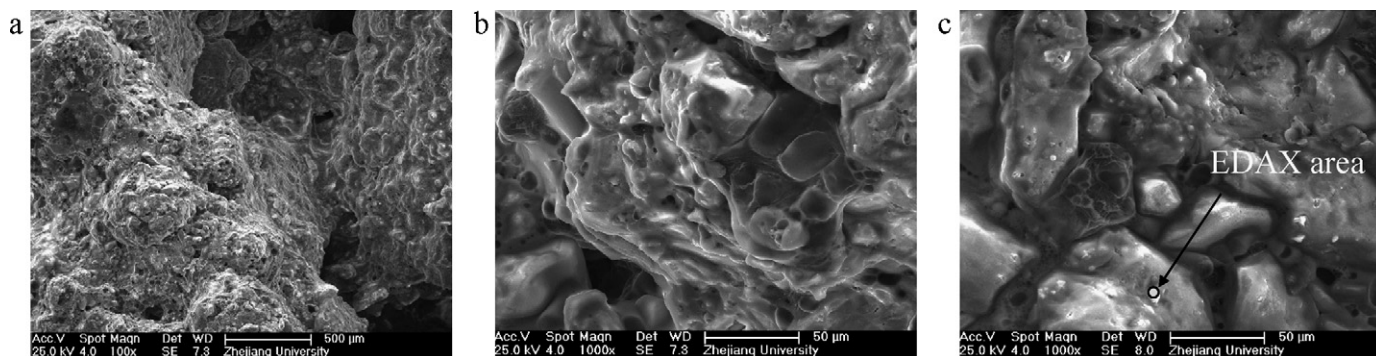


Fig. 4. Morphology of the NaBH₄-NaPAA composite after releasing 10% H₂: (a) top view in low magnification; (b) top view in high magnification; and (c) cross-sectional view.

Table 2

Composition evaluation of the composite before and after hydrolysis reaction.

Element	Crystal area marked in Fig. 3(b)		White spot area marked in Fig. 4(c)	
	wt.%	at.%	wt.%	at.%
C	14.45	23.13	15.13	21.67
O	14.85	17.83	45.28	48.70
Na	70.70	59.04	39.59	29.63
Atomic ratio of C to O	1:0.77		1:2.25	

From the cross-sectional view of the NaBH₄-NaPAA composite after part of the borohydride was hydrolyzed, the hydrogen bubbles were generated in the NaPAA matrix. Small hydrogen bubbles merged into a big bubble so that the inner surface appeared smooth. This observation suggests that the NaPAA matrix was the site of borohydride hydrolysis. The NaPAA matrix functioned by dis-

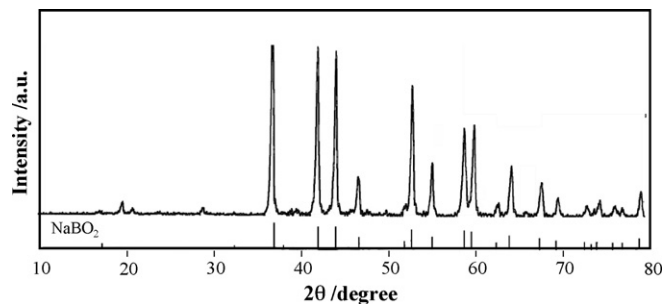
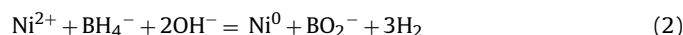


Fig. 5. XRD pattern of the substance extracted by water from the NaBH₄-NaPAA composite after hydrolysis.

tributing the catalyst precursor solution (NiCl₂ solution). When the precursor solution reached the NaBH₄ crystals through the NaPAA matrix, the NaBH₄ crystals dissolved to form BH₄⁻ ions, meanwhile Ni(II) was chemically reduced to metallic Ni [9]:



The metallic Ni formed was distributed homogeneously into the NaPAA matrix.

The results suggest that hydrogen evolution from the NaBH₄-NaPAA composite takes place through the following steps:

- (1) Catalyst precursor solution diffuses through the NaBH₄-NaPAA composite, contacting the NaBH₄ crystals through NaPAA.
- (2) Metallic Ni forms in the NaPAA matrix.
- (3) Dissolved NaBH₄ contacts the metallic Ni surface where borohydride hydrolysis occurs.
- (4) Hydrogen bubbles are generated on the metallic Ni.
- (5) Small hydrogen bubbles merge into big bubbles, which rise and release the hydrogen, leaving sodium borate in the NaPAA matrix.

A scheme of hydrogen evolution from the NaBH₄-NaPAA composite is summarized in Fig. 6.

3.2. Hydrogen evolution kinetics

According to the proposed mechanism, water distribution plays an important role in the hydrogen evolution from the composite. Fig. 7 gives a comparison of the hydrogen evolution behavior of the NaBH₄-NaPAA composite with that of the corresponding alkaline borohydride gel. The same amount of water (30 g) and sodium borohydride (0.2 g) was used for the borohydride hydrolyses. No

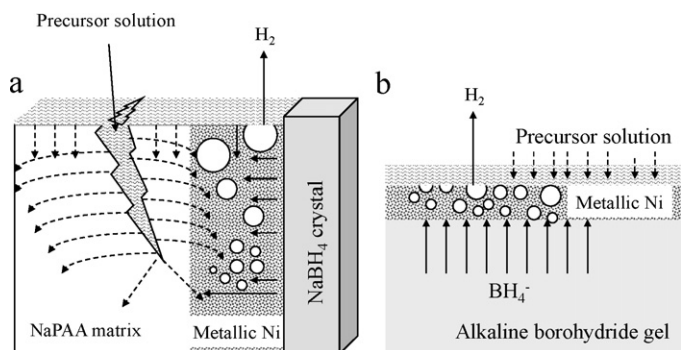


Fig. 6. Schemes for hydrogen evolution from (a) the NaBH₄-NaPAA composite and (b) the alkaline borohydride gel.

water was present in the NaBH₄-NaPAA composite. On the other hand, the precursor solution contained one-third of the initial water (10 g), and the alkaline borohydride gel was two-thirds. Hydrogen was rapidly evolved from the NaBH₄-NaPAA composite after adding the precursor solution, whereas, hydrogen releases from the alkaline borohydride gel started only after a certain incubation time. As shown in Fig. 6, metallic Ni could be formed anywhere in the NaPAA matrix of the NaBH₄-NaPAA composite. However, metallic Ni could be formed only on the surface of the alkaline borohydride gel. BH₄⁻ ions had to move a long distance from the gel interior to the surface. As a result, the hydrogen evolution from the alkaline borohydride gel was slower than that from the NaBH₄-NaPAA composite.

Fig. 8 shows the influence of water content in the NiCl₂ precursor solution on the hydrogen evolution amount and rate. The hydrogen evolution amount and rate increased with the water content in the NiCl₂ precursor solution. The NiCl₂ precursor solution may be absorbed by NaPAA and then localized by the NaPAA when a small amount of water was added, so that only part of the NaBH₄ reacted with the water, thereby decreasing the hydrogen evolution amount and rate. Diffusion of the NiCl₂ precursor solution into the NaPAA matrix controlled the rate of borohydride hydrolysis reaction. Increasing the water content in the PAA matrix improved the diffusion of the NiCl₂ precursor solution so well that well-scattered metallic Ni formed in the whole NaPAA matrix. This hastened the borohydride hydrolysis. Therefore, the kinetics of the hydrogen evolution was improved by increasing water content in the precursor solution.

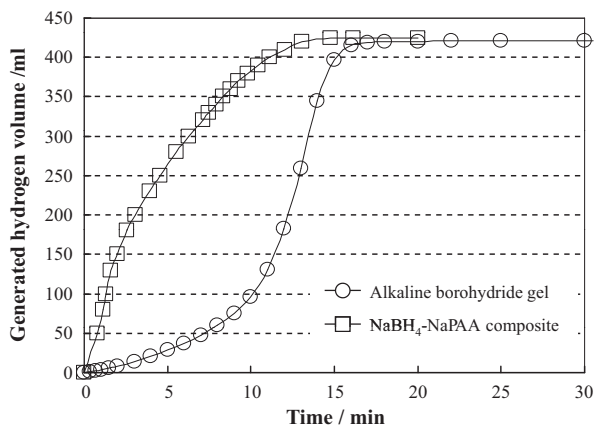


Fig. 7. Comparison of hydrogen evolution from the NaBH₄-NaPAA composite with that from the corresponding alkaline borohydride gel at 25 °C. The NiCl₂ precursor solution contains 54 mg NiCl₂ (0.1 g of NiCl₂·6H₂O). Both samples contain 0.2 g NaBH₄.

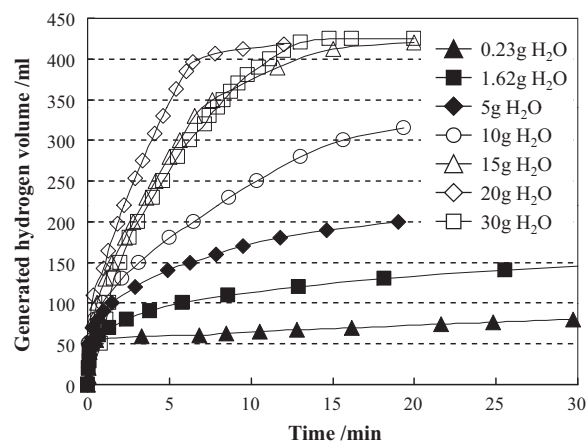


Fig. 8. Hydrogen evolution behavior from the NaBH₄-NaPAA composite at 25 °C when the NiCl₂ precursor solution contains 54 mg NiCl₂ (0.1 g of NiCl₂·6H₂O) and different amounts of water. The NaBH₄-NaPAA composite contains 0.2 g NaBH₄.

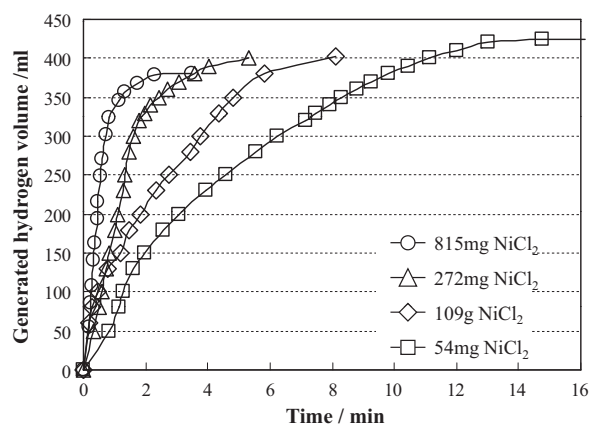


Fig. 9. Hydrogen evolution behavior from the NaBH₄-NaPAA composite at 25 °C when the NiCl₂ precursor solution contains 30 g water and different amounts of NiCl₂. The NaBH₄-NaPAA composite contains 0.2 g NaBH₄.

The effect of water content in the precursor solution on the improvement of hydrogen evolution rate was decreased when more than 15 g water was added. This was because the NaPAA matrix could not absorb all of the precursor solution, which in turn decreased the amount of formed catalyst in the NaPAA matrix. On the other hand, Ni(II) had to move a long distance through the NaPAA matrix toward the NaBH₄. Therefore, with free precursor solution, further increase of water content in the precursor solution would negatively affect the hydrogen evolution kinetics.

Fig. 9 shows the hydrogen evolution behavior of the NaBH₄-NaPAA composite when the NiCl₂ precursor solution contains more NiCl₂. The hydrogen evolution rate increased with the NiCl₂ content in the precursor solution. This result could be attributed to the fact that the more NiCl₂ the precursor solution contains, the more the metallic Ni catalyst is formed. However, the hydrogen generation volume would be decreased somewhat because part of the NaBH₄ is used for the reduction of Ni(II) to Ni [9].

4. Conclusions

A composite material was prepared by ball milling sodium borohydride with NaPAA. The composite exhibited a higher hydrogen evolution rate than the corresponding alkaline borohydride gel. The water and NiCl₂ contents in the precursor solution play an important role in the hydrogen evolution. The hydrogen evolution rate

increases with the increase of the water and NiCl_2 content in the precursor solution. However, once the SAP ceases to absorb the precursor solution, further increase of water content in the precursor solution would exert a negative affect on the hydrogen evolution kinetics.

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