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Combined Hydrogen Generation from Al/$NiCl_2$ Powder and Alkaline $NaBH_4$ Solution for Portable Fuel Cell

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Abstract: *Hydrolysis of Al and $NaBH_4$ for hydrogen generation has obtained considerable attention as a portable hydrogen source system. In this paper, we report a new combined hydrogen generation from Al powder and alkaline $NaBH_4$ solution activated by $NiCl_2$ additive. The system is characterized as the followed features: the interaction of Al/$NaBH_4$ hydrolysis, catalytic effect of Ni_2B for Al and $NaBH_4$, Al hydrolysis stimulated by NaOH solution. The effects which affect the hydrogen generation performance of the system were studied. The results showed that a favorable combination of high hydrogen yield and high hydrogen generation rate might be obtained via the optimized composition design. Therefore, the system may be developed as a portable hydrogen source system.*

Keywords: Hydrogen generation, Al/$NaBH_4$ system, catalytic effect, $NiCl_2$ additive

1. INTRODUCTION

Hydrogen storage is a barrier which limits the application of proton exchange fuel cell (PEMFC) at an industrial scale. The potential hydrogen sources from the hydrolysis of Al/$NaBH_4$ system have been widely studied [1, 2]. Al/$NaBH_4$ system has high theoretic hydrogen density about 3.7~10.8 wt%, with good stability at air. Aluminum can be stable due to the alumina layer covered on Al surface and $NaBH_4$ can be stored in alkaline solution. Most of the research efforts have been developed to obtain high activated catalysts, which stimulate the hydrolysis reactions of Al and $NaBH_4$.

The reactivity of aluminum can be improved by physical and chemical methods. Generally, aluminum has good hydrogen generation performance in alkaline solution. Many works [3–5] introduced hydrolysis of aluminum and aluminum alloys to produce hydrogen in NaOH solution. There existed polymeric aluminate ions in the hydrolysis byproducts, which could act as nuclei for $Al(OH)_3$ crystallization, prevent the $Al(OH)_3$ precipitation on Al surface and stimulate Al hydrolysis [6]. There is an advantage that the hydrogen generation rate can be controlled by tuning the concentration and quality of NaOH solution. The hydrogen generation performance of aluminum powder can be further improved with the presence of additives in the electrolyte. Dai et al [7] found that the addition of a small amount of Na_2SnO_3 into alkaline solution could greatly stimulate Al hydrolysis. The hydrolysis byproduct Sn could act as a cathode and accelerated the electrochemical corrosion of aluminum therefore.

The hydrogen generation performance of $NaBH_4$ can be improved by the catalytic effect of transition metals and metal boride such as Pt/C, Ru/Al_2O_3,Co-B, Ni-B, etc [8]. Pt- and Ru-based catalyst have high reactivity for $NaBH_4$ hydrolysis, but they are also expensive. Ni-based catalyst is a good promotor for $NaBH_4$ hydrolysis and it is low cost, compared to Pt- , Ru- and Co-based catalysts. Many efforts have been developed to improve the reactivity of Ni-based catalysts. Liu et al [9] found that hydrogen generation rate of 0.3-1.5 L/min g (catalyst) were obtained at 20 °C, using Raney Ni, Raney $Ni_{25}Co_{75}$, Raney $Ni_{50}Co_{50}$ and Raney $Ni_{75}Co_{25}$ for $NaBH_4$ hydrolysis. Wu et al [10] prepared Ni-B catalyst which could give high hydrogen generation rate from $NaBH_4$ hydrolysis and successive hydrogen supply to a 2.2 kW PEMFC at a hydrogen utilization of 100%. Approximate 403 L /min.g (catalyst) and 357 L /min.g (catalyst) hydrogen generation rate of $NaBH_4$ solution could be achieved using $NiCl_2^{25}AlCl_3^{75}$ and $NiCl_2^{25}AlCl_3^{75}$ [11]. However, low hydrogen storage density has to be achieved because hydrolysis byproduct $NaBO_2$ has low solubility and limits $NaBH_4$ concentration therefore.

In this paper, a new composite of Al/$NiCl_2$ powder and $NaBH_4$

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alkaline solution was used to improve high hydrogen generation density. The hydrogen generation performance can be regulated via changing Al/$NiCl_2$ amount, $NaBH_4$/NaOH concentration. Compared with conventional $NaBH_4$- or Al-based systems, the newly developed system has significant advantages in terms of hydrogen generation amount and rate with high efficiency. The combination of these advantages makes the Al/$NiCl_2$/$NaBH_4$/NaOH mixture promising for portable hydrogen source applications.

2. EXPERIMENTAL

2.1. Chemical materials

Al powder (99.9% purity and particle size of about 10 um; Angang Group Aluminum Powder Co., Ltd, China), NaOH (98%, purity), $NiCl_2$ (99.0% AR), and $NaBH_4$ (98% purity; China Chemical Company Ltd) were used as starting materials. The Al/$NiCl_2$ powder mixture were hand-milled using an agate jar, then the mixture was pressed into a tablet in a stainless steel mold (the diameter was 10 mm) under 1 ton pressure. The alkaline $NaBH_4$ solution was prepared as the follows: $NaBH_4$, 5, 10, 15, 20 wt%; NaOH, 5, 10, 15, 20 wt%. The alkaline $NaBH_4$ solution was used as $NaBH_4$-5 wt%, NaOH- 5wt% if no special state was elaborated.

2.2. Hydrogen generation performance testing

The experimental equipment used for hydrogen generation was described in the previous work [3]. The mass of Al/$NiCl_2$ powder mixture was o.26 g, including 0.2 g Al and 0.06 g $NiCl_2$ if no special state was elaborated. The alkaline $NaBH_4$ solution was 4 ml. At 30^0C, 4 ml alkaline $NaBH_4$ solution was dumped into a 30 ml crucible which was placed in a constant- temperature bath. Then Al/$NiCl_2$ powder mixture was thrown into the crucible. The generated hydrogen flowed through a condenser and then was collected using dewatering method at 25 $^{\circ}$C and 1 atm. The reaction time began with the first bubble, and the final volume of the produced hydrogen was collected after one hour of reaction. Powder X-ray diffraction (XRD) studies were carried out in an X-ray diffractometer (RIGAKU, Japan, model D/MAX2550V/PC). Microstructure studies (EDX analysis) were performed on model JSM−5610LV from JEOL Company, which was equipped with INCA energy dispersive X-ray spectroscopy measurements (EDS).

3. RESULTS AND DISCUSSION

3.1. Effect of Al amount

Fig. 1 shows effect of Al amount on hydrogen generation performance of Al/$NaBH_4$ system. As the Al amount able to react with alkaline solution increases, hydrogen generation rate become faster. The maximum hydrogen generation rate of the system increases from 290 ml/min.g to 490, 590 and 741 ml/min.g when Al amount increases from 0.1 g to 0.2, 0.3 and 0.4 g. The maximum hydrogen generation rate follows a linear relationship on the initial Al mass to the power of 2/3 in Fig.1b. Similar results have also been reported by Soler et al and Hu et al [12, 13]. It can be also found that hydrogen generation amount increases from 785 ml/g to 897, 1021 and 1145 ml/g within 1 h when Al amount increases from 0.1 g to 0.2, 0.3 and 0.4 g. Approximate 120 ml hydrogen is increased with 0.1 g Al amount continuously added. There exists a linear relationship between increased hydrogen generation amount within 1 h and Al amount.

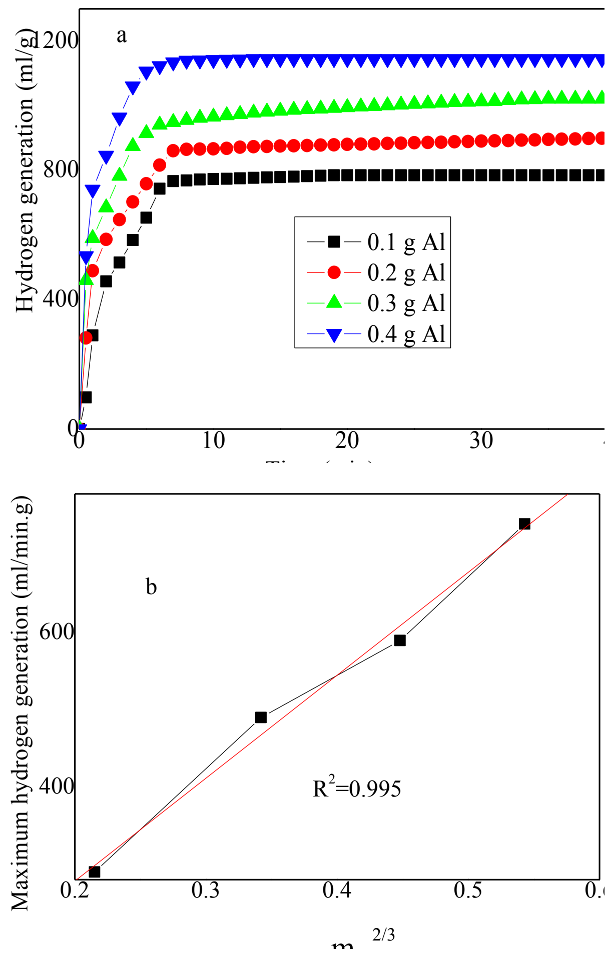

Figure 1. Hydrogen generation curves of Al/$NaBH_4$ system with different Al amount.

3.2. Effect of NaOH concentration

Fig. 2 shows effect of NaOH concentration on the hydrogen generation performance of Al/$NaBH_4$ system. Hydrogen yield is increased from 98% to 100% and hydrogen generation rate is steadily increased by increasing NaOH concentration. For 5 wt%, 10 wt%, 15wt% and 20 wt% of NaOH solution, the maximum hydrogen generation rate is corresponded to 490, 526, 616 and 720 ml/min.g, respectively. NaOH acts as a catalyst in Al hydrolysis and higher NaOH concentration means to more NaOH amount in the same solution volume. Therefore, high NaOH concentration is beneficial to hydrogen generation. As Al hydrolysis is an exothermic reaction, the temperature increase leads to improve the hydrolysis kinetics of Al/$NaBH_4$ system. The positive effect of NaOH is quite interesting since it compensates a possible negative effect caused by reduced activity of water and lowered solubility of the reaction product at higher hydroxide concentration in some degrees. The improved reactivity of Al/$NaBH_4$ system with high NaOH concentration was also obtained by the surface reactions of nickel-based catalyst and hydroxide ions [14].

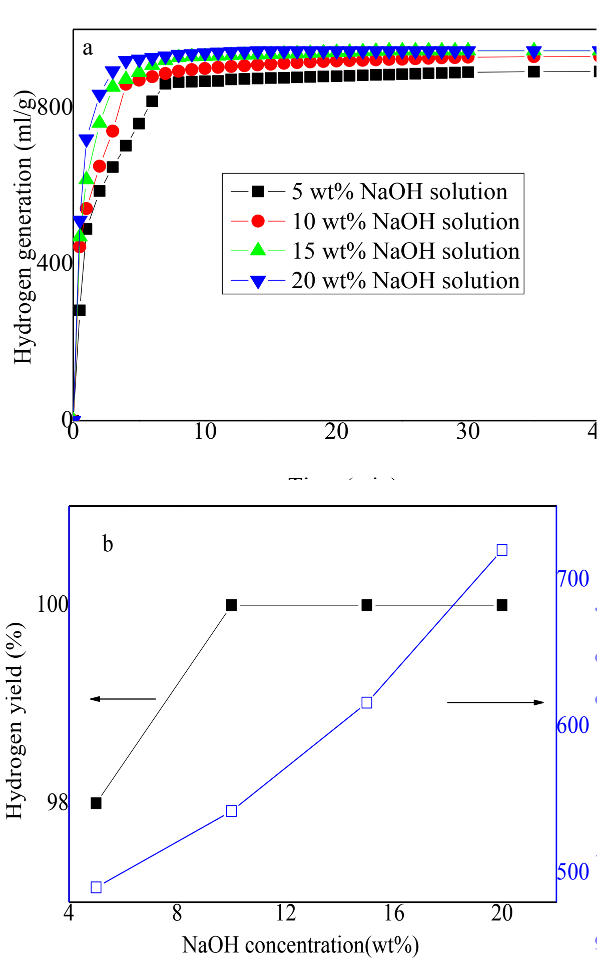

Figure 2. Hydrogen generation curves of Al/NaBH$_4$ system with different NaOH concentration.

3.3. Effect of NaBH$_4$ concentration

Fig. 3 shows hydrogen generation performance obtained with different concentration of NaBH$_4$. The hydrogen generation amount is increased with increasing NaBH$_4$ concentration. This is probably due to the fact that high NaBH$_4$ concentration means to more NaBH$_4$, which reacts with water to generate hydrogen. Hydrogen generation amount are 897, 1422, 1976 and 2186 ml/g within 1 h when their NaBH$_4$ concentrations in 4 ml solution are 5, 10, 15 and 20 wt%. Their efficiency is 98%, 100%, 100% and 93%, respectively. Hydrogen yield is increased firstly and then decreased with the increase of NaBH$_4$ concentration. As the hydrolysis reaction proceeds, the concentration of hydrolysis NaBO$_2$ increases the alkaline which stimulates Al hydrolysis. When the continuous increase of NaBO$_2$ eventually exceeds its solubility limit, NaBO$_2$ crystal precipitates out of solution, blocks catalysts sites and decreases catalyst reactivity. Fig. 4 shows SEM images of hydrolysis byproducts with different NaBH$_4$. It is clearly confirmed that the particle size is increased evidently as the solid-state NaBO$_2$ covers on the surface of catalyst and Al(OH)$_3$. The similar explanation was also proposed by Pinto AMFR et al [15], when using nickel-based catalyst.

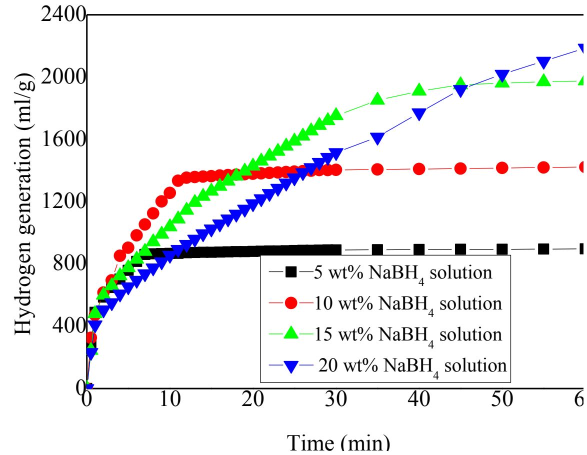

Figure 3. Hydrogen generation curves of Al/NaBH$_4$ system with different NaBH$_4$ concentration.

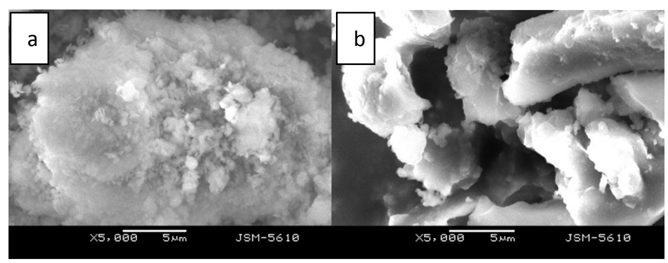

Figure 4. SEM images of hydrolysis byproducts of Al/NaBH$_4$ system with different NaBH$_4$ concentration. a, 5 wt%; b, 20 wt%.

3.4. Effect of NiCl$_2$ amount

Fig. 5 shows effect of NiCl$_2$ amount on hydrogen generation performance of Al/NaBH$_4$ system. Hydrogen generation amount has no evident change with increasing NiCl$_2$ amount, but hydrogen generation rate is proportional to NiCl$_2$ amount. The inflection point in Fig.5 comes beforehand with NiCl$_2$ amount increased. NiCl$_2$ is a good promoter for NaBH$_4$ hydrolysis. Its hydrolysis byproduct NixB also stimulated NaBH$_4$ hydrolysis. In addition, NixB deposited on Al powder surface and functioned as cathodes of micro-galvanic cell to stimulate Al hydrolysis. More NiCl$_2$ amount resulted in more hydrolysis byproduct NixB. Therefore, high reactivity of Al/NaBH$_4$ system can be obtained with increasing NiCl$_2$ amount. However, uncontrollable hydrogen generation rate occur with NiCl$_2$ amount increasing continuously. So the suitable NiCl$_2$ amount should be pursued.

There exist complex hydrolysis processes in the hydrolysis of Al-NiCl$_2$ powder and NaBH$_4$ alkaline solution, where chemical reactions and electrochemical corrosion are combined together. Chemical reactions include Al hydrolysis activated by alkaline solution and NaBH$_4$ catalyzed by NixB and Al(OH)$_3$. Their hydrolysis mechanism can be depicted in the followed reactions [1-4]. The catalyst comes from the reaction [5].

$$2Al + 2NaOH + 6H_2O \rightarrow 2NaAl(OH)_4 + 3H_2 \quad (1)$$

$$NaAl(OH)_4 \leftrightarrow NaOH + Al(OH)_3 \quad (2)$$

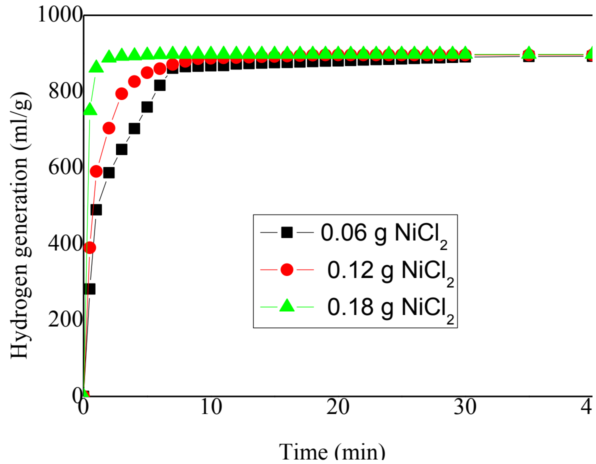

Figure 5. Hydrogen generation curves of Al/$NaBH_4$ system with different $NiCl_2$ amounts.

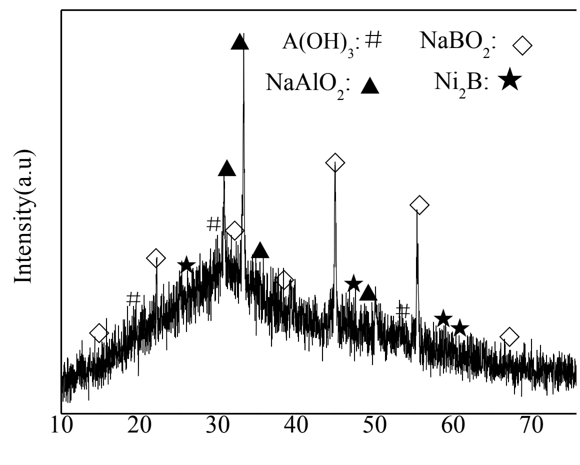

Figure 6. XRD patterns of hydrolysis byproducts of Al/$NiCl_2$ powder and $NaBH_4$ alkaline solution.

$$2Al + 6H_2O \xrightarrow{Al(OH)_3+NixB} 3H_2 + 2Al(OH)_3 \quad (3)$$

$$NaBH_4 + H_2O \rightarrow NaBO_2 + 4H_2 \quad (4)$$

$$NaBH_4 + xNiCl_2 + H_2O \rightarrow NaB_4O_7 + NixB + NaCl + H_2 \quad (5)$$

There also exists the electrochemical corrosion of Al. The electrochemical corrosion can be elaborated in reactions [6-8].

$$\text{Anodereaction}: \ 2Al + 6OH^- - 6e \rightarrow 2Al(OH)_3 \quad (6)$$

$$\text{Cathode reaction}: 6H_2O\,(NixB) + 6e \rightarrow 3H_2 + 6OH^- \quad (7)$$

$$\text{Total reaction}: \ 2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \quad (8)$$

The hydrolysis byproducts can be identified in Fig. 6, where the peaks of $Al(OH)_3$, $NaBO_2$, $NaAlO_2$, etc, are found. There existed polymeric aluminate ions in hydrolysis byproduct solution, including a lot of aluminate–hydroxide and aluminate–aluminate associates, which could form nuclei in further polymerization for the partial precipitation of $Al(OH)_3$ [16]. The form of anionic hydrogen bonded complexes could be stabilized by alkaline concentration, which could be strengthened by $NaBH_4$ hydrolysis as the hydrolysis byproduct $NaBO_2$ presents alkaline. On the contrary, polymeric aluminate ions covered on NixB surface and forms high activated catalyst, which improves the hydrolysis kinetic of $NaBH_4$.

4. CONCLUSION

The hydrogen generation characteristics of Al/$NiCl_2$ powder and $NaBH_4$ alkaline solution were evaluated. High hydrogen generation amount and rate of Al/$NaBH_4$ system have revealed a promising system to supply hydrogen for fuel cell. This process could increase hydrogen storage density and reduce production costs compared to processes based on hydrolysis of chemical hydrides as raw materials for hydrogen generation. The optimized composite including 0.2 g Al, 0.06 g $NiCl_2$ and 4 ml $NaBH_4$(15 wt%)-NaOH (5 wt%) solution can produce 1976 ml/g hydrogen at 30 ^{0}C, with 100% efficiency. It has been shown that the hydrogen generation performance can be regulated with the variations of the experimental parameters such as $NaBH_4$ concentration, NaOH concentration, Al and $NiCl_2$ amount. A hydrolysis mechanism unifying the behavior of the interaction between Al/$NaBH_4$ activated by NaOH and $NiCl_2$ is proposed.

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