Journal of Power Sources 219 (2012) 16–21

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Effect of $Al(OH)_3$ on the hydrogen generation of aluminum–water system

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## HIGHLIGHTS

- ► Novel effect of $Al(OH)_3$ powders on $Al/H_2O$ system for hydrogen generation was demonstrated.
- ► Fine and poor crystalline $Al(OH)_3$ powder acts an effective additive to the $Al/H_2O$ system.
- ► A proposed reaction mechanism for the enhancement of hydrogen generation was given.
- ► The reaction is able to rapidly produce hydrogen in a speed of 70% yield within 30 min.

## ARTICLE INFO

*Article history:*
Received 10 May 2012
Received in revised form
14 June 2012
Accepted 16 June 2012
Available online 24 July 2012

*Keywords:*
Bayerite
Aluminum
Hydrogen generation
Water

## ABSTRACT

Many metal oxides effectively modify metallic aluminum (Al) powders to produce hydrogen in neutral water at room temperature. In this study, hydrogen is generated even more rapidly from the reacted solution when the by-product $Al(OH)_3$ (bayerite) is present. The influence of $Al(OH)_3$ on the hydrogen generation during the aluminum/water reaction is highly dependent on the surface area and the crystallinity of $Al(OH)_3$. High surface area and poor crystallinity of $Al(OH)_3$ render the system a rapid hydrogen generation rate. The self-catalytic phenomenon can be explained by the formation of AlO(OH) (boehmite) from the reaction of by-product β-$Al(OH)_3$ and the surface passive oxide layer $Al_2O_3$. Furthermore, by taking advantage of the exothermic heat from the Al/water reaction, hydrogen yield is able to reach 70% within 30 min in a common aqueous solution ($pH < 10$) containing fine $Al(OH)_3$. This hydrogen generation technology relies on common, nontoxic, noncorrosive additives and is therefore a very promising system for creating a use-on-demand hydrogen source.

## 1. Introduction

The corrosion of metal Al in aqueous alkaline solutions has long been known as a good way to generate hydrogen to produce clean fuel [1]. Recently, there has been increasing interest in the reaction of the Al/water system for generating hydrogen [2–13] using either Al–Ga alloys [2], Al–Ga–In alloys [3], KCl/NaCl [4,5] or metallic oxide modifiers such as γ-$Al_2O_3$ and calcined boehmite AlO(OH) [6–12]. We have reported that many metallic oxide–modified Al exhibited far better hydrogen generation than those of pristine Al in pure water at room temperature [13]. The key issue in the $Al/H_2O$ reaction is breaking the surface's $Al_2O_3$ passive layer. Oxide modifiers or catalysts mixed with Al powders are an excellent way to produce hydrogen in neutral water at room temperature [6–13]. However, the size of the metallic Al particles, the choice of modifier materials, the size of the modifier particles, the mixing duration, the reaction temperature, and the purity of water all influence the corrosion of metal Al in water and therefore influence hydrogen production. The optimal conditions for generating an adequate amount of hydrogen to meet the use-on-demand system is still challenging for the $Al/H_2O$ system using oxide modifiers.

One gram of Al will produce 1.36 l of $H_2$ when completely reacted with water in ambient conditions. However, the direct reaction of metallic Al with pure water is difficult due to the surface's passive $Al_2O_3$ layer. Grinding can remove the oxide layer and expose a fresh surface of aluminum metal. Hydrogen will then be generated according to reaction (1):

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \qquad (1)$$

However, the surface will be passivated quickly by the increasing $Al(OH)_3$ (bayerite) layer.

Reaction (1) generates hydrogen easily under ambient conditions when modifiers are used; however, this reaction takes many hours to reach 100% yield [7–13]. Deng et al. [7–10] confirmed the role of the catalyst/modifier γ-$Al_2O_3$ in enhancing the hydrogen

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http://dx.doi.org/10.1016/j.jpowsour.2012.06.077

production rate and the effect of elevated temperatures. The mechanism by which $\gamma$-$Al_2O_3$–modified Al powders produce hydrogen when reacted with water can be explained by the uniform corrosion model [8,14]. Using modifiers such as $\gamma$-$Al_2O_3$ [7–10] or $TiO_2$ [13] causes the dense passive alumina layer to transform into boehmite (AlO(OH)) according to the following reaction:

$$Al_2O_3 + H_2O \rightarrow 2AlO(OH) \qquad (2)$$

Furthermore, the boehmite will then react with metal Al to generate hydrogen:

$$2Al + 6AlO(OH) \rightarrow 4Al_2O_3 + 3H_2 \qquad (3)$$

In fact, the combination of reaction (2) × 4 and reaction (3) results in reaction (4), which is thermodynamically unfavorable at room temperature but is favorable between 277 °C and 477 °C [15].

$$2Al + 4H_2O \rightarrow 2AlO(OH) + 3H_2 \qquad (4)$$

In a recent finding [16], sodium stannate–doped sodium hydroxide solution effectively promoted hydrogen generation from the $Al/H_2O$ system by weakening the oxide layer using sodium hydroxide and oxidizing Al by reducing the $Sn(OH)_6{}^{-2}$ ions. However, the continuous and subsequent hydrogen generation reactions require more sodium stannate, and the accumulation of Sn metal waste could also interfere with the practical application of this system. A fascinating report by Rosenband [17] showed that 6-μm-sized Al in water could yield 100% hydrogen in less than 5 min by their in-house activated treatment on Al powders using a lithium-based thermo-chemical process. Sodium aluminate ($NaAlO_2$) was also demonstrated an excellent alternative way other than NaOH to produce hydrogen in short time [18]. Especially, when 0.01 M $NaAlO_2$ combined and 20 g $dm^{-3}$ $Al(OH)_3$ suspension, the system reached a maximum rate of 221 $cm^3$ $min^{-1}$ and 100% yield at pH ca. 12.1 in 77 min [19]. Thus, a use-on-demand hydrogen source that uses the Al/water system could be realized in near future. However, these systems relied on high pH solution ($pH > 12$) which might also be corrosive to the environment. Since the dissociation of $NaAlO_2$ in water can lead to the formation of $Na^+$, $OH^-$ and AlO(OH) species, the generation of hydrogen is likely due to the high pH value. The role of AlO(OH) in this case has been overlooked. It is challenging to produce hydrogen rapidly from Al/water system without the use of high pH alkaline solution.

In this study, we started from a $TiO_2$–modified Al powders which produced hydrogen in water easily [13]. The system can continuously generate hydrogen in a neutral water system at room temperature by just adding additional batches of Al, i.e., it self-catalytically generates hydrogen at an increasingly rapid rate without requiring the high pH alkaline solution, thereby reducing the cost of producing hydrogen as well as the corrosive problem to the environment. The key to this issue is the reaction kinetics of $Al(OH)_3$.

## 2. Experimental procedures

Deionized (DI) water ($pH = \sim 7.0$, resistivity > 18 MΩ cm) and tap water (pH = 6.3–7.5, resistivity < 4.5 kΩ cm) were used throughout this study. Metallic Al powders with a particle size of 45 μm (Alfa Aesar, 325 mesh, 99.5% purity) were used for all of the experiments. Metallic Al powder (1 g) was hand-mixed with 1 g modifier $TiO_2$ nanocrystals (P90, Degussa, 22 nm) or reagent $TiO_2$ powders (Shimakyu's Pure Chemicals, 99%, 375 ± 75 μm) for 3 min to create the starting materials. The reagent $TiO_2$–modified Al powders were added to 200 ml of deionized water and sealed in a conical flask. After the completion of this initial reaction, the 1st batch of unmodified Al (1 g) powders and later batches (also pristine Al powders) were added consecutively to the same flask after the completion of the previous reaction, which allowed the accumulation of the by-product $Al(OH_3)$ from previous reactions, thereby increasing its overall concentration in the flask. All of the experiments were carried out at 25 °C ± 1 °C using circulating water bath. No magnetic stirring was employed within the reaction flask. The hydrogen generated was measured using a silicone tube passing through a water bath at room temperature to a precision gas flow meter (Alicat Scientific, Inc.) that automatically recorded the output data in a notebook computer every second until the reaction reached 100% yield (hydrogen) (1360 ml $g^{-1}$ Al). The cooling water bath is used to minimize the water vapor. Similar experiments were also carried out for the P90–modified Al system in tap water.

Two commercial reagent $Al(OH)_3$ powders (Acros, USA, 5 μm, 99% purity, and NanoAmor, USA, 0.5 μm, 98% purity) were also used to compare their effects on the reaction of the $Al/H_2O$ system. The size effect of $Al(OH)_3$ was tested as follows. First, two self-made $Al(OH)_3$ powders were obtained from as-received 5-μm $Al(OH)_3$ commercial powders. That is, the Acros 5-μm $Al(OH)_3$ powders (2.88 g) and deionized water (200 ml) were mixed and stirred for 24 h. The solution was divided into the "top" 100 ml and "bottom" 100 ml immediately after the stirring process. Both solutions were dried, and the powders obtained (0.13 g) were employed to test their effect on hydrogen generation. These four dried powders (i.e., 5 μm, "top", "bottom", and 0.5 μm) were hand-mixed with Al (1 g) and added to 50 ml deionized water to measure their ability to generate hydrogen. The "top" $Al(OH)_3$ powder is smaller than that of "bottom" one after 24 h stirring, as seen in the FESEM images in Section 3.2. The BET surface area analysis for the "Acros" 5-μm, "top", "bottom", and the "NanoAmor" 0.5-μm, $Al(OH)_3$ powders were 0.32 $m^2\,g^{-1}$, 6.65 $m^2\,g^{-1}$, 1.83 $m^2\,g^{-1}$, and 6.25 $m^2\,g^{-1}$, respectively. The 5-μm $Al(OH)_3$ powders clearly broke down and their surface area increased after stirring for 24 h. The hydrogen generation results will be detailed in Section 3.2.

For the experiments of different Al/water weight ratios on the hydrogen generation rate without temperature control, 3 g of metal Al powders were added into a reduced amount of water to evaluate the effect of the heat from the in-situ exothermic reaction on hydrogen generation. The weight ratio of Al to deionized water was varied between 1:5, 1:10, 1:20, and 1:30 (i.e., 3 g Al in 15 ml, 30 ml, 60 ml and 90 ml of water), where 20 g $Al(OH)_3$ (NanoAmor, USA, 0.5 μm, 98% purity) was first added right before the addition of the Al powders. All of the experiments were carried out at room temperature (25 °C ± 1 °C) using circulating water bath. The water displacement method was used to measure hydrogen generation using two 2000-ml cylinder meters (reading data error of less than 20 ml) because of the speed of the hydrogen generation. After reacting with water, the product powders were characterized with an analytical PW3040/60 X'Pert Pro X-ray diffractometer using Cu K$\alpha$ radiation and a Ni filter over the angular range of 10°–80° ($2\theta$) at a scanning rate of 4° $min^{-1}$ and a step size of 0.01°. Field-emission scanning electron microscopy (FESEM, JEOL JSM 7600F) was employed to characterize the morphology of the powders. The surface areas of all $Al(OH)_3$ powders were measured using nitrogen adsorption–desorption isotherms on an ASAP 2020 (Micromeritics Instruments, USA) apparatus. All of the samples were degassed at 120 °C prior to the Brunauer–Emmett–Teller (BET) measurements.

## 3. Results and discussion

### 3.1. Enhanced hydrogen generation from the addition of consecutive Al batches

Fig. 1 shows the amount of hydrogen generation from the reaction of $TiO_2$ (reagent)–modified Al powders and deionized

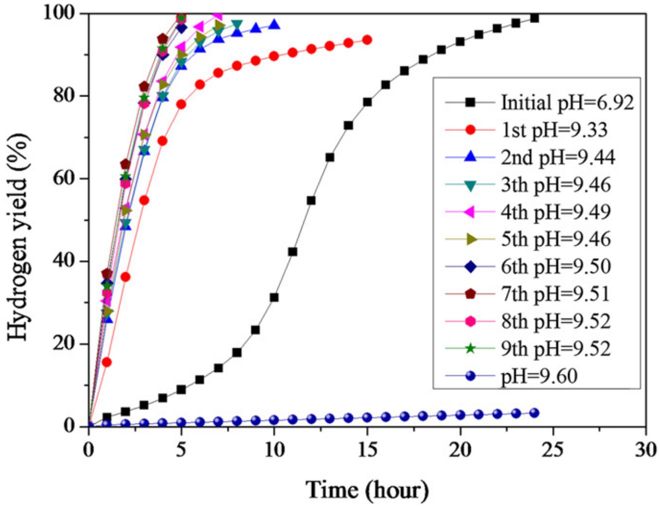

**Fig. 1.** $TiO_2$ (reagent)–modified Al (1 g, initial) and consecutive batches of Al (1 g, 1st and after) in deionized water at room temperature. The batch "pH = 9.60" was carried out for comparison purpose only, which is simply a basic solution.

water (200 ml) at 25 °C ± 1 °C (Al:$H_2O$ = 1:200). The initial batch of modified Al (1 g) powder corroded away 50% approximately 12 h after adding it to the deionized water. For the 1st batch of unmodified Al powder (1 g), the 50% yield of hydrogen occurred at approximately 3 h. For the 2nd and 3rd batches of pristine Al powders, the 50% yield of hydrogen occurred at approximately 2 h and reacted increasingly faster than those of the initial and 1st batch. The 4th, 5th, and 6th batches of unmodified Al powders yielded 50% hydrogen at 2 h, 1.5 h, and 1.5 h, respectively. The 7th, 8th and 9th batches of unmodified Al powders had almost identical generation curves over time and yielded 50% hydrogen in less than 1.5 h. Thus, hydrogen generation was accelerated as the consecutive batches of unmodified Al powders were added to the solution and the by-product $Al(OH)_3$ accumulated. The hydrogen generation rate reached a maximum after the 7th consecutive batch, resulting in 8.5 ml $min^{-1}$ $g^{-1}$ Al calculated from the 50% yield.

Fig. 1 also shows the increasing pH values during hydrogen generation from the reaction of reagent $TiO_2$–modified Al powders and the subsequent unmodified Al batches in deionized water. The pH values for the solution after the termination of reaction were recorded for each Al batch. The pH value increased slightly from the initial pH of 6.92 to 9.52. The slight increase of the pH value was considered to be due to the limited dissociation of the by-product $Al(OH)_3$ in water. However, the pH value ultimately reaches equilibrium, and the generation rate of hydrogen no longer increases. To elucidate the effect of the pH value alone on the Al/$H_2O$ reaction, a clear deionized water (200 ml) at pH 9.60 was prepared using NaOH (Sigma–Aldrich). However, this high pH did not assist hydrogen generation (see curve "pH = 9.60" in Fig. 1).

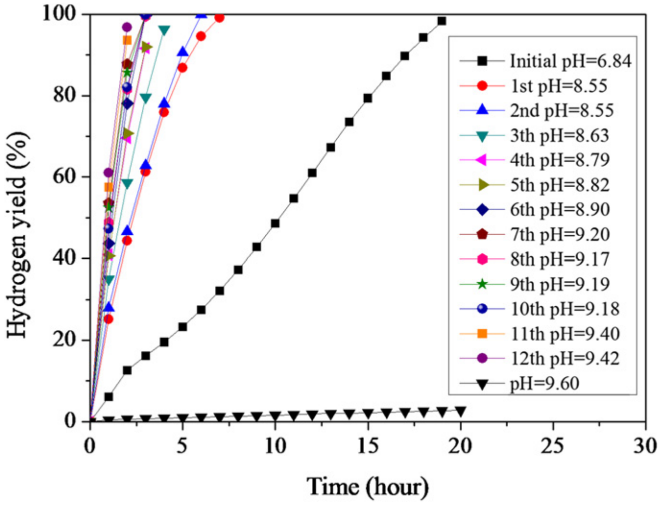

**Fig. 2.** $TiO_2$ (P90)–modified Al (1 g, initial) and consecutive batches of pristine Al (1 g, 1st and after) in tap water at room temperature. The batch "pH = 9.60" was carried out for comparison purpose only, which is purely aqueous alkaline solution.

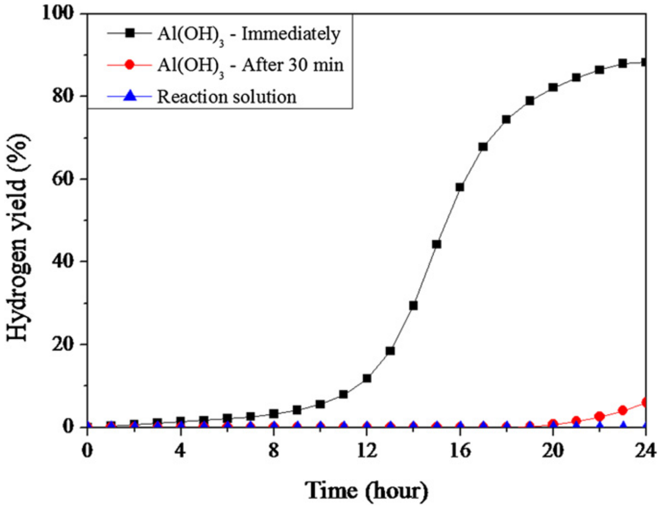

**Fig. 3.** Effect of filtered reaction solution and two different $Al(OH)_3$ powders on the hydrogen generation of Al/$H_2O$ system.

Fig. 2 shows that the reaction of $TiO_2$ (P90)–modified Al powders in neutral tap water (200 ml) at 25 °C ± 1 °C (Al:$H_2O$ = 1:200) generates hydrogen in a manner similar to the systems in Fig. 1. The initial modified batch of Al (1 g) powder had corroded 50% approximately 10 h after adding it to the tap water. However, for the 1st batch of unmodified Al powder, the 50% yield of hydrogen occurred at approximately 2.5 h, which was the same for the 2nd batch; both were much faster than that of the initial batch. The 3rd, 4th, 5th and 6th batches of unmodified Al powders yielded 50% hydrogen at 1.5 h, 1 h, 1 h and 1 h, respectively. The generation curves over time were almost identical for the 7th–12th batches of unmodified Al powders, resulting in 50% yield in less

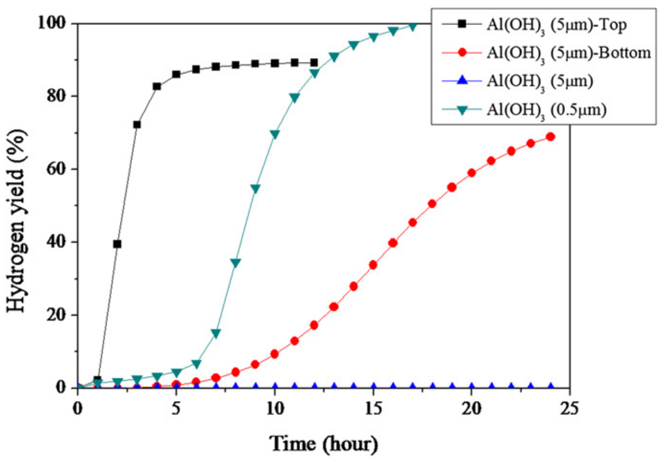

**Fig. 4.** Effect of different sized commercial $Al(OH)_3$ powders on the hydrogen generation on Al/$H_2O$ system.

than 1 h. Thus, hydrogen generation was accelerated as the consecutive batches of unmodified Al powders were added to the solution, and the rate reached its maximum ~12.3 ml $\text{min}^{-1}$ $\text{g}^{-1}$ Al calculated from 50% yield of hydrogen for the 7th–12th batches.

Fig. 2 also shows the pH changes during the hydrogen generation from the reaction of $TiO_2$ (P90)–modified Al powders and the subsequent batches of unmodified Al powders in neutral tap water. The pH values of the solutions after the termination of reaction were recorded for each Al batch. The pH value increased slightly from its initial pH of 6.84 to 9.42. Again, the slight increase of pH value was considered to be due to the limited dissociation of the by-product $Al(OH)_3$ in water. However, the pH value ultimately reaches equilibrium, and the generation rate of hydrogen no longer increases. Clear tap water with pH at 9.60 was also prepared using NaOH (Sigma–Aldrich) to determine the effect of pH value alone on the reaction. However, pH at 9.60 does not assist the hydrogen generation, as shown by the curve "pH = 9.60" in Fig. 2.

From literature [1,6], to assist hydrogen generation from $Al/H_2O$ reaction, alkaline solution at pH greater than 11 is desired. pH lower than 10 shows little effect on hydrogen generation as the curve "pH = 9.60" shown above. Obviously, the by-product $Al(OH)_3$ plays an important role on the consecutive runs of corrosion reactions. However, the effect of $Al(OH)_3$ on the reaction of Al/water for the enhanced hydrogen generation is clearly not due to the increased pH of the solution; the alternative factors affecting hydrogen production deserved further studies. Although the initial batch of Al was modified by $TiO_2$, the later experiments show that $TiO_2$ is not the major contributor to the consecutive enhanced hydrogen generation. More $TiO_2$ actually deteriorates the hydrogen generation rate of the later consecutive reactions. In fact, the initial batch of Al could be modified by using commercial $Al(OH)_3$ powders and the results as Figs. 1 and 2 are still valid.

### 3.2. *The role of $Al(OH)_3$ in the solution for the subsequent batches*

Two $Al(OH)_3$ aqueous solutions were prepared by adding the commercial as-received $Al(OH)_3$ powders (Acros, 5 μm, 2.88 g, gibbsite phase) into a 200 ml deionized water and stirred for 1 h to

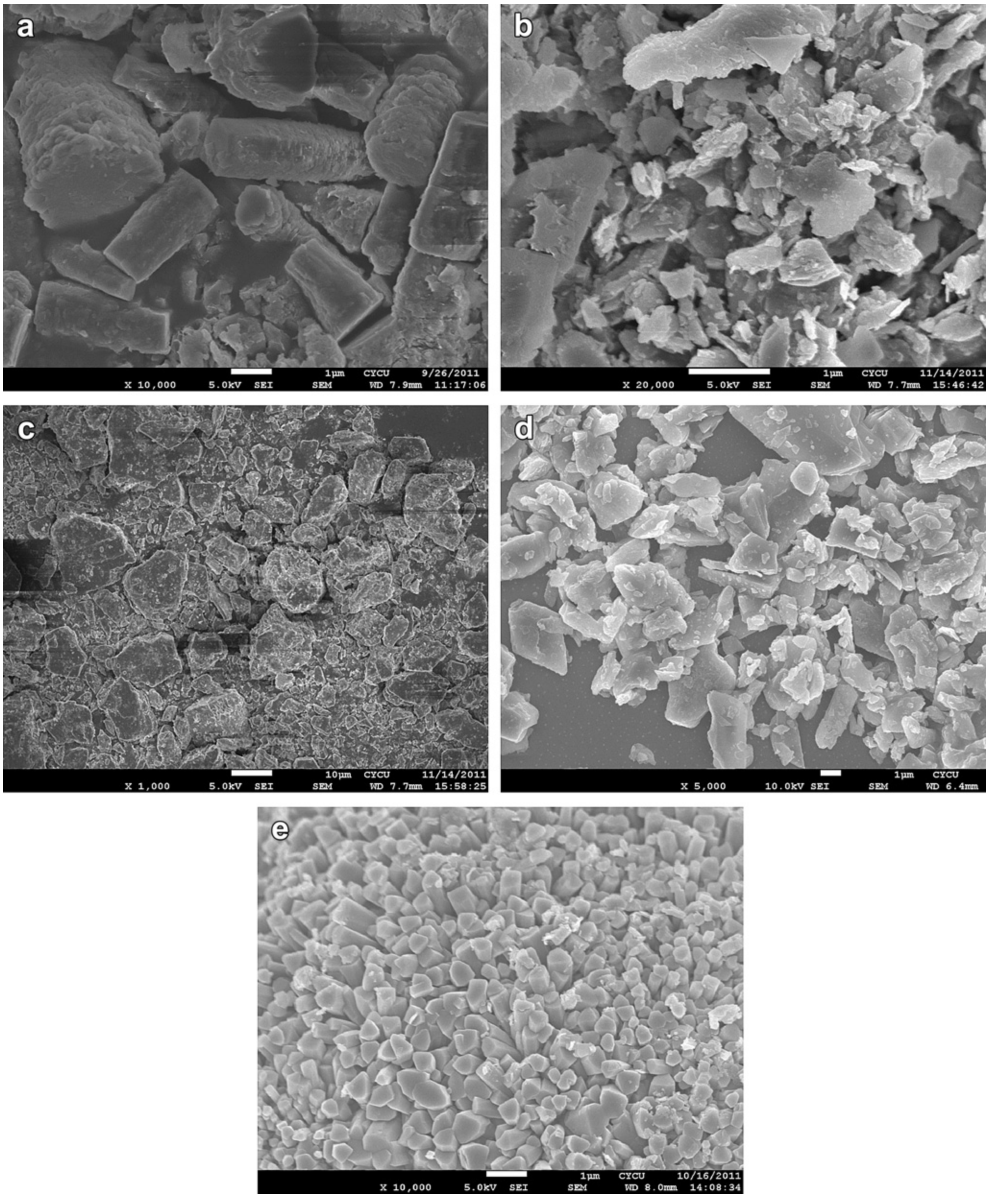

**Fig. 5.** FESEM for $Al(OH)_3$ powders, (a) commercial as-received 5 μm, (b) top from stirred 5 μm for 24 h, (c) bottom from stirred 5 μm for 24 h, (d) commercial as-received 0.5 μm, and (e) rod-like $Al(OH)_3$ powders on Al surface after reaction.

evaluate the role of $Al(OH)_3$ on the hydrogen generation. The upper 100 ml aqueous solution of the stirred $Al(OH)_3$ solution was taken immediately and 30 min after settlement using pipet. Fig. 3 shows the distinct differences in these two $Al(OH)_3$ solutions on the hydrogen generation from the reaction of unmodified Al (1 g) and the solution. The $Al(OH)_3$ aqueous solution taken after 30 min settlement did not show significant hydrogen generation even after 20 h reaction time. The curve "reaction solution" in Fig. 3 shows the hydrogen generation behavior from the reaction of 1 g pristine Al with a previously reacted solution (200 ml) that was filtered and had no visible $Al(OH)_3$ residuals. Neither the pH value (9.33) nor the ions in the solution assisted in generating hydrogen. Thus, the $Al(OH)_3$ residuals must help generate hydrogen. The solubility of $Al(OH)_3$ in the two solutions should be the same, and the clear solution without the solid $Al(OH)_3$ particles exerted little effect on the Al powders to generate hydrogen. Fig. 3 clearly shows the small white $Al(OH)_3$ particles exhibit significant effects on the Al surface and greatly enhance the hydrogen generation reaction.

Fig. 4 shows the effect of the two stirred $Al(OH)_3$ powders ("top" and "bottom", stirred for 24 h, see Section 2) and the two commercial as-received $Al(OH)_3$ powders on hydrogen generation. Clearly, the as-received 5-μm $Al(OH)_3$ powders exerted little effect on hydrogen generation from the Al/water system. However, when the 5-μm $Al(OH)_3$ powders were stirred in water and divided into "top" and "bottom" parts, "top" part exerted significant effects on the metal Al surface and improved the Al/water reaction. The "top" $Al(OH)_3$ powder is a breakdown species from as-received 5-μm. As stated in Section 2, Experimental procedure, that the surface area of "top" was much higher than that of "bottom" and original as-received 5-μm after 24 h stirring. Their images were shown in the following FESEM images, Fig. 5 and will be discussed shortly. The commercial as-received 0.5 μm $Al(OH)_3$ powders also showed a typical three-stage curve of hydrogen generation [11]. i.e. the "induction period", "fast reaction", and "slow reaction". The effect of as-received 0.5 μm $Al(OH)_3$ seems less effective than that of "top" sample, though their surface areas were similar, 6.25 $m^2\ g^{-1}$ vs. 6.65 $m^2\ g^{-1}$, respectively. The "induction period" of "top" sample in Fig. 3 was very short. Similarly, the "induction period" of consecutive batches in Figs. 1 and 2 were almost not present. There must be a good reason for this behavior that it happened right away when pristine Al contacted $Al(OH)_3$ aqueous solution.

Fig. 5 (a)–(e) shows all of the $Al(OH)_3$ powders obtained in this study. Fig. 5 (a), (b) and (c) shows the FESEM images for the as-received 5-μm $Al(OH)_3$ powders, and their "top" and "bottom" counterparts. The powder from the "top" of the solution is much smaller than that from the "bottom", which consisted of very large particles. Fig. 5 (d) and (e) shows the as-received 0.5-μm $Al(OH)_3$ powders and the fine, rod-like $Al(OH)_3$ product on the surface of the Al powder after reaction, respectively. These images are consisted with those of gibbsite and bayerite reported in the literature [20]. XRD was performed to evaluate the differences in crystallinity of these powders. Fig. 6 (a)–(f) shows the crystalline phase of commercial as-received $Al(OH)_3$ powders and the by-product from Al/water reaction. It turned out that the by-product from Al/water reaction was β-$Al(OH)_3$, bayerite and the commercial as-received $Al(OH)_3$ powders were all $\alpha$ phase, gibbsite. As shown in Fig. 6, the 5-μm $Al(OH)_3$ powders and "bottom" powders exhibited strong crystallinity. The "top", 0.5-μm $Al(OH)_3$ and β-$Al(OH)_3$ from Al/water reaction exhibited relatively poor crystallinity. After stirring for 24 h, the smaller-sized particles in the 5-μm $Al(OH)_3$ powders settled down more slowly that the larger ones. Fig. 4 demonstrated that the smaller-sized $Al(OH)_3$ powder with higher surface area (as the "top" sample shown) was important for enhancing the hydrogen generation of the Al/water system. Figs. 1 and 2 showed that the by-product β-$Al(OH)_3$ from the $Al/H_2O$ reaction effectively promotes hydrogen generation. The BET surface area of the by-product β-$Al(OH)_3$ from the Al/water reaction was measured to 29.92 $m^2\ g^{-1}$. The summary data of all $Al(OH)_3$ powders used in this study is shown in Table 1. From these results, it is clear that the solid $Al(OH)_3$ material with poor crystallinity as well as large surface area are important for catalyzing the reaction rate of Al/water system.

### 3.3. *Catalytic mechanism of $Al(OH)_3$*

The key to improving the rate of hydrogen generation is disrupting the protective passive $Al_2O_3$ layer on the surface of metal Al powder, whether that happens through a phase change or whether it is broken by the modifiers. The uniform corrosion mechanism states that the entire native oxide film is hydrated at room temperature in the initial stage [8,14] when modifiers are added, according to reaction (2). AlO(OH) (boehmite) greatly facilitates the production of hydrogen in the $Al/H_2O$ system at room temperature, while the 5-μm $Al(OH)_3$ did not [13]. Once the AlO(OH) (boehmite) was formed, the front of it reacted with the Al to produce $Al_2O_3$ and hydrogen in the contact area (reaction (3)). Reactions (2) and (3) continued until all of the Al metal was completely consumed, as long as the boehmite was still being produced from reaction (2).

The above reactions occurred when the initial 1 g of modified Al was added to water. However, when the 1st 1 g of unmodified Al was put in the same flask after the completion of the initial batch, the hydrogen generation was greatly enhanced due to the fine by-product β-$Al(OH)_3$, as shown in Figs. 1 and 2. The hydrogen generation reaction is increasingly rapid as the later batches of Al are added to the same flask. This result contradicts the report by Soler et al. [19], where the consecutive experiments performed after the first run showed lower rates. They claimed that the slower hydrogen production rates of the later runs were smaller because of the slower diffusion of species in a more viscous media due to the accumulated $Al(OH)_3$ mud in the 75 ml solution. We thought that the contradiction may come from the water quantity (200 ml) used in our study, where rapid diffusion was possible.

We propose a mechanism for these rapid hydrogen generations as shown in the following reaction (5):

$$Al_2O_3 + Al(OH)_3 \rightarrow 3AlO(OH) \quad \Delta G = -39.4\ \text{kJ mol}^{-1} \tag{5}$$

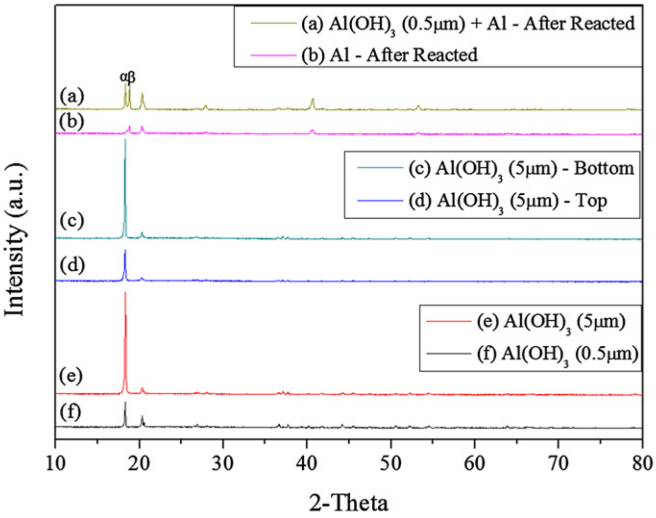

**Fig. 6.** XRD for (a) by-product of Al/water after reaction using as-received 0.5 μm $Al(OH)_3$, (b) by-product of Al/water after reaction, (c) the filtrated residuals from "bottom" sample, (d) the filtrated residuals from "top" sample, (e) as-received 5 μm $Al(OH)_3$, and (f) as-received 0.5 μm $Al(OH)_3$.

**Table 1**
Summary of $Al(OH)_3$ powders used in this study.

| ID | Commercial as-received 5 μm (Acros) | "Top" of 5 μm (Acros) | "Bottom" of 5 μm (Acros) | Commercial as-received 0.5 μm (NanoAmor) | By-product after Al/water reaction |
|---|---|---|---|---|---|
| Surface area ($m^2\ g^{-1}$) | 0.32 | 6.65 | 1.83 | 6.25 | 29.92 |
| Crystalline phase | Gibbsite | Gibbsite | Gibbsite | Gibbsite | Bayerite |
| Assigned name | $\alpha$-$Al(OH)_3$ | $\alpha$-$Al(OH)_3$ | $\alpha$-$Al(OH)_3$ | $\alpha$-$Al(OH)_3$ | $\beta$-$Al(OH)_3$ |
| Crystallinity | Very strong | Poor | Very strong | Poor | Very poor |

The free energy change was calculated based on the data of γ-alumina, bayerite, and boehmite from Ref. [21]. When the fine β-$Al(OH)_3$ powders in water contact the $Al_2O_3$ surface layer of metallic Al, these two reactants form AlO(OH) according to reaction (5), where β-$Al(OH)_3$ may simply lose its $OH^-$ and $H^+$ and become one AlO(OH). The species of $OH^-$ and $H^+$ were highly mobile and migrated into the $Al_2O_3$ layer and formed the other two AlO(OH), whose reaction formula could also be described in reaction (2). It is also possible that the fine and poor crystalline $Al(OH)_3$ particles enhance the ionic migration of $H^+$ ions from the bulk $H_2O$ to the Al surface. It's known from Bunker's report [14] that the hydroxide ions (or water molecules) are the mobile species in the films (rather than $H^+$, $O^{2-}$, or $Al^{3+}$) and that transport rates are sufficiently rapid to account for the kinetics of Al corrosion and pitting processes. Coarse $Al(OH)_3$ exhibited little effect on the hydrogen production due to its low reactivity. The coarse crystalline $Al(OH)_3$ particles require at least 1 h to be broken down in the water and become effective for generating hydrogen from the Al/water system. The by-product β-$Al(OH)_3$ from the reaction of Al/water is poorly crystalline and has a large surface area; thus, this by-product is quite effective for allowing reaction (5) to proceed. To compare the effect between gibbsite (α) and bayerite (β) is trivial, since their crystal structure differ only in the way that the double layers of coordinated $OH^-$ and $Al^{+3}$ are stacked to form the three-dimensional crystal units [20]. It is the surface area of $Al(OH)_3$ that highly dominates the hydrogen generation of Al/water system. By utilizing the in-situ self-heating exothermic reaction with a large quantity of initial Al powder and a minimum water content (3 g Al:15 g $H_2O$) containing fine β-$Al(OH)_3$, we are able to produce more than 70% yield hydrogen within 30 min without using alkaline solution (pH $<$ 10). The setup is able to produce hydrogen rapidly and yet no corrosive problem to the environment, making it an ideal candidate of hydrogen source for a use-on-demand system.

## 4. Conclusions

We have demonstrated the novel effect of $Al(OH)_3$ powders on the $Al/H_2O$ system for generating hydrogen. Fine, poorly crystalline $Al(OH)_3$ powder is an effective additive to the $Al/H_2O$ system. We also proposed a reaction mechanism to explain the enhancement of hydrogen generation in this system. By using high surface area, poor crystalline $Al(OH)_3$ powders in aqueous solution, $Al_2O_3$ surface layer of metallic Al powders are readily reacted, making rapid hydrogen generation possible without using highly corrosive alkaline solution. Further promotion of hydrogen generation rate could be achieved by taking advantage of its in-situ exothermic reaction as well as special designed $Al(OH)_3$ powders having high surface area.

## Acknowledgments

This work was supported financially by the National Science Council (NSC99-2113-M-033-003-MY3) and the CYCU Distinctive Research Area project (grant CYCU-98-CR-CH).

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