# Al Surface Modification by a Facile Route

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A facile route was used to modify Al particle surfaces by putting Al particles into an Al(OH)<sub>3</sub> suspension, which was produced by the reaction of Al powder with water under vacuum at a mild temperature, then drying and heat-treating under vacuum at elevated temperature. The modified Al powder has a good reaction activity with water to generate hydrogen, and its reaction rate depends on the sizes of Al particles used to produce Al(OH)<sub>3</sub> suspension. The reaction induction time of the modified Al powder prepared using the Al(OH)<sub>3</sub> suspension produced by the reaction of Al with water is obviously shorter than that prepared using the Al(OH)<sub>3</sub> suspension formed by the direct addition of a commercial Al(OH)<sub>3</sub> powder, because the in situ formed Al(OH)<sub>3</sub> has a finer microstructure. As the present method has no complicated processing procedure and the Al-water reaction byproduct can be reused to modify Al, it is an economically viable way to fabricate the activated Al powder for commercial applications.

# I. Introduction

H YDROGEN is an ideal fuel due to its high calorific value and environmentally benign oxidation products, but the hydrogen storage and distribution are still a problem. Therefore, hydrogen-storage materials and hydrogen-generation materials have received much attention. Metal Al is an ideal *in situ* hydrogen-generation material for portable and kW-grade fuel cells due to its high electron density and relative low cost,<sup>1,2</sup> 1 kg Al reacts with water to generate as much as 0.11 kg H<sub>2</sub>. However, a compact and strongly adhesive passive film is developed on Al surfaces upon their exposure to atmosphere or aqueous solutions, inhibiting the direct reaction of Al with water.

In the past few years, different methods, based on the disruption of the passive oxide film on Al particles, have been proposed for hydrogen generation using Al with water, for example, Al reacts in an alkaline solution,<sup>3,4</sup> alloying Al by doping Ga, In, Bi, Sn, etc.,<sup>5–9</sup> mechanically milling metal Al with selected oxides, <sup>10–13</sup> and Al surface modification, <sup>14–17</sup> etc. Among the above Al-activated methods, Al surface modification is a relatively cheap and viable method for practical application from the viewpoint of environmental concerns and commercial cost, because the adopted modification agents, oxides, are cheap and the reaction solutions are chemically neutral.<sup>1</sup> However, the complicated ceramic processing procedure (e.g., ball-milling and cold pressing)<sup>16,17</sup> for fabricating the modified Al powder is a barrier for its large-scale production.

In this work, a new wet chemical method was used to modify Al particle surfaces. In this method, Al powder is put into an  $Al(OH)_3$  suspension, which is preliminarily produced

by the reaction of Al powder with water under vacuum at a mild temperature. The suspension with the Al powder is filtered, dried, and heat-treated under vacuum at elevated temperature, to finally produce the modified Al powder. In an industrial cycle, the above  $Al(OH)_3$  suspension could be the byproduct of hydrogen generation by the reaction of a modified Al powder with water. As the present method is simple and streamlined, it provides a viable way for the large-scale production of modified Al powders in commercial applications.

# **II. Experimental Procedure**

Four kinds of Al powders with the average sizes of 72.94 nm (Shanghai St-nano Science and Technology Co., Shanghai, China), 2.25 µm (99.9% purity; Henan Yuan Yang Aluminum Industry Co., Changheng, China), 7.29, 24.94 µm (99.9% purity; High Purity Chemical Co., Tokyo, Japan), and Al(OH)<sub>3</sub> (99.99% purity, 2.5 µm; High Purity Chemical Co.) were used in the present work. Two different ways were adopted to prepare Al(OH)<sub>3</sub> suspensions. One way is to use the reaction of Al powder with water at 40°C under an initial pressure of 0.04 bar,<sup>15</sup> where 0.6 g of pure Al powder was added into a closed glass reactor with 250 mL of deionized water and stirred so that metal Al could completely react with water and become Al(OH)<sub>3</sub> suspension. Another way is the direct addition of commercial Al(OH)<sub>3</sub> powder into deionized water to form Al(OH)<sub>3</sub> suspension. The concentration of  $Al(OH)_3$  in the suspensions prepared by the above two ways is almost the same.

A suitable amount of 7.29 µm Al powder was added into the above Al(OH)<sub>3</sub> suspensions, then ultrasonically dispersed for 2 min and filtered by a filter paper. The obtained wet mixtures of Al + Al(OH)<sub>3</sub> were dried at 60°C for 20 min, then heated at a rate of 1°C/min, and held at a temperature of 400°C under vacuum (<10<sup>-4</sup> bar) for 1 h. The mixtures became  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified Al powders (GMAPs). The as-received GMAPs were sieved using a 100-mesh nylon sieve before the experimental tests. All the GMAPs in this research have the same composition of 67 vol% Al + 33 vol%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (this composition is similar to that in some Al/A<sub>2</sub>O<sub>3</sub> composites).<sup>18,19</sup>

The hydrogen-generation experiment of GMAPs with water was carried out in a closed glass reactor with a volume of ~560 mL, which is airtight and could keep a constant gas pressure for more than 1 week.<sup>16</sup> The reaction temperature was controlled by a thermostat water bath with an accuracy of  $\pm 1^{\circ}$ C. 0.2 g of GMAP was suspended in 250 mL of deionized water in each test. A magnetic agitation bar with a speed of ~500 rpm was used to stir the mixture of water and GMAP. At the beginning, the reactor was evacuated to a low vacuum of 0.04 bar. As the reaction of Al with water produces only one kind of gas, that is, H<sub>2</sub>,<sup>1</sup> the hydrogen evolution could be determined by the gas pressure in the reactor, which was measured by a manometer with an accuracy of 0.2 kPa (Type: LEO 2, Keller Co., Winterthur, Switzerland). The measurement uncertainty of the system is <0.5%.

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According to the ideal-gas equation, hydrogen yield  $\boldsymbol{\alpha}$  can be written

$$\alpha = \frac{(P - P_{\text{initial}})(V_{\text{reactor}} - V_{\text{H}_2\text{O}} - V_{\text{Al}})}{n_0 \text{RT}}$$
(1)

where *P* is the total gas pressure in the reactor;  $P_{\text{initial}}$  is the initial gas pressure in the reactor, which was measured before the hydrogen-generation test;  $V_{\text{reactor}}$ ,  $V_{\text{H}_2\text{O}}$ , and  $V_{\text{Al}}$  are the volumes of the reactor, water, and Al powder, respectively;  $n_0$  is the theoretical hydrogen moles obtained by reacting all of the metal Al in GMAP; *R* is the gas constant and *T* is the reaction temperature. Moreover, at least two identical tests were carried out to check the reproducibility of each hydrogen-generation curve.

An X-ray diffractometry (XRD; Model No. D/max-2200, Rigaku Co., Tokyo, Japan) was used to analyze the phases in GMAPs and those after reaction with water. Scanning electron microscopy (SEM) was used to observe the morphologies of GMAPs.

# III. Results and Discussion

Figure 1 shows the morphologies of the GMAPs prepared using the Al(OH)<sub>3</sub> suspensions produced by the reaction of different size Al powders with water and the direct addition of pure Al(OH)<sub>3</sub> powder. It can be seen that after modification, there are some  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains covering Al particles. This coating was produced by the decomposition of Al (OH)<sub>3</sub> phases during the heat treatment.<sup>14</sup> However, the coverage of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains on Al particles is different for different GMAPs. Fine  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains relatively uniformly cover on Al particle surfaces of the GMAPs prepared using the Al(OH)<sub>3</sub> suspensions produced by 72.94 nm and 2.25 µm Al powders [arrows in Figs. 1(a) and (b)], but part of Al particle surfaces of the GMAPs prepared using the Al(OH)<sub>3</sub> suspensions produced by 7.29 µm Al powder, 24.94 µm Al powder, and pure Al(OH)<sub>3</sub> powder are bare and not covered by  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains [arrows in Figs 1(c)–(e)]. It seems that the coverage uniformity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains on Al particle surfaces decreases with increasing size of Al particles used to prepare Al(OH)3 suspensions. Among five GMAPs in Fig. 1, the Al surface modification is the worst when the commercial  $Al(OH)_3$  powder was used to form the  $Al(OH)_3$  suspension.

Figure 2 shows the hydrogen evolution from deionized water using the above different GMAPs at 25°C. It can be seen that all the GMAPs could react with water and generate hydrogen. Conversely, the pure 7.29 µm Al powder could not react with water within 80 h under the above condition (the result is not shown in Fig. 2). However, the reaction induction time of GMAP and its total reaction time with water strongly depend on the raw materials used to prepare the Al(OH)<sub>3</sub> suspensions. Generally speaking, the reaction induction time of GMAP decreases with decreasing size of Al particles used to prepare the Al(OH)<sub>3</sub> suspensions, and the GMAP prepared by pure Al(OH)<sub>3</sub> powder has the longest induction time. At the same time, it is noted that there is almost no induction time for the GMAPs prepared using the Al(OH)<sub>3</sub> suspensions produced by 72.94 nm and 2.25 µm Al powders, and the difference in their reaction dynamics is small. This implies that when the sizes of Al particles used to prepare the Al(OH)<sub>3</sub> suspension are down to a specific value, the Al surface modification effect tends to reach saturation and stabilize. In this case, one can optimize Al surface modification by choosing a suitable sized Al powder to prepare Al (OH)<sub>3</sub> suspension.

Figure 3 shows the hydrogen evolution from deionized water using the GMAP prepared using the Al(OH)<sub>3</sub> suspension produced by 2.25 µm Al powder at three different temperatures. It can be seen that the hydrogen-generation rate of GMAP with water increases with increasing the reaction temperature. At 50°C, 85% of metal Al in GMAP was consumed within 3 h, implying that the hydrogen-generation rate of GMAP could satisfy the requirement of portable fuel cells. As the reaction of Al with water is exothermal and its reaction heat reaches as high as 426.5 kJ/mol,<sup>1</sup> the reaction of Al with water is self-heating, especially if the Al-to-H<sub>2</sub>O weight ratio varies from 1:5 to 1:10 in a practical application. In this case, the water temperature would increase with the reaction progress, leading to the increase in the hydrogengeneration rate of Al with water. In fact, the experiment of Jung et al.<sup>20</sup> indicated that the reaction temperature of Al with water could increase from room temperature to >80°C in a model device.



**Fig. 1.** SEM micrographs of the GMAPs prepared using the Al(OH)<sub>3</sub> suspensions produced by (a) 72.94 nm Al powder, (b) 2.25 μm Al powder, (c) 7.29 μm Al powder, (d) 24.94 μm Al powder, and (d) pure Al(OH)<sub>3</sub> powder, respectively.



**Fig. 2.**  $H_2$  evolution from deionized water using the GMAPs prepared using the Al(OH)<sub>3</sub> suspensions produced by 72.94 nm Al powder, 2.25 µm Al powder, 7.29 µm Al powder, 24.94 µm Al powder, and pure Al(OH)<sub>3</sub> powder, respectively, where the initial pressure is 0.04 bar and the reaction temperature is 25°C.



Fig. 3.  $H_2$  evolution from deionized water using the GMAP prepared using the Al(OH)<sub>3</sub> suspension produced by 2.25  $\mu$ m Al powder, where the initial pressure is 0.04 bar and three reaction temperatures of 25°C, 36°C, and 50°C are used.

Figure 4 shows the X-ray diffraction patterns of GMAPs and their products obtained after reaction with water. It can be seen that there is an  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase in the GMAP prepared using the Al(OH)<sub>3</sub> suspension produced by the direct addition of pure Al(OH)<sub>3</sub> powder [Fig. 4(e)], implying that its Al(OH)<sub>3</sub> phase has decomposed into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase and covered on Al particle surfaces. However, there is no clear  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase in the GMAP prepared using the Al(OH)<sub>3</sub> suspension produced by the reaction of  $2.25 \ \mu m$  Al powder with water [Fig. 4(a)]. To clarify whether the  $2.25 \ \mu m$ Al-produced Al(OH)<sub>3</sub> phase has transformed into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase, its filtered Al(OH)<sub>3</sub> powder was heat-treated using the same procedure to prepare GMAPs, and the phase compositions of the calcined powder are shown in Fig. 4(g). Figure 4(g) indicates that there is a clear  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase in the calcined powder and its diffraction peaks are very wide, implying that the produced  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains are very fine, which is believed to be the cause that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> diffraction peaks are not clear in Fig. 1(a). Figure 4 also indicates that the reaction by-products of all the GMAPs with water at different temperatures are bayerite

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \uparrow$$
<sup>(2)</sup>

It means that the reaction suspensions of GMAPs with water could be reused to modify the Al and to generate hydrogen.



**Fig. 4.** X-ray patterns of (a) as-received GMAP prepared using the Al(OH)<sub>3</sub> suspension produced by 2.25  $\mu$ m Al powder, (b) that in (a) after reaction in deionized water at 25°C for 32.6 h, (c) that in (a) after reaction at 36°C for 22.1 h, (d) that in (a) after reaction at 50°C for 11.2 h, (e) as-received GMAP prepared using the Al(OH)<sub>3</sub> suspension produced by pure Al(OH)<sub>3</sub> powder, (f) that in (e) after reaction at 25°C for 53.3 h, and (g)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder prepared by calcining Al(OH)<sub>3</sub> produced by 2.25  $\mu$ m Al powder, where the initial pressure for reaction tests is 0.04 bar.

Previous works<sup>15,16</sup> showed that Al surface modification is due to the dense passive oxide films on Al particle surfaces becoming the loose transition Al2O3 phases with the assistance of modification agents. Therefore, the uniform distribution of the modification agents on Al particle surfaces is important to get a high-quality GMAP. In this work, the Al(OH)<sub>3</sub> suspensions produced by the reaction of Al with water were used to modify Al particle surfaces. However, the Al(OH)<sub>3</sub> particle sizes in suspensions strongly depend on the reacted Al particle sizes, as evidenced in Fig. 4 of Ref. [21], where the larger Al particles reacted to produce larger Al(OH)<sub>3</sub> particles. This means that the Al (OH)<sub>3</sub> suspension prepared by the larger sized Al powder has a larger Al(OH)<sub>3</sub> particle size. As the Al(OH)<sub>3</sub> particles  $\frac{14}{14}$ retained their original morphology after decomposition<sup>1</sup> and the contact area between the larger particles is small, the coverage of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains on Al particles in GMAPs decreases with increasing size of Al particles to produce Al (OH)<sub>3</sub> suspension, as shown in Fig. 1. This is why the reaction induction time of GMAP and its total reaction time with water decrease with decreasing the sizes of Al particles to prepare Al(OH)<sub>3</sub> suspension (Fig. 2). Because the commercial Al(OH)<sub>3</sub> powder has a large average size of 2.5 µm, its  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> coverage in GMAP is the worst [Fig. 1(e)]. Moreover, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains produced by *in situ* formed Al (OH)<sub>3</sub> using Al-water reaction have more fine structures than those produced by the commercial Al(OH)<sub>3</sub> powder (Fig. 4). These  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> grains have a higher activity and a larger contact area with Al particles; therefore the reaction activity of the GMAP prepared by pure Al(OH)<sub>3</sub> powder is relatively poor (Fig. 2).<sup>16</sup>

#### IV. Conclusions

In this work, a facile wet chemical method was adopted to modify the Al particle surfaces, using an Al(OH)<sub>3</sub> suspension produced by the reaction of Al powder with water under vacuum at a mild temperature. The modified Al powder has a good reaction activity with water to generate hydrogen, its reaction induction time and total reaction time decrease with decreasing the sizes of Al particles used to prepare Al(OH)<sub>3</sub> suspension. The reaction activity of the modified Al powder prepared using the Al(OH)<sub>3</sub> suspension produced by the reaction of Al with water is obviously better than that for a powder prepared using suspension with a commercial Al (OH)<sub>3</sub> powder because the *in situ* formed Al(OH)<sub>3</sub> has a finer microstructure, leading to a good  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> coverage on Al particles. As the present method has no complicated procedure and the Al-water reaction by-product can be reused to modify Al, it provides a viable way to fabricate the modified Al powder for commercial applications.

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