

Physicochemical Mechanism for the Continuous Reaction of γ-Al₂O₃-Modified Aluminum Powder with Water

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Previous experiments showed that γ -Al₂O₃-modified Al powder could continuously react with water and generate hydrogen at room temperature under atmospheric pressure. In this work, a possible physicochemical mechanism is proposed. It reveals that a passive oxide film on Al particle surfaces is hydrated in water. OH⁻ ions are the main mobile species in the hydrated oxide film. When the hydrated front meets the metal Al surface, OHions react with Al and release H2. Because of the limited Hsoluble capacity in small Al particles and the low permeability of the hydrated oxide film toward H^+ species, H_2 molecules accumulate and form small H₂ gas bubbles at the Al:Al₂O₃ interface. When the reaction equilibrium pressure in H₂ bubbles exceeds a critical gas pressure that the hydrated oxide film can sustain, the film on the Al particle surfaces breaks and the reaction of Al with water continues. As the surface oxide layer on modified Al particles has a lower tensile strength, the critical gas pressure in H₂ bubbles is lower so that under an ambient condition, the reaction of modified Al particles with water is continuous. The proposed mechanism was further confirmed by a new experiment showing that the as-received Al powder could continuously react with water at temperatures above 40°C and under low vacuum, because the vacuum makes the critical gas pressure in H₂ bubbles decrease as well.

I. Introduction

CMALL fuel cells are being exploited as energy suppliers for D portable devices, i.e., the 4C devices (Computers, Camcorders, Cellular phones, Cordless tools).^{1,2} An advantage of portable fuel cells is that they could work uninterruptedly if the fuel supply is continuous. Moreover, fuel cells have a higher energy density than the rechargeable Li-ion batteries. Theoretically, portable fuel cells, once filled with the fuel, could work for a time interval of 10-20 times longer than the Li-ion batteries with the same weight and output.³⁻⁵ Nowadays, it is popular to develop direct methanol fuel cells (DMFC) for portable devices, which use methanol as a fuel. However, the large methanol crossover rate and CO poisoning effect are two barriers for DMFC in obtaining high efficiency and output.^{6,7} If pure hydrogen is used as a fuel, the above technological barriers disappear. However, the present hydrogen storage materials are very difficult to use as hydrogen sources for portable fuel cells, because the storage and release of hydrogen by these materials need a special temperature and pressure^{3,8} that imply adding some extra components in the application. These extra parts are unaffordable by volume and cost for small fuel cells. Therefore, it is of significance to develop hydrogen-generation materials for portable application.

In the past few years, there was considerable endeavor in this field. The main research was focused on chemical hydrides, i.e., NaBH₄, KBH₄, LiH, NaH, MgH₂, etc.^{9,10} Chemical hydrides are very reactive toward hydrolysis in water, which results in the release of large amounts of hydrogen gas. Among these chemical hydrides, NaBH₄ is the most valuable material for this application. Usually, NaBH4 dissolves in and reacts with water in the presence of a catalyst and gives up its hydrogen.^{11,12} Theoretically, the reaction of NaBH4 with water produces 10.8 wt% hydrogen. However, a definite amount of NaOH is needed to stabilize the NaBH₄ solution, because NaBH₄ reacts slowly with pure water until $\sim 7\%$ of NaBH₄ is consumed.¹¹ Furthermore, an optimum solution with the composition of 20 wt% NaBH₄/ 10 wt% NaOH/70 wt% H2O is usually adopted in the application due to the limited solubility of byproduct NaBO₂ in water.12 This implies that the practically generated hydrogen is ${\sim}4$ wt% using the NaBH4 solution. Moreover, the current high price of NaBH₄ (US 55 kg⁻¹) attenuates its competitiveness for commercial applications.¹²

In our previous work,¹³ metal Al particle surfaces were modified by fine γ -Al₂O₃ grains using a mixture of Al and Al(OH)₃ powder through a ceramic processing procedure.^{14–16} It was found that γ -Al₂O₃-modified Al powder could continuously react with water and generate hydrogen under ambient conditions. In contrast to NaBH₄, metal Al powder is cheaper; no catalyst or NaOH is required to promote the reaction with water. The reaction of metal Al with water produces ~4.8 wt% hydrogen. This makes the modified Al powder a more economically viable material for hydrogen generation for portable fuel cells.

In this work, a possible physicochemical mechanism is proposed to explain the reaction between the modified Al powder with water. The analyses predict the critical conditions (pressure, temperature) under which the reaction occurs. In order to verify the mechanism, a new experiment was designed to show that the as-received Al powder reacts with water at temperatures above 40° C under low vacuum.

II. Physicochemical Mechanism

(1) Hydration Reaction and H_2 Bubbles

The exceptional corrosion resistance of metal Al is critically dependent on the presence of a passive oxide film that is formed on its surface.¹⁷ When metal Al is placed in water, a hydration reaction occurs on the surface oxide film,¹⁸ which was recently documented by Bunker *et al.*¹⁹ using secondary ion mass spectrometry. For a dense oxide such as Al₂O₃, hydration primarily involves the disruption of Al–O–Al bonds via hydrolysis to form Al–OH species. Extensive hydration eventually produces

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(b) AlOOH film growth and formation of H_2 bubbles $6AlOOH + 2Al \rightarrow 4Al_2O_3 + 3H_2 \uparrow$



Fig. 1. Schematic representation of the hydration reaction inside the passive oxide film on the Al particle surface: (a) induction stage in which no film growth occurs, and (b) hydration eventually leads to film growth, while the hydroxide is reduced by Al to regenerate the oxide and generate H_2 at the Al:Al₂O₃ interface. These H_2 molecules then accumulate and form H_2 bubbles. The short arrows represent the movement of the hydration front.

oxyhydroxide or hydroxide phases such as AlOOH and Al(OH)₃ that are thermodynamically more stable than Al₂O₃ at room temperature. The results of Bunker *et al.*¹⁹ suggest that OH⁻ ions (or H₂O molecules) are the mobile species in the films (rather than H⁺, O²⁻, or Al³⁺), and their transport rates are sufficiently rapid to account for the kinetics of Al corrosion process.

The hydration of Al particles in water involves two stages, as shown in Fig. 1. In the initial stage, the following hydration reaction occurs at room temperature:^{13,19}

$$Al_2O_3 + H_2O \to 2AlOOH \tag{1}$$

This stage is the induction stage during which no film growth occurs (Fig. 1(a)). When the entire native oxide film is hydrated at the initial stage, the hydration front meets the metal Al surface. Although hydrolysis creates hydroxyl groups, other reactions can eliminate hydroxide ions and regenerate oxide structures. In fact, aluminum hydroxide phases are known to be thermodynamically unstable in contact with metal Al_{20}^{20} which is similar to what happens when water encounters a clean Al surface.²¹ OH⁻ ions are anionic defects that could be driven

to the Al:Al₂O₃ interface under an internal anodic potential.¹⁹ At the metal Al surface, OH^- ions would react with Al by an electrochemical process and form oxides and H₂ molecules (see Fig. 1(b) of Bunker *et al.*¹⁹). The overall reactions can be written

$$6\text{AlOOH} + 2\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 3\text{H}_2\uparrow$$
(2)

If the generated H_2 at Al:Al₂O₃ completely diffuses away through hydration oxide film or into metal Al bulk, there would be no H_2 accumulating at the Al:Al₂O₃ interface. In this case, the film will grow, because the newly generated Al₂O₃ layer is subsequently hydrated. However, if the above conditions are not satisfied, that is, the generated H_2 at the Al:Al₂O₃ interface cannot diffuse away, then these H_2 molecules will accumulate and form small H_2 gas bubbles at the Al:Al₂O₃ interface (Fig. 1(b)).

For the oxidation reaction at the Al surface, Eq. (2), the reaction rate can be written²²

$$\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}t} = K_0 e^{-E_a/RT} [\mathrm{AlOOH}]^m \tag{3}$$

where [H₂] and [AlOOH] represent the moles of H₂ and AlOOH per area at the Al:Al₂O₃ interface, respectively; K_0 is the maximum reaction rate constant, E_a is the activation energy for reaction, and *R* is the gas constant; and *m* is the reaction order that depends on the reaction mechanism, which can be determined experimentally. As the generated H₂ at the Al:Al₂O₃ interface will diffuse through the hydrated oxide film or into metal Al, the net H₂ amount accumulating at Al:Al₂O₃ interface of a spherical Al particle with radius *r* is

$$S_{\rm H_2}(t) = 4\pi r^2 \int_0^t \left\{ \frac{\mathrm{d}[{\rm H_2}]}{\mathrm{d}t} - J_{\rm film}(t)/2 - J_{\rm Al}(t)/2 \right\} \mathrm{d}t \qquad (4)$$

where $J_{\text{film}}(t)$ and $J_{\text{AI}}(t)$ are the H⁺ diffusion fluxes through hydrated oxide film and into Al bulk, respectively. In the steady-state diffusion, Fick's first law can be used

$$J = -D_0 \mathrm{e}^{-(Q/RT)} \frac{\partial C}{\partial x} \tag{5}$$

where D_0 is the maximum diffusion coefficient, Q is the activation energy for diffusion, C is the concentration of matter, and x is the position.

The related experiments^{23,24} showed that hydrogen permeability through the Al₂O₃ film is 100–2000 times lower than that through metal Al. Therefore, most of the generated H₂ at the Al:Al₂O₃ interface firstly diffuses into the bulk Al metal, and the H₂ diffusing through the hydrated oxide film could be negligible.¹⁹ Then, Eq. (4) can be simplified as

$$S_{\rm H_2}(t) = 4\pi r^2 \int_0^t \left\{ \frac{d[{\rm H_2}]}{dt} - J_{\rm Al}(t)/2 \right\} dt$$
 (6)

However, the solubility of H in metal Al is extremely low (with atomic H/Al fractions in the range of $10^{-6}-10^{-8}$)^{23,25}, and the volume of small metal Al particle is limited. Therefore, after an initial time, t_s , the Al particle will be saturated in H. The time t_s can be determined by

$$\int_0^{t_s} 4\pi r^2 J_{\rm Al}(t) \mathrm{d}t = \frac{4}{3}\pi r^3 C_0 \tag{7}$$

where C_0 is the saturation concentration of H in metal Al. If the H⁺ ion diffusion flux is simplified to be a constant, J_{Al} , then

$$t_{\rm s} = \frac{rC_0}{3J_{\rm Al}} \tag{8}$$

Equation (8) indicates that the time of H^+ ion diffusion saturation in an Al particle is proportional to its radius and

inversely proportional to the H^+ ion diffusion flux. After the time, t_s , no H^+ ions could diffuse into metal Al particle.

In fact, the accumulated H₂ molecules will self-assemble many small uniformly distributed H₂ bubbles at the Al:Al₂O₃ interface.^{19,26} If the hydrated oxide film is not broken during H₂ bubble generation, the reaction will reach an equilibrium in the light of the reaction kinetics²² at a time after H⁺ ion diffusion reaches the saturation in the Al particle. At the same time, the gas pressure in H₂ bubbles reaches an equilibrium pressure, $P_{H_2}^{e}$.²² As the diffusion of H⁺ ions in the hydrated oxide film is very

As the diffusion of H⁻ lons in the hydrated oxide him is very slow, the reaction at the Al:Al₂O₃ interface almost stops in the equilibrium state. If the accumulated H₂ molecules are assumed to be $S_{H_2}^e$ at the equilibrium state, then

$$S_{\rm H_2}^e = 4\pi r^2 \left\{ \int_0^{t_{\rm s}} \left\{ \frac{{\rm d}[{\rm H_2}]}{{\rm d}t} - J_{\rm Al}(t)/2 \right\} {\rm d}t + \int_{t_{\rm s}}^{t_{\rm s}+t_{\rm e}} \frac{{\rm d}[{\rm H_2}]}{{\rm d}t} {\rm d}t \right\}$$
(9)

where t_e is the time interval from the H⁺ diffusion saturation in the Al particle to the time that the interface reaction reaches equilibrium. Figure 1(a) indicates that there is an induction time, t_i , that is, the hydration time of the native oxide film, after which H₂ generation at the Al:Al₂O₃ interface starts. It can be understood that the total time counted from adding the Al powder to water up to the time at which the interface reaction reaches equilibrium is

$$t_0 = t_i + t_s + t_e \tag{10}$$

(2) Critical Conditions for H_2 Bubble Break

Figure 2(a) shows the forces that the hydrated oxide film underwent above an ellipsoidal H₂ bubble with semi-axis lengths *a* and *b* at the Al:Al₂O₃ interface. Because the tensile stress in the film decreases with the position away from the bubble, as an approximation, it is assumed that the maximum tensile stress, $\sigma_{\rm h}$, in the film is at the circle with a radius *a* above the H₂ bubble. The force balance in the film can be written

$$2\pi ah\sigma_{\rm h}\cos\theta + \pi a^2 P_{\rm atm} = \pi a^2 P_{\rm H_2} \tag{11}$$

where *h* is the thickness of the hydrated oxide film, P_{atm} and P_{H_2} are the environmental gas pressure and that in the H₂ bubble, respectively. θ is the angle between the stress vector $\vec{\sigma}_h$ and the axis normal to the film, and θ depends on the shape of the H₂ bubble, the radius of the Al particle, and the mechanical modulus of the film, etc. The maximum stress in the film is as follows:

$$\sigma_{\rm h} = \frac{a(P_{\rm H_2} - P_{\rm atm})}{2h\cos\theta} \tag{12}$$

If σ_h exceeds the tensile strength of the film, σ_c , then the hydrated oxide film will be broken. Equation (12) can be rearranged as

$$P_{\rm H_2}^{\rm c} = P_{\rm atm} + \frac{2h\sigma_{\rm c}\cos\theta}{a} \tag{13}$$



Fig. 2. Schematic representation of (a) the forces that the hydrated oxide film underwent above an ellipsoidal H_2 bubble at the Al:Al₂O₃ interface, and (b) the reaction of metal Al with water in the Al particle continues after the hydrated oxide film is broken.

 $P_{H_2}^c$ is the critical gas pressure in the H₂ bubble that leads to the breakage of the hydrated oxide film.

Equation (13) indicates that the critical gas pressure in the H_2 bubble depends on the environmental gas pressure and the tensile strength of the hydrated oxide film.

If the reaction equilibrium pressure in the H₂ bubble, $P_{H_2}^e$, is higher than the critical gas pressure, $P_{H_2}^e$, then the hydrated oxide film on the Al particle surfaces will be broken. After the film is broken, Al and water will directly make contact and react

$$Al + 2H_2O \rightarrow AlOOH + \frac{3}{2}H_2 \uparrow$$
 (14)

Because the reaction byproduct AlOOH does not dissolve in water, the AlOOH grains would cover the metal Al surface.²¹ When all the H₂O molecules between the newly formed AlOOH grains and the metal Al surface react away, a new layer of AlOOH would cover the metal Al surface. Then the above-described process will repeat,²⁷ as shown in Fig. 2(b). This implies that the reaction of Al particles with water continues until the entire Al is consumed. It should be mentioned that the phase constituents of the newly formed AlOOH layer are different from those on the original Al particle surfaces, as evidenced by the previous work.¹³ Moreover, the new AlOOH layer is probably slightly loose and has a lower tensile strength, because it is formed accompanied by H₂ bubble generation.

(3) Direct Reaction of Modified Al Powder with Water

In our previous work,¹³ metal Al particle surfaces were modified by fine γ -Al₂O₃ grains using a mixture of Al and Al(OH)₃ powders, which was pressureless sintered at a temperature of 600°C in vacuum. Because the decomposition of Al(OH)₃ produced a γ -Al₂O₃ phase during heating,¹⁴⁻¹⁶ all the constituents on the original Al particle surfaces were transformed into the γ -Al₂O₃ phase after sintering. Under ambient conditions, there was no obvious reaction between the as-received Al powder and distilled water.¹³ This implies that the reaction equilibrium pressure in H₂ bubbles in original Al particles is lower than the critical gas pressure in Eq. (13). In this case, the hydration reaction almost ceases when the gas pressure in the H₂ bubble reaches the reaction equilibrium pressure.

After the surface modification of metal Al powder by fine γ - Al_2O_3 grains, the oxide layer on the Al particle surfaces becomes loose, as shown in Fig. 3(a).¹³ This means that the strength of the surface oxide film on the modified Al particles decreases relative to that of the original Al particles. As the critical gas pressure in the H₂ bubble decreases linearly with decreasing tensile strength of the surface oxide film (Eq. (13)), it can be understood that the critical gas pressure in the modified Al particles is lower than that in the original Al particles. In this case, it is possible that the reaction equilibrium pressure in the modified Al particles exceeds the critical gas pressure. Therefore, the γ -Al₂O₃-modified Al powder could continuously react with water and generate hydrogen at room temperature under atmospheric pressure.¹³ Figure 3(b) shows the loose and fiber-like pseudoboehmite grains on a reacted Al particle surface,¹³ which is believed to be formed by the breakage of H2 bubbles and the hydrated oxide film. Moreover, our experiments also showed that under ambient conditions there is an incubation time (15-25 min) for hydrogen generation when the modified Al powder is placed in water, which is consistent with the prediction in Section II(1).

In fact, there are two ways to decrease the critical gas pressure in the H₂ bubble so that the direct reaction of Al powder with water can be realized (Eq. (13)). One way is to decrease the tensile strength of the surface oxide film, which has been confirmed by our previous experiments.¹³ Another way is to decrease the environmental gas pressure, $P_{\rm atm}$. In order to verify this prediction, the new experiment was performed to show that the asreceived Al powder reacts with water at a mild temperature and under low vacuum.



Fig. 3. TEM micrographs of (a) γ -Al₂O₃-modified Al powder with the composition of 72 wt% Al+28 wt% γ -Al₂O₃, and (b) the modified Al powder in (a) after a reaction in distilled water for 40 h at room temperature under atmospheric pressure.

III. Reaction of As-Received Al Powder with Water Under Low Vacuum

(1) Experimental Procedure

The Al powder used in the present experiment is the same as that in the previous work¹³ (highly pure Al powder, 99.9% purity, 3 µm; High Purity Chemical Co., Tokyo, Japan). The hydrogengeneration experiment of Al powder with water was carried out at room temperature (18°C), 40°, and 50°C, using 0.5 g Al powder suspended in 270 mL of distilled water in a pyrex glass cell. At the beginning of the experiment, the glass cell was evacuated to a low vacuum of ~ 3 kPa (~ 0.03 atmospheric pressure) and this vacuum state was retained for 30 min in order to eliminate the residual air. Then, the evacuation was stopped and the detection of evolved gases began. The gases evolved were determined by a thermal conductivity detector (TCD) gas chromatograph (Model No. GC-8A, Shimadzu, Kyoto, Japan), which was connected to a glass-made gas circulating line attached to the pyrex glass cell. The measurement uncertainties were about 0.05%. The schematic representation of the present hydrogen-generation equipment can be found in Hara et al.²

An X-ray diffractometer (XRD; Model No. RINT2000, Rigaku Co., Tokyo, Japan) was used to analyze the phases in the as-received Al powder, and those after a reaction at different temperatures. TEM was used to observe the morphologies of Al powder before and after reacting with distilled water.

(2) Results

Figure 4 shows the evolution and pressure of the gases from the distilled water containing as-received Al powder at room temperature, 40° , and 50° C, under low vacuum. In addition to hydrogen, no large amount of other gases (N2, O2, and H2O vapor) could be detected during the reaction. At room temperature, almost no generated hydrogen was found, and the change in gas pressure was very small. However, by increasing the temperature up to 40°C, after an incubation time of ~ 2 h, hydrogen generation was obvious, and at the same time, the gas pressure increased rapidly. When the temperature was up to 50°C, hydrogen generation was more rapid and the incubation time was significantly shortened in comparison with 40°C. In Fig. 4, ~64% of metal Al was consumed at 40°C within 8 h. If the reaction time is long enough, it is believed that metal Al powder would completely react with water. However, there was no obvious hydrogen generation when the as-received Al powder was placed in 75°C distilled water for 10 h under atmospheric pressure, indicating that low vacuum at the beginning is the key for the reaction of Al powder with water.

Figure 5 shows the XRD of Al powder before and after reaction with water. It can be seen that the surface layer of the original Al particles has complex phase constituents. However,



Fig. 4. (a) H_2 evolution from distilled water using as-received Al powder at room temperature (RT), 40° and 50° C, and (b) gas pressure corresponding to the experimental data in (a), where the Al powder used in each test was 0.5 g.

after reaction with water at room temperature, the diffraction peaks corresponding to those in the original Al particle surface disappeared. After the Al powder reacted with water at 40°C, all the phases in original Al powder were transformed into bayerite, indicating that at 40°C, metal Al reacted with water and generated hydrogen and bayerite. The overall reaction is

$$2\mathrm{Al} + 6\mathrm{H}_2\mathrm{O} \to 2\mathrm{Al}(\mathrm{OH})_3 + 3\mathrm{H}_2 \uparrow \tag{15}$$

This reaction produces 3.7 wt% hydrogen (weight ratio of generated H₂ to Al and H₂O). The reaction byproduct bayerite is chemically neutral,¹⁷ and could be reduced to metal Al for recycle by molten-electrolytic technology.

(3) Analyses

The phase constituents on the surface oxide film of the original Al particles disappeared after reaction at room temperature (Fig. 5), indicating that a hydration reaction occurred. This is confirmed by the TEM observations in Figs. 6(a) and (b), because the Al particle surfaces showed no obvious change after reaction with water at room temperature. The hydrated product at room temperature is probably pseudoboehmite, because the weak diffraction intensity¹³ and small amount (3–4 nm thick)¹⁹ of pseudoboehmite make its diffraction peaks invisible. But above 40°C, the hydrated product is Al(OH)₃ (Fig. 5).

At room temperature and under low vacuum, no hydrogen was detected (Fig. 4(a)), indicating that the reaction equilibrium pressure in the H₂ bubble is still lower than the critical gas pressure, although the critical gas pressure decreases in vacuum (Eq. (13)). However, when the temperature increases, the hydration reaction and the movement of OH⁻ ions in the oxide film become active so that the Al(OH)₃ moles per area at the Al:Al₂O₃ interface increase and the reaction rate at the Al:Al₂O₃ interface (Eq. (3)) increases. In this case, the accumulated H₂ molecules in



Fig. 5. X-ray patterns for (a) as-received Al powder and those (b) after reaction with distilled water at room temperature for 23 h, and (c) after reaction with distilled water at 40°C for 8 h, where the gas pressure was \sim 3 kPa at the beginning of the reaction in the glass cell.

the H₂ bubbles increase. From the ideal gas equation

$$PV = nRT \tag{16}$$

(*n* is the gas moles), it is clear that the reaction equilibrium pressure increases with temperature if the H_2 bubble volume is constant. In this case, it is possible that the reaction equilibrium pressure exceeds the critical gas pressure. This is the reason why as-received Al powder could continuously react with water and generate H_2 above 40°C and under low vacuum. The above result verifies the prediction in Eq. (13) that the vacuum could decrease the critical gas pressure. Moreover, the loose morphology of the reaction byproduct bayerite in Figs. 6(c) and (d) is further evidence of the breakage of H_2 bubbles and the hydrated oxide films.

The incubation time strongly depends on the temperature because it depends on the diffusivity of the mobile species (Eq. (8)). When the temperature increases, the diffusivity increases (Eq. (5)) and the incubation time decreases. This theoretical prediction is in good agreement with the experimental results in Fig. 4(a), because the incubation time at 50°C is obviously shorter than that at 40°C.

The accessory of portable fuel cells should be simple and cheap, that is, the modified Al powder is a feasible hydrogengeneration material for portable application, because it works under ambient conditions. Nevertheless, if the Al hydrogen-generation method is used in automobile or other large vehicles, it is possible and affordable to add a vacuum pump to draw hydrogen from the direct reaction of pure Al powder with water at a mild temperature.

IV. Conclusions

In this work, the physicochemical mechanism for the continuous reaction of γ -Al₂O₃-modified Al powder with water was investigated. The analyses reveal that

(1) When metal Al powder is placed in water, the surface oxide film on the Al particles is hydrated, and OH^- ions are the



Fig. 6. TEM micrographs of (a) as-received Al powder and those (b) after reaction with distilled water at room temperature for 23 h, and (c) and (d) after reaction with distilled water at 40°C for 8 h, where the gas pressure was ~ 3 kPa at the beginning of the reaction in the glass cell.

mobile species in the hydrated oxide film. After the native oxide film is completely hydrated, the hydrated front contacts the metal Al surface. The electrochemical reaction of OH- ions with metal Al releases H₂ at the Al:Al₂O₃ interface; H₂ molecules accumulate due to the low diffusivity of H⁺ through the Al₂O₃ film and the limited soluble capacity of the small Al particles for H. Accumulated H₂ molecules form small uniformly distributed H₂ bubbles at the Al:Al₂O₃ interface. Subsequently, the gas pressure in the H₂ bubbles reaches the reaction equilibrium pressure.

(2) There is a critical gas pressure in H_2 bubbles, which depends on the environmental pressure and the tensile strength of the hydrated oxide film. When the reaction equilibrium pressure in the H₂ bubble exceeds the critical gas pressure, the hydrated oxide film breaks and the Al powder continuously reacts with water and generates hydrogen.

(3) After surface modification of the Al particles by fine γ -Al₂O₃ grains, the tensile strength of the surface oxide film decreases so that the reaction equilibrium pressure in the H₂ bubble exceeds the critical gas pressure. This results in the γ-Al₂O₃-modified Al powder continuously reacting with water under ambient conditions.

(4) The existence of critical gas pressure in the H_2 bubbles was further confirmed by a new experiment showing that the as-received Al powder could continuously react with water at temperatures above 40°C and under low vacuum, because the vacuum decreases the critical gas pressure.

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