

Hydrogen Generation by Accelerating Aluminum Corrosion in Water with Alumina

J. Skrovan, A. Alfantazi, and T. Troczynski

Abstract—For relatively small particles of aluminum (<60 μm), a measurable percentage of the aluminum (>5%) is observed to corrode before passivation occurs at moderate temperatures (>50°C) in de-ionized water within one hour. Physical contact with alumina powder results in a significant increase in both the rate of corrosion and the extent of corrosion before passivation. Whereas the resulting release of hydrogen gas could be of commercial interest for portable hydrogen supply systems, the fundamental aspects of Al corrosion acceleration in presence of dispersed alumina particles are equally important. This paper investigates the effects of various amounts of alumina on the corrosion rate of aluminum powders in water and the effect of multiple additions of aluminum into a single reactor.

Keywords—Alumina, Aluminum, Corrosion, Hydrogen

I. INTRODUCTION

WITH the current concern with global warming, air pollution, and diminishing reserves of fossil fuels, there has been increased emphasis on transitioning to a hydrogen economy. Hydrogen is made at large scale today (mostly from natural gas) for use in chemical processes such as oil refining and ammonia production [1]. About 1% of U.S. primary energy use (~ 5% of U.S. natural gas use) goes to hydrogen production for chemical applications [2]. However, if hydrogen is to be widely used as a future energy carrier, storage will be needed to meet time-varying demands for fuel and allow for mobile energy sources. Methods of interest include compression, liquefaction, physisorption, metallic hydrides, and complex hydrides [3]. The most common storage solution for small systems is currently pressure cylinders and industry has set a target of a cylinder with a gravimetric storage density of 6 mass % and a volumetric storage density of 30 kg/m^3 [4].

Aluminum being a reactive metal will readily form aluminum hydroxide when placed into water with a resulting release of H_2 gas [5]. Looking at a mass balance equation we can calculate that aluminum could have an equivalent storage density of 11 mass%, well above current storage targets. This equates to roughly 1.25 liters of hydrogen per gram of aluminum [6]. However in practice aluminum is almost always found with a protective Al_2O_3 oxide layer covering the bulk material due to reaction with oxygen in the atmosphere.

J. Skrovan is with King Fahd University Of Petroleum & Minerals, Department of Mechanical Engineering, KFUPM Box 903, Dhahran 31261, Saudi Arabia (e-mail: skrovan@kfupm.edu.sa).

A. Alfantazi is with the University of British Columbia, Department of Materials Engineering, 6350 Stores Road, Vancouver, BC Canada V6T 2G9

T. Troczynski is with the University of British Columbia, Department of Materials Engineering, 6350 Stores Road, Vancouver, BC Canada V6T 2G9

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This layer is non-soluble and prevents or retards the Al-water reaction. In near neutral pH pure water systems, aluminum is reported to form various aluminum hydroxides depending on water temperature and pressure all of which form a passivating layer that grows to at most a couple of micrometres thickness before the reaction stops [7]. For this reason aluminum has not traditionally been viewed as a practical source for hydrogen generation.

To prevent passivation and use aluminum as a hydrogen source the most common approach has involved alkali solutions, typically NaOH [8] - [11]. However, strongly alkali solutions present problems for use in portable and household applications where possible spills present safety concerns. To corrode aluminum in neutral pH solutions several different methods are reported to be under investigation. The use of Ga and In to accelerate aluminum corrosion suffers from the high cost of the alloying element. The addition of just 5 wt% Ga to aluminum increases the cost of the Al alloy by 10 times [6], [12]. Other researchers have milled aluminum with Bi to create a galvanic cell within the alloy [13], or with alumina [14] to increase surface area. Additives to the aluminum unfortunately decrease the available hydrogen per gram of powder as well as adding cost and additional preparation steps. If the secondary additive to the milling is a water soluble salt then it can be removed from the aluminum after milling so the resulting powder has increased surface area without a weight penalty, but again at the cost of increased processing steps [15], [16].

Widespread use of aluminum as a hydrogen source would be facilitated by a process that uses water without acidic or alkaline additives, aluminum without expensive alloying elements or preprocessing requirements, and does not require or generate toxic products. In this paper the addition of alumina powder in the reaction vessel is shown to promote the corrosion of aluminum and generate commercially useable quantities of hydrogen. Earlier work using alumina to promote the corrosion of Al reported by Deng [12] uses a sintering step where the alumina is thought to weaken the protective oxide on the aluminum particle. This work gives evidence that the sintering step is not necessary and another mechanism is responsible for the enhanced corrosion seen with Al/alumina mixtures.

The by products of the aluminum water reaction, namely aluminum hydroxides, are non-toxic and already make up a significant portion of the earth's crust so disposal after use or in the event of spills is not complicated and requires no special handling. Unlike other complex hydrides that are being investigated as hydrogen sources such as sodium borohydride, there already exists a commercial process for recycling the spent oxide back into aluminum. One of the

major commercial challenges with using sodium borohydride is lack of a viable method for recovering sodium borohydride from the spent reaction products. With aluminum there already exists a worldwide network of aluminum smelters that can accept the aluminum hydroxide as a feed stock with reduced processing compared to bauxite ore that is normally used. It should be noted that because of aluminum's electronegativity, direct reduction of aluminum oxide back to aluminum is not currently practical for small portable systems. All such reduction utilizes high temperature and intermediate chemical compounds such as cryolite or carbon. At this point a recycle stream of the spent oxide back to commercial aluminum smelters would be more practical than onboard regeneration.

II. EXPERIMENTAL PROCEDURES

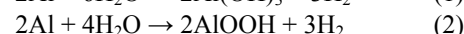
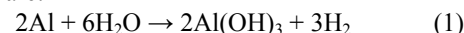
All experiments used atomized aluminum powder from Alcoa, 101 common grade, 99.7% Al, main impurities: Fe (max 0.25%) and Si (max 0.15%) as well as 0.6% Al₂O₃ on the surface of powder particles. Aluminum powder had an average particle diameter of 40 μm and is either used loose in water when hydrogen is being collected or it is compacted in a die to 350 kg cm⁻² and the resulting pellet used in an electrochemical cell. Al powder was hand mixed with Al₂O₃ powder (ALCOA A-16SG, 99.8% calcined alumina), using a glass rod. For hydrogen evolution testing the solution (typically 75ml of de-ionized (DI) water (1Mohm)), was added to a 200ml Pyrex beaker and heated on an electric hot plate/stirrer (Barnstead Thermolyne). The temperature was measured while heating to starting temperature with a removable thermometer, but was not controlled during the reaction which allowed for higher temperatures to be reached depending on the amount of aluminum and rate of reaction. Once the solution was at temperature the powder was added and the beaker stoppered with a #12 rubber stopper. A Pyrex tube through the center of the stopper allowed evolving gas to flow through a ¼ inch inner diameter tube from the beaker and into an inverted graduated cylinder. Corrosion of loose powder was measured by capturing evolved hydrogen in a water filled inverted graduated cylinder, the downward displacement of water indicating the amount of evolved hydrogen with approximately 5 ml initially lost to clear the tubing between beaker and cylinder. Gas analysis performed by Global Hydrogen Technologies detected only hydrogen gas and some residual air from the collection process.

A Princeton Applied Research potentiostat model 273A was used for electrochemical work with a standard three electrode corrosion cell using a Ag/AgCl reference electrode. All potentials are graphed versus standard hydrogen electrode (SHE). The corrosion cell was jacketed and a variable temperature controller circulated water around the cell to maintain cell temperature to within 0.5°C of set point. Potentiodynamic tests were run at 0.5 mV s⁻¹. The working electrode had a 0.833 cm² exposed surface, but current densities are reported as an apparent current because solution

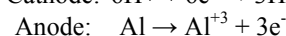
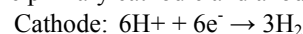
penetration into the powder pellet made determination of the actual surface area exposed to solution indeterminate.

III. RESULTS AND DISCUSSIONS

When looking at Al/Alumina samples in water above 50°C the hydrogen evolution is fairly rapid and can be measured by the displacement of water by H₂ in an inverted graduated cylinder. From the gas evolution rate the aluminum corrosion rate and the percent of aluminum that has reacted in the sample can be calculated. The two reactions depending on the water temperature are:



In both cases the primary cathodic and anodic reactions are:



The difference between eq. (1) and eq. (2) is that eq. (2) consumes less water to produce the same amount of hydrogen which might be important in portable applications where weight must be conserved. Eq. (2) also forms a different aluminum hydroxide (AlOOH), which is typically seen for aluminum reactions in water at temperatures above 70°C [15] – [17]. When studying the effect of ball milling (BM) aluminum with alumina powder in earlier work [16], [18], tests were also run with an aluminum/alumina mixture that had not been BM to serve as a control for the BM samples and to compare with the straight powder samples. Because of the ductile nature of aluminum, a pure aluminum pellet was considered likely to compress into a less porous pellet during compaction and this porosity might be a difference between the pure aluminum pellet and the BM sample. It was still somewhat surprising when the non-ball milled sample showed a higher corrosion rate than the straight aluminum powder (Fig. 1).

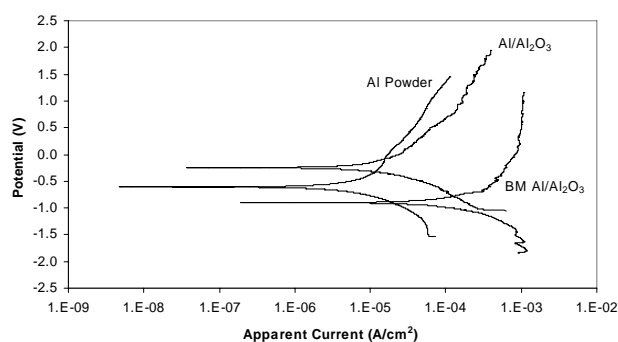


Fig. 1 Potentiodynamic curve of an aluminum/alumina mixture in water compared to aluminum powder and a ball milled (BM) aluminum/alumina mixture.

With only one half the aluminum present as in the 100% sample the corrosion rate was expected to be lower for the aluminum/alumina sample. To see a higher rate implied that the oxide was providing a pathway for greater solution penetration of the pellet, exposing greater overall aluminum surface, or that the oxide was facilitating the corrosion from

the available surface.

To investigate the role the alumina might play and confirm the first results, samples of varying oxide percentage composition were prepared and tested (Fig. 2). If the oxide was only serving as a solution pathway to aluminum deeper within the pellet then a point of diminishing returns might stabilize or reverse the apparent acceleration of corrosion seen in the first test. Instead an increased corrosion rate was seen with each increase in the amount of oxide in the pellet. This suggested that the oxide was promoting the aluminum corrosion, but did not rule out that it simply allowed for more surface area of aluminum particles to be exposed to water. To test this idea, corrosion rates for loose powder in a beaker were measured by the evolution of hydrogen, where it was assumed that all of the available aluminum was exposed to water regardless of the presence of oxide.

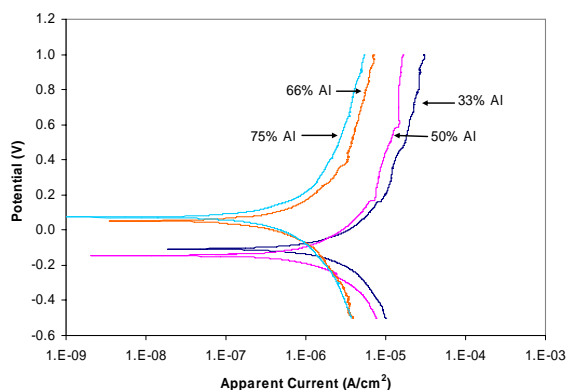


Fig. 2 - Potentiodynamic scans for aluminum/alumina pellets in DI water with the amount of aluminum varying from 33% to 75%

Fig. 3 shows the hydrogen evolution from 0.5g of aluminum powder placed in 65°C DI water with time. There is a clear and dramatic increase in the amount of hydrogen evolved when the aluminum powder was added with 5g of Al_2O_3 powder. This increase while slower than that seen with the BM systems did result in the aluminum powder reaching corrosion levels and thus evolved hydrogen amounts equal to or greater than that seen with the BM systems.

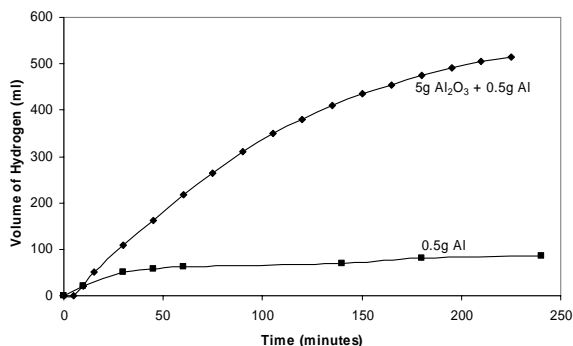


Fig. 3 - Hydrogen evolution from 0.5g of aluminum powder in 75ml of 65°C DI water with 5g of alumina powder added

Previous researchers [9] who studied the effect of alumina to accelerate aluminum corrosion were sintering the alumina and aluminum and proposed a corrosion mechanism involving the weakening of the native oxide layer on the aluminum particle by the sintering process. They did not report any results for unsintered powders such as used in this study. This result shows that the sintering processing steps are not necessary to promote the increased corrosion rate needed for hydrogen generation.

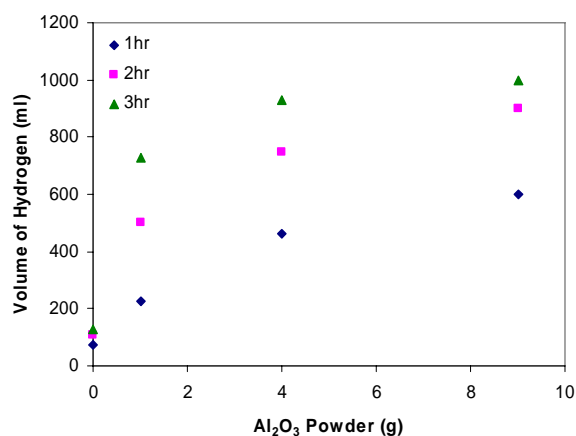


Fig. 4 - Volume of hydrogen released in one, two, and three hours after immersion in 65°C water as a function of the number of grams of Al_2O_3 powder added to 1 gram of aluminum powder

As can be seen in Fig. 4, the corrosion rate for a given amount of aluminum powder continues to increase although with diminishing returns as the amount of oxide added to the beaker is increased. It can also be noted that all the oxide amounts showed a much higher hydrogen evolution in the second and third hours of immersion, and the rapid fall-off in hydrogen evolution seen with the pure aluminum (zero oxide point), which is attributed to aluminum passivation, is no longer observed when alumina is present. This corrosion acceleration is not just a mechanical effect of being buried by a secondary particle. Fig. 5 shows the effect of aluminum powder mixed with various other powders (SiO_2 , CuO , La_2O_3 , and SiC), none of which show noticeably more hydrogen evolution than that seen by just aluminum powder in water.

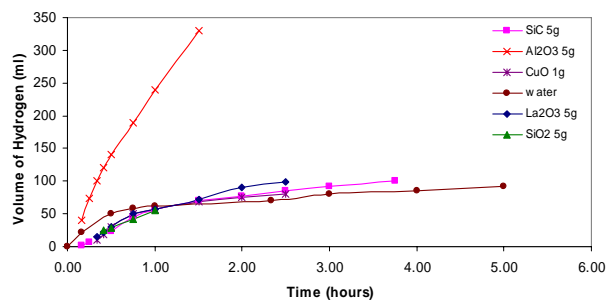


Fig. 5 - Volume of hydrogen released with time for 0.5g Al in 70°C water with additions of Al_2O_3 , SiC , CuO , La_2O_3 , and SiO_2

While the effect of alumina on aluminum corrosion is very interesting and invites an explanation, if new alumina is needed with each batch of aluminum powder then it will not be a useful method for hydrogen production because of the weight inefficiency in transporting the inert alumina in addition to the aluminum powder. To be a commercially useful technology the alumina should be reusable, allowing multiple additions of aluminum powder without loss of corrosion rate or total efficiency. As seen in Fig. 6, subsequent additions of 0.5g aluminum powder to a beaker containing 5g of Al_2O_3 not only maintain the rate of corrosion seen earlier, but accelerate the corrosion rate with the first 3 runs and then remain constant with a total corrosion in the first hour above that seen for the 50/50 BM mixtures [16].

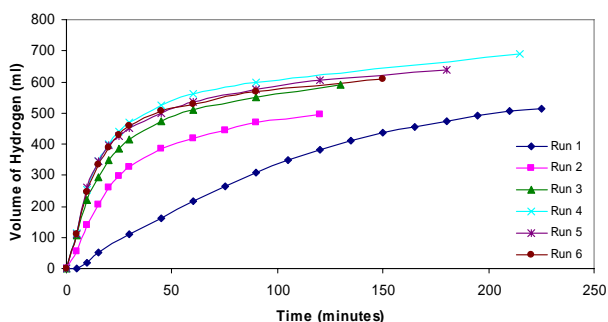


Fig. 6 Volume of hydrogen released from 5g Al_2O_3 in 75ml of 65°C DI water with the addition of 0.5g Al powder at the start of each run, run 6 started one day later

A similar addition of 0.5g of aluminum, into 75ml of water containing 5g of alumina, every 30 minutes show that by the third run over 90% of the theoretical maximum hydrogen is evolving each time (Fig. 7). This was maintained without pausing for 13 runs without loss of hydrogen evolution rate, and continued over the next two days for a total of 21 runs without loss of the catalytic role the alumina played. These tests were carried out on a hotplate which established the starting temperature at 65°C, although the exothermic nature of the reaction would cause the temperature to increase during the reaction. A portable system for hydrogen generation would not want to need continual heating so a test was also run with an insulated beaker.

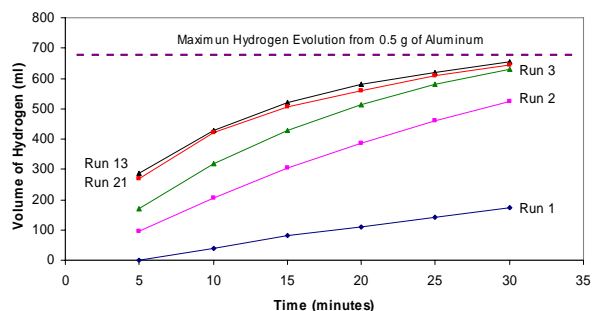


Fig. 7 Volume of hydrogen evolved when 0.5g of Al powder is added every 30 minutes to 5g alumina in 75ml of 65°C DI water

A test was started on a hotplate for the first 4 runs as in the previous test, but with the beaker insulated. At the start of run 5, the beaker was removed from the hotplate and set on the counter and aluminum added every 5 minutes (Fig. 8). In addition to demonstrating the ability to run without external heat, this tests shows that if a long term demand for hydrogen allows for time to stabilize a batch system, then overall hydrogen production rates can be set by the rate at which aluminum is fed into the system. A small hydrogen tank added to the system would allow for instant startup, with heat from the fuel cell starting the batch reactor with the flow of hydrogen produced controlled by the speed aluminum is added to the reaction chamber. When demand is turned off the remaining un-reacted aluminum in the chamber would finish producing hydrogen to refill the startup tank and ready the system for the next start.

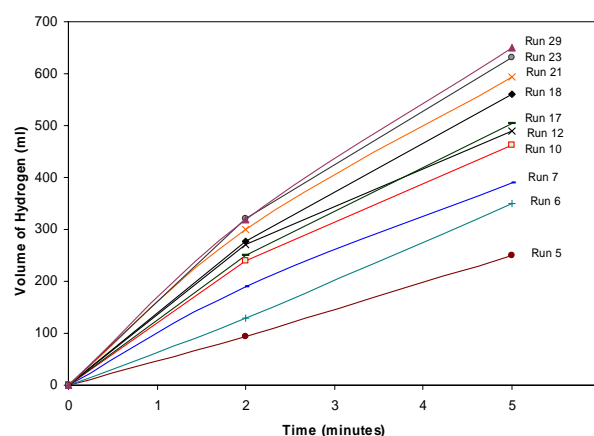


Fig. 8 Volume of hydrogen released with the addition of 0.5g Al every 5 minutes to 5g Alumina in 75ml of DI water in insulated beaker

With multiple runs in one beaker where aluminum is added before the prior reaction is complete (both Fig. 7 and 8) it is important to remember that there will be ongoing generation from earlier additions that increase the output seen from the later runs. This is offset by hydrogen lost when the beaker is opened to add new aluminum and the need to reclear water from the tube to the collection cylinder. More accurate determination of evolved hydrogen with time would be possible with an improved reactor setup allowing aluminum addition without opening the reaction chamber. However the stabilization at near the maximum yield expected (Fig. 7) indicates these additional losses are not excessive. One of the additional differences in the system with subsequent runs is the presence of aluminum hydroxide produced earlier. To test if this would help explain the acceleration seen with multiple runs a 0.5M boehmite solution was used to run a cathodic polarization curve on an aluminum powder pellet and this was compared with an aluminum powder pellet run in a 0.045 M KCl solution. Both solutions were at 25°C and de-aerated with N_2 for 1 hour while the solution was stirred (Fig. 9). The boehmite solution showed an increased cathodic current by ~1 order of magnitude, with the open circuit potential being

almost identical to the aluminum control sample. Furthermore, the sample in the boehmite solution showed the effect of bringing fresh boehmite to the aluminum surface with the current increasing as the solution stirring was increased and then dropping when the stirring was turned off which is typical of a sample influenced by a concentration gradient.

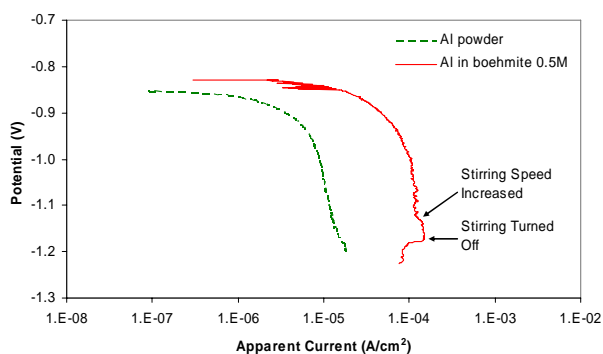


Fig. 9 Cathodic polarization scans of aluminum powder in 0.045 M KCl and 0.5 M boehmite solutions at 25°C

The effect of the boehmite solution was also tested on loose aluminum powder (see Fig. 10). Compared to water with 5g of alumina present, the corrosion of 0.5g Al powder was much quicker in a 0.5 M boehmite solution without alumina, but the solution quickly gelled and the hydrogen evolution was hindered. The addition of alumina gave intermediate results, with the boehmite giving increased initial hydrogen evolution and the oxide preventing the rapid gelling of the solution.

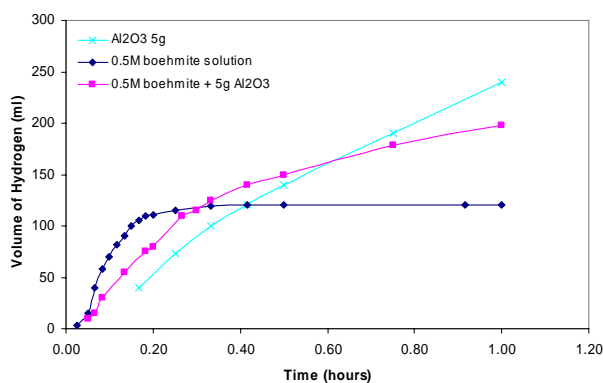


Fig. 10 Hydrogen evolution with time from 0.5 g of aluminum powder in DI water with 5g of Al_2O_3 compared to 0.5 g of aluminum powder in a 0.5 M Boehmite solution with and without the 5 g of alumina

The addition of alumina to the water increased the pH from approximately 7 to around 8.2 for 5g of alumina into 100 ml of water. This increase is thought to occur because alumina will attract a surface layer of H^+ ions when at a pH below its iso-electric point. The high surface area (approximately $9\text{m}^2/\text{g}$) [16] and the high zeta potential of alumina may adsorb enough H^+ ions to shift the measured pH. One of the possible explanations for the effect of alumina on aluminum that is being investigated is the alumina provides a source of H^+ ions to carry away the electrons given up by the anodic aluminum

reaction. Additional runs show a continuing increase in pH to slightly above 9 as a result of the aluminum hydroxide formation or as a side effect of the hydrogen evolution. This increase in pH may also contribute to the increased corrosion rate seen in subsequent runs. The increase in pH alone is not enough to account for the greater corrosion rate. The maximum pH seen after multiple runs was below 9.5; previous work looking at the corrosion rate of aluminum powder in NaOH solutions showed no increase at pH values up to 10, and the rate at a pH of 11 was below that seen in these tests [16].

IV. CONCLUSION

The addition of a loose alumina powder will accelerate the corrosion of aluminum in water and it is not necessary to pretreat the aluminum by ball milling or sintering it with the alumina. The acceleration of corrosion increases with increasing amounts of alumina. The catalytic effect of the alumina is not depleted and the same alumina can be used for multiple batches of aluminum powder. As subsequent runs are performed the corrosion rate initially increases and then stabilizes by the fourth run. This increase is hypothesized to result from the formation of aluminum hydroxide particles during the initial runs. The rate increases until over 95% of the available aluminum is corroding within 30 minutes if run in a batch mode and hydrogen generation rate can be controlled by the feed rate of aluminum. The reaction is exothermic and will sustain itself without external heating once initiated. This indicates that a simple reactor for generating hydrogen from water and aluminum can be built without the need for expensive additives, extensive pretreatments, and toxic or alkaline solutions. These results also point to the need for further study of the corrosive properties of small particles of oxide as nano-technology becomes more widespread.

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