Generating Hydrogen on Demand by Splitting Water with Al Rich Alloys

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ABSTRACT

Our group has been pioneering the production of on-demand hydrogen using aluminum-gallium alloys to split water into hydrogen, heat, and alumina. Recently, we have found that we can split water on demand using solid alloys of 95 wt% aluminum (Al), and 5 wt% of a gallium-indium-tin alloy (Ga-In-Sn). This is both a technological breakthrough and an economic viability breakthrough since the more expensive Ga-In-Sn component is in small proportion. Since pure alumina can be reduced for about \$0.30/lb, and the 5% component can reclaimed at about \$0.0625/lb, we can show this technology is capable of delivering energy at \$0.10/kWh.

Keywords: splitting-water, hydrogen, aluminum

1 INTRODUCTION

Safe hydrogen storage, transportation, and delivery are the goals of state of the art research in hydrogen systems and applications. In this paper, a means of safely producing hydrogen gas on demand is discussed. The method utilized involves the depassivation of aluminum by alloying with pure gallium or gallium-indium-tin. The depassivated aluminum alloy is then able to reduce water, producing hydrogen gas, alumina, and heat. The advantages of this method are that energy is stored in relatively safe materials at an energy density significantly higher than that of modern chemical batteries. Additionally, the gravimetric and volumetric fuel density of the alloy shows promise in meeting the Department of Energy's targets for on board hydrogen storage systems for 2010 and beyond. Lastly, recovery and recycling of the reaction byproducts can yield an energy cost as low as \$0.10/kWh, providing an economically viable scenario for a sustainable hydrogen fuel delivery system.

2 REACTION MECHANISMS

It is well established that aluminum is thermodynamically capable of splitting water. In practice, however, bulk aluminum does not split water very well due to its surface being passivated by a thin layer of aluminum oxide. In the late 1960's Jerry Woodall discovered that liquid alloys of gallium and aluminum are capable of splitting water. This is believed to be because the gallium acts to disrupt the passivating oxide that forms on aluminum, allowing all of the aluminum contained in the gallium alloy to react. When water is added to this liquid system, aluminum that reaches the alloy surface will reduce the water releasing hydrogen gas. More aluminum will reach the surface by means of random thermal motion and split more water until the liquid alloy is depleted of aluminum.

Recently, progress has been made in increasing the wt% aluminum content (up to 95 wt%) in the alloys such that the alloys exist as a solid at room temperature. These solid alloys will also split water and produce alumina, hydrogen, and heat. We currently believe this to be a result of a liquid phase existing in the grain boundaries of the material, allowing the alloy to react in a similar manner to the liquid phase alloy previously discussed.

The other components of the alloy, Ga, In, and Sn remain unused during the reaction of the aluminum due to the fact that these elements are thermodynamically unable to reduce water. Instead, these elements are dispersed among the many small grains of alumina that result from the reaction and can be separated by a centrifuge. This easy recovery is an important consequence of the reaction because it allows for subsequent reuse of the inert elements.

3 FABRICATION

The alloys used for testing were both supplied by KB Alloys, (Robards, KY), and made in-house using a small laboratory furnace with an oxygen free nitrogen atmosphere. To make the 50 wt% Al alloys, a composition of 50 wt% Al, 34 wt% Ga, 11 wt% In, and 5 wt% Sn was used at a process temperature of about 550 ºC. To make the 95 wt% Al alloys, a composition of 95 wt% Al, 3.4 wt% Ga, 1.1 wt% In, and 0.5 wt% Sn was used at a process temperature of approximately 750 ºC. Typical process times are 8 to 10 hours in length. After baking, the alloys are cooled by quenching in a stainless steel basin. Note that the ratio Ga:In:Sn is kept constant among the alloys tested.

4 ENERGY DENSITY AND VOLUMETRIC/GRAVIMETRIC H_2 CONTENT

The stoichiometric equation for the reaction of aluminum with water is given in equation (1) with the enthalpy value calculated using the standard molar enthalpy (heat) of formation at 298.15 K for each chemical [1].

$$Al + {}^{3}/_{2}\, H_2O \rightarrow {}^{1}/_{2}\, Al_2O_3 + {}^{3}/_{2}\, H_2 + 409.15\ \text{kJ/mol} \quad (1)$$

Burning the hydrogen produced from reacting 1 mole of aluminum with water will produce about 428.7 kJ, as shown in equation (2).

$$^{3}/_{2}\ H_2 + {}^{3}/_{4}\ O_2 \rightarrow {}^{3}/_{2}\ H_2O + 428.7\ \text{kJ/mol} \qquad (2)$$

Thus there is approximately 837.85 kJ of usable energy in every mole of aluminum. Alloying aluminum with gallium, indium, and tin provides access to this energy. Assuming the total energy content of aluminum to be as calculated above, a typical 95 wt% aluminum alloy can have an total energy density as high as 8.18 kWh/kg.

Water reacts in a 3:2 molar ratio with Al, however the molecular weight of water is roughly two-thirds that of Al. Thus it takes approximately 1 gram of water to react 1 gram of Al to completion. Applying this approximation to a sample of 95 wt% aluminum alloy, it takes 0.95 grams (equivalently, 0.95 mL) of water to completely react 1 gram of alloy and produce approximately 0.106 grams of hydrogen. Assuming the density of the alloy can be approximated as a weighted average of the densities of its constituent elements, we arrive at 2.88 g/cc for a typical 95 wt% aluminum alloy. Summing the volume of alloy and water necessary to produce these 0.106 grams of hydrogen, we arrive at a theoretical volumetric density of 0.0817 kg H_2 per liter of alloy.

Similarly we can calculate the gravimetric density of H_2using the same assumptions. 1 gram of alloy will react with 0.95 grams of water to produce 0.106 grams of hydrogen, giving us a theoretical H_2 gravimetric density of 0.0516 kg H_2 per kilogram of alloy. This number could be increased however, if a system was designed in such a way that 50% of the water necessary to complete the reaction was derived from the spent H_2 fuel that has been combusted to H_2O. In this case, the gravimetric hydrogen density would start at 0.0670 and decrease down to 0.0516 kg H_2 per kilogram of alloy as the system converts aluminum in the alloy to alumina (the combustion of H_2 and recycling the water produced essentially brings in additional oxygen weight from outside the system as the alloy is used up).

Storage Parameter	Units	2007	2010	2015
System Gravimetric Capacity	kWh/kg (kg H_2 / kg sytem)	1.5 (0.045)	3 (0.060)	6 (0.090)
System Volumetric Capacity	kWh/L (kg H_2 / L sytem)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost	\$/kWh net (\$/kg H_2)	6 (200)	4 (133)	2 (67)

Table 1: DOE Technical Targets For On Board Hydrogen Storage Systems [2].

Though to date there has not been a complete system designed around this method of producing hydrogen, these volumetric and gravimetric numbers show promise for meeting the 2010 and 2015 Department of Energy's targets for on board hydrogen storage systems as seen in table 1.

5 FINANCIAL VIABILITY

We will now examine the financial viability of using a 95-5 alloy to store energy. In order to make aluminum to customer's specifications, aluminum companies refine bauxite until it becomes high purity alumina with an average particle size of 120 microns. This alumina gets shipped to the 9 foundries around the world where it is reduced to aluminum metal containing additive metals to customer specifications during the smelting process to reduce alumina to aluminum.

Bauxite to alumina	$0.20
Alumina purification and particle resizing	$0.60
Electrolysis of alumina to aluminum	$0.30
Total:	$1.10

Table 2: Component Cost per Pound of Aluminum

The process of reacting our aluminum alloys with water results in high purity alumina, so the only step in this process required to recharge the aluminum is the electrolysis of alumina to aluminum. A test case can be analyzed where 20 reaction cycles (1 initial + 19 recycled) are performed. For this test case, a 95 wt% aluminum alloy will be evaluated. Aluminum will be treated as 20 lbs of active aluminum. This “active aluminum” is simply 1 lb reacted 20 times. The Ga-In-Sn used in the reaction will total approximately 0.05 lbs and an assumed 0.1% loss will be replenished each recycle step. The cost per pound of Ga-In-Sn at current shelf price is $125. At a price of $1.10 per lb Al, and a recycle cost of $0.30/lb, we can calculate the average cost per pound of alloy for our test case over 20 uses. The average cost per pound of alloy becomes approximately $0.67 (or $1.47/kg of alloy). Figure 1 shows the cost per kg of alloy over N recycles.

After a sufficient number of recycles, the average cost per kg of alloy drops to about $0.64. At the assumed energy density of 8.18 kWh/kg for 95 wt% aluminum, the cost per kWh reaches $0.078. This analysis can be compared to gasoline at $3.50 per gallon which has a cost per kWh of $0.10.

Since 1 kg of this alloy can theoretically produce up to 0.106 kg of hydrogen gas, we arrive at a cost of approximately $6.04 / kg H_2, which compares nicely to the DOE system cost target of $67/kg H_2 by 2015 featured in table 1.

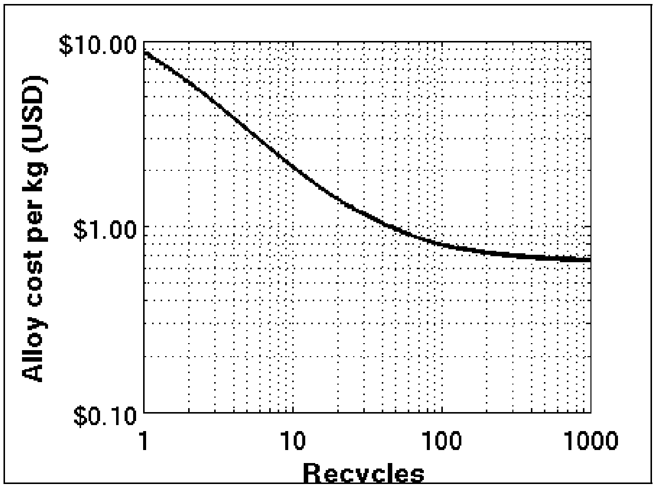

Figure 1: Amortization of materials.

6 KINETICS STUDIES

We have constructed an experimental setup designed to capture the hydrogen produced by the alloy-water reaction and measure the quantity of hydrogen produced as a function of time. Currently, we have plotted these curves for our 50 wt% aluminum sample, and hope to extrapolate rate constants from these curves in the near future. We then plan to move on to study the 95 wt% alloy in detail, as this is the more economically viable of the two alloys.

Figure 2 shows the volume of hydrogen produced at standard pressure and temperature from a 0.102 gram sample of 50 wt% aluminum alloy as a function of time.

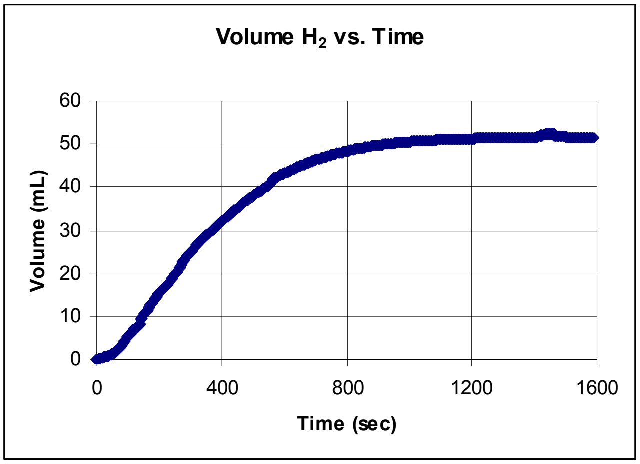

Figure 2: Hydrogen yield as a function of time

In this plot, 72% of the theoretical yield for the alloy was produced within the first 20 minutes of reaction. In many of our trials thus far, the reaction of this alloy goes to 100% after waiting a sufficient length of time. We expect to improve upon these rates as we improve our understanding of the microstructure of these alloys and the associated underlying mechanics of the alloys' reaction with water.

7 CONCLUSIONS

High wt% aluminum alloys show great promise as an energy storage material. The volumetric and gravimetric hydrogen content of the alloy-water system is sufficiently high to merit continued study and characterization of its properties. Furthermore, the ability to make the process very cost effective by means of recycling and reusing the waste products makes an aluminum-enabled hydrogen economy financially feasible while simultaneously making it sustainable.

REFERENCES

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