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Hydrogen Generation Through Aluminum, Aluminum Alloys In Aqueous Solution

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Abstract : Hydrogen has been identified as an alternative to substitute the non-sustainable fossil fuel. Ongoing research is underway to develop environmentally friendly and economical hydrogen production technologies that are essential for the hydrogen economy. One of the promising ways to produce hydrogen is to use aluminum or its alloys to reduce water or hydrocarbons to generate hydrogen. In the present work production of hydrogen using aluminum and aluminum alloys (Al/Si) with aqueous alkaline solutions has been performed. Effect of aluminum concentration, aluminum alloy concentration, corrosion time and pH on generation of hydrogen has been studied. SEM is used to study the changes in surface properties of metal occurring due to corrosion. The obtained result shows that Al/Si alloy produces more hydrogen than aluminum, although with a low reaction efficiency reaching a hydrogen production yield upto 14 % at pH 12. In principle, this method does not consume alkali because the aluminate salts produced in the hydrogen generation undergo a decomposition reaction that regenerates the alkali. This process is based on aluminum corrosion, consuming only water and aluminum which are cheaper raw materials than other compounds used for in situ hydrogen generation, such as chemical hydrides. As a consequence, this process could be a feasible alternative for CO_2 free hydrogen production for fuel cell application.
Keywords : Hydrogen, aluminum alloy, Al/Si alloy, corrosion.

Introduction

The current fossil-fuel based economy is generally considered unsustainable due to resource as well as environmental constraints. One possible alternative is the development of a hydrogen-based economy, as hydrogen is an abundant and environmentally friendly fuel. However, it should be noted that free hydrogen does not occur naturally, and needs to be generated by various means. Hydrogen should therefore not be considered a primary energy source (eg. coal), but rather, an energy carrier. The need for high pressure storage systems is one impediment to the large-scale utilization of hydrogen as a fuel. The production of on-demand hydrogen, thereby bypassing the storage system requirement, could greatly aid in making the hydrogen economy a reality.

A lot of researchers have recently focused their interests on the generation of hydrogen by the hydrolysis of metal or metal hydrides[1-4,5]. Hydrogen can be generated from hydrolysis reaction through corrosion of active metals such as, Al, Na, Zn, Mg etc. in an alkaline water[3,6,7]. These metals are considered to be one of the most attractive hydrogen production systems at very low cost. Among them, Al is the second most abundant element in the Earth`s crust following silicon, and it is electrochemically very active (EAl3+/Al = -1.66). So, Al can be used as a safe, simple, low-cost, and practical material for hydrogen production.

Production of hydrogen using corrosion produces on-demand hydrogen for fuel cells through the use of aluminum which reacts with water under certain conditions to produce hydrogen using the following reaction.

$2Al + 6H_2O + 2NaOH = 2NaAl(OH)_4 + 3H_2$ (1)
$NaAl(OH)_4 = NaOH + Al(OH)_3$ (2)
$2Al + 6H_2O = 2 Al(OH)_3 + 3H_2$ (3)

This can be used for applications as small as portable handheld devices, onboard generation for vehicles, or as large as a hydrogen refueling center. However, the utilization of aluminum for generating on-demand hydrogen is critically dependent on the control of the rate of hydrogen generation from the reaction. Decreasing the aluminum particle size can result in increased reaction rates due to higher reactant surface area. It should be noted that in general, aluminum-water reactions for hydrogen generation have been extensively studied and reported in literature. However, there is a dearth of literature on the use of aluminum particles at the nano-scale in particular. Experiment were conducted to identify the salient parameters that influence the mixture proportions (Aluminum/Aluminum alloy powder, NaOH, Deionized water) on the properties of low cost hydrogen production through corrosion of Aluminum and Aluminum alloy. Corrosion properties of Aluminum and Aluminum alloy powder or what percentage of corrosion occurred from the reaction was also studied.

Experimental Procedure

Different proportions of materials was added to deionized water and influence of processing parameters i.e. curing time, curing temperature, water content of mixture and corrosion etc. was studied and analyzed. To study the effect of alkaline solution, sodium-based solutions were chosen because they were cheaper as well as more reactive than others like potassium-based solutions. The sodium hydroxide solids were in flakes form (3 mm), with a density of 1.33, 98% purity, and obtained from Finar Chemical Ltd, Ahmedabad INDIA. The sodium hydroxide (NaOH) solution was prepared by dissolving either the flakes or the pellets in water. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, M.

The reactor was a triple-neck 200 ml round-bottomed glass vessel. The reaction was initiated by introducing aluminum and aluminum alloy particles through the central vessel neck into the alkaline solution poured in the vessel from beforehand. After particle introduction, the neck was immediately corked to prevent any gas leakage. Tubing (40 cm length and 8 mm I.D.) inserted in one of the adjacent neck corks routed the evolving hydrogen gas through water bath at room temperature in order to cool it and was collected into an inverted 1000 ml measuring cylinder.

The evolving hydrogen displaced the water in the measuring cylinder, and the changing water level in the measuring cylinder was measured as a function of time. The rate of change of the water level provided an indication of the rate of hydrogen generation from the reaction, and the difference between the initial and final water levels in the measuring cylinder indicated the total hydrogen yield. For experiments using less than 5 ml of solution, the aluminum particles were introduced into the empty glass vessel first, and the alkaline solution was injected into the vessel subsequently.

Solid byproducts of the hydrogen generation reactions were analyzed with Scanning Electron Microscopy (SEM) for crystalline species identification. For SEM analysis of the byproducts, the solid mixture remaining in the reactor was filtered using a vacuum pump and a funnel provided with a filter plate. Solids were dried in an oven at 75 ◦C under air for approximately 24 h to remove humidity.

Result And Discussion

Using the triple-neck glass vessel reactor, multiple experiments were conducted in order to gain familiarity with the reaction under consideration, confirm basic trends described in literature, and draw qualitative conclusions about certain factors affecting the rate and yield of the reaction. 76.7 ml of hydrogen was produced in 15 minutes using 0.1 gm Al powder with water having pH 7.2 at the room temperature (34^oC) (Figure 1). The initial reaction rate was found to be very slow. As the time proceeds, the rate of reaction goes on increasing. The reason behind this result was that rate of corrosion of hydrogen was low initially and as time proceeds, it increases.

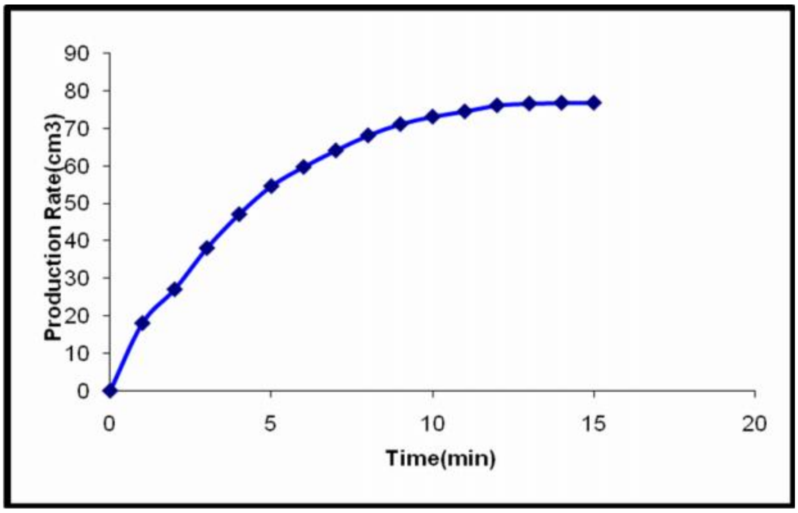


Figure 1: Hydrogen production using 0.1 gm Al powder at pH =7.2.

The characteristic morphology of original Aluminum powder is shown in SEM image Figure (6). It can be seen that it consists of a series of spherical vitreous particle of different size (diameters ranging from 10 µm to 200 µm). Although usually hollow, some of these spheres may contain other particle of smaller size in their interiors. Figure (6) also shows the changes detected in Aluminum powder microstructure after the attack. Some of the reacted Aluminum particles coexisting with the unreacted spheres and even with the particles partially covered with reaction products may be seen in the picture.

Figure (2) shows the rate of hydrogen production using 0.1gm aluminum powder with 75 ml of aqueous NaOH of pH 12.1. Analyzing the above experiment, it may be concluded that the rate of production of H_2 during the first second (i.e.; 0-1) is very high i.e. the rate of corrosion of Al is very high. From first minute to sixth minute, the production rate goes on decreasing after that it increases slightly then again it decreases and after 12th minute, the production remains constant with time. The production rate of hydrogen is about 151 ml in 15 minutes. Figure (6) shows the SEM analysis of the surface after corrosion at pH 12.1.

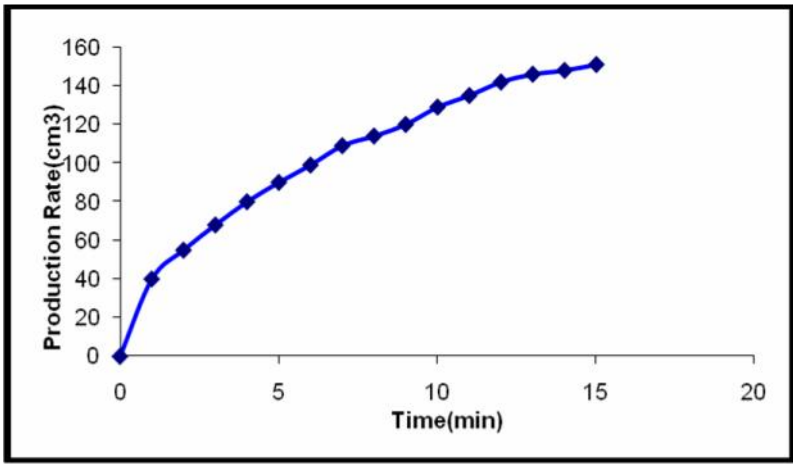


Figure 2: Hydrogen production using 0.1 gm Al Powder at pH 12.1

Figure (3) shows the effect of increase of Al concentration on the amount of hydrogen produced. 0.2 gm of Aluminum powder was treated with 75 ml of NaOH solution at 12.1 pH. Analyzing the above experiment it may be concluded that the initial production rate of H_2 was very high, i.e. 85 ml to 223 ml as time was raised from 1 to 4 minutes. After that it goes on decreasing as the time proceeds. Figure (6) shows the SEM analysis of the present case.

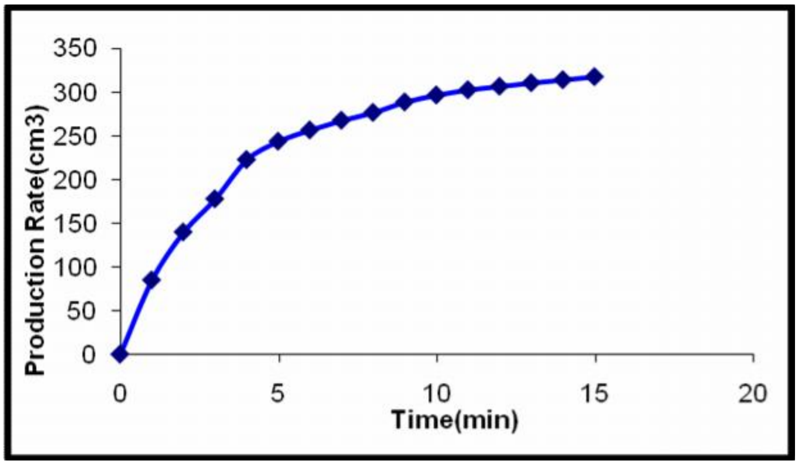


Figure 3: Hydrogen production using 0.2 gm Al Powder at pH 12.1

Figure (4-5) shows the effect of aluminum silicone alloys on the production of hydrogen. 0.1gm aluminum alloy powder was contacted with 75 ml of aqueous NaOH of pH 12.1. It may be seen that the rate of production of H_2 during the first second (i.e.; 0-1) is very high i.e. the rate of corrosion of Al is very high. From third minute to sixth minute, the production rate goes on decreasing after that it increases slightly then again it decreases and after 12th minute, the production remains constant with time. And the production rate of hydrogen is about 476 ml in 15 minutes. SEM Image of surface microstructure is shown in Figure (6). Effect of increasing Aluminum alloy concentration is also reported in Figure (5). It can be seen that the rate of production of H_2 using 0.2gm Al alloy is higher than 0.2gm Al i.e. alloy of Al corrode more than Al. The SEM microstructure is shown in Figure (6).

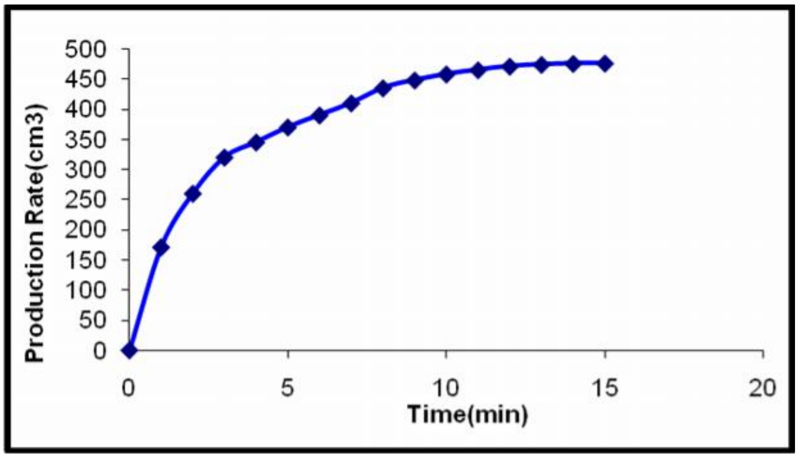


Figure 4: Hydrogen production using 0.1 gm Al Alloy Powder in 75 ml of Aqueous Solution of NaOH

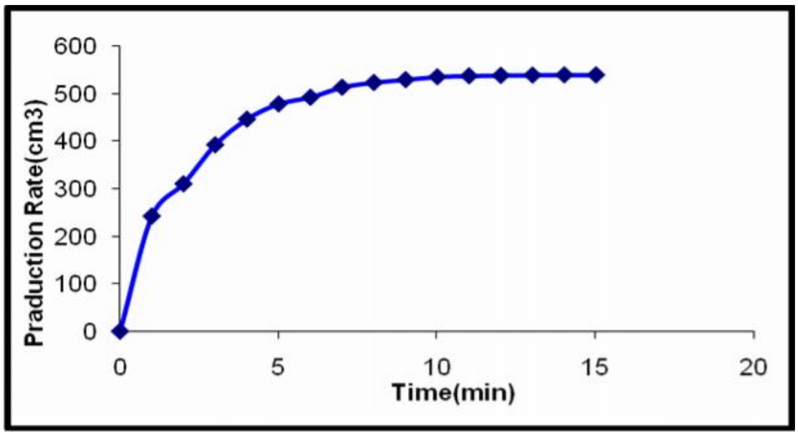
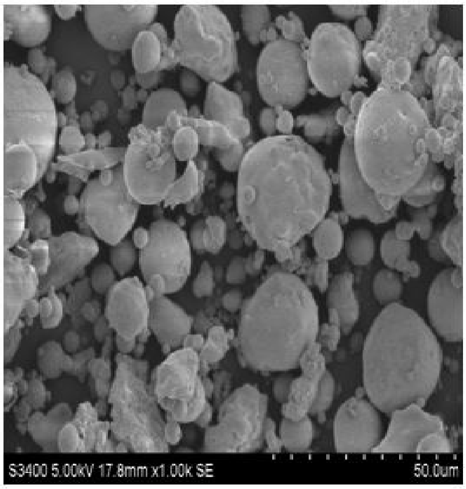
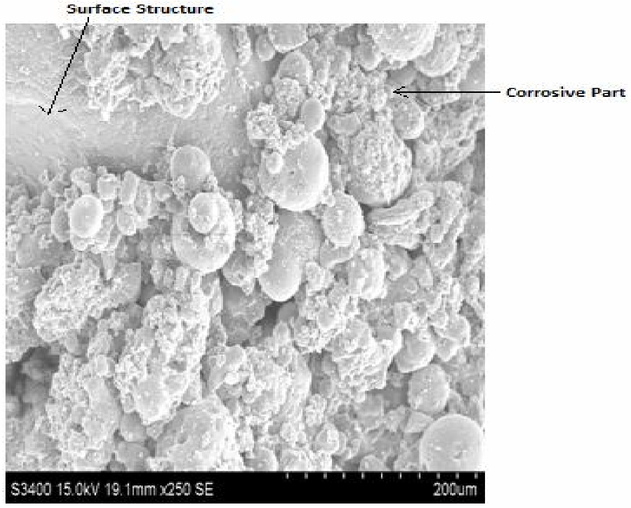


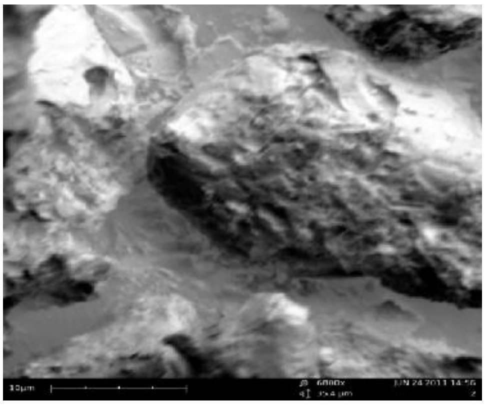
Figure 5: Hydrogen production using 0.2 gm Al Alloy Powder in 75 ml of Aqueous Solution of NaOH



a)



b)



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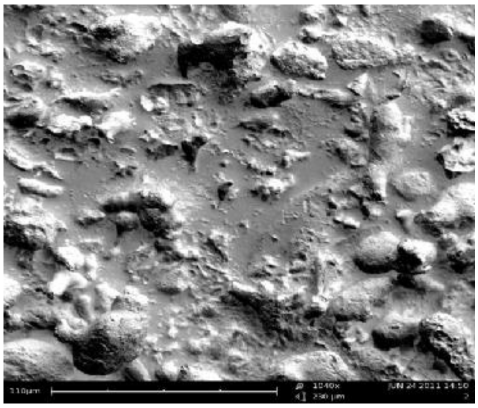
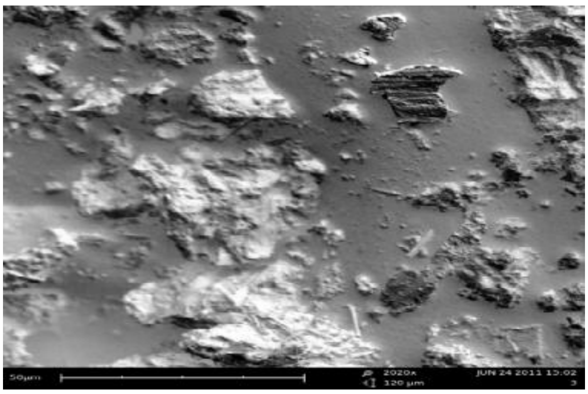
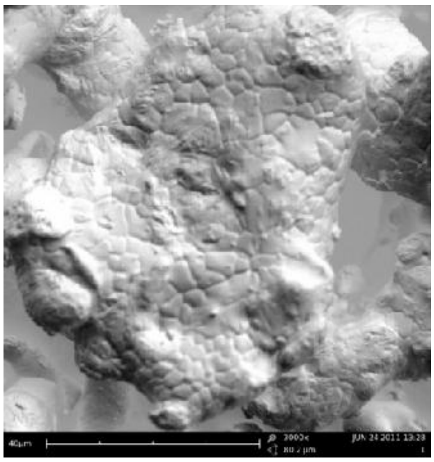


d)



e)



f)

Figure 6: SEM of Microstructures Morphology of Aluminum surfaces (a) As Received fine particles and (b) After leaching with water at pH 7.2 for 15 min (c) 0.1gm Al Leached With aq. NaOH (solution pH 12.1) (d) 0.2gm Al Leached With aq. NaOH (solution pH 12.1) (e) 0.1gm Al Alloy (f) 0.2gm Al Alloy

Table (1) show the overview of the amount of hydrogen produced using various conditions studied in the present paper.

Table 1: Overview of hydrogen production using aluminum corrosion

S.No.	Amt. of Al/Al alloy	pH	Amt. of H_2 (cm^3)
1.	0.1 gm Al powder (only water)	7.2	73
2.	0.1 gm Al powder (Alkaline)	12.1	152
3.	0.2 gm Al powder (Alkaline)	12.1	319
4.	0.1 gm Al alloy powder (Alkaline)	12.1	457
5.	0.2 gm Al alloy powder (Alkaline)	12.1	530

Conclusion

SEM, analysis shows the corrosion in Aluminum and Aluminum alloy by addition of NaOH. SEM analysis gives the microstructure of the surface, which shows the corrosive part of the content. The high activity of aluminum makes it able to extract hydrogen from different sources including water or alkaline water hence, aluminum and it's alloys are rather useful for hydrogen production. Higher pH shows more basic solution, hence better result is obtained at solution having higher pH. Higher quantity of Al alloys gives better result as compare to higher quantity of using aluminum powder because corrosion occurs more in Al alloys solution which produces higher hydrogen rate.

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