Short communication

Hydrogen from aluminium in a flow reactor for fuel cell applications

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Abstract

Aluminium appears to be a promising material for on-board hydrogen generation in fuel cell applications given the comparatively large amount of hydrogen produced per gram of aluminium in a safe system. A microfuel processor with aluminium and water as reactants is developed in a flow reactor for application in portable power sources. Two types of reactor are used. One reactor permits the direct feeding of liquid water in channels containing aluminium pellets, whereas the other utilizes the heat produced from the reaction to vapourize liquid water before entry into the reactor. Two additives, namely, calcium oxide (CaO) and sodium hydroxide (NaOH), are used to enhance the reaction rate. A maximum conversion of 78.6% with respect to aluminium is achieved when the water entering in the reactor is vapourized partially. In the case of liquid water entering the reactor, the conversion is 74.4%.
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1. Introduction

Hydrogen is the best fuel for obtaining high performance from fuel cells. In order to use this fuel in microfuel cells for application in portable electronics, there is a need for hydrogen storage. The problem is that it is difficult to find a way to store or produce sufficient pure hydrogen in the laptop. One could imagine putting a tank of hydrogen in the laptop and refilling it at filling stations, rather like those proposed for cars. In practice, however, the explosive nature of hydrogen rules out this possibility. For example, a laptop with a hydrogen cylinder would not be allowed on an aeroplane. In fact, of possible fuels, so far only formic acid and methanol have been approved by the dangerous-goods committee of the International Civil Aviation Organization for use on aeroplanes and storage in luggage. Therefore, two good options are the installation of a microfuel processor before a microfuel cell that provides the facility to select a fuel (e.g., methanol, ethanol) other than hydrogen without changing the feed (i.e., hydrogen) for the fuel cell, or the direct use of methanol, ethanol and formic acid. The former system requires high temperature to reform the hydrocarbon (e.g., methanol and ethanol) into hydrogen and this makes the sys-

tem complicated and extra power is consumed. The reformate gas also contains about 25% of impurities (e.g., CO_2) and this decreases the fuel cell efficiency. The system also needs some extra time to commence hydrogen production. The direct use of alcohol gives a very low power density in addition to poor kinetics at the anode and a hydrocarbon crossover problem through the membrane. Another possible way to use hydrogen directly in a microfuel cell is to find an effective hydrogen storage material in terms of both volumetric and gravimetric capacity. Some new technologies, such as hydrogen storage in metals and alloys, graphite adsorbents or carbon nanotubes are being explored but they are still far from practical realization [1,2].

Hydrogen production from aluminium can provide an alternative means to produce on-board pure hydrogen for feeding to a microfuel cell [3]. Aluminium offers a promising hydrogen source with high power density as the hydrogen produced per 1 g aluminium is quite high ($0.001245 \, m^3$ hydrogen, which is close to 95% of the theoretical maximum). This method is also suitable as a mode of hydrogen supply in oil refineries in order to reduce CO_2 emission by replacing conventional hydrocarbon reforming, a process that produces 7 tonnes of CO_2 for each ton of hydrogen generated.

Hydrogen is generated through the Al oxidation reaction:

$$Al + 3H_2O \rightarrow Al(OH)_3 + \tfrac{3}{2}H_2 \tag{1}$$
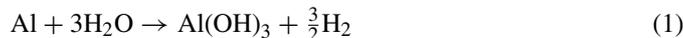
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It is claimed that sodium hydroxide acts as a catalyst as it is consumed in the hydrogen-generating reaction (2) and can be regenerated by reaction (3):

$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2 \qquad (2)$$

$$NaAl(OH)_4 \rightarrow NaOH + Al(OH)_3 \qquad (3)$$
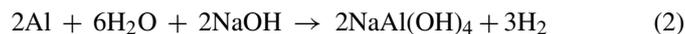
Hitachi Maxell has developed a device capable of generating hydrogen just by mixing Al powder into water [4]. Their main aim was to improve the reactivity of aluminium by using activated fine particles obtained by milling aluminium alloy in water. The activation procedure comprised a thermal shock treatment wherein the fine particles were repeatedly heated and cooled down rapidly followed by storing in refrigerator [5]. This method is intriguing because it requires only inexpensive Al and water, with no catalyst. It is obvious that the particle size is the determining factor for obtaining hydrogen via this route. The advantages of using aluminium powder for hydrogen generation is low cost, high efficiency, pure hydrogen with high humidity, and simple changeability.

There is one report of hydrogen generation from aluminium and water with a high concentration of caustic soda as a catalyst [6]. Aluminium foil, electrical wire, beverage cans and other similar aluminium waste were used as the fuel cartridge. The main disadvantage was the employment of a high concentration of caustic soda which is very harmful to handle. The reaction is also very difficult to control.

In an another attempt, an inorganic salt (e.g., NaCl, NaNO₃, KCl) may be mixed with aluminium to obtain a uniform mixture of powder, which requires little heat to start the evolution of hydrogen and produce hydrogen continuously. The minimum temperature required for this purpose is ~55 °C [7], but it produces hydrogen without adding sodium hydroxide. Kravchenko et al. [8] used aluminium-based composites doped with gallium, indium, zinc or tin in various proportions. In this case, there is no need for other additives like NaOH or inorganic salt. The high reactivity of the prepared alloys with water is due to the presence of dispersed solid phases based on non-equilibrium solid solutions of aluminium and a liquid phase distributed over the grain boundary space. The maximum amount of hydrogen obtained from 1 g of metal composite is 0.001 m³. Fan et al. [9] also used Al alloy with Ga, Sn, In, Zn, Ge, Sb, Mg, Pb and Bi (prepared by mechanical milling) for hydrogen generation in pure water. Among all the above Al alloys, Al–Bi alloy produced 80% of the expected amount of hydrogen. The addition of Zn accelerated the hydrolysis rate of Al–Bi alloy. Soler et al. [10] used commercial aluminium and aluminium alloys with aqueous solutions of different bases (e.g., potassium hydroxide, calcium hydroxide). The maximum conversion of aluminium was 76% in a batch reactor after 100 min that contained 0.21 g of Al/Si alloy in saturated calcium hydroxide solution. Hu et al. [11] reported the evolution of hydrogen from a Ni/Al alloy. The effects of different aspects such as composition and particle size of the Ni–Al alloy, the concentration of the NaOH aqueous solution and the temperature were investigated.

Based on the above literature, it is clear that there has been no attempt to control the flow rate of hydrogen generated from an aluminium–water system. Such control is essential for an on-board hydrogen source for fuel cells in portable electronic devices. The main objective of the present work is to develop an improved system for hydrogen production using aluminium oxidation by water. A flow-type reactor has been used for this purpose. Two different types of reactor configuration and two types of additive (NaOH and CaO) are used in order to control the hydrogen flow rate.

2. Experimental

Fig. 1 shows the experimental set-up of the flow-type reactor. It consisted of one fuel cartridge in which an aqueous solution of sodium hydroxide was stored. Various concentrations of sodium hydroxide were used. In the case of the experiment with NaOH only (where no CaO was used), the concentrations of sodium hydroxide were 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%, respectively, whereas only 5 wt.% of NaOH was used when different amounts of CaO were mixed with Al powder. The aqueous solution of NaOH was pumped via micro-pump (Star Micronics, Japan; model number SDMP 301D) into in the reactor. The liquid feed rate was always maintained at 0.2×10^{-6} m³ min⁻¹. The reactor was made of stainless steel and had three channels. The width of each channel and each fin in the reactor side was 0.012 m and 0.002 m, respectively. The length and depth of the channel is 0.03 m and 0.008 m, respectively. On the vapourizer side of the plate, there were 14 micro-channels. The micro-channels had same dimension (0.001 m) in width and depth of the channel as well as similar width of the fin (Fig. 1b). The channels alignment in the vapourizer side was perpendicular with respect to the alignment of the channels in the reactor side. Aluminium (purity of 99.0%) with a particle size of 200 mesh was purchased from Samchun Chemical. At first, aluminium was palletized by compacting at different pressures using a mould and hydraulic press. The width and length of the pellet is 0.010 m and 0.028 m, respectively. In each pellet, the amount of aluminium or a mixture of aluminium and CaO was always 1.5 g.

One thermocouple of type K at the outlet point inside the reactor was fixed in order to monitor the temperature of the system. The produced gas stream was directed through a cold trap to remove liquid components and then passed to the mass-flow controller (CNL, Korea) for measuring flow. The mass-flow controller was interfaced with a computer in order to record and store the data. The produced gas was also passed through an on-line micro-gas chromatograph for analysis of H₂, CO and CO₂. The micro-gas chromatograph (Varian CP-4900) was equipped with a Molecular Sieve 5A and Porapak Q column and a TCD detector using Argon as the carrier gas.

The conversion of Al or the total evolution of hydrogen/versus the expected amount of hydrogen was calculated based on the point at which the reaction almost stops (i.e., the flow rate of hydrogen was less than 2×10^{-6} m³ min⁻¹). In this case, the theoretical amount of hydrogen produced per gram of aluminium was considered to be 1.245×10^{-3} m³.
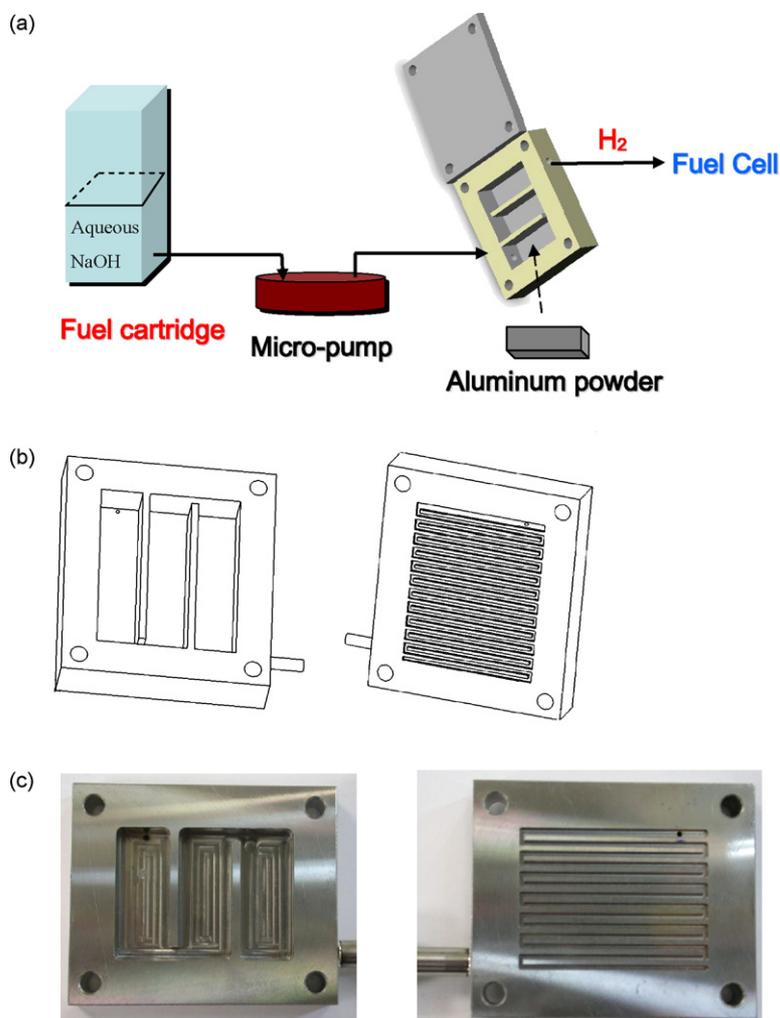
Fig. 1. (a) Experimental set-up with reactor (b) another type of reactor with partial vapourization of aqueous NaOH entering in reactor (c) photograph of reactor side and vapourizer side.

3. Results and discussion

Initially, the calibration was made for the micro-pump (Fig. 2). It was found that the desired flow rate of aqueous NaOH of 0.2×10^{-6} m^3 min^{-1} could be achieved at 80 V (40 Hz frequency). At first, the experiment was made with the reactor where there was no provision of vapourizing the liquid feed. Only one additive (NaOH) was used for the initial phase of the experiments, i.e., the aluminium pellets were made of pure aluminium. Fig. 3 shows one typical curve of hydrogen evolution and the temperature of the reactor with time for 15 wt.% of NaOH and a pelletizing pressure of 1500 kgf cm^{-2}. The reaction rate is very fast (in which the evolution of 30% of the expected amount of hydrogen is released) for about 40 min, after that hydrogen evolution is almost constant. The maximum temperature obtained is 58.2 °C (Table 1). The total evolution of hydrogen is 47.3% of the expected amount of hydrogen with 15 wt.% of aqueous NaOH. The produced gas is 99.1% hydrogen and 0.9% CO_2 obtained from analysis by micro-gas chromatography. The small amount of CO_2 is due to the presence of small amounts of contaminants in the aluminium powder. Fur-
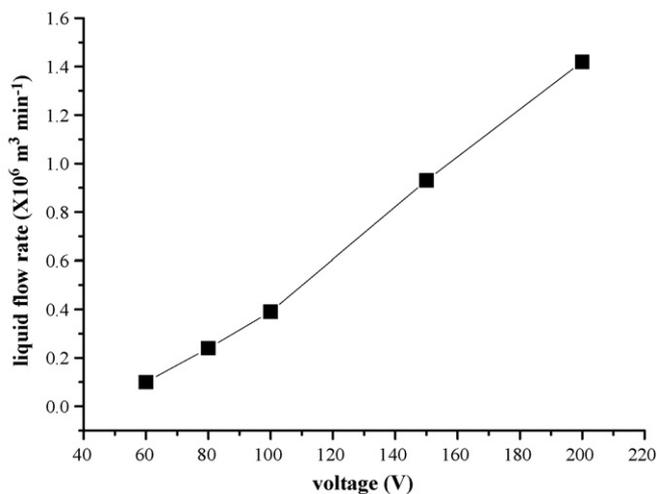

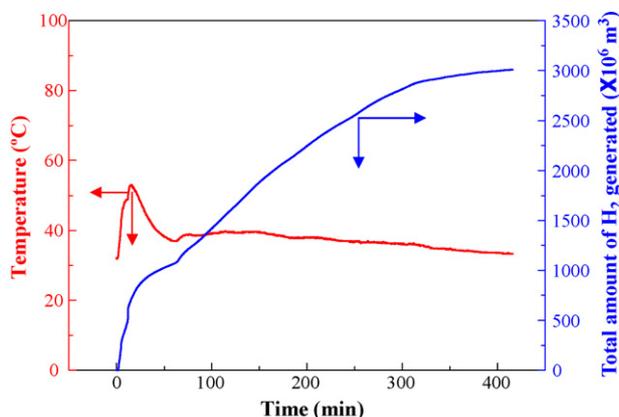Fig. 2. Calibration of micro-pump at different applied voltages at 40 Hz frequency.

Fig. 3. Hydrogen production curve and temperature of reaction (feed rate: $0.2 \times 10^{-6}\,m^3\,min^{-1}$; NaOH concentration: 15 wt.%; pelletizing pressure: $1500\,kgf\,cm^{-2}$).

Table 1
Amount of hydrogen evolved and maximum temperature in reaction of Al with water in various concentrations of NaOH (feed rate: $0.2 \times 10^{-6}\,m^3\,min^{-1}$ and pelletizing pressure: $1500\,kgf\,cm^{-2}$)

NaOH concentration (wt.%)	Total amount of H_2 generation ($\times 10^3\,m^3$)	Maximum temperature (°C)	Conversion (%)
5	1.47	49.7	26.3
10	2.05	52.4	36.6
15	2.65	58.2	47.3
20	1.15	53.7	–

ther increase in NaOH concentration (i.e., 20 wt.%) reduces the aluminium pellets to a powder form (which blocks the channels very easily) and the flow rate of hydrogen is very high for a few seconds which is not possible to measure. The addition of CaO to the Al powder before pelletizing enables the system to handle of low concentration of NaOH. Various proportions of CaO were added to the Al powder (Table 2). The maximum conversion of Al is 74.4%, which is far better in comparison with the value obtained without using CaO at the same pelletizing pressure. This conversion is achieved at a feed rate of $0.2 \times 10^{-6}\,m^3\,min^{-1}$ with a 5 wt.% aqueous NaOH solution. The pellets were formed with a CaO:Al weight ratio of 0.5 and a pelletizing pressure of $1500\,kgf\,cm^{-2}$. The maximum

Table 2
Amount of hydrogen evolved and maximum temperature in reaction of Al with water after adding of various amounts of CaO to Al powder during pelletization (feed rate: $0.2 \times 10^{-6}\,m^3\,min^{-1}$; NaOH concentration: 5 wt.%; pelletizing pressure: $1500\,kgf\,cm^{-2}$)

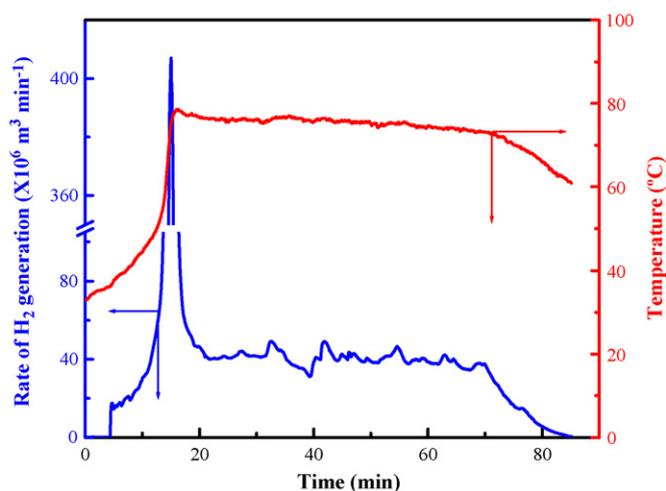| CaO:Al weight ratio	Total amount of H_2 generation ($\times 10^3\,m^3$)	Maximum temperature (°C)	Conversion (%)
0	1.47	49.7	26.3
0.1	3.22	74.6	63.3
0.3	2.82	81.1	65.4
0.5	2.78	84.5	74.4

Fig. 4. Rate of hydrogen evolution and temperature of reaction with feed rate of $0.2 \times 10^{-6}\,m^3\,min^{-1}$, 5 wt.% concentration of NaOH, CaO:Al weight ratio of 0.1 and pelletizing pressure of $1500\,kgf\,cm^{-2}$.

temperature obtained in the reaction is also high due to high exothermicity of the reaction between CaO and water to form $Ca(OH)_2$. Further increase in the amount of CaO in the Al powder increases the rate of reaction, which is difficult to control. It is also found that as the CaO proportion is increased in the Al:CaO mixture, the maximum reaction temperature is also increased. CaO helps to enhance the reaction rate of Al with water. As aluminium oxidizes, a skin of oxide layer forms on its surface and prevents further contact between aluminium and water. Once contacted with water, CaO causes a very substantial increase of pH (i.e., creates an alkaline environment) which stimulates the corrosion of Al with an accompanying release of hydrogen, because the oxide layer is being dissolved at the surface in alkaline environment. More importantly, CaO powder has a non-hygroscopic nature which makes it possible to mix in aluminium powder very efficiently and to store the mixture of Al and CaO for a long time. Fig. 4 shows the hydrogen evolution rate with CaO/Al pellets in a weight ratio of 0.1 where the pellets were made under a pressure of $1500\,kgf\,cm^{-2}$. Initially, the flow rate of hydrogen rises to a very high value for about 20 min. After that, the flow rate is constant at $40 \times 10^{-6}\,m^3\,min^{-1}$ for about 50 min. The uncontrolled flow rate at the initial point may be due to non-uniform exposure of the water phase on the aluminium pellets for entering the feed in the reactor as liquid phase. Table 3 shows the conversion of aluminium at different pelletizing pressures. It is interesting to note that the applied pressure

Table 3
Amount of hydrogen evolved and maximum temperature in reaction of Al with water at different pelletizing pressure (feed rate; $0.2 \times 10^{-6}\,m^3\,min^{-1}$; NaOH concentration: 5 wt.%; CaO:Al weight ratio: 0.3)

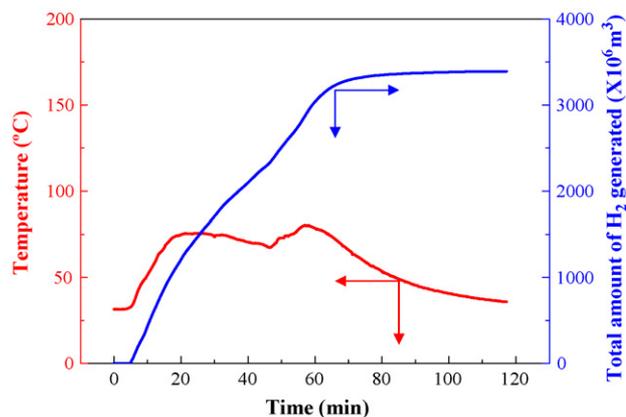| Pressure ($kgf\,cm^{-2}$)	Total amount of H_2 generation ($\times 10^3\,m^3$)	Conversion (%)
1000	2.56	59.4
1500	2.82	65.4
2000	3.17	73.5
2500	2.91	67.5

Fig. 5. Hydrogen evolution profile and temperature of reaction with time at feed rate of $0.2 \times 10^{-6} \, m^3 \, min^{-1}$, 5 wt.% concentration of NaOH, CaO:Al weight ratio of 0.3 and pelletizing pressure of 1500 kgf cm^{-2} (conversion of aluminium: 78.6%).

has a profound effect on the conversion of aluminium. This is mainly due to variation in the pore size of the pellets at different applied pressures. There should be one optimized pressure where the pore size does not prevent blockage the reactant (i.e., aqueous NaOH) to the next layer of the aluminium pellet after reaction of the first layer to form Al(OH)$_3$ and the pellet should not make powders easily during the reaction. Table 3 shows the optimum applied pressure of 2000 kgf cm^{-2}. In this condition, the hydrogen flow rate is comparatively uniform. There was also an attempt to quantify the production of hydrogen without using NaOH solution (i.e., only flow of water) in a mixture of Al and CaO. Initially, it starts hydrogen production as CaO reacts to form Ca(OH)$_2$ and, consequently, increases pH. In this case, the hydrogen evolution rate is very small from a mixture of CaO and Al (weight ratio of 0.5). This is due to the possible formation of an insoluble compound such as Ca$_2$Al(OH)$_7$·2H$_2$O or Ca$_3$Al$_2$(OH)$_{12}$, which hinders the access of hydroxide to the oxide layer covering the metallic aluminium surface. Further increase in the amount of CaO in the Al/CaO mixture increases the rate of hydrogen evolution, but it is a very uncontrollable and high temperature operation and the total conversion is low.

It should be mentioned that all the above results were obtained from a reactor where there is no provision for vapourizing the liquid feed (Fig. 1a). In the next step, a new design of reactor is used (Fig. 1b and c) where there is a provision of preheating the aqueous NaOH solution before coming into contact with Al/CaO pellets. This preheating is made possible by utilization of the heat produced by the reaction of water with Al/CaO itself. The hydrogen evolution is more uniform compared to previous experiment (Fig. 3), as shown in Fig. 5. The maximum conversion of Al is also higher (78.6%) compared with the conversion achieved in the previous reactor under at any condition. The partial vapourization of aqueous NaOH makes the reactants more

uniformly distributed over the pellets and increases the penetrating capability of the reactants inside the pellets from the Al(OH)$_3$ layer to the fresh Al particle. In order to obtain a more uniform flow of hydrogen production with time, there is further work in progress to make pellets with interior cracking and the use of a heater for complete vapourization of the liquid feed.

4. Conclusions

A hydrogen-generating system for portable PEMFCs has been developed by using a flow-type reactor in which aluminium and water are used as fuels. By adding NaOH to the water and doping a promoter material (CaO) into the aluminium, the reaction rate as well as the total amount of produced hydrogen is increased because of chemical etching by NaOH and CaO. For liquid feed entering in the reactor, the conversion is 74.4%. The combination of the two additives (CaO and NaOH) is more efficient for obtaining maximum conversion of aluminium. Hydrogen can be generated constantly through the improvement of design of the reactor. One type of reactor has the provision of partial vapourization of the reactor feed before entry into the reactor. Considerable progress has been made in terms of conversion and flow uniformity by using this reactor. A maximum conversion of 78.6% is achieved. Further work is in progress to attain more uniform hydrogen production.

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