

Aluminum-Based Hydrogen Generator for a Mini-Type Proton Exchange Membrane Fuel Cell with an Innovative Flow Field Plate

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An orientation-free mini-type hydrogen generator, which produces high purity hydrogen from a chemical reaction between aluminum and a sodium hydroxide (NaOH) solution, is designed and fabricated with an innovative perforated flow field plate and tested for a range of related parameters. An examination of the effects of the solution concentration and feeding rate, the initial temperature of the sodium hydroxide solution, as well as the open hole ratio of the perforated flow field plate on the PEM fuel cell performance, is quantitatively made. The results indicate that, with a suitable open ratio of the perforated flow field plate, there is a substantial increase in fuel cell performance, in terms of power density, limiting current density and cell impedance, as compared to previous studies. It is found that the maximum power density can reach to 75 mWcm^{-2} and the limiting current density is up to 375 mAcm^{-2} at optimum condition for the present aluminum-based hydrogen generator coupled with a PEM fuel cell.

Keywords: Mini Hydrogen Generator, Proton Exchange Membrane Fuel Cell, Aluminum, Sodium Hydroxide.

1. INTRODUCTION

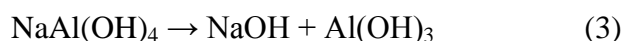
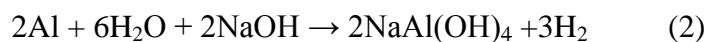
Due to the depletion of fossil fuels, especially oil and natural gas, and the concern over carbon dioxide (CO₂) emissions, there is an urgent need for sustainable and clean fuel substitutes for our future energy supply. Hydrogen has been proven to be a promising alternative fuel source because of its high heating value and regeneration capability. In addition, hydrogen has also been found to be the best fuel for fuel cells. On-board hydrogen production has received a lot of attention because it can generate/fuel the hydrogen where/when it is needed. It is long recognized that there are three methods

of hydrogen production on-board; all are through displacement of hydrogen from water. Normally, interaction of activated aluminum and its alloy with water, and hydrogen from sodium borates in the presence of water and corresponding catalysts [1]. Among many fuel cell applications, hydrogen production from a sodium hydroxide-assisted aluminum-water reaction provides possibly the best method to generate hydrogen on-board for a μ PEM fuel cell [2-4], because the aluminum can be found from the recycle soft drink cans and the hydrogen produced is quite high. Today, hydrogen and methanol are mainly used as fuel for portable and micro fuel cells. The former can be achieved via hydrogen production from aluminum to produce on-board pure hydrogen for feeding to a micro fuel cell.

Generally, hydrogen is generated via the aluminum oxidation reaction:



while sodium hydroxide acts as a catalyst as it is depleted in the hydrogen-generating reaction (2) and, most importantly, can be regenerated by reaction (3):



Adding Eqs. (2) and (3) together yields the overall reaction in Eq. (1). Therefore, essentially, only water is spent during the entire process. Owing to the extremely higher corrosiveness of NaOH, producing hydrogen via the above reaction is not recommended for use in vehicles or in household power systems. Except for this major drawback, this method is, thus far, the only way by which the hydrogen yield target of 6.0 wt.% for hydrogen storage systems set by the US Department of Energy can possibly be reached [4].

There is a surprising lack of papers in the open literature available on the change in the anode/cathode flow field plate configuration when anode fuel hydrogen feeds through an aluminum (Al)-based H_2 generator [5-6]. In fact, a special anode/cathode flow field plate design, like the present study using a perforated plate rather than the conventional flow field plate [7-9], could greatly improve conventional fuel cell performance.

In this work, we have proposed a mini aluminum-based hydrogen generator for a PEM fuel cell with a new and innovative (perforated) anode/cathode flow field plate. The main objective was to examine how the cell performance would be improved through such a new/innovative flow plate with an aluminum-based hydrogen generator.

2. EXPERIMENTAL PROCEDURE

2.1 Al-based hydrogen generator and perforated flow plate fabrication

Fig. (1) shows the schematic diagram and prototype of the hydrogen generator used in this study, respectively. Fig. 1(a) presents the front view of the system, and in Fig. 1(b) the decomposition

of the system is schematically illustrated. The hydrogen generator consists of the solution storage tank, and the hydrogen generation container.

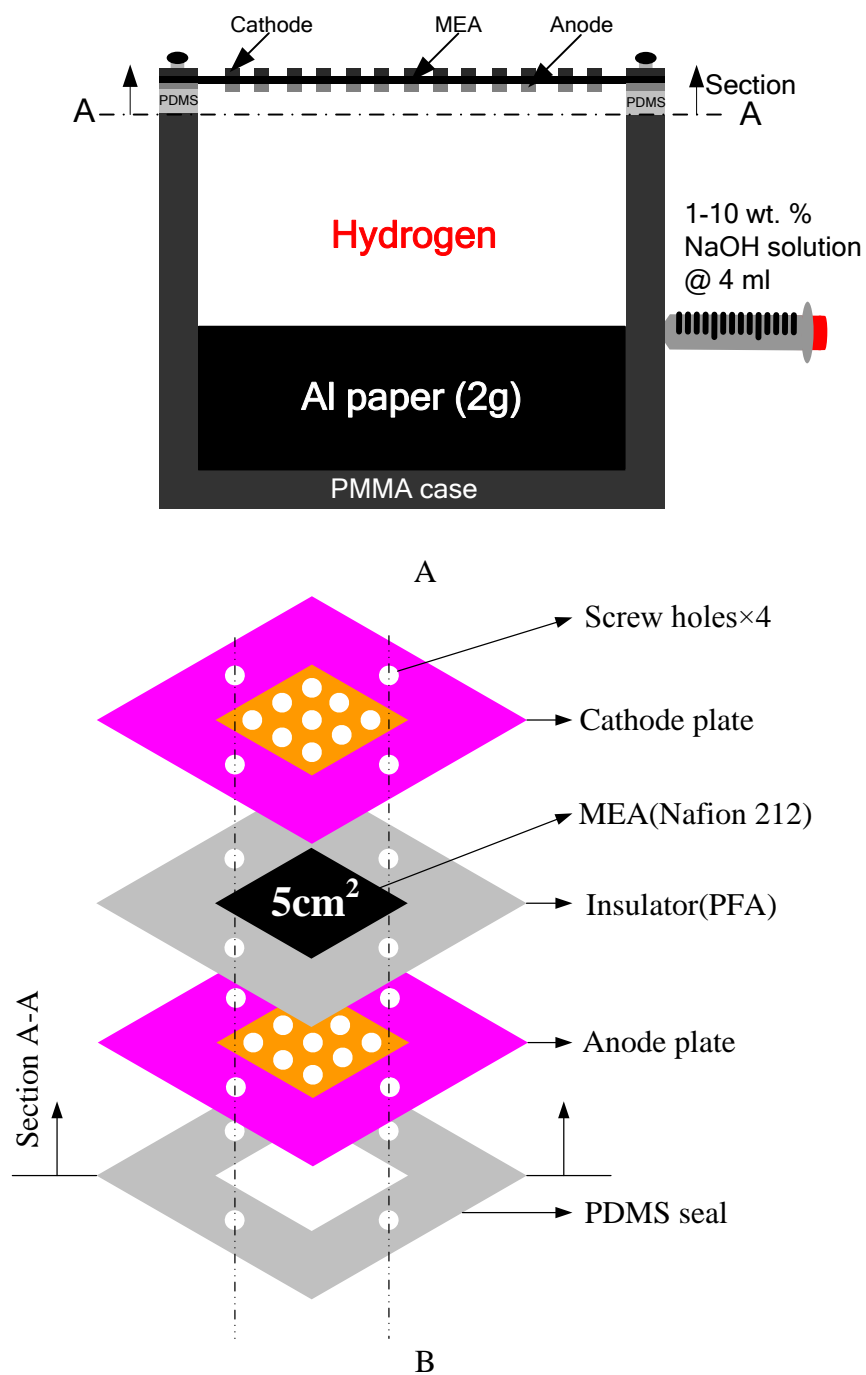


Figure 1. (a) Structure of mini-type PEM fuel cell with hydrogen generator system, and (b) schematic of the present mini-type PEM fuel cell system.

In addition to the above-stated hydrogen generator, the microfabrication of the flow field plate structures, such as the copper sheet flow field plate using deep UV lithography has also been proposed.

SU-8 (2100) materials were chosen for prototyping the perforated geometric structures for the flow path.

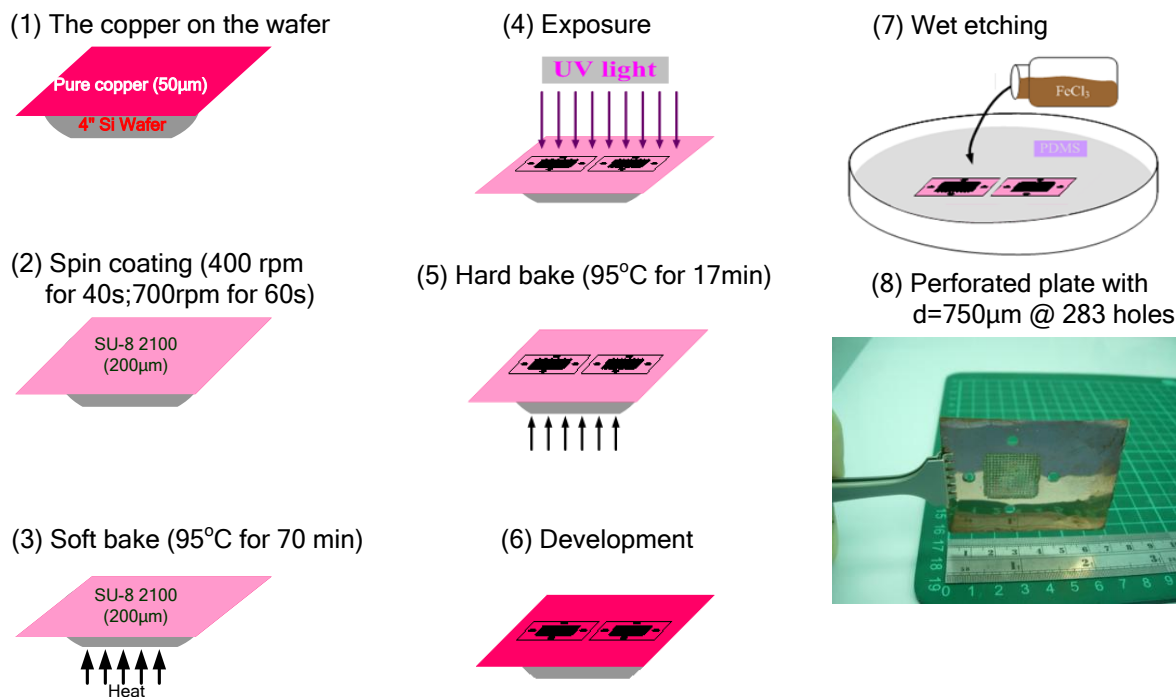


Figure 2. Micro-fabrication processes of the perforated plates.

Table 1. Different hole open ratios arranged in the study.

Perforated holes plates (Both anode and cathode)				
Hole diameter	Open ratio / %	holes		
750 µm	25	283		
	35	396		
	50	566		
Cathode of perforated holes plates (35% @ 396 holes)				
	Case	Open ratio / %	A / mm	B / mm
Anode (One hole)	Case 1	25	11.18	11.18
	Case 2	35	13.23	13.23
	Case 3	45	15	15
	Case 4	50	15.81	15.81
	Case 5	55	16.58	16.58
Anode of perforated holes plates (35% @ 396 holes)				
	Case	Open ratio / %	A / mm	B / mm
Cathode (One hole)	Case 6	25	11.18	11.18
	Case 7	35	13.23	13.23
	Case 8	45	15	15
	Case 9	50	15.81	15.81
	Case 10	55	16.58	16.58

Table 2. Micro fabrication parameters and conditions.

PR coating	SU-8 2100
PR property	Negative
PR type	Thick film
Dehydration bake (°C)	150
Spin coating speed (rpm)	400 (40sec) ; 700 (60sec)
Thickness (µm)	200
Soft bake (95°C) (min)	70
UV light wave length (nm)	365
Light intensity (mWcm ⁻²)	17
Exposure time (s)	35
Hard bake (95°C) (min)	17
Development (min)	3
Etching solution	FeCl ₃ solution
Color	Brown
Sp Gr 15°C/4°C	1.432-1.47
Concentration of FeCl ₃ solution	40-41%

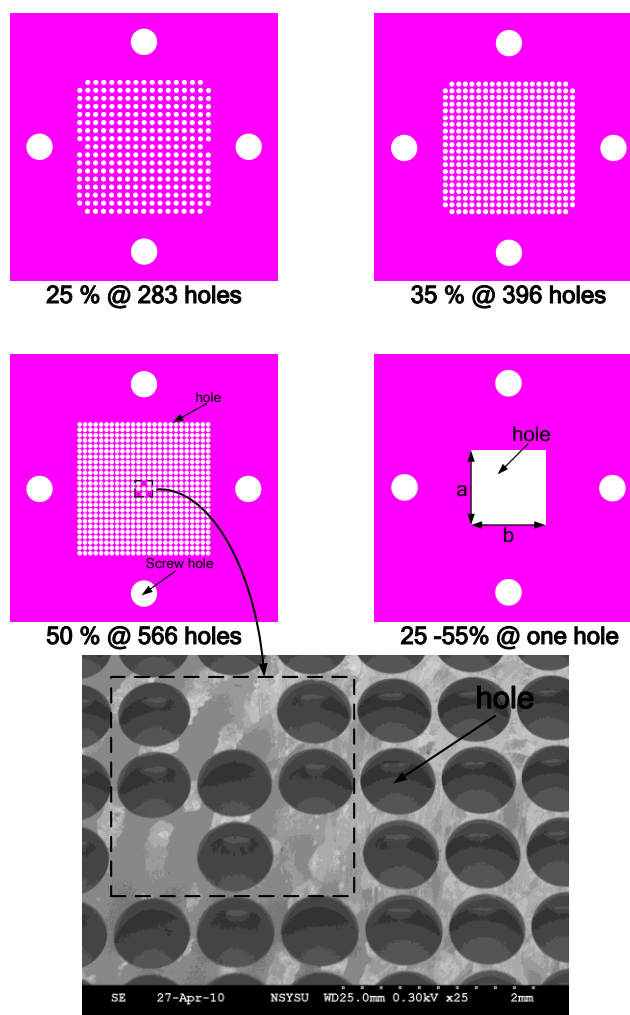


Figure 3. Design of the perforated plates.

As shown in Fig. 2, several different numbers of holes with different sized perforated copper plates were made via wet etching with FeCl_3 with a specific weight of 1.43-1.47 and an average concentration of 4-5% as supplied by Hou Jan Industrial Co. (Taiwan).

The detailed geometric parameters (for instance, the number of holes, open hole ratio, etc.) and fabrication parameters are listed in Tables 1 and 2, respectively. Fig. 2 summarizes and highlights the salient steps in the fabrication sequence of the perforated flow plate. The resultant four different perforated plates, with typical SEM images, are shown in Fig. 3.

2.2 Chemicals

Sodium hydroxide powder was supplied by Kojima Chemical Works Co. (Taiwan). Deionized water was used to prepare all the aqueous solutions in concentrations of from 1~10 wt.%. Pure aluminum thin foils (purity 99.0%), about 10 μm in thickness with a 2.25 cm width and 2.25 cm length, having a varied weight of 0.1 to 2 g, were obtained from Diamond Co. The detailed solution formulas with relevant parameters are presented in Table 3.

Table 3. Specification of hydrogen generator.

Case material	PMMA
Shape size	40 / mm×40 / mm×40 / mm
Internal size	22.4 / mm×22.4 / mm×30 / mm
Active area	5 / cm ²
Chemical reaction of hydrogen production	
NaOH solution	1-10 wt. %
Volume of solution	4 / ml
Aluminum paper	2 / g

The different concentrations with a constant volume of 4 ml of NaOH solution were injected into the reactor (solution storage tank and hydrogen generator) while the system was in operation. The aluminum used was obtained from household aluminum foil and treated with concentrated sulfuric acid to remove the paint and plastic film.

2.3 Test facility and instrumentation

A single PEM fuel cell, with an active area of 2.25 cm x 2.25 cm, was used coupled with the above-stated hydrogen generator. The MEA consisted of an E-Tek Nafion 212 membrane in combination with platinum loading (Lynntech) of 0.5 mgcm⁻² on the anode and cathode, respectively. Two 290 μm carbon papers (ELAT), serving as gas diffusion layers (GDLs), were added into and made part of the MEA. The specifications of the μPEM fuel cell system are listed in Table 4. Fig. 4 shows the experimental set-up that comprised a chemical reaction for hydrogen production with a

PEM fuel cell. Also illustrated in Fig. 4 are the relevant electric load cells (KFM 2150, Ki Kusui, Japan) and instrumentation used in this study.

Table 4. Specification of μ PEM fuel cell system.

MEAs	E-Tek ES12E-W-5L Nafion 212
Anode	Pt on carbon ($0.5 / \text{mgcm}^{-2}$)
Cathode	Pt on carbon ($0.5 / \text{mgcm}^{-2}$)
GDL	
Anode	Carbon paper based material ($290 / \mu\text{m}$)
Cathode	Carbon paper based material ($290 / \mu\text{m}$)
Active area	$5 / \text{cm}^2$
Cell numbers	Single cell
Electrode plates	
Anode and Cathode	Perforated holes plates
Material	Pure copper
Size	$40 / \text{mm} \times 40 / \text{mm} \times 50 / \mu\text{m}$

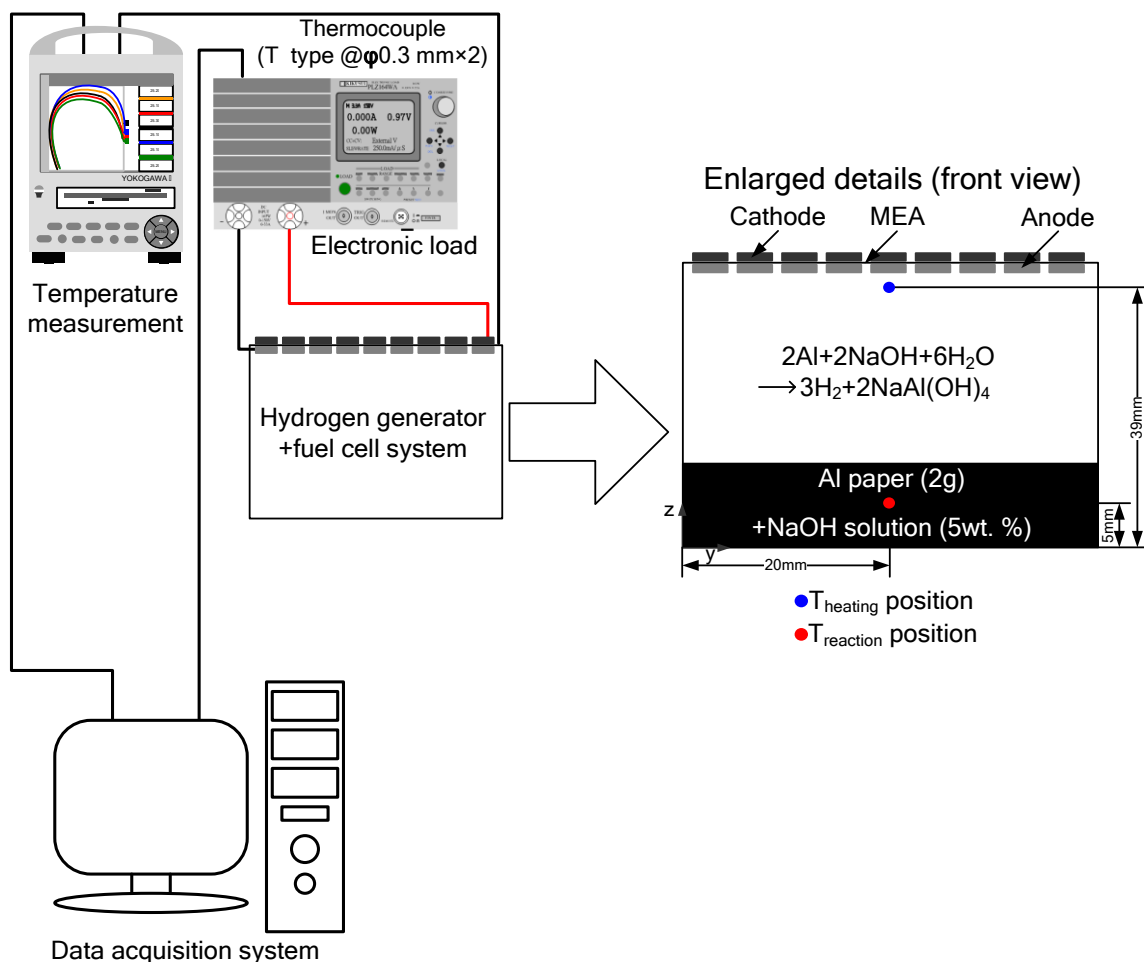


Figure 4. The schematics of the present test loop.

Two 0.3 mm thermocouples of Type T at the hydrogen-generating chamber and solution storage tank, whose relative positions are shown in Fig. 4, were placed in order to monitor the respective temperatures (chemical reaction temperature vs. hydrogen product temperature) of the system. Fig. 4 also shows the flow loop and measuring system for the present system. For generating hydrogen, the sodium hydroxide solution was injected into the storage chamber and the hydrogen-generating chamber, via a syringe pump and a plastic tube, and reacted with the pure aluminum foil, as mentioned previously.

2.4 Calibration and assessment of hydrogen generation

The produced H_2 gas stream was directed through the perforated plate used as an anode/or cathode for the PEM fuel cell. The equipment (not shown), used to quantify the hydrogen production rates and yield separately as a function of time, collected the H_2 gas into an upside-down $2dm^{-3}$ graduated cylinder full of water, which was itself submerged in a container full of water. As the hydrogen gas accumulated into the cylinder full of water, the H_2 gas from the cylinder displaced the water; thus, the volume of H_2 gas produced could be measured.

The generated hydrogen could also be measured by hydrogen pressure gauges (0-10 MPa), and the hydrogen volume was calculated from the equation:

$$V_{H_2} = P_a \times T_1 \times (2050 - V_{al} - V_{water}) / (P_1 \times T_0) [10],$$

where $P_a = 1$ atm (101.35 kPa), $T_0 = 298.15$ K, and T_1 and P_1 are the experimental temperature and pressure, respectively.

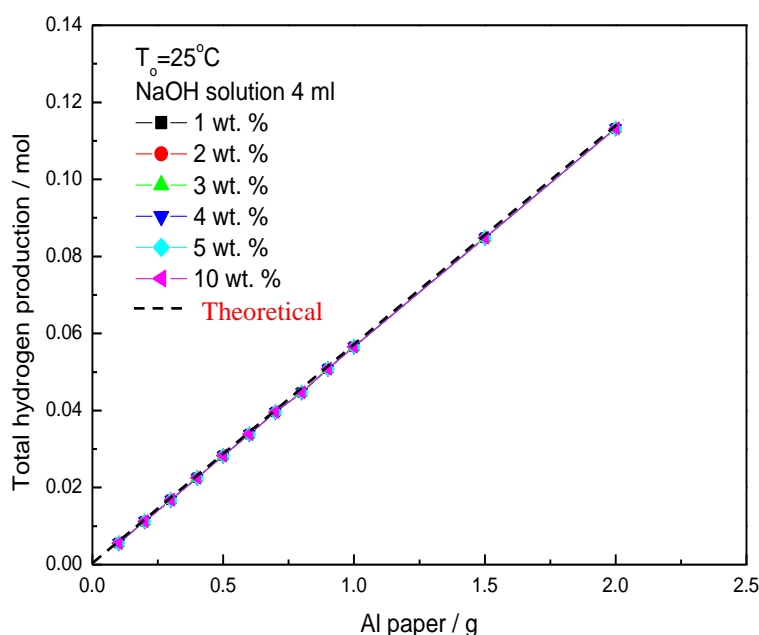


Figure 5. Effect of Al paper weight on total hydrogen production.

V_{al} and V_{water} are given. T_1 and P_1 were obtained by taking an average value by measuring the temperature and pressure near the internal bottom or top of the generator through the two thermocouples and pressure gauges, respectively. In order to secure an optimum operating condition, a set of preliminary tests was made. Through careful examination and analysis, an optimal working condition was found with 4 ml NaOH solution of 5 wt.% concentration for 2 g of household aluminum foil. The results obtained from the preliminary experiments carried out using 2 g of Al foil with a NaOH concentration of 1%–10% at a volume of 4 ml are shown in Fig. 5, along with the results from the theoretical calculations for comparison, and the agreement was good. The volume of hydrogen generated seemed to be independent of the NaOH solution concentration. This result differed from previous studies [5] which found that an increase in KOH concentration produced an increase in the hydrogen production rate. While the production rate increased when the temperature was higher, this may have been due to the low NaOH concentration used in this study as compared to that in Wang et al. [4], in which the hydrogen generation rate was steadily increased by increasing the sodium hydroxide concentration from 9 wt.% to 25 wt.%. The rate of hydrogen conversion generation, based on the aluminum used, was calculated based on the reaction steps, and the volume of hydrogen produced (via collection of hydrogen gas over water) per gram of aluminum was about 1331 ml under the present working conditions.

3. RESULTS AND DISCUSSION

According to the basic chemical reaction in Eq. (1), the products of the reaction include hydrogen and water, as well as heat. During the experiments, hydrogen from the hydrogen generator was fed as the fuel to the perforated flow plate (anode and the cathode) with air as the oxidant. The results obtained on the effects of the parameters used in this study are presented and discussed below. Prior to the formal runs, different placement tests of the system were made and were found to be orientation free (not shown).

3.1 Effect of weight of Al paper and NaOH solution concentration on H_2 generation

Our tests indicated that the hydrogen generation rate increased as the sodium hydroxide solution injection rate increased (not shown). The stoichiometric feeding rate of the NaOH solution was found to be 4 ml for 2 g of aluminum paper, while still meeting the present fuel cell demand. As stated previously, the volume of H_2 produced was about 1331 mlg^{-1} Al with proper corrections for water vapor, which was slightly lower than the theoretical value of 1348 mlg^{-1} Al. The deviation of about 1.3% was due to possible experimental errors. Owing to an exothermic reaction, the reaction temperature of the gas and the solution contained in the chamber increased to about 40°C to 95°C from an ambient temperature of 25°C based on different concentration of NaOH solution. But it will be cooled down to the ambient temperature again after 150 min. Fig. 5 shows the effect of Al by paper weight on the total volume of hydrogen produced. The experimental results seemed consistently lower

than the theoretical values; nevertheless, with such a negligible deviation, they could be considered equal. Furthermore, the concentration of the NaOH solution appeared to have no significance.

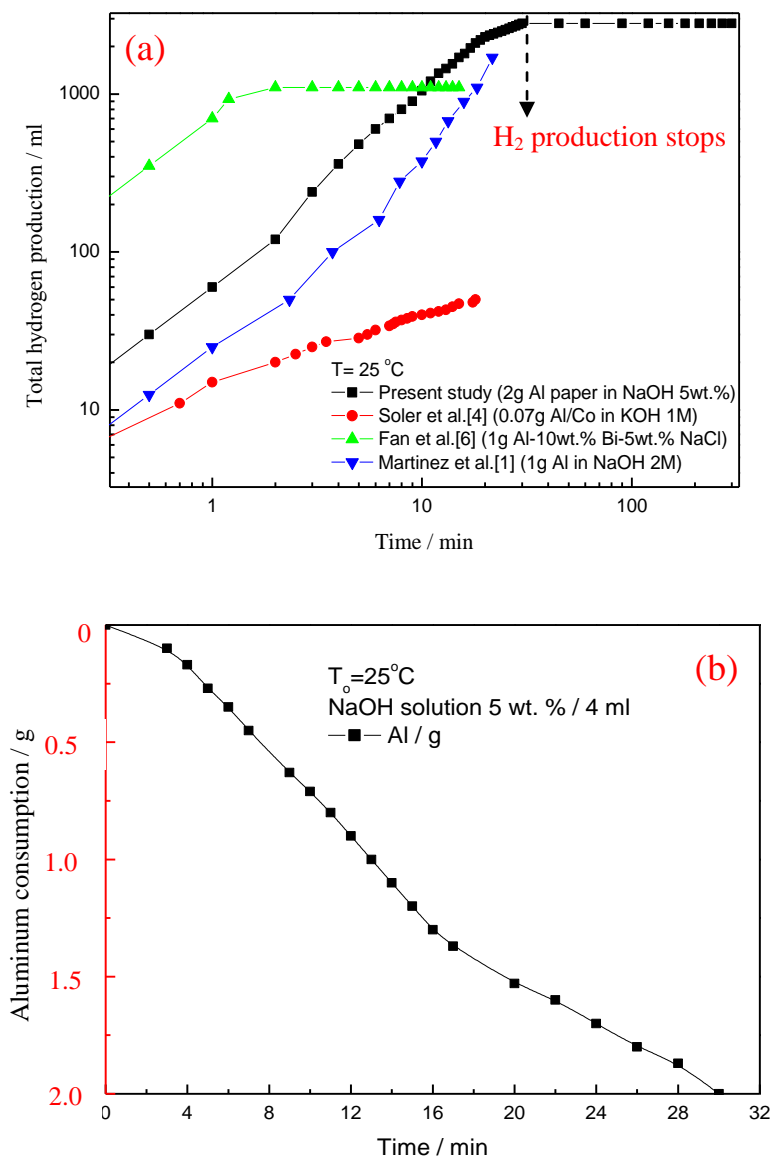


Figure 6. (a) H₂ production vs time (b) Al consumption rate during the H₂ production.

The time history for the hydrogen production is shown in Fig. 6(a), together with previous results from Soler et al. [5], Martinez et al. [2], and Fan et al. [10] for comparison. In the present study it was found that H₂ production would stop after 30 min, which was much longer than in the studies of previous investigators. Strictly speaking, the present results were similar to those reported by Soler et al. [5], although with a much shorter hydrogen production time, but with the same tendency for an increase in H₂ production as time went on until production ceased. A close examination of Fig. 6(b) reveals that the Al consumption obviously decreased over time. Again, it took about 30 min (28 min, in fact) for complete Al depletion. This again verified the results shown in Fig. 6(a).

3.2 Reaction/hydrogen heating temperature

There were two reaction mechanisms involved in the present H₂ product based on the NaOH concentration, as depicted in Figs. 7(a) and (b), respectively.

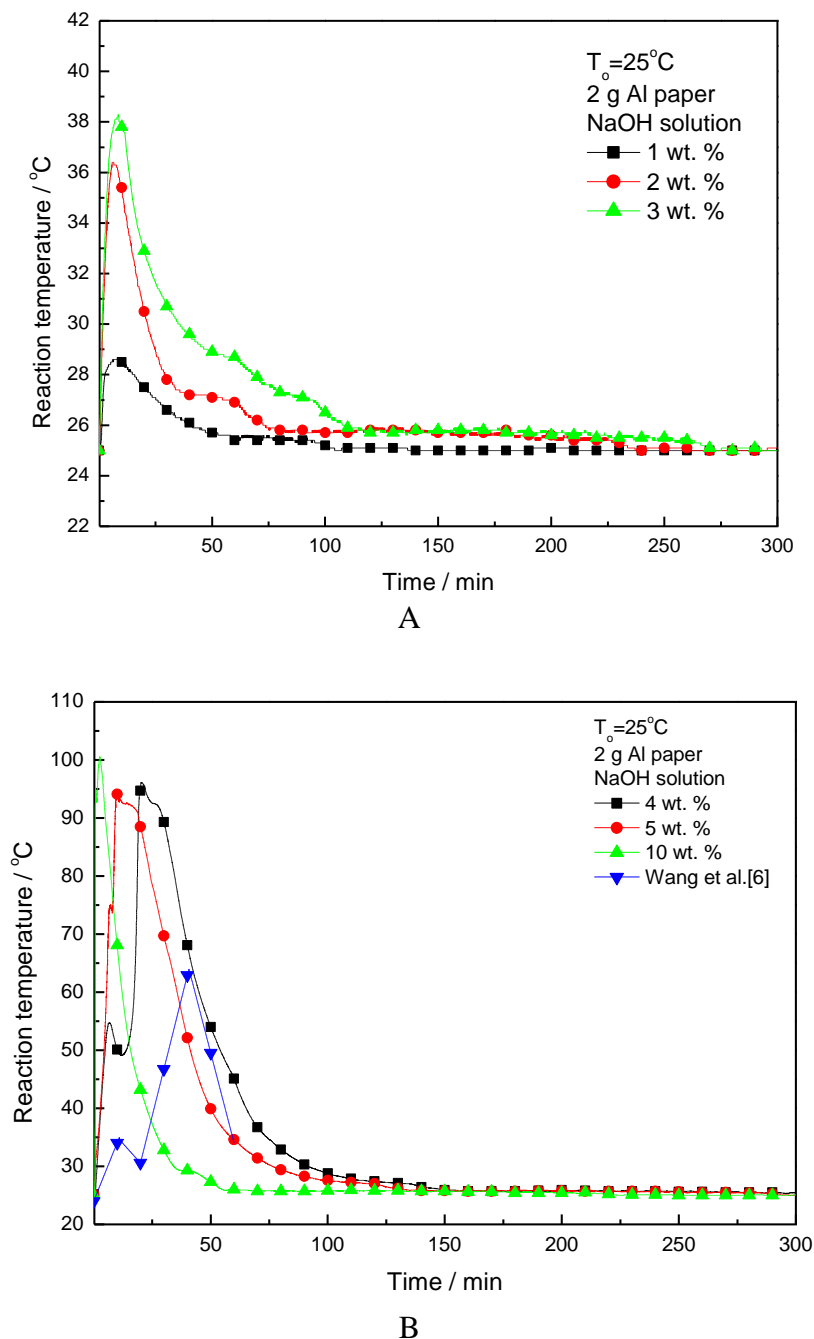
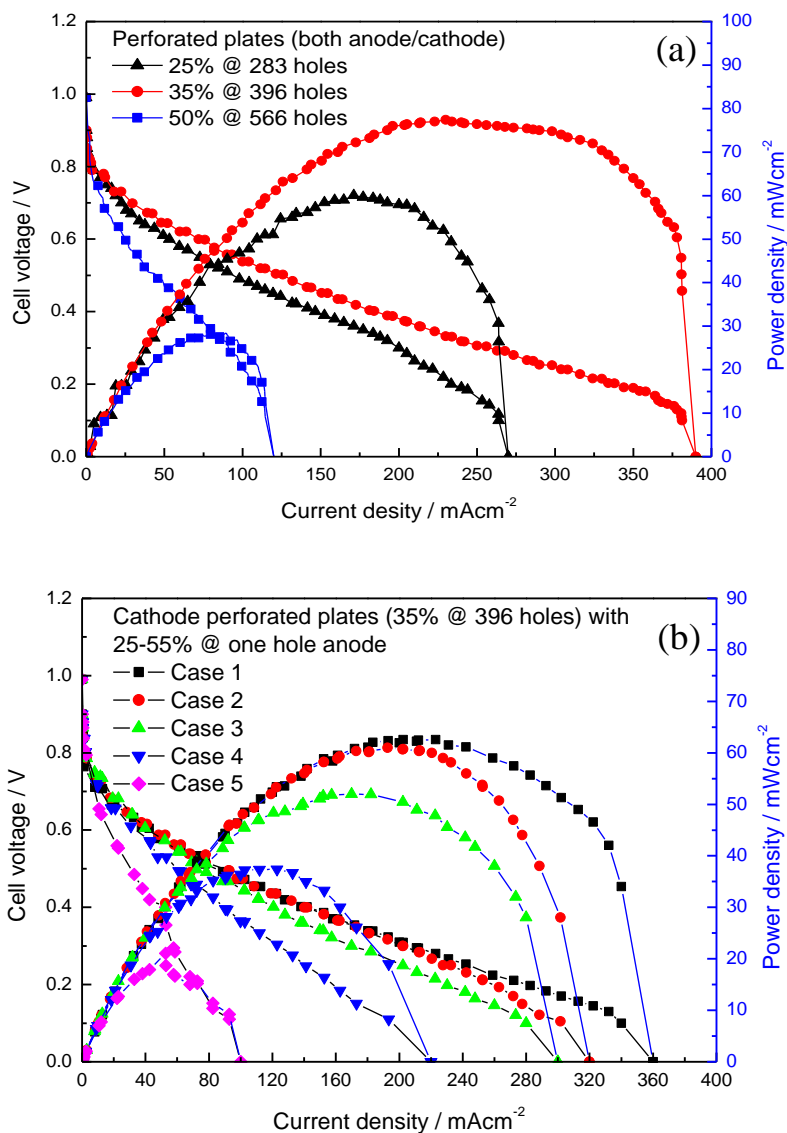


Figure 7. Reaction temperature history (a) NaOH solution 1-3 wt. % and (b) NaOH solution 4-10 wt. %.

Fig. 7(a) shows the hydrogen temperature curves in the hydrogen generator with a 1~3 wt.% NaOH solution at the initial temperature of about 25°C. Clearly, the temperature solution exhibited a

similar trend for the three different weight concentrations of NaOH solution, with a common sharp temperature peak at a different magnitude (e.g., at 38°C, 3wt.% of NaOH solution was found at 10 min), which mainly resulted from a vigorous exothermic reaction of the accumulated NaOH solution towards the beginning, at about 10 min. Then, as the accumulated NaOH solution was depleted, the generator temperature gradually decreased and eventually (about 150 min later) leveled off at about 25°C. On the other hand, with a slightly higher NaOH solution concentration (≥ 4 wt.%), a slightly different NaOH solution temperature history occurred and a double and moderate peak appeared instead of the sharp peak, as in Fig. 7(b). The magnitude of the second peak was much higher than that of the first. A similar situation occurred for Wang et al. [6]. Further inspection of Fig. 7(b) shows that, with a 4 wt.% NaOH solution, the second peak temperature reached 95°C at 25 min (vs 55°C at 10 min for first peak). Compared to the corresponding H₂ production curve in Fig. 6(a), it was found that the H₂ production rate then stabilized and became uniform ($t > 10$ min).

3.3 Single cell polarization curves with perforated flow fields



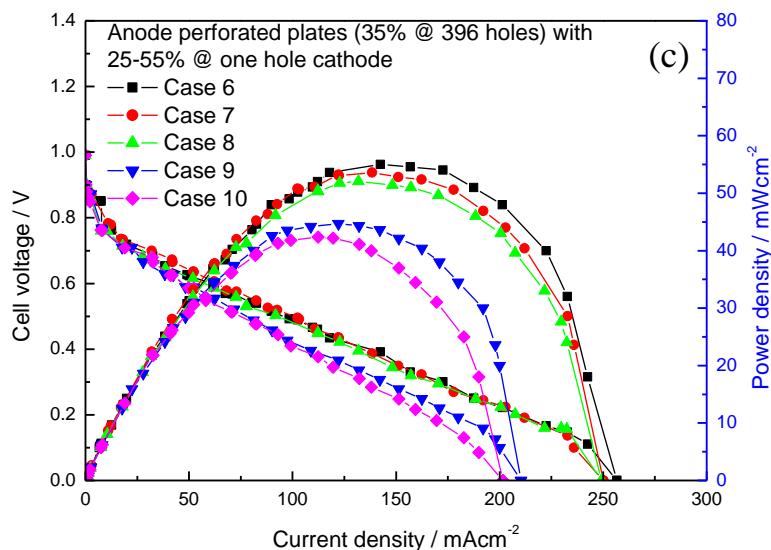


Figure 8. Cell performance of mini-type PEM fuel cell with different open ratio perforated plates.

Under the different flow fields, as listed in Table 1, the single cell performance with different open ratios could be measured (as shown in Fig. 8(a) for both the anode and cathode, in 8(b) for the cathode and in 8(c) for the anode). Basically, the cell performance for the three cases under study was similar. A single cell fuelled by a hydrogen generator in the present study seemed to result in the same performance trend as that of the usual steel conventional bottle with a slightly higher open circuit voltage (OCV) and larger limiting current density. Although we had three different flow field configurations, all the data presented showed a unique result, i.e., that an open ratio of 35% resulted in a superior performance. With both new electrodes (new flow plates design) being used, the limiting current could be reached at about 390 mAcm^{-2} , and the maximum power density of 75 mWcm^{-2} was found at a 35% open ratio of the perforated plate, as depicted in Fig. 8(a). Taking a closeup examination of Fig. 8(a), it was found that the cell had the best performance with an open ratio of 35% on both the anode and cathode. In comparing Figs. 8(b) and (c) it was also found that, with the same open ratio and other parameters, the limiting current density and maximum power density of the cathode's perforated flow plate were greatly improved compared to those of the anode.

Fig. 9 shows the effect of hole pitch of the flow plate on cell performance. Again, it was found that an open ratio of 35% for a 1 mm hole pitch gave the highest maximum power density and limiting current density for both the anode/cathode perforated plates. Based on this plot, an optimum pitch value could finally be found. More data are presented in Figs. 10(a) and (b) from the extensive examination of the effect of the open ratio on cell impedance, limiting current density and maximum power density. Again, it was shown that the lower the impedance, the higher the maximum power density and limiting current density. Furthermore, an optimum open ratio of 35% again occurred at the highest limiting current density and maximum power density, as expected.

Based on the aforementioned VI curve, Fig. 11 shows the cell performance for the previous study [11] and the comparison with the optimum perforated flow field plate of the present study. It is seen that the present design has a quite superior performance in both power density and limit current

density to the conventional PEM fuel cell with a traditional serpentine flow field on both anode and cathode. The present optimum design can reach near 375 mAcm^{-2} in current density and 75 mWcm^{-2} for maximum power density.

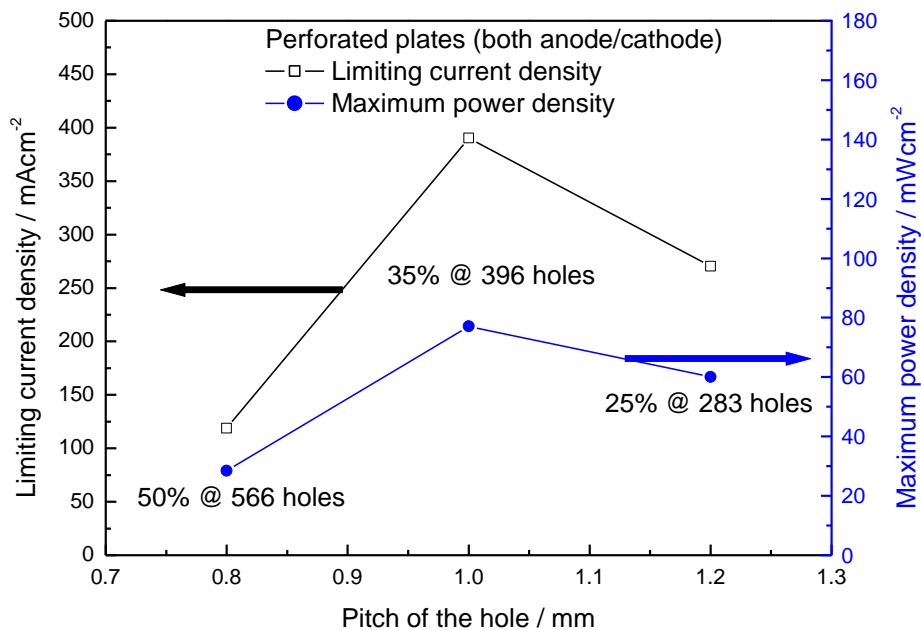
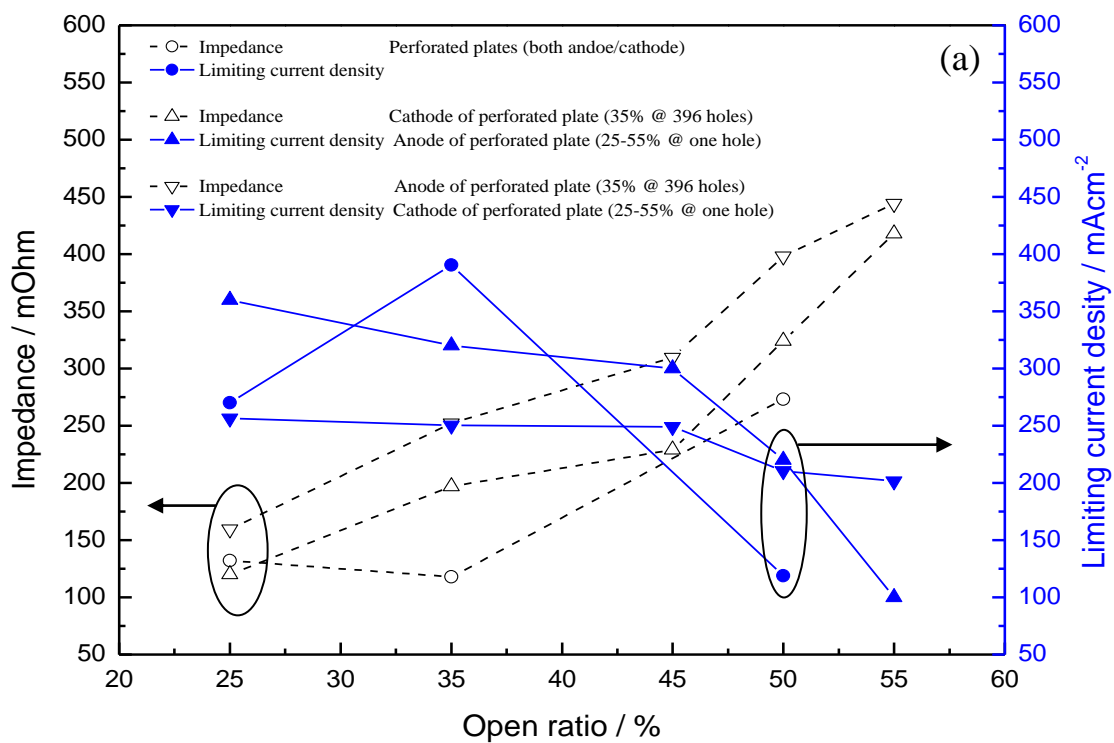


Figure 9. Effect of distance from center of circle to center of circle (pitch) on the limiting current density and maximum power density.



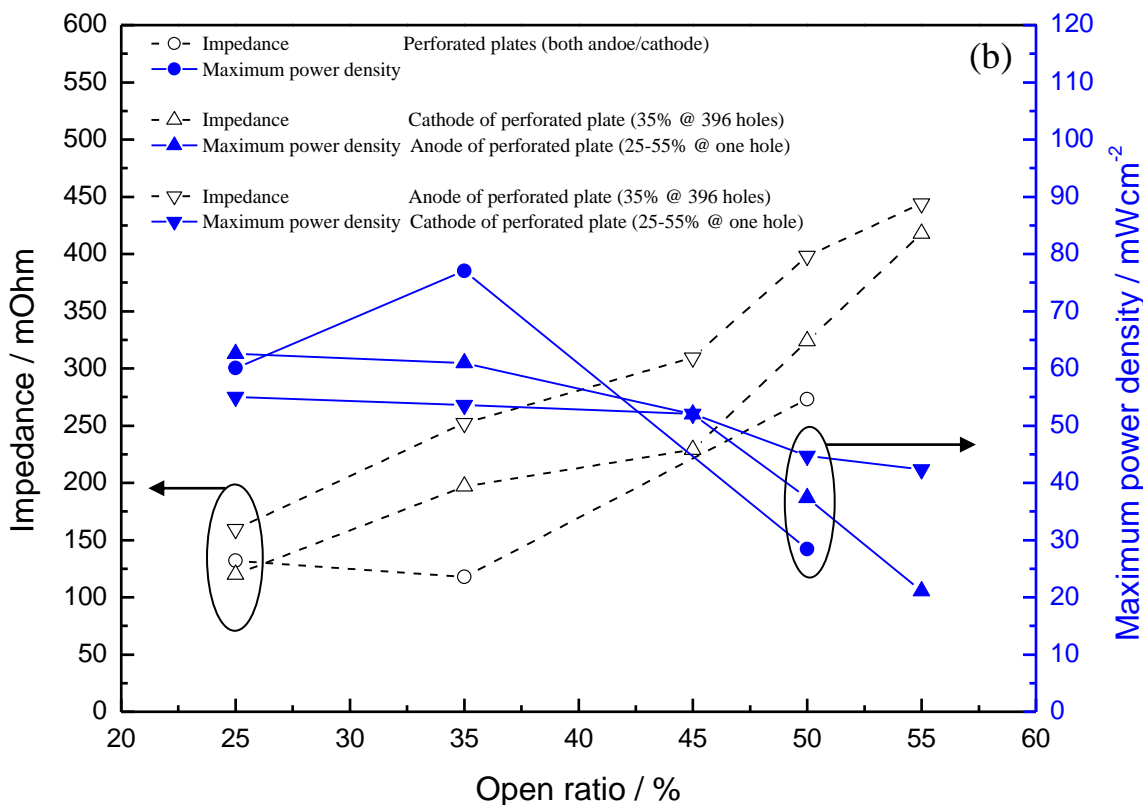


Figure 10. Effect of open ratio on cell impedance, limiting current density, and power density for mini-type PEM fuel cell system.

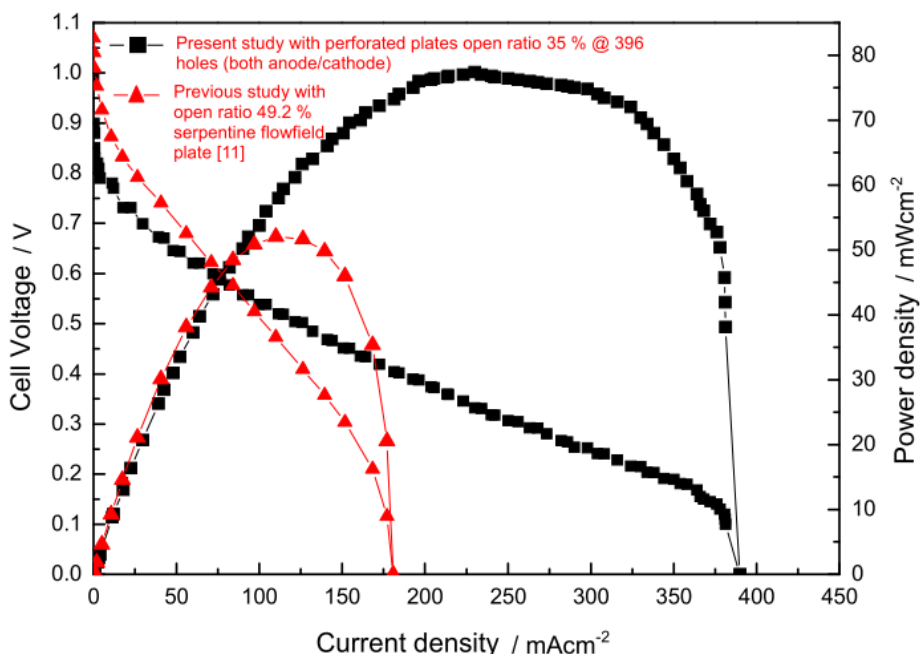


Figure 11. Compare cell performance with different hydrogen generation in the micro PEM fuel cell.

The cell voltage and current evolution curve were plotted against time duration, as illustrated in Figs. 12(a) and (b), respectively, together with the conventional PEM fuel cell results for comparison. Data were recorded at a constant voltage of 0.5 V for voltage vs time and current density vs time under closed circuit condition with an electric load. After about 30 min, the cell voltage ceased to drop

because the limited aluminum was completely depleted, while the conventional PEM fuel cell continued operating, as expected. Still, after 30 min, the present hydrogen generating system had a superior performance in cell voltage or cell current density as compared to the conventional PEM fuel cell [11].

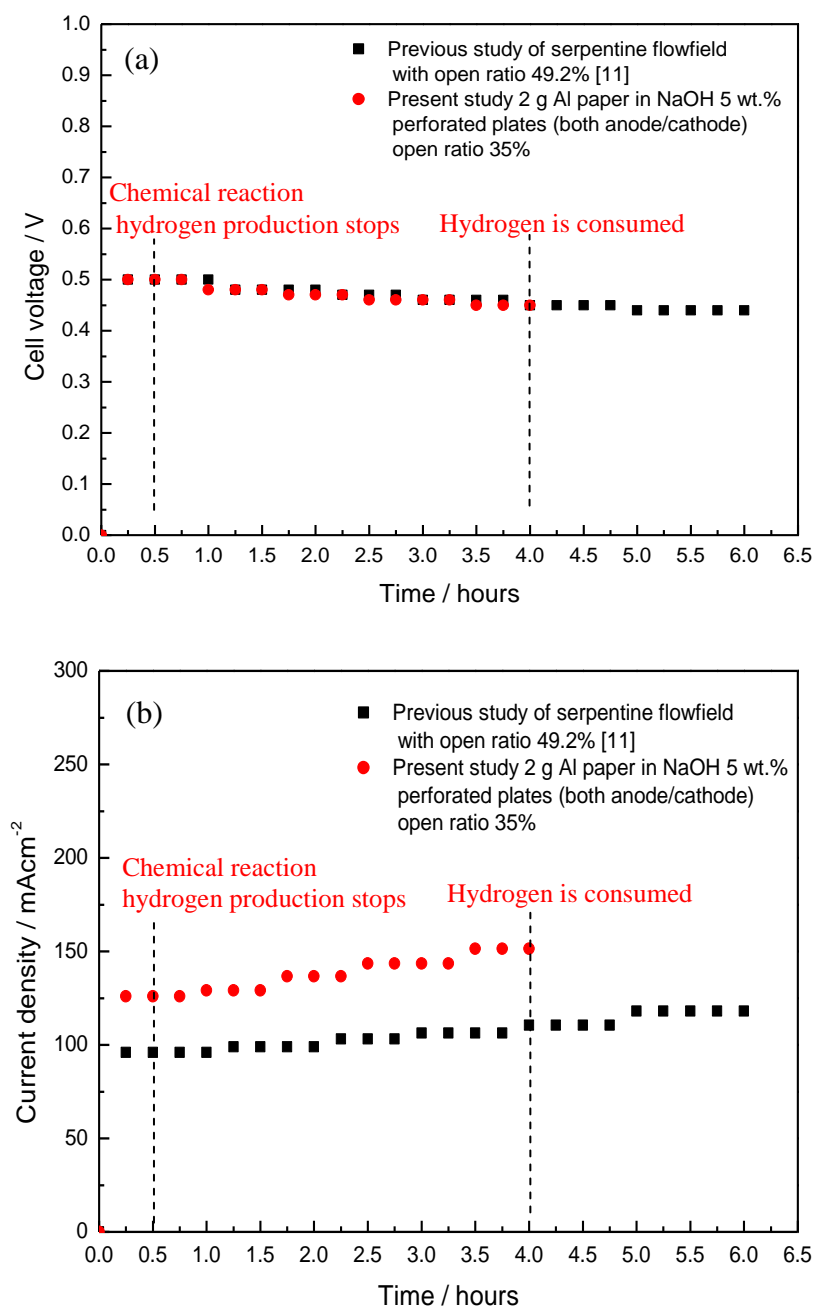


Figure 12. Constant cell voltage 0.5 V as hydrogen is consumed in the PEM fuel cell (a) voltage vs time (b) current vs time.

The foregoing results and discussion have shown that the present hydrogen production system worked well. Once the proper amounts of aluminum (2 g) and NaOH solution (4 ml) of 5 wt.% concentration mixture were fed, it could continue running 4 or 5 h with/without electrical load before

the fuel regenerated. In addition, it was proven that the purity of the H₂ generated in the system was high enough to trigger a mini PEM fuel cell system. With the unique characterization of the recovery and recyclability of the present fuel, the hydrogen production could successfully power a conventional PEM fuel cell with a much better cell performance as compared to the conventional PEM fuel cell with a serpentine flow plate.

3.4 Startup (transient) behavior

The time history of the cell voltage and the current density are significant for the real application of PEM fuel cells, especially during the cell/stack startup. Fig. 11 shows a plot of cell voltage versus current during the startup period ($t \leq 30$ min, this study), and the cell voltage and current time evolution of at least 4 h for the present hydrogen generated case for fuel supplied by hydrogen generator or conventional steel bottle, respectively. Further, as one can see in Figs. 12(a) and (b), the rate of hydrogen depletion was similar for both fuel feedings. In addition, except for the cell voltage (Fig. 11), the current density was about 20% greater than the current obtained from the conventional PEM fuel cell [11]. This is partly because the produced hydrogen has the moisture contained (~30% relative humidity) which helps to keep the polymer electrolyte humidified, and partly because the perforated flowfield plates were used in this study which would enhance the electrochemical reaction of the fuel cell. The detailed behavior with the corresponding operating conditions is shown Fig. 12(b). Based on Figs. 12(a) and (b), it could further be proven that the present mini hydrogen generator, plus a PEM fuel cell, could be operated and run successfully and smoothly. The advantages of this type of PEM fuel cell have also been shown. For instance, and most importantly, the aluminum and sodium hydroxide (NaOH solution) regenerated and was ready for use in the next cycle, and the aluminum could be secured from recycled cans and household aluminum foil.

4. CONCLUSION

A mini-type hydrogen generator, in which aluminum and NaOH solutions were used as fuel and catalyst, respectively, was designed, fabricated and tested, coupled with a PEM fuel cell with an innovative flow plate. Attention was paid to the flow field plate design. In addition, the effect of the system parameters on hydrogen production rates, reaction temperature and cell performance was studied extensively. An optimal perforated open hole ratio (35% for 396 holes) for both the anode and cathode was found to significantly improve the cell performance, especially for the average power density (about 60% increase) and the limiting current density (about 200% increase), with a secured high purity of hydrogen produced. The system operated for 4~5 h each time once fed the proper (2 g aluminum + 4 ml (5 wt.%) NaOH solution in this study) fuel.

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