



Short communication

A mini-type hydrogen generator from aluminum for proton exchange membrane fuel cells

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ABSTRACT

A safe and simple hydrogen generator, which produced hydrogen by chemical reaction of aluminum and sodium hydroxide solution, was proposed for proton exchange membrane fuel cells. The effects of concentration, dropping rate and initial temperature of sodium hydroxide solution on hydrogen generation rate were investigated. The results showed that about 38 ml min⁻¹ of hydrogen generation rate was obtained with 25 wt.% concentration and 0.01 ml s⁻¹ dropping rate of sodium hydroxide solution. The cell fueled by hydrogen from the generator exhibited performance improvement at low current densities, which was mainly due to the humidified hydrogen reduced the protonic resistivity of the proton exchange membrane. The hydrogen generator could stably operate a single cell under 500 mA for nearly 5 h with about 77% hydrogen utilization ratio.

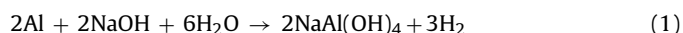
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1. Introduction

The use of fossil fuels, especially oil and natural gas, in recent years has accelerated, which is triggering a global energy and environment crisis. In response to the crisis, fuel cell has attracted much attention due to its high efficiency and low pollution [1,2]. Among the various types of fuel considered for fuel cell, hydrogen is highly desired because hydrogen-powered fuel cells can operate very efficiently with very high power density (Table 1) [3]. However, for applications, especially portable applications, of the hydrogen-powered fuel cells, it is a big challenge to supply hydrogen to the fuel cells safely and economically. Hydrogen storage in tanks, in hydrogen-storing alloys, and on activated carbon or nanoscale materials such as carbon nanotubes, is not suitable for portable applications due to the low volumetric and gravimetric efficiency as well as the associated safety issues [4–7]. Generating hydrogen on-board, instead, is desirable for portable hydrogen-powered fuel cells. Although hydrogen generation from sodium borohydride has recently been explored for fuel cell applications [8–10], deactivation of catalysts, treatment of by-products, high cost and proper control of reaction rates are still possible problems that affect the practical feasibility [11].

Hydrogen production from aluminum provides a promising alternative means to produce hydrogen on-board for portable fuel

cells, because aluminum is relatively cheaper and the hydrogen produced per 1 g aluminum is quite high. By this method, hydrogen was produced through the reaction of aluminum and sodium hydroxide solution:



According to Eq. (1), 1 g aluminum can produce 0.056 mol hydrogen that corresponds approximately to 1.371 hydrogen (at 298 K, 1 atm) [12]. Jung et al. [13] has reported a hydrogen generator from aluminum to supply pure hydrogen to a micro-fuel cell. It is noteworthy, however, that Jung et al. used a micro-pump to pump the aqueous solution of NaOH to the hydrogen generator, which increased the power loss and the complexity of the system, and in addition, replacement of aluminum powders was not quite convenient. For the viable application of hydrogen generator from aluminum for portable fuel cells, a simple and easy-controlled generator has to be developed.

In this paper, a mini-type hydrogen generator was designed and fabricated, aiming at supplying hydrogen to a portable proton exchange membrane fuel cell (PEMFC) conveniently. To lower the cost of hydrogen generation, aluminum alloy with 99% weight percent of aluminum, instead of pure aluminum, was used as the raw material. Due to its quite low cost, the generator can be replaced by a new one when aluminum was completely consumed. Hydrogen generation rate of the generator was automatically controlled by the pressure difference. Firstly, the effects of concentration, dropping rate and initial temperature of sodium hydroxide solu-

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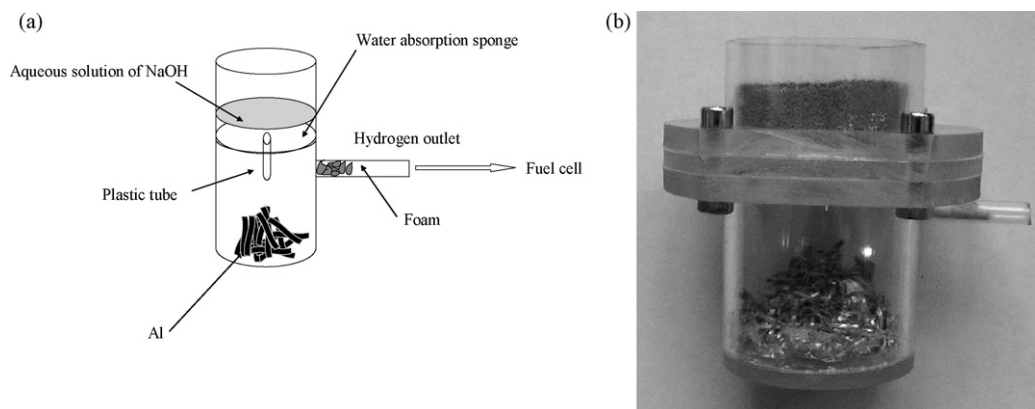


Fig. 1. Schematic diagram and the actual laboratory prototype of the hydrogen generator. (a) Schematic diagram of hydrogen generator and (b) actual laboratory prototype of the hydrogen generator.

tion on the hydrogen generation rate, as well as the temperature variation of the generator during hydrogen producing, were systematically investigated. Then, the hydrogen generator was applied to a portable PEMFC and performance of the PEMFC was evaluated. It was demonstrated that the developed hydrogen generator was suitable for portable fuel cell applications.

2. Experimental

2.1. Working principle and fabrication of hydrogen generator

Fig. 1 shows the schematic diagram and the actual laboratory prototype of the hydrogen generator. The generator consisted of three parts, which were solution-storage chamber, hydrogen-generating chamber and hydrogen-filtering chamber. On the top of the generator, there was a chamber in which an aqueous solution of sodium hydroxide was stored. Below this solution-storage chamber was the hydrogen-generating chamber, where aluminum alloy was stored and hydrogen was produced by the reaction of aluminum alloy and the sodium hydroxide solution provided by the solution-storage chamber. On the upper part of the hydrogen-generating chamber, there was a hydrogen outlet tube called hydrogen filtering chamber, where some foam was placed to prevent the solid products from entering the fuel cell and purify the generated hydrogen.

For generating hydrogen, sodium hydroxide solution was dropped from the solution-storage chamber to the hydrogen-generating chamber via a plastic tube, and reacted with the aluminum alloy. To overcome the effect of liquid gravity on the dropping rate, a porous water absorption sponge was put in the

solution-storage chamber. By this method, sodium hydroxide solution was filled in the pores of the sponge and dropped almost at a constant rate. The plastic tube connected the solution-storage chamber and hydrogen-generating chamber was thin with the inner diameter of 0.5 mm. In addition, the two ends of the tube were cut into sharp tines which could reduce the effect of liquid surface tension and guarantee the sodium hydroxide solution to drop continuously. Aluminum alloy used in the hydrogen generator was in the form of rods which were obtained by wringing together some aluminum alloy strips with about 0.3 mm thickness, 1 mm width and 20 mm length. All the aluminum alloy rods were bundled at one end using a rubber ring, and the bundled end was towards the plastic tube. By this means, nearly all the aluminum can be reacted as the sodium hydroxide solution dropped on the surface of the bundled aluminum rods. Fig. 2 shows the appearances of aluminum alloy strips and the reaction product after hydrogen generation. Hydrogen generation rate could be automatically adjusted by the pressure variation in the hydrogen-generating chamber. As PEMFC was operated under high current densities, more hydrogen was consumed, and the pressure of the hydrogen-generating chamber was lower than that of the solution-storage chamber, which would lead to quicker NaOH solution dropping and thus higher hydrogen generation rate. As the PEMFC was operated under low current density or stopped, the pressure of the hydrogen-generating chamber was higher than that of the solution-storage chamber, which would automatically reduce or stop the NaOH solution dropping and the hydrogen generation.

The prototype hydrogen generator, shown in Fig. 1(b), was made by organic glass. The solution-storage chamber and the hydrogen-generating chamber were sealed by two flanges. Between the two flanges, there was a thin board where the plastic tube was fitted. It is noteworthy that this prototype hydrogen generator was just an experimental demonstrating device and for practical applications, the generator can be manufactured by mold casting method using plastic as raw materials.

2.2. Assessment of hydrogen generation and single cell test

Effects of concentration, dropping rate and initial temperature of the sodium hydroxide solution on the hydrogen generation rate were systematically investigated. During the investigation, 25 wt.%, 17 wt.% and 9 wt.% of the sodium hydroxide solution were used. The dropping rate of sodium hydroxide solution was controlled by inserting a nickel thread into the plastic tube, and different lengths of the nickel thread in the tube led to different dropping rates of sodium hydroxide solution. The temperature of the hydrogen generator was detected by a thermocouple, which was inserted in

Table 1
Energy density of various fuels

Fuel	Energy density (Wh kg ⁻¹)	Comments
Compressed hydrogen	500–1,000	5000 psig, value includes container weight
Sodium borohydride	3,600	[NaBH ₄ + 2H ₂ O] weight only
Methanol	5,500	Based on lower heating value of fuel
Most liquid hydrocarbons	~12,400	Based on lower heating value of fuel
Hydrogen gas	33,200	Unpacked
Nuclear material	2,800,000	Raw power

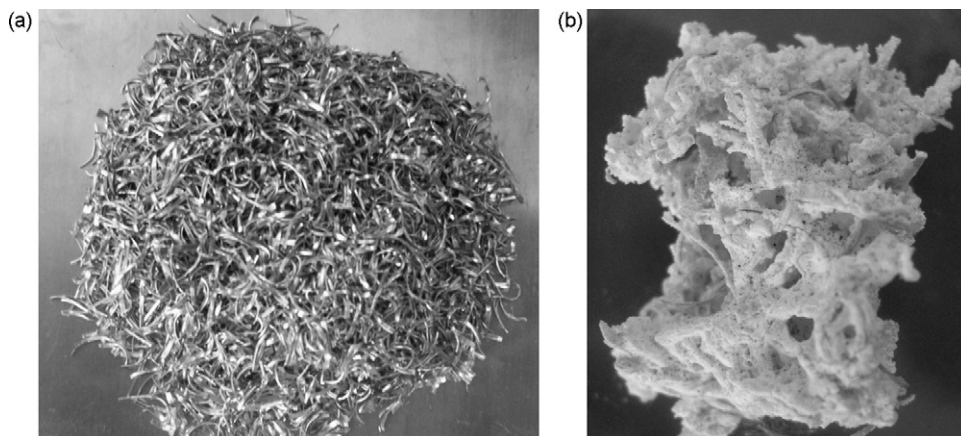


Fig. 2. Appearances of aluminum alloy strips and the reaction product after hydrogen generation (a) aluminum alloy strips and (b) reaction product.

the hydrogen-generating chamber and sealed carefully. In addition, hydrogen generation rate was measured by a gas flowmeter.

The MEA with an active area of $1.0\text{ cm} \times 4.0\text{ cm}$ for single cell test was prepared as described in the previous article [14]. Both the anode and cathode gas diffusion layers (GDL) consisted of 30 wt.% PTFE bonded carbon paper (TGP-H-090, Toray) as backing layers and 20 wt.% PTFE contained carbon black (XC-72, Cabot) as microporous layers (MPL). The catalyst layer consisted of 20 wt.% Pt/C (E-TEK), PTFE and Nafion (20:5:2) with 0.3 mg cm^{-2} Pt loading for the cathode, and 20 wt.% Pt/C and Nafion (3:1) with Pt loading of 0.2 mg cm^{-2} for the anode, respectively. The MEAs were finally obtained by hot-pressing the treated Nafion 112 membrane [14], the anode and the cathode at $135\text{ }^{\circ}\text{C}$ with a pressure of 0.8 MPa for 2 min. The single cell was tested at $25\text{ }^{\circ}\text{C}$ by Neware Cell Test equipment (SHENZHEN, China). During the test, hydrogen from either the hydrogen generator or a steel bottle was fed to the anode as the fuel, and the cathode was open with air as the oxidant.

3. Results and discussion

3.1. Effect of sodium hydroxide concentration on the hydrogen generation rate

Fig. 3 shows the effect of sodium hydroxide concentration on the hydrogen generation rate. Clearly, the hydrogen generation rate was steadily increased by increasing the sodium hydroxide con-

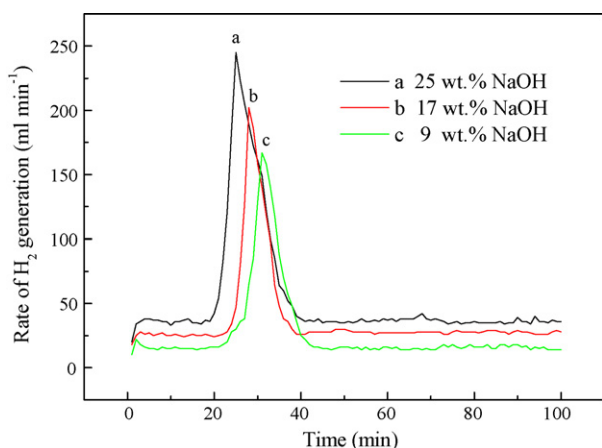


Fig. 3. Effect of sodium hydroxide concentration on the hydrogen generation rate with 0.01 ml s^{-1} dropping rate of sodium hydroxide solution.

centration. For 25 wt.%, 17 wt.% and 9 wt.% of sodium hydroxide solution, the hydrogen generation rates were about 38 ml min^{-1} , 28 ml min^{-1} , and 15 ml min^{-1} , respectively. It was interesting that there was a sharp peak in each hydrogen generation curve. More interestingly, with decrease in the sodium hydroxide concentration, the peak appearance was delayed and the peak value was reduced. The appearance of the hydrogen generation peak was probably due to the fact that the H_2 generating reaction started from room temperature at which the reaction kinetics was slow, and some dropped sodium hydroxide solution unreacted and accumulated. With the reaction going, the temperature in the generator was increased gradually because the reaction between aluminum and sodium hydroxide solution was an exothermic reaction. The temperature increase resulted in the speed-up of the reaction, which led to that both the unreacted and fresh sodium hydroxide solution reacted vigorously, and therefore, a sharp hydrogen generation peak appeared. As the accumulated sodium hydroxide was completely consumed, a stable hydrogen generation rate was obtained because of the almost constant temperature in the generator. It was understandable that, for the case of high concentration of sodium hydroxide solution, more NaOH solution accumulated and thus, the peak appeared more quickly and the peak value was higher. It was reported that sodium hydroxide acted as a catalyst in the reaction between aluminum and water, and therefore, high concentration of sodium hydroxide solution was beneficial to hydrogen generation. However, the concentration of sodium hydroxide solution has to be optimized in view of the stability of hydrogen generation.

3.2. Effect of sodium hydroxide dropping rate on hydrogen generation rate

Fig. 4 shows the effect of sodium hydroxide dropping rate on hydrogen generation rate. The hydrogen generation rate was increased with the increase in sodium hydroxide dropping rate. Specifically, the hydrogen generation rate was, respectively, about 16 ml min^{-1} , 38 ml min^{-1} and $40\text{--}70\text{ ml min}^{-1}$ for 0.005 ml s^{-1} , 0.01 ml s^{-1} and 0.017 ml s^{-1} dropping rates of sodium hydroxide solution. For the case of 0.017 ml s^{-1} dropping rate of sodium hydroxide solution, the hydrogen generation rate was fluctuating due to the vigorous reaction. Similarly to the case of sodium hydroxide concentration, with increasing of sodium hydroxide dropping rate, the peak value was enhanced and the peak appearance was brought forward for the hydrogen generation rate. For the application of the generator, appropriate dropping rate of sodium hydroxide solution has to be adopted in order to meet the fuel cell demand.

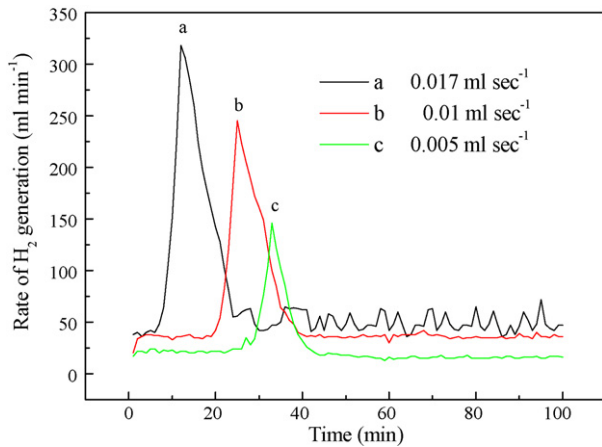


Fig. 4. Effect of dropping rate for sodium hydroxide solution on the hydrogen generation rate.

3.3. Effect of initial temperature for sodium hydroxide solution on the hydrogen generation rate

To confirm the reason for the appearance of the hydrogen generation peak, sodium hydroxide solution was preheated to different temperatures, and then reacted with aluminum. The effect of the initial temperature of sodium hydroxide solution on the hydrogen generation rate was illustrated in Fig. 5. With increasing of the initial temperature of sodium hydroxide solution, there was a little increase of the hydrogen generation rate in the beginning; afterward, the peak of hydrogen generation was obviously delayed and reduced, and finally, the hydrogen generation rate was almost unchanged. This observation could be explained as: for higher initial temperature of sodium hydroxide solution, more sodium hydroxide solution was consumed and more hydrogen was produced in the beginning; afterward, more consumption of sodium hydroxide solution led to less accumulated NaOH solution, which decreased and delayed the hydrogen generation peak; finally, the generator temperature came to a stabilized value and the hydrogen generation tend to a constant rate. From the above observation and explanation, it can be concluded that high initial temperature of sodium hydroxide solution was beneficial to stable hydrogen generation.

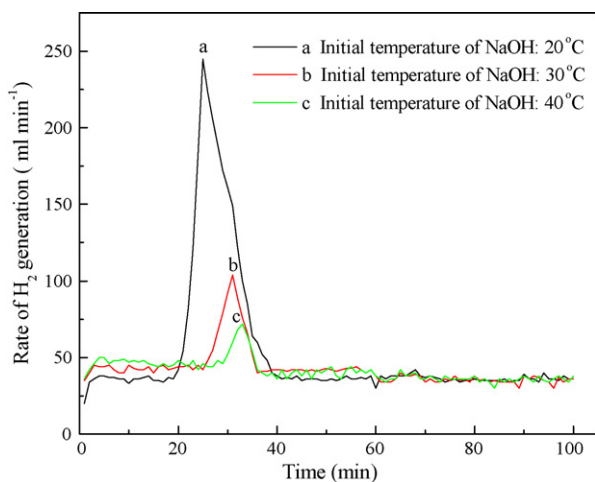


Fig. 5. Effect of initial temperature for sodium hydroxide solution on the hydrogen generation rate with 25 wt.% concentration and 0.01 ml s^{-1} dropping rate of sodium hydroxide solution.

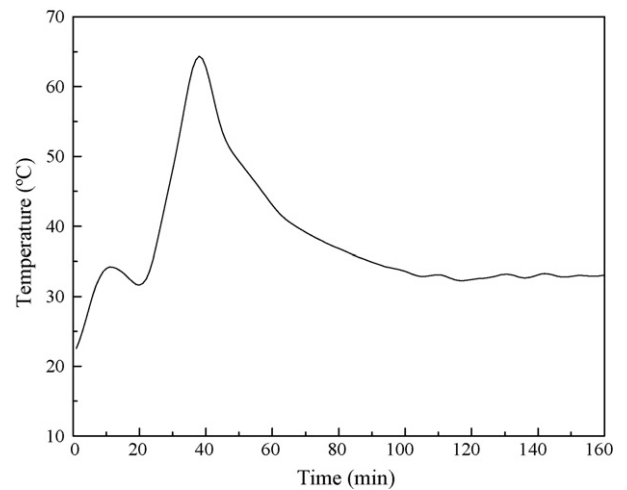


Fig. 6. Temperature evolution during hydrogen generation.

3.4. Temperature evolution during hydrogen generation

The temperature evolution during the hydrogen generation was recorded and presented in Fig. 6. Clearly, the temperature evolution exhibited a similar trend to the case of hydrogen generation rate. A sharp temperature peak, which mainly resulted from vigorous reaction of the accumulated sodium hydroxide solution in the beginning, appeared at about 40 min. Then, as the accumulated sodium hydroxide solution was consumed, the generator temperature decreased, and finally, stabilized at about 35°C .

3.5. Single cell polarization curves

The performance of single cell with hydrogen fed by the hydrogen generator and a steel bottle were compared and illustrated in Fig. 7. Basically, the cell performances for both cases of hydrogen generator and steel bottle were similar. However, the voltage of the cell fueled by the hydrogen generator was slightly higher than that fueled by the steel bottle at low current densities, which probably resulted from the difference in water content of the hydrogen fuel. For steel bottle, hydrogen was unhumidified. For hydrogen generator, however, some water in the sodium hydroxide solution was unavoidably evaporated at the reaction temperature of about 35°C during the hydrogen generating, and therefore, hydrogen was humidified indirectly. As the cell was operated at low current densities, less water was produced at the cathode and

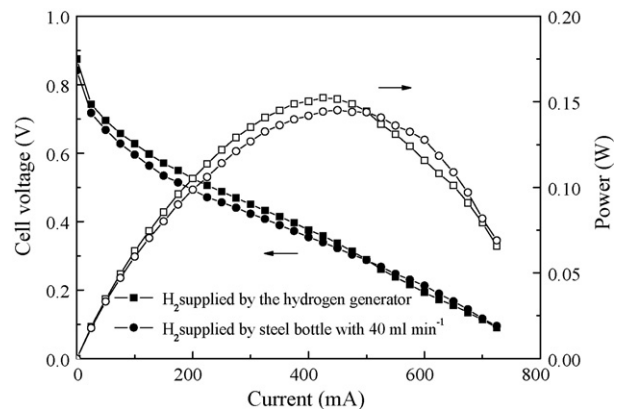


Fig. 7. Polarization curves and power curves of the single cell supplied by both the hydrogen generator and steel bottle.

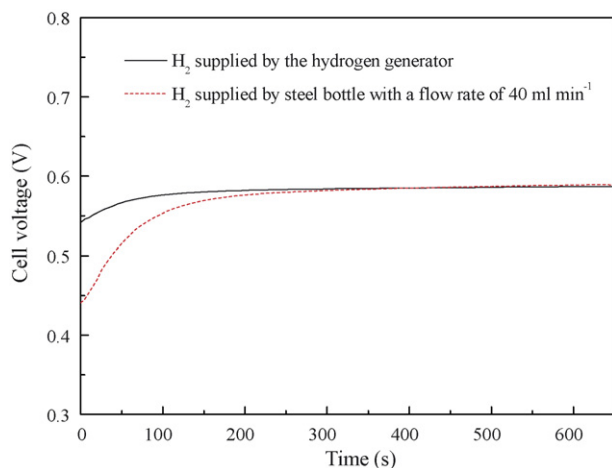


Fig. 8. Startup behavior of the single cell supplied by both the hydrogen generator and steel bottle.

the electrolyte membrane could not be fully humidified, leading to significantly high protonic resistivity. In contrast to the case of steel bottle which supplied dry hydrogen, the protonic resistivity of the membrane could be somewhat reduced for the case of hydrogen generator because some humidified hydrogen was supplied, and therefore higher cell voltage was obtained. As the cell was operated at high current densities, however, much water was produced at the cathode and the membrane was almost fully humidified. In this case, hydrogen humidification would not play a key role in the cell performance, and thus the single cell performances for both cases were similar.

3.6. Single cell startup behavior

Startup behavior was significant to practical application of PEMFC. Fig. 8 presents the startup behavior of the single cell fueled by the hydrogen generator and the steel bottle with a flow rate of 40 ml min⁻¹ under 500 mA. Clearly, the fuel cell fueled by the hydrogen generator showed better startup performance than that fueled by the steel bottle. During the cell startup, the water content of the membrane and the temperature of the cell were both low, and the hydrogen generator could supply hydrogen with higher humidity and temperature to the fuel cell, which, on one hand, increased the water content of the membrane, reducing the membrane resistance, and on the other hand, increased the temperature of the cell, promoting the electrochemical reaction rate. Therefore, the developed hydrogen generator could improve the fuel cell startup performance.

3.7. Single cell performance operated under constant current

Fig. 9 shows the performance of the single cell operated under 500 mA until the aluminum was completely consumed. The results indicated that the single cell fueled by the hydrogen generator could operate stably for nearly 5 h. According to the hydrogen generation reaction, 6 g aluminum used in this experiment can produce 8220 ml hydrogen (298 K, 1 atm) and support the cell operating under 500 mA for 6.5 h, theoretically. In this case, therefore, the hydrogen utilization ratio was calculated to be about 77%, and this ratio was higher if considering the initial ejecting process of air from the hydrogen generator. It is noteworthy that although the above results and discussions were just based on the single cell test, the hydrogen generation rate of 38 ml min⁻¹ was also successfully applied to PEMFC stack fabricated in our lab.

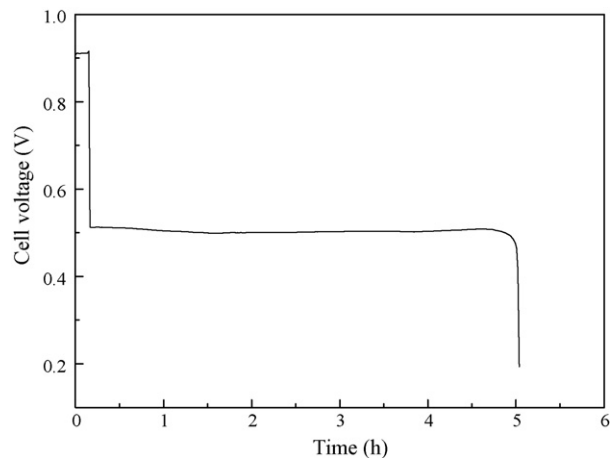


Fig. 9. Performance of the single cell under 500 mA.

4. Conclusions

A mini-type hydrogen generator for micro-PEMFCs was designed, fabricated and evaluated. Hydrogen generation rate was significantly affected by the concentration and dropping rate of sodium hydroxide solution. Increasing the initial temperature of sodium hydroxide solution can significantly reduce the effect of sodium hydroxide accumulation. The cell fueled by the hydrogen generator, mainly due to the humidified hydrogen indirectly, performed better than that fueled by steel bottle at low current densities. The cell startup performance can also be improved by the hydrogen generator because of the increased hydrogen humidity and temperature. The hydrogen generator can operate a single cell stably until aluminum was completely consumed, and the hydrogen utilization ratio can reach above 77%. This simple and cheap generator can be a good hydrogen source for micro-PEMFC.

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