Feasibility of on-board hydrogen production from hydrolysis of Al–Fe alloy for PEMFCs

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Abstract

The feasibility of using the hydrolysis of Al alloys in an on-board hydrogen generation system for PEMFCs is investigated. Hydrogen produced by the hydrolysis of Al–Fe alloys is supplied directly to a PEMFC. The weight-normalized hydrogen generation rate of sheet Al–1Fe is higher than that of cubic Al–1Fe alloy, and its hydrogen generation rate changes little during hydrolysis in alkali water. Furthermore, during the hydrolysis reaction, the water temperature is stable. Hence, Al–1Fe in sheet form is suitable as a source for on-board hydrogen production from hydrolysis in alkali water. At a current of 10 A, the PEMFC presents a voltage of about 0.71 V, which remains stable for 37 min. However, after 37 min, the cell voltage decreases dramatically to 0 V due to a reduction in hydrogen feeding rate by exhaustion of Al–1Fe. It is particularly notable that on-board hydrogen production using the hydrolysis of Al–Fe alloy exhibits self-humidification, supplying humidity automatically without a humidifier.

1. Introduction

Hydrogen is a clean energy carrier with high energy density and zero emission. It has immense potential as a clean energy source for electrical devices and vehicles because its chemical energy can be easily converted to electric energy by polymer electrolyte membrane (PEM) fuel cells. To ensure PEM fuel cells function successfully, it is important to develop a convenient and safe H2 storage and production system with high capacity using liquid hydrogen vessels, metal hydrides, and carbon nanotubes. However, in terms of specific energy density, their hydrogen storage density is not sufficient and their market price is too high for commercial applications. In the last ten years, chemical hydrides, such as NaBH4 [1–4], LiBH4, NaH, NaAlH4, and NH3BH3 [5–7] that can directly produce hydrogen on board have received much attention. The chemical hydrides can feed H2 directly into PEMFCs without a H2 storage system. However, the present cost of chemical hydrides is very high for commercial applications because the hydrogen generation reaction is a self-consuming one-pot process. Meanwhile, an on-board hydrogen production method via the hydrolysis of electrochemically active metals such as aluminum [8–18] has been developed because it is economical compared to chemical hydrides [9]. One kilogram of aluminum can generate about 0.110 kg H2, 1370 L H2 (at 1 atm, 298 °C) [8,9]. The hydrolysis reaction of Al in alkaline solution has been described to be as follows [8]:

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A recent, commercially available electric car powered by fuel cells with a driving range of 400 km requires about 4 kg of hydrogen, which can be produced by 36 kg of aluminum with hydrolysis, assuming a conversion yield of 100% [9]. Furthermore, if waste aluminum containing a small amount of Fe, Cu, and Sn is used instead of primary aluminum, the price decreases even further by 30%. However, the hydrogen generation rate by hydrolysis of Al is too low to operate common electronic devices using PEMFCs, unless the volume and weight of aluminum increase dramatically. To solve this problem, many researchers [8,10–15] have developed Al or Al alloys in powder form; these powders show a high rate of hydrolysis due to their large surface areas. However, because the powders of Al and Al alloys are explosive when they come into contact with moisture or a little heat, it is difficult to store these compounds safely. Additionally, these materials are expensive due to complex manufacturing processes. As one of the methods to solve this problem, the development of safe and economical bulk-formed Al and Al alloys with high performance for hydrogen generation has proven to be a challenge. In a previous study [16], we designed bulk Al–xFe alloys (0 (pure Al), 1, 3, 6 wt.%) for on-board hydrogen production from hydrolysis. Among them, the Al alloy containing 1 wt.% Fe showed the highest hydrogen generation rate; about 4 times than pure Al, and 1.5 times than Al-3 and 6 wt.% Fe. The difference was due to that of the corrosion behavior related with H₂ production mechanism. On the other hand, it has hardly been reported that hydrogen produced directly from the hydrolysis of bulk Al alloys to feed PEMFCs except a few researches [17,18]. To confirm the possibility of its practical use, it is necessary to investigate the feasibility of an on-board hydrogen generation system from hydrolysis by bulk Al alloys to PEMFCs. Moreover, in this paper, the effect of self-humidification on the cell performance of a single PEM fuel cell was examined.

2. Experimental

2.1. Preparation of materials

Al–Fe alloys containing 1 wt.% Fe, which showed the highest hydrogen generation kinetics in alkaline water in previous research [16], were prepared from commercial pure Al (99.9%) and Al–Fe master alloy (Al-50 wt.% Fe). To fabricate casting alloys, pure Al and Al–Fe master alloy were melted at 1300 °C. The fused alloy was poured into a stainless steel mold and air-cooled to 20 °C in the mold. From the phase diagram of Al–Fe [19], it is expected that an Al matrix and Al₃Fe precipitates are formed. A sheet of Al–1Fe alloy was fabricated to compare its hydrogen generation properties with those of cubic-shaped Al alloys. A 5-mm-thick sheet of bulk Al–1Fe thickness was hot-rolled 5 times at 500 °C and then annealed at 500 °C for 1 h. A 1-mm-thick Al–1Fe sheet was then prepared.

2.2. Analyses

The surface morphology of the Al alloys in bulk form was analyzed using scanning electron microscopy (SEM) after 3 min etching at 25 °C in 10 wt.% NaOH solution. To measure the hydrogen generation kinetics from the hydrolysis of Al alloys in alkaline water, hydrogen generation tests were performed in 50 ml 10 wt.% NaOH solution at 50 °C. The volume and rate of generated hydrogen gas were measured by a mass flow meter (MFM), and converted to the value obtained at 25 °C. The reactor was immersed in a water bath to stabilize the temperature, and no stirring was carried out in the reactor. The photograph of the experimental setup for the measurement of H₂ generation rates was shown in Fig. 1(a).

2.3. Connection with single PEM fuel cell

To investigate the feasibility of on-board hydrogen production from hydrolysis of Al–1Fe alloy to a PEMFC, a single cell, which can be connected directly to the hydrogen production reactor, was prepared as shown in Fig. 1(b). The single cell consisted of metal end plates, carbon gas diffusion layers (GDLs), carbon bipolar plates, and a commercial MEA (GORE™). The MEA contained 0.4 mg Pt/C catalyst in both the anode and cathode. Its active area was 5 × 5 cm². To activate the MEA incipiently, H₂ gas and air with more than 95% relative humidity (RH) were supplied into the anode and cathode, respectively, for 20 h. Then, the gas flow rate of H₂ was 413 ml min⁻¹, and the flow rate of air was 1280 ml min⁻¹. After activation, all experiments using the single PEM fuel cell were conducted.

![Fig. 1 – Photograph of the experimental setup for (a) the measurement method of H₂ production rates and (b) the connection of the Al hydrolysis-reactor with a single PEMFC.](image-url)
3. Results and discussion

3.1. Surface morphologies of Al–1Fe alloys

Fig. 2 shows the surface morphologies of the cubic Al–1Fe and sheet Al–1Fe after chemical etching for 3 min in 10 wt.% NaOH solution. A cubic Al–1Fe alloy has small precipitates distributed along the grain boundary as shown in Fig. 2(a). However, in sheet Al–1Fe alloys (Fig. 2(b)), a rough layer with plate-like precipitates randomly distributed is observed. The phase of the precipitates was confirmed to be Al$_3$Fe by TEM diffraction patterns (shown in Fig. 2(a)). From the previous results [16], it was found that the hydrolysis of cubic Al–1Fe with Al$_3$Fe precipitates distributed along the grain boundary is affected by both intergranular and galvanic corrosion. On the other hand, the hydrolysis reaction in sheet Al–1Fe might be affected by only galvanic corrosion. Therefore, the weight-normalized hydrogen generation rate of sheet Al–1Fe must be higher than that of bulk Al–1Fe. However, the weight-normalized hydrogen generation rate of sheet Al–1Fe must be higher than that of bulk Al–1Fe alloy because the sheet form has a larger surface area per weight than the cubic form.

3.2. Hydrogen generation kinetics of Al–1Fe alloys

Fig. 3 shows the effects of the morphology of Al–Fe alloys on the weight-normalized hydrogen generation kinetics in a solution of 10 wt.% NaOH at 50 °C. The overall reaction time from beginning to end for the hydrolysis of cubic Al–1Fe was about 130 min, and the reaction time of sheet Al–1Fe was about 60 min. The total hydrogen generation volumes (measured at 25 °C) of cubic Al–1Fe and sheet Al–1Fe are similar: 1175 ml g$^{-1}$ and 1150 ml g$^{-1}$, respectively. The conversion yield of the cubic Al–1Fe and sheet Al–1Fe was calculated to 86.6 and 84.7%, respectively. As expected, the weight-normalized hydrogen generation rate of sheet Al–1Fe alloy is shown to be 2.2 times higher than that of cubic Al–1Fe alloy. Therefore, it is notable that the sheet Al–1Fe alloy is more valuable as on-board hydrogen generation material than cubic Al–1Fe alloy because it can allow the on-board hydrogen production reactor to be small and light. Moreover, sheet Al–1Fe shows very stable hydrogen generation behavior during the overall hydrolysis reaction. As shown in Fig. 4, the hydrogen generation rate, which is the slope (hydrogen generation volume/time) in the graph of Fig. 3(b), shows little change during the overall reaction. Furthermore, during the hydrolysis reaction, the reaction temperature is also very stable. In the first 3 min, the temperature increases from 49 to 52 °C. However, the temperature then remains constant at 52 °C, as shown in Fig. 4. Hence, it is concluded that hydrogen production from the hydrolysis of sheet Al–1Fe alloy is a suitable method for supplying hydrogen directly into PEMFCs.

3.3. Effect of anode gas flow rate on the cell performance

On the other hand, to obtain 10 A (400 mA cm$^{-2}$) from a single PEM fuel cell, hydrogen should be supplied at least at a rate of 76.0 ml min$^{-1}$ (stoichiometric ratio (SR) is 1.0 at 25 °C). Fig. 5 shows the polarization curve (I–V curve) of a single PEM fuel cell, which demonstrates the effect of hydrogen supply rate on the cell performance. Hydrogen generated from a high-pressure H$_2$ tank was fed into the single cell. The hydrogen supply rate was controlled from SR 1.0 to SR 1.8 by the mass flow controller (MFC). When hydrogen was supplied at SR 1.0, the cell voltage decreased dramatically to 0.58 V at 10 A. However, with a further increase in the rate to SR 1.1, the cell voltage was increased stably to 0.7 V at 10 A. From these results, it was found that a hydrogen flow rate greater than SR 1.1 (83.6 ml min$^{-1}$) should be supplied continuously to obtain 10 A stably from the cell. When considering that the cell’s average hydrogen generation rate during the overall hydrolysis reaction (for 60 min) is about 17.5 ml min$^{-1}$ g$^{-1}$ (5-mm-thick sheet Al–1Fe) at 25 °C (from Fig. 4), approximately 5 g of the sheet Al–1Fe, which can produce hydrogen by the rate of 87.5 ml min$^{-1}$, is needed to operate the PEMFC with high efficiency at 10 A for 1 h.

3.4. Production of power from the hydrolysis by sheet Al alloy via a PEM fuel cell

To investigate the feasibility of on-board hydrogen production from the hydrolysis of sheet Al–1Fe alloy and the supply of hydrogen directly to a PEMFC, the single cell, which can be connected directly to the hydrogen production reactor, was prepared. To obtain the constant power from operating the PEMFC stably for a long time, it is important that the hydrogen generation rate be controlled stably. From the results of
Section 3.1, it seems that Al–1Fe in sheet form, which showed stable hydrogen generation kinetics, is more suitable for this application than bulk Al–1Fe. Fig. 6 shows the stoichiometric ratio (SR) of hydrogen generation from the hydrolysis of a 5-g Al–1Fe alloy sheet with reaction time, which is converted to the value obtained at 0°C. In the first 3 min, the SR of hydrogen increased from 1.0 to 1.2. This might have been due to an increase in the water temperature, as presented in Fig. 4. However, from 3 min to 57 min, the SR gradually decreased from 1.2 to 0.85. This may be attributed to the formation of Al(OH)3 on the surface of Al and a decrease in the active Al area [12,13]. From 57 min to end, the hydrogen generation rate decreased dramatically due to a decrease in the amount of active Al. Therefore, it is understood that the intervals between 0 min and 40 min will be suitable to the operation of the PEMFC at 10 A because the SRs during the intervals were greater than 1.0. Fig. 6 shows the cell voltage measured at a current of 10 A for the single cell when supplying the hydrogen generated from the hydrolysis of a 5-g sheet of Al–1Fe alloy in 10 wt.% NaOH solution at 50°C. The single cell stably exhibited a voltage of about 0.71 V for 37 min. However, from 37 min to 39 min, the cell voltage decreased from 0.71 V to 0.55 V. After 39 min of hydrolysis, the cell voltage decreased dramatically to 0 V. This might have been due to the decrease in the hydrogen generation rate to below SR 1.0 (~76 ml min^-1 at 25°C).

3.5. Self-humidification of the hydrolysis by Al alloys

Fig. 7 shows the effects of relative humidity (RH) of the H2 gas supplied into the anode on the cell performance. As hydrogen gas with about 0% RH was fed into the anode, the cell voltage was 0.605 V at 10 A. However, as the RH was increased from 0% to 50%, the cell voltage increased by 6% to 0.640 V. With a further increase of RH to 100%, the cell voltage increased by 13% to 0.725 V. Accordingly, it was found that the humidity of H2 gas largely affects cell performance. Fig. 7(d) presents the I–V curve obtained when directly supplying the hydrogen generated from the hydrolysis of sheet Al–1Fe alloy in 10 wt.% NaOH solution at 50°C.
Fig. 7 – The effects of relative humidity (RH) of H₂ gas supplied into the anode on the cell performance, the humidity of the anode H₂ gas; (a) 0%, (b) 50%, (c) 100%, and (d) H₂ self-humidified from the hydrolysis of a sheet of Al–1Fe alloy in alkaline water with 10 wt.% NaOH at 50 °C.

alkaline water with 10 wt.% NaOH at 50 °C without passing a humidifier. At 10 A, the cell voltage was 0.648 V, which is close to the value when H₂ gas with RH 50% is supplied to the anode. Accordingly, it was noted that the on-board hydrogen production using the hydrolysis of the Al–1Fe alloy exhibits self-humidification, supplying humidity automatically without a humidifier.

4. Conclusions

We examined the feasibility of an on-board hydrogen generation system from the hydrolysis of Al–Fe alloys and the direct supply of generated hydrogen to a PEMFC. The weight-normalized hydrogen generation rate of sheet Al–1Fe was higher than that of cubic Al–1Fe alloy, and its hydrogen generation rate changed little during hydrolysis in alkaline water. Furthermore, the water temperature remained stable during the hydrolysis reaction. Hence, it was determined that the sheet Al–1Fe is suitable as a source for on-board hydrogen production from hydrolysis in alkaline water. At a current of 10 A, the PEMFC studied stably exhibited a voltage of about 0.71 V for 37 min. However, after 37 min, the cell voltage decreased dramatically to 0 V due to a reduction in hydrogen feeding rate by exhaustion of Al–1Fe and covering of Al(OH)₃ on the surface. It should be noted that the on-board hydrogen production system using the hydrolysis of the Al–1Fe alloy exhibited self-humidification, supplying humidity automatically without a humidifier.

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