Abstract

In this paper, the effectiveness analysis of hydrogen energy systems including a fuel cell for hydrogen control and energy management by using chemical hydrides hydrolysis reaction with a stainless steel catalyst inside the reactor is proposed. The hydrogen energy systems included hydrogen storage of metal hydride to transfer the system’s heat energy to the hydrogen storage and exit. The metal hydride not only recycled the heat energy from fuel cell but also averages the hydrogen supply of magnesium hydrolysis reaction which setup as a reactor. Experimental results prove that our prototype, can reach its hydrogen production efficiency by the chemical reaction about 97%. In this study, the user in on-demand period knows the data on the amount of hydrogen flow rate, the electricity from fuel cell, the temperatures of fuel cell, reactor, and metal hydride hydrogen storage, and recycled heat energy storage capacity information by the system interface.

Key Words: hydrogen generation control, hydrogen, energy Systems.

1. Introduction

Hydrogen has been identified as a promising energy carrier for the future because it offers the potential for fuel-efficient, emissions-free applications and can be produced from multiple primary energy sources. Utilizing clean hydrogen sources by fuel cell offers the potential to reduce greenhouse gas emissions and pollution. Nevertheless, many critical technical challenges need to be overcome before a hydrogen-based energy economy could become viable [1–5]. Hydrogen produced by chemical conversion of an energy source, can be used by the fuel cells to generate electricity to power devices. However, on-board hydrogen storage is one of the most challenging technical barriers to the implementation of the hydrogen economy. To achieve reasonable fuel efficiency and space-saving, weight and volume for on-board hydrogen storage system must be limited. As a result, the U.S. Department of Energy’s Freedom Car Program targets [2] dictate that the gravimetric density of a hydrogen storage system should be at least 6 wt. % by weight, and the volumetric density should be at least 45 g H₂/liter by 2010. The targets for 2015 are 9 wt. % for gravimetric density and 81 g H₂/liter for volumetric density.

Existing hydrogen storage methods include compressed hydrogen, liquid hydrogen, metal hydrides and chemical hydrides [3]. Sodium borohydride (NaBH₄) systems have attracted much attention because of their intrinsic safety and easy handling of fuel compared to other options [4, 5]. This process is a famous method for hydrolyzing to generation high-quality hydrogen gas without polluting emissions. However, one of main shortcomings is the production cost of sodium borohydride (NaBH₄) is too high, at around US$ 80 dollars/kg [6]. The generation of hydrogen gas by the hydrolysis of high energy ball-milled Mg-based materials in pure water and potassium chloride aqueous solution has been studied [7]. When the Mg powders were milled for 0-10 hours, the generation rate of hydrogen gas increased with time period up to 15-60 minutes. Wang et al. [8] generating hydrogen gas from aluminum fine powders of 180-425 μm in diameter in aqueous sodium hydroxide. The generation rate of hydrogen gas increased with reaction time up to 9 minutes, and beyond this time it started to decrease rapidly. Uan et al. [9] studied the possibility of generating hydrogen gas from low grade magnesium waste scraps. Only high grade magnesium scraps is being recycled and more than half of the remaining low grade magnesium scraps cannot be processed economically because the refining technology cannot clean the range of scrap produced. The experimental results [9] indicated that this method for generating hydrogen promotes the recycling of the end-of-
life magnesium products. As a result, Magnesium scraps were considered commercially viable in the emerging fuel cell industry [10–11].

However, unstable for generating hydrogen gas can lead to fuel cell output current fluctuated. Insufficient chemical reaction of generating hydrogen and the formation of magnesium hydroxide can slow down fuel cell operation and performance in various ways, such as reducing output power or the effectiveness and thus obstructing the fuel cell output its electricity. Therefore, an effective, low-cost process for producing hydrogen is a basic requirement for commercializing fuel cells.

1.1 Magnesium Scraps for Hydrogen Generation Catalyzed by Stainles Steel Net in an Aqueous Sodium Chloride Solution

This work focused on the generation of hydrogen from waste metallic magnesium (Mg) scraps catalyzed by a stainless steel net in an aqueous sodium chloride solution. This reaction of the corrosion of magnesium (Mg) has been suggested to be catalyzed herein by stainless steel net in sodium chloride solution to promote significantly the rate of generation of H₂. Therefore, the chemical reaction may be expressed as [9]

\[
\text{Mg}^{(s)} + 2\text{H}_2\text{O}^{(f)} \xrightarrow{\text{Catalyst}} \text{H}_2^{(g)} + \text{Mg(OH)}_2^{(s)} + \Delta H
\]

In this reaction, magnesium (Mg) is the anode and the stainless steel net is the cathode. The enthalpies of chemical reaction was exothermic process by the value of \(\Delta H = -353 \text{ kJ/mole} \) [9]. The by-product, magnesium hydroxide is a non-toxic compound, which is commonly used as flame retardant [9]. Additionally, the chloride ions (Cl\(^-)\) attracted to the anode (Mg) are typically not oxidized to chloride gas because the half reaction occurs at a very noble potential below which the (Cl\(^-)\) is stable. Theoretically one gram magnesium can produce one liter of hydrogen at normal temperature and pressure (NTP), because the density of hydrogen is 0.084 kg/m³ at NTP [12]. According to the experimental results, the average cumulative volume of hydrogen generation was 27 liters by using 27.6 grams of Mg as listed in Table 1. Therefore, in the present study the efficiency of hydrogen production by the chemical reaction was 97% at NTP.

Fig. 1 shows data on the generation of hydrogen gas as a function of time. During the initial 0–120 seconds of the reaction, the average rate of H\(_2\) generation increased to 0.9 liter per minute and then rapidly diminished to 0.4-0.2 liter/minute due to form an insulator of magnesium hydroxide Mg(OH)\(_2\) which would hinder the catalyst to react continuously with magnesium scraps. The magnesium scraps were corroded easily via its high activity. However, if we put magnesium scraps in an aqueous sodium chloride solution, their surface of magnesium hydroxide should be destroyed and then corroded continuously. This corrosion for magnesium scraps in an aqueous solution generated hydrogen and magnesium hydroxyl Mg(OH)\(_2\). Magnesium scraps began to decompose into Mg\(^{2+}\) and electron e\(^-\) as soon as contacting with water. If the aqueous solution contained a lot of hydrogen ion and then the electron e\(^-\) would react with hydrogen ion H\(^+\) to form hydrogen gas. As a result, magnesium scraps in an aqueous solution will generate Mg\(^{2+}\), OH and H\(_2\). As the corrosion proceeded it would consume hydrogen ion H\(^+\) and generate hydroxyl OH\(^-\). Noted that increased the concentration of hydroxyl would increase the PH value. If the PH value was more than 11.5, the magnesium ion would react with hydroxyl to form magnesium hydroxide as an insulator. As shown in Fig. 1, the rate of hydrogen generation rapidly diminished after 120 seconds. The corrosion reaction will go forward in an aqueous solution unless the PH value is less than 8.5. Fig. 2 presents the cumulative volume of hydrogen generation versus time catalyzed by stainless steel in an aqueous solution of 3.5 wt. % sodium chloride.

![Fig. 1: hydrogen generation rate as a function of time.](image-url)

According to “metal hydride” as a buffer responded that the hydrogen supply for Mg scraps directly reacting in an aqueous sodium chloride solution catalyzed by stainless steel has not been not on demand, may solve the problem which because the fuel cell under the variation of load cannot supply its power continuously. The effects of temperature for releasing hydrogen gas and hydrogen generation weight percentage are compared with some metal hydrides [14]. The characteristics of these hydrides proved satisfactory for hydrogen storage, which needs the hydride to have the following properties including high hydrogen capacity, fast kinetics of hydrogenation and dehydrogenation, easy activation and minimal deterioration during hydrogenation cycling. The AB5 type metal hydrides which used as a buffer has excellent hydrogenation performance at ambient temperatures and hydrogen capacity typically in the range of 1–1.5 wt.% [15, 16].
1.2 PEM Fuel Cell

PEM fuel cell employs a thin polymer membrane as an electrolyte. The fuel cell needs a hydrogen pressure of minimum 1.2 bar to operate. Protons are the ionic charge carrier in a PEM fuel cell, the electrochemical reactions are

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O + \text{Electricity} + \text{Heat} \]  

It can be seen that the power and the efficiency of the PEM fuel cell. These calculations are based on considering a single cell. The electric power of fuel cell stack \( P \), efficiency \( \eta \), \( \dot{n}_h \) hydrogen \( H_2 \) usage by using the unit mole/second of the mole flow rate and \( \dot{n}_a \) air usage of mole flow rate were theoretically calculated by [12]

\[ P = V_c I_c N_c \]  

\[ \eta = \left( \frac{H_i V_c}{1.25} \right) \times 100\% \]  

\[ \dot{n}_h = \lambda \times \left( \frac{I_c N_c}{2F} \right) \]  

\[ \dot{n}_a = \lambda \times \left( \frac{I_c N_c}{0.21 \times 4F} \right) \]

where \( V_c \) is the cell voltage, \( I_c \) the cell current, \( N_c \) the number of cells, \( \mu_c \) the fuel utilization (typically about 0.95), \( F \) the Faraday’s constant (96498), \( \lambda \) the stoichiometry ratio 2.0 for hydrogen, and 1.25 the cell thermodynamic voltage which is the reversible thermodynamic cell voltage relative to the lower heating value (LHV). Because the cases in which water finally ends in liquid form were so few, it was not worth considering here. According to the mole proportion of air, the mole ratio of oxygen is 0.21. In the present study, the fuel cell for cathode using air as reactant for the stoichiometry ratio 1.5 is operated below 100°C, so that liquid water is produced.

The linear relationship between the hydrogen molar flow rate \( \dot{n}_h \) through the fuel cell and current \( I_c \) generated by the fuel cell is the sum of the reactor and metal hydride.

As a result, a mass flow controller uses here for controlling the output power of fuel cell.

\[ \dot{n}_h = \dot{n}_r + \dot{n}_m \]  

In addition to the rate of usage of hydrogen, it is often also useful to know the electrical energy that could be produced from a given mass/mole or volume of hydrogen. It clearly follows that the difference between the actual cell voltage and this voltage represents the energy that is not converted into electricity because the energy that is converted into heat instead. The thermal power \( Q \) generated by the fuel cell is given the following equation

\[ Q = \dot{n}_h \Delta H - P = P\left(\frac{1.25}{V_c} - 1\right) \]

Where \( \Delta H \) is the enthalpy of the hydrogen. The specific enthalpy of hydrogen at LHV is \( 1.21 \times 10^8 \) J/kg [12]. It also means that energy is leaving the fuel cell in three forms which are electricity, sensible heat and the latent heat of water vapor. Therefore the thermal power of sensible heat released from the fuel cell which is transferred partly to metal hydride hydrogen stocker and reactor, and the rest is transferred to the ambient environment. This relationship is denoted by,

\[ Q = Q_r + Q_a + Q_m \]  

In Eq. (9), \( Q_r \) is the rate energy exchange with reactor, and \( Q_m \) the thermal power transferred between the fuel cell stack and the ambient environment according to

\[ Q_r = hA(T_c - T_r) \]  

\[ Q_m = hA(T_a - T_r) \]

In these equations, \( T_c, T_r, \) and \( T_a \) are the temperatures for fuel cell, reactor, and ambient, respectively, and \( h \) is the overall heat transfer coefficient of heat exchange and \( A \) the effective area of the heat transfer.

1.3 Integration of Hydrogen Energy Systems

The experiment set up is carried on the hydrogen energy systems as shown in Fig. 3 by recycling the fuel cell’s heat energy to storage in the metal hydride canister in order to control hydrogen flow rate for transferring into electricity. The metal hydride hydrogen storage as a buffer not only recycles the heat energy from fuel cell but also averages the hydrogen supply when magnesium directly reacts with 3.5 wt.% sodium chloride solution catalyzed by stainless-steel (S.S.) net. As shown in Fig. 1, the rate of hydrogen generation increased in the initial stage of 0~120 seconds, and then reduced rapidly to 0.4~0.2 liter/minute. The excessive hydrogen coming from the chemical hydrides is amenable to be stored in a metal hydride and used afterwards to produce electricity by using the PEM fuel cell. Once the excessive hydrogen is stored it can be fed in the right stoichiometric ratio with oxygen by air.
The heat energy can be stored in metal hydride when the fuel cell discharges heat and the metal hydride emits immediately hydrogen gas on the absorption fuel cell heat energy to replenish the hydrogen gas which magnesium reacting in an aqueous sodium chloride solution catalyzed by stainless steel net has insufficiency of the hydrogen supply. In contrast, the chemical hydride reactor produces excess the hydrogen supply when the load is reduced. As long as the hydrogen pressure is greater than that of metal hydride a bit, the hydrogen will enter metal hydride and simultaneously emit the quantity of heat energy. In this reversible process, the hydrogen has not been consumed but stored in metal hydride to constitute a heat energy accumulator together.

With the increasingly wide range of applications for hydrogen energy, the integrated heat and electrical energy of hydrogen energy systems not only employ a metal hydride hydrogen stocker as a buffer for recycling the heat energy but also control the input hydrogen flow rate by transferring hydrogen into electricity. The integration of heat/electrical energy and metal hydride hydrogen storage enables a high efficiency hydrogen generation units located in a small volume to conduct on-demand monitoring with electricity power through a mass flow controller module, transmitting data back to computer. Considering the instability of hydrogen generation system for magnesium reacting in an aqueous sodium chloride solution catalyzed stainless steel net, this study also added a metal hydride on the availability of controlling input hydrogen flow rate and recycling heat energy from the fuel cell.

2. Experiment

2.1 Apparatus

The fuel cell stack was a 30W water-cooled PEMFC stack made by APFCT, and integrated by high efficiency micro heat pipes of heat exchangers. The nominal power was 30W at 60°C and 1.2 bar, with 10 cells and an active area of 25 cm². Air was supplied to stack by blowers, and hydrogen was supplied from the metal hydride canister 10 liters in the beginning until the stack’s temperature over 60°C transferring heat energy to enhancement of the hydrogen generation together through a mass flow controller. The fuel cell stack temperature was controlled by a heat exchanger, additionally cooling water circulated with a small pump.

Fig. 3 shows the setup that integrates the chemical hydride reactor for hydrogen generation and metal hydride stocker as a buffer and a PEM fuel cell stack for output power. This figure also shows the water and heat energy balance between the PEM fuel cell stack, hydrogen gas stocker of metal hydride and reactor by a heat exchanger driven by circulating pumps. The chemical reaction that governs the hydrogen generation by reacting magnesium (Mg) with water is given by Eq. (1).

2.2 Operation and Characterisation

The PEM fuel cell stack was operated with a heat exchanger which cooling water temperature of maximum 60°C and 1.2 bar by a pressure regulator. The 10 liters metal hydride and 30W PEM fuel cell were operated in start-up cycles from room temperature and up to fuel cell operation temperature at 60°C.

Fig. 4: the currents under average 0.3 liter/minute hydrogen generation speed with/without metal hydrides.

2.3 Experimental Results

As shown in Fig. 4, the output current of fuel cell increased initially from zero to 2A in 3 minutes and remained in the range of 1.9–2.1A, and then decreased rapidly when the time over half an hour due to inadequate of hydrogen supply. During the same period, the output current of fuel cell was generated stably at the value of 1.5A with metal hydride. Such a generator can supply hydrogen fuel continuously and on-demand to the anodic compartment of a solid polymer fuel cell, even from ambient temperature and requiring only a small amount of power for pumping (less than 2W). The generator,
consisting of a minimum of components, micro heat pipes of heat exchanger for example, is designed to minimize the overall volume and for a future integration with a fuel cell into a power generator. Hydrogen generator works properly and its dynamic response and performance look adequate to be coupled with a solid polymer fuel cell. Measured conversions for 97% are promising, and its proprietary catalyst shows a good chemical stability in the present study.

3. Conclusion

The hydrogen energy systems not only recycles the heat energy from fuel cell but also averages the hydrogen supply of magnesium scraps directly reacting with water which setup as a reactor. Experimental results prove that our prototype, can reach its hydrogen production efficiency by the chemical reaction about 97%. In this study, we could show that the user in on-demand period knows the data on the amount of hydrogen flow rate, the efficiency by the chemical reaction about 97%. In this study, we could show that the user in on-demand period knows the data on the amount of hydrogen flow rate, the efficiency by the chemical reaction about 97%. In this study, we could show that the user in on-demand period knows the data on the amount of hydrogen flow rate, the efficiency by the chemical reaction about 97%.

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5. References


Table 1 Magnesium scraps with stainless steel net catalyst

<table>
<thead>
<tr>
<th>Mg scraps sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg scrap (including S.S.net)</td>
<td>48.2g</td>
<td>49.4g</td>
<td>39.1g</td>
<td>58.7g</td>
<td>49.8g</td>
<td>53.5g</td>
<td>54.6g</td>
<td>51.5g</td>
<td>33.8g</td>
<td>37.2g</td>
</tr>
<tr>
<td>Hydrogen generation (in10hours)</td>
<td>1.0L</td>
<td>1.1L</td>
<td>0.7L</td>
<td>1.4L</td>
<td>1.1L</td>
<td>1.2L</td>
<td>1.3L</td>
<td>1.1L</td>
<td>0.5L</td>
<td>0.6L</td>
</tr>
</tbody>
</table>

L: liter