Abstract

Magnesium hydride, MgH$_2$, is a promising candidate for hydrogen carrier in the next generation energy network. Along with abundance of raw material and ease of handling, high hydrogen capacity of MgH$_2$ is suitable for the H$_2$ source of fuel cell or hydrogen engine. We have succeeded in producing MgH$_2$ powder in industrial scale, based on thermodynamic equilibrium technique. To solve the problem of poor kinetics of MgH$_2$ in hydrogen release, we adopted hydrolysis process, which can attain hydrogen production yield up to 15.2 mass% below 100 deg.C. Application examples of cartridge-type hydrogen reactors to portable power generators and personal vehicles combined with polymer electrolyte fuel cells are presented. The hydrolysis product Mg(OH)$_2$ can be re-used for other applications, or regenerated to Mg or MgH$_2$ by plasma process. Finally, a comprehensive recycling system for MgH$_2$ is proposed.

1. Introduction

There is a growing concern on hydrogen economy due to the fear of global warming and limited fossil fuel resources [1]. Along with electricity, hydrogen is considered as secondary energy which can complement the deficit of renewable primary energy. In order to utilize hydrogen energy effectively, it is indispensable to develop a carrier in which hydrogen can be safely stored with high density. As the carrier will be used globally, abundance of material and cost are crucial factors. Several types of hydrogen carriers have been proposed such as metal [2], organic [3], or inorganic [4] hydrides, and methane [5].

Magnesium and its alloys have been widely utilized as a lightweight structural material. But they also possess attractive features as an energy storage material.

In this paper, the use of magnesium hydride MgH$_2$ as a promising hydrogen carrier for future hydrogen economy is proposed.
Following the industrial process of MgH$_2$ production and the hydrogen extraction based on hydrolysis, application examples as portable batteries and personal vehicles combined with polymer electrolyte fuel cells (PEFC) will be presented. Finally, a comprehensive recycling system for MgH$_2$ is proposed.

2. MgH$_2$ as Hydrogen Carrier

It is a world-wide consensus that the future energy resource is not fossil fuel but renewable energy such as solar, wind or geothermal heat. These renewable energy sources are low in density, and intermittent by nature. Therefore, it is necessary to transform renewable (primary) energy to highly dense, usable (secondary) energy. Electricity and hydrogen are suitable for secondary energy. However, they have some problems regarding large-scale storage and transport for long distance.

Recently, magnesium and its alloys have attracted attention as energy storage materials;
(a) Abundant raw material (earth’s crust contains 2wt% Mg, sea water contains 0.13% Mg or total of 1800 Tton [6,7]),
(b) Stable in contact with air,
(c) Environment and human friendly (a vital component of a healthy human diet),
(d) High storage capacities of hydrogen as much as 7.6wt% (110kg-H$_2$/m$^3$),
(e) Low negative electrode potential, suitable for battery (Mg $\rightarrow$ Mg$^{2+}$ + 2e ; $E_0$=-2.37V vs. SHE)
(f) High oxidation heat (Mg + H$_2$O $\rightarrow$ MgO + H$_2$ ; $\Delta$H = -360 kJ/mol)

Among them, (d)-(f) are particularly of interest. As for (e), sea-water battery and sacrificial anode are good examples. Now Mg-ion battery [8] and Mg-air battery [9] have been proposed, aiming for post Li-ion batteries. As for (f), Yabe [7,10] propose magnesium as fuel for power generation plants. While (e) and (f) need further studies for commercialization, (d), hydrogen storage material for fuel cell, is an emerging item as the market is rapidly expanding [11].

3. Production of MgH$_2$

So far, thermal decomposition reaction of diethyl magnesium MgEt$_2$ (Equation 1) and direct hydrogenation (Equation 2) are used for the synthesis of MgH$_2$ [6];
\[ \text{MgEt}_2 \rightarrow \text{MgH}_2 + 2\text{C}_2\text{H}_4 \quad (1) \]
\[ \text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2 \quad (2) \]

The former process produces reactive MgH$_2$ that makes handling difficult. Akiyama and co-workers have developed direct hydrogenation processes by means of combustion synthesis [12] and hydrogen CVD [13]. Filament MgH$_2$, and later, granule MgH$_2$ were successfully synthesized using a hydrogenation furnace shown in Figure 1. Here, an industrial process of MgH$_2$ utilizing thermal equilibrium process co-developed with Akiyama [14,15] is mainly presented.

Usually, Mg powder slowly reacts with hydrogen under 250-400 deg.C and high H$_2$
pressure. It is difficult to accomplish hydrogenation at once. Then a procedure called ‘activation process’ in which adsorption-desorption of hydrogen to Mg is applied for numerous times under specific condition to enhance sorption kinetics.

![Diagram of hydrogenation furnace for magnesium](image1)

Figure 1: Schematic diagram of hydrogenation furnace for magnesium [12].

![Equilibrium diagram of MgH2 and (Mg+H2)](image2)

Figure 2: Equilibrium diagram of MgH2 and (Mg+H2).

The basic idea of our proposed process can be explained with Mg-MgH2 equilibrium, shown in Figure 2. First, raw material mainly consisting Mg powder is kept at Region (I) in which Mg and H2 are thermodynamically stable. Under such condition, surface film is effectively removed. Next, the chamber atmosphere is changed to Region (II) in which MgH2 is preferentially formed. By going back and forth between Regions (I) and (II), MgH2 is produced with lower cost and higher efficiency compared to traditional activation process. Modifying the lab-furnace shown in Figure 1 to a small-scale batch furnace made it possible to produce 5 kg of MgH2. The average production yield attains 95.8 % with a good reproducibility. Figure 3 shows XRD chart of obtained MgH2. The result of a commercially available MgH2 reagent is also shown for reference. Both samples show peaks at the same diffraction angles.
4. Hydrogen Production by Hydrolysis of MgH$_2$

Mg based hydrogen storage materials have been studied for more than 40 years [16]. Mg can absorb 7.6wt% of H$_2$, which is one of the largest capacity among metal hydrides. However, sluggish desorption kinetics of H$_2$ in temperature higher than 300 deg.C is the main obstacle for further development or commercialization.

Magnesium, along with other alkali or alkali-earth metals such as Li or Ca, is thermodynamically unstable that is readily oxidized with water to magnesium hydroxide Mg(OH)$_2$ accompanied by H$_2$ gas evolution. Its hydride MgH$_2$ also reacts with water but generates twice in H$_2$ volume, which is summarized in Table 1.

Table 1: Hydrogen volume generated from Mg and MgH$_2$ (wt%).

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Include H$_2$O</th>
<th>Exclude H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg + 2H$_2$O $\rightarrow$ Mg(OH)$_2$ + H$_2$</td>
<td>3.3</td>
<td>8.2 (3)</td>
</tr>
<tr>
<td>MgH$_2$ + 2H$_2$O $\rightarrow$ Mg(OH)$_2$ + 2H$_2$</td>
<td>6.4</td>
<td>15.2 (4)</td>
</tr>
</tbody>
</table>

Fuel cell (FC) is an electric power generator utilizing electrochemical reaction of H$_2$ and O$_2$. Combined with exhaust heat, it reaches high energy efficiency without CO$_2$ gas emission. During the FC operation, water is generated as a byproduct. If this water is recovered for the hydrolysis reaction (4), maximum H$_2$ gas volume of 15.2% could be attained. In addition, the reaction proceeds under 100 deg.C, which is particularly suitable for H$_2$ source of polymer electrolyte FC (PEFC) used in small-middle scale batteries for mobile phone, notebook PC and electric vehicles.

H$_2$ generation utilizing hydrolysis reaction of metal hydrides has been proposed for LiH-NaH[17], NaBH$_4$[18] and MgH$_2$ [19-25] systems. The common drawback of hydrolysis process compared to conventional physical H$_2$ generation from metal hydrides is that the reaction is irreversible. As a result, the obtained hydroxide should be reduced to metal or metal hydride by putting external energy, or re-used for other applications. This issue will be discussed in Section 6.

In case of MgH$_2$ application, the surface is gradually covered with Mg(OH)$_2$ film and the reaction is slowed down. The addition of organic acid [19], foreign metallic particles which works as galvanic cathode to Mg [20], chlorides [21] or ammonium salts [22], ball milling with CaH$_2$[23] or graphite [24] are actively investigated. We are also trying to improve the hydrogen kinetics by pulverization, addition of acids and ultrasonic radiation [25].

Figure 4 shows the influence of the particle
size and temperature on hydrogen production yield (HPY) of MgH\textsubscript{2}. Here, HPY is calculated as follows:

\[
\text{HPY(\%)} = \frac{[\text{H}_2 \text{ gas collected after 60 min. of operation}]}{[\text{theoretical value calculated from Eq.(4)}]}.
\]

It is interesting to note that HPY shows maxima at frequency of 28 and 100kHz, suggesting the presence of optimum frequency for detaching H\textsubscript{2} bubbles or viscous Mg(OH)\textsubscript{2} at Mg-solution interface [26]. The addition of citric acid and MgCl\textsubscript{2} break the surface film that accelerates depassivation even at lower temperature.

5. Development of Mag-H\textsubscript{2} Reactor and its Application

5.1 Development of Mag-H\textsubscript{2} Reactor

Mag-H\textsubscript{2} reactor is an apparatus for providing H\textsubscript{2} gas on-demand utilizing the hydrolysis of MgH\textsubscript{2}. The process flow for generating electricity combined with FC is shown in Figure 5.

Table 3 shows the specification of Mag-H\textsubscript{2} reactor. MHR3, which is suitable for educational purpose, equips three fuel tubes inside the cartridge, and each tube contains 6 MgH\textsubscript{2} pellets. The type of fuel cell is PEFC, with cell capacity of 30W, and output power is 150Wh.

Table 2: Effect of temperature and ultrasonic wave radiation on HPY. (Note: figures in Bold indicate HPY higher than 80%.)

<table>
<thead>
<tr>
<th>Additives</th>
<th>Temp. (deg.C)</th>
<th>Grain size (\mu m)</th>
<th>Ultrasonic wave frequency (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>20</td>
<td>61.4</td>
<td>&lt;1%</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>61.4</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>92</td>
<td>61.4</td>
<td>11</td>
</tr>
<tr>
<td>Citric acid (15%)</td>
<td>20</td>
<td>61.4</td>
<td>2.0</td>
</tr>
<tr>
<td>MgCl\textsubscript{2} (10%)</td>
<td>70</td>
<td>61.4</td>
<td>11</td>
</tr>
<tr>
<td>MgCl\textsubscript{2} (1%)</td>
<td>70</td>
<td>61.4</td>
<td>57</td>
</tr>
</tbody>
</table>
Figure 5: Process flow of Mag-H2 reactor to generate electricity with FC.

H₂O is supplied from reservoir to the bottom of reactor through water tube.

H₂ is generated by the hydrolysis of MgH₂ inside fuel tubes.

After passing through a dryer, H₂ gas is introduced to FC.

FC generates electricity.

Hydrolysis of MgH₂ continues with keeping the water level of fuel tubes.

If there is no need of electricity, H₂ partial pressure inside the reactor increases, which pushes out H₂O in water tube.

FC stops generation of electricity.

Figure 6: Mag-H2 reactor (MHR30).

Figure 6 shows the appearance of Mag-H2 reactor (MHR30). Depending on the application or operation mode, adequate amount of MgH₂ powder or pellet can be selected.

<table>
<thead>
<tr>
<th>Mag-H2 reactor</th>
<th>Main application</th>
<th>Fuel tube ( - )</th>
<th>Fuel cell capacity ( W )</th>
<th>Output power ( Wh )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHR3</td>
<td>Educational kit</td>
<td>3</td>
<td>30</td>
<td>150</td>
</tr>
<tr>
<td>MHR10</td>
<td>Portable power generator</td>
<td>10</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>MHR30</td>
<td>Commuter car</td>
<td>25</td>
<td>300</td>
<td>1,250</td>
</tr>
</tbody>
</table>

Table 3: Type and specification of Mag-H2 reactor.
5.2 Application Examples

In collaboration with several industrial partners and universities, following products are under development.

Educational kit

The education about low-carbon society based on hydrogen and FC technologies is important. There are growing needs of experiment demonstration on hydrogen driven FC at schools. Figure 7 shows a prototype of such system.

Portable power supply (Emergency power supply)

The utilization of portable power supply for outdoors, at rural/remote/mountainous regions or emergency battery at disaster is getting popular. MgH₂ fuel can be stored for a long period and the cartridge system is particularly convenient for on-demand use. Figure 8 shows a prototype of portable power supply.

Blow cleaner, lawn mower

As these apparatus are often used in urban areas, the noise, vibration, and exhaust gas during their operation may cause problems. A prototype developed with a partner showed in Figure 9.

Commuter car

In response to the needs of personal vehicle to relieve congestion in urban area and electric wheel chair for disabled people, several types of FC driven vehicles are being developed. Figure 10 shows a schematic diagram and actual driving of SUZUKI senior car equipped with MHR30 and FC.

![Figure 7: FC system for educational use.](image)
Figure 8: Portable power supply.

(a) Blow cleaner equipped with Mag-H2 and FC  
(b) Lawn mower equipped with Mag-H2, FC and solar panel.

Figure 9: Blow cleaner and lawn mower equipped with Mag-H2 FC.

(a) Schematic  
(b) Actual driving

Figure 10: Installation of Mag-H2 reactor and FC to SUZUKI senior car.
6. Recycle/re-use of Mg(OH)$_2$

In the proposed system, MgH$_2$ is transformed to Mg(OH)$_2$ by hydrolysis reaction. It will not be eco-friendly nor practical system without re-using/recycling them. We are also aggressively engaged in the research about re-using/recycling Mg(OH)$_2$ or MgO.

6.1 Cascade recycle of MgO/Mg(OH)$_2$

MgO is widely used as a chemical agent, of which the world consumption is in tens of megatons [6]. Main applications are;
- Additives for mortar in construction,
- Mild neutralizing agent in medicine,
- Heat resistant bricks,
- Additives for plastics.

Hydration-dehydration reaction of MgO and Mg(OH)$_2$ are reversible, which can be applied as a heat-pump operated around 300 deg.C [27]. In addition, MgO and Mg(OH)$_2$ react with CO$_2$ to carbonates, which are expected to work as fixing agents for greenhouse CO$_2$ gas [28]. As the reaction is exothermic, the heat can be used for other applications.

6.2 Regeneration to Mg/MgH$_2$

Electric refining of anhydrous MgCl$_2$ and thermal reduction of magnesite under 1200-1500 deg.C in presence of ferrosilicon alloy are current production technologies for Mg ingot, which could be adapted for the regeneration of Mg(OH)$_2$/MgO. Yabe proposes thermal reduction of MgO by solar-powered laser [7]. We are developing a reduction process from Mg(OH)$_2$/MgO to Mg, or further to MgH$_2$ by reactive hydrogen plasma. A schematic diagram is shown in Figure 11. The advantages of this system are the creation of H radical atmosphere with temperature more than 2000 deg.C, and ease of intermittent operation.

![Figure 11: Schematic diagram of plasma-assisted regeneration system.](image)

7. Future Development

MgH$_2$ is stable in dry atmosphere which does not require special handling or storage compared to compressed or liquefied H$_2$. Therefore cartridge type MgH$_2$ can be sold at usual glossary stores and kept at homes or warehouses. We are planning to scale up this technology according to the size of FC and its requirement, shown in Figure 12. The application to mobile electric devices such as mobile phone or notebook PC, and electric...
vehicle are particularly promising.

Finally, a comprehensive recycling system of MgH₂ is proposed, which is shown in Figure 13. Among them, following three issues are considered as main tasks to be accomplished:
- Cost down of MgH₂. A production furnace with 50 kg MgH₂ batch capacity has been recently constructed. Initial trials showed satisfactory results. The full-scale operation is planned in March 2010.
- Recycle of used Mg(OH)₂ by cascading re-use or regeneration by plasma process.
- Continuous effort for exploring application and market that will provoke a large-scale production-distribution of Mg, MgH₂, and Mg(OH)₂.

We hope that our technology would provide another prospect in Mg industry, and eventually contribute to the realization of a clean H₂ economy.

Figure 12: Perspective of Mag-H₂ reactor +FC application.
Figure 13: Comprehensive recycling process of MgH₂

References