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Industrial production of MgH_2 and its application

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ABSTRACT

A process for the industrial production of magnesium hydride (MgH_2) based on a thermal equilibrium method and its application to portable hydrogen sources is proposed. Mg powders and tablets compressed with mechanically ground Mg ribbons were successfully hydrogenated in a 50-kg-batch furnace. The resultant MgH_2 showed a hydrogen yield of around 96% with good reproducibility. The compression ratio of Mg tablets was found to be an important factor in the hydrogenation yield. A hydrolysis technique using citric acid as an additive was employed to generate hydrogen under 373 K. Increasing the concentration of citric acid and the temperature accelerated the hydrolysis reactivity. A hydrogen reactor utilizing hydraulic head pressure was developed. It generated hydrogen continuously for 1 h at a flow rate of 100 ml min^{-1} with hydrolysis of 5 g of tablet-form MgH_2. The conversion yield was around 70%, regardless of the flow rate.

1. Introduction

Mg-based hydrides are promising candidates for hydrogen storage applications because of their high gravimetric/volumetric hydrogen storage capacity and the low cost of the raw material [1–7]. On the other hand, high absorption/desorption temperature and sluggish reaction kinetics require complex procedures such as tailoring Mg alloys and compounds or by producing nanometer-size grains through reactive ball milling [1,2]. Some procedures have been proven to be effective in reducing the absorption temperature while the desorption temperature remains high. Few companies produce MgH_2 on a commercial basis, apart from chemical reagent suppliers. This can be partly explained by the complex activation treatment required for hydrogenation [3] and the careful handling of Mg powder, which poses the potential hazard of dust explosion [4]. Akiyama et al. [5] have proposed hydriding chemical vapor deposition directly synthesizing single-crystal nano-sized MgH_2 fibers via gas phase reaction. The resultant MgH_2 showed a plateau of 7.6 wt% at 578 K in the *P*–*C*–*T* curve without any activation treatment. In collaboration with Akiyama, the present authors have developed an industrial process for producing MgH_2 by utilizing thermal equilibrium between $\{Mg + H_2\}$ and $\{MgH_2\}$ [6,7]. Mg powders were hydrogenated at controlled temperature and hydrogen pressure in a 5-kg-batch furnace. Twenty-four consecutive trials provided an average hydrogenation yield of 96%. In this article, the scalability of this process is verified with a 50-kg-batch furnace using Mg tablets and powder as samples.

The hydrolysis of alkali, alkali-earth metal hydrides, or borohydrides has recently attracted attention as a method of hydrogen production for small to medium-sized polymer electrolyte fuel cells (PEFCs). Hydrolysis with LiH or CaH_2 is violent and often becomes uncontrollable, while $NaBH_4$ [8] shows more controllable reactivity in the presence of a catalyst. In the case of MgH_2, the reaction can be expressed as

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2, \quad \Delta H = -268\,\mathrm{kJ\,mol\text{-}MgH_2}^{-1} \tag{1}$$

Several hydrolysis studies of MgH_2 have been conducted using ball-milled MgH_2 powder supplemented with graphite [9] or rare-earth metal [10]. The compounds generate hydrogen in pure water at room temperature. There have been no studies on how to control such high reactivity for practical applications. In this study, hydrolysis was investigated with tablet-type MgH_2 in citric acid. Citric acid is a weak organic acid that is extensively used in the food and beverage industry. Its solution can be easily prepared without the need for handling the dangerous concentrated acid. After characterizing the process parameters, a portable reactor that generates hydrogen at a constant rate was developed.

2. Experimental

Some 99.8%-purity Mg powder (Chuo-kosan, Japan) with a 200 mesh (<75 μm) was used. Tablet-form Mg was prepared by grinding a 99.8% Mg ingot (Chuo-kosan, Japan) into ribbons of thickness less than 150 μm. These ribbons were then compressed in a Ø10 mm steel mold. The compression ratio was controlled by applying pressure. The apparent density was calculated by the weight and volume.

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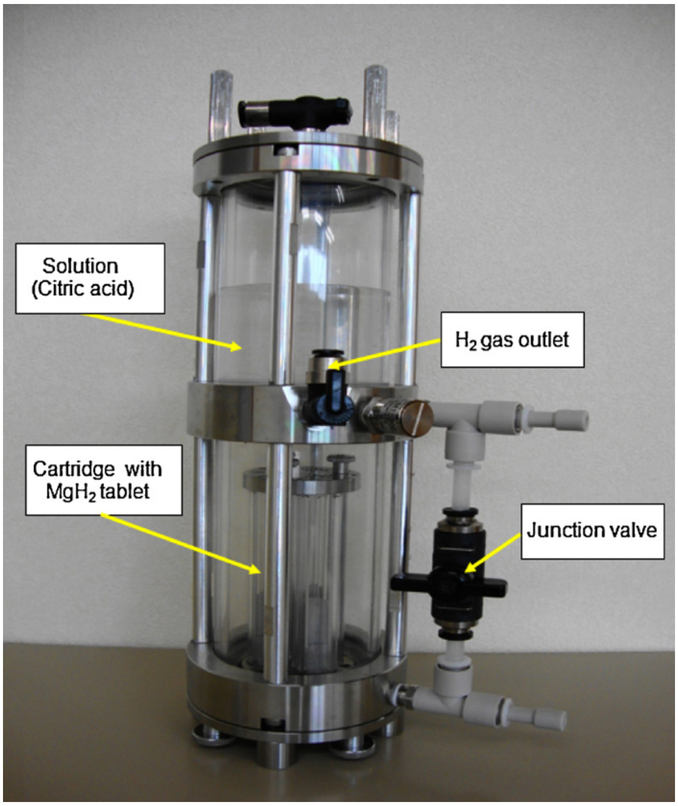

Fig. 1. MgH_2–hydrogen reactor (MHR) for hydrolysis of MgH_2 tablet in citric acid.

The hydrogenation of Mg samples was conducted based on a thermal equilibrium method [6,7]. Powder and tablet Mg were placed on trays inside a 50 kg hydrogenation furnace. After purging with Ar, the furnace was filled with 99.9999% hydrogen with a pressure of less than 2 MPa. The temperature of the process was controlled so as to remain near the boundary between the regions $\{MgH_2\}$ and $\{Mg + H_2\}$ in the thermal equilibrium diagram, and maintained for 30–45 h. The hydrogen consumption behavior was monitored by a pressure gauge. Afterward, the furnace was gradually cooled down to room temperature. The hydrogenation yield (%) was calculated via the weight difference of Mg samples before/after the process.

One MgH_2 tablet (~1.7 g) was placed into a 200 ml Pyrex glass flask. Some 55 ml of 0.52–1.04 mol l^{-1} citric acid solution prepared by reagent grade chemicals and de-ionized water was added to react with the tablet. The experiment was carried out under atmospheric pressure and a temperature of 299–343 K in a water bath. In addition, 200 mg MgH_2 powder in 10 ml citric acid was studied. The hydrogen that emerged from the flask was collected in an inverted mess cylinder to measure the quantity. The amount of hydrogen produced was expressed by conversion yield (%), which is defined as the volume of produced hydrogen over the theoretical volume of hydrogen, and by hydrogen generation rate (ml min^{-1} g $MgH_2{}^{-1}$), and all materials were assumed to react during hydrolysis reaction (1).

A hydraulic head-type MgH_2 reactor (MHR) consisting of two containers, shown in Fig. 1, was developed. Three pieces of MgH_2 tablets (~5 g) were placed in the lower container, and 100 ml of 1.04 mol l^{-1} citric acid was poured into the upper container. By manipulating the pressure in the upper and lower containers, a suitable amount of citric acid descended to continue hydrolysis in the lower container. The initial pressure was set to 0.06–0.08 MPa. The hydrogen generation rate was regulated to 50, 100, and 150 ml min^{-1} by a flow meter equipped with a control valve. The time taken for the pressure in the lower container to decrease to below 0.02 MPa was monitored. For reference, hydrolysis with MHR under atmospheric pressure without flow control (open system, the same experiment as with the flask) was also conducted. The experiment was repeated at least three times to confirm reproducibility.

3. Results and discussions

3.1. Hydrogenation of Mg in 50-kg-batch furnace

Table 1 shows the result of four batch trials with a load of up to 23 kg of powder and tablet Mg. The hydrogenation yield was a minimum of 93% and averaged 97%. X-ray powder diffraction was also measured to detect only those peaks related to Mg and MgH_2. The presence of oxide thus seems negligible. The variation from batch to batch was slightly higher than the previous trials with a 5-kg-batch furnace. Fig. 2 shows the relationship between the density of Mg tablet and hydrogenation yield for various hydrogenation periods. Longer hydrogenation gave better yields. The positive effect of tablet density on hydrogenation yield is evident. Generally, hydrogen absorption in metal improves remarkably with plastic deformation, which introduces lattice defects to function as trap sites for hydrogen. In hydrogen storage studies, accumulative roll bonding or severe plastic deformation have been found to improve absorption characteristics such as ease of activation or higher capacity [11]. The pressure applied to fabricate Mg tablets certainly induces plastic deformation inside Mg ribbons and resultant lattice defects. Considering the Mg density of 1.74 g cm^{-3}, Mg tablets with apparent density of 1.2–1.5 g cm^{-3} would provide the optimum condition for hydrogenation by creating numerous lattice defects while maintaining sufficient voids for hydrogen diffusion. Hereafter, MgH_2 tablets with 95% hydrogenation yield were employed.

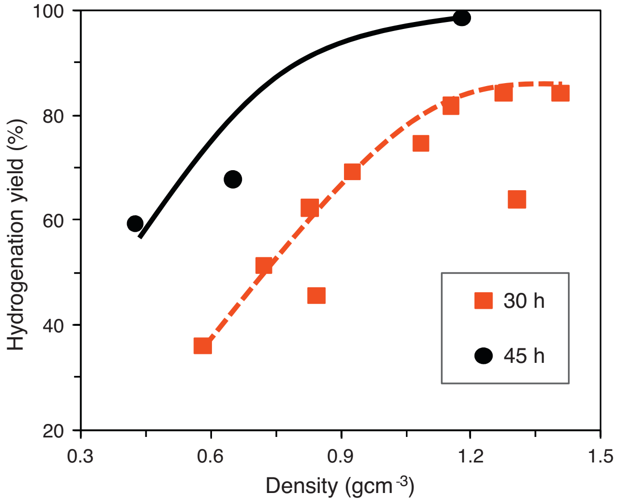

Fig. 2. Relation between density of Mg tablet and hydrogenation yield. Hydrogenation was carried out for 30 h and 45 h.

3.2. Hydrolysis of MgH_2 with citric acid

Fig. 3 shows an example of the hydrolysis behavior of MgH_2 in citric acid. The conversion yield follows a parabolic curve; the increase is reduced at longer hydrolysis periods. Some researchers have attempted to analyze the trajectory by curve fitting based on the Avrami–Erofeev reaction [9,10]. The hydrogen generation rate was 161 ml min^{-1} g^{-1} initially and decreased to 3 ml min^{-1} g^{-1} after 60 min, 1.9% of the initial rate.

Table 2 summarizes the effect of process parameters on the time required to attain a conversion yield of 80% after 60 min, and an average generation rate within 60 min. For reference, the results of MgH_2 powder are also mentioned. Hydrolysis with MgH_2 powder completed within a minute, and the yield reached 100%. On the other hand, MgH_2 tablet reaction required a much longer period. The average hydrogen generation rate was proportional to the concentration of citric acid. Increasing the preset temperature was also effective in improving hydrolysis kinetics. Note that the hydrolysis reaction (1) is highly exothermic; the actual solution temperature would not be the same as that of the water bath once the reaction had started. Nevertheless, the results suggest that the heat is effective in continuing the reaction. The temperature dependence

Table 1
Hydrogenation yield of Mg powder and tablet at 50 kg batch furnace. Hydrogenation was carried out for 45 h.

RUN	Total Mg (kg)	Mg powder		Mg tablet	
		Weight (kg)	Hydrogenation (%)	Weight (kg)	Hydrogenation (%)
1	8	8	97.6	0.1	98.4
2	15	15	93.2	0.3	95.3
3	16	16	100.0	0.2	99.0
4	23	17	93.1	5.6	97.9
Average			96.0		97.7

Table 2
Effect of process parameters on hydrolysis of MgH_2.

MgH_2	Citric acid (mol l^{-1})	Temperature (K)	*t* at conversion yield = 80% (min)	Conversion yield after *t* = 60 min (%)	Average H_2 rate (ml min^{-1} g^{-1})
Powder	0.26	299	0.6	100.0	2.87×10^3
	0.52	299	0.1	99.6	9.06×10^3
Tablet	0.52	299	60<	53.9	16.2
	0.78	299	60<	70.0	21.1
	1.04	299	35.3	86.0	24.3
	0.78	313	60<	75.1	22.7
	0.78	323	60<	78.9	23.4
	0.78	333	48.0	83.2	24.7
	0.78	343	25.4	92.5	27.6

of the solubility of Mg byproduct would undoubtedly influence this behavior.

3.3. Hydrogen generation with MHR using MgH_2 tablet

As shown in Table 2, MgH_2 powder is more reactive than in tablet form. However, from the viewpoint of reaction control, tablet MgH_2 is advantageous. With our designed MHR, the height of the solution level in the lower container changes according to the hydraulic head pressure of the higher and lower containers. If the hydrolysis reaction proceeds a little further, the pressure increases to push the solution to the upper container. As a result, the surface area in contact with the solution drops, and the reaction ceases. In addition, tablets prepared by Mg ribbons greatly reduce the risk of dust explosion during handling and associated cost. Thus, tablet MgH_2 was used in MHR studies.

Fig. 4 shows of the time taken for hydrogen generation with MHR under various flow rates. The average conversion yield was also plotted. During operation, hydrogen flow was almost steady once it was set, while the pressure decreased gradually with time. When the pressure in the lower container decreased to 0.04 MPa, flow rate adjustment with a control valve became necessary. In general, the MHR supplied a constant flow of hydrogen autonomously until 90% of the total duration. The obtained conversion yield of around 70% was similar under all conditions and was close to the value obtained with the open system. These findings indicate that the MHR can work as a hydrogen generator with simple control. The present capacity of hydrogen production is sufficient for PEFCs of 5–10 W. Since it is possible to scale up the MHR system without major modifications, applications to small to medium-sized PEFCs are promising.

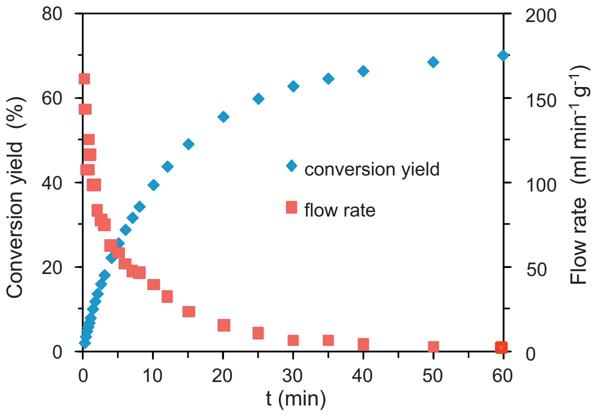

Fig. 3. Change of conversion yield and hydrogen flow rate with time. Hydrolysis was carried out with 1 g MgH_2 tablet in 33 ml of 1.04 mol l^{-1} citric acid, *T* = 299 K, under open condition.

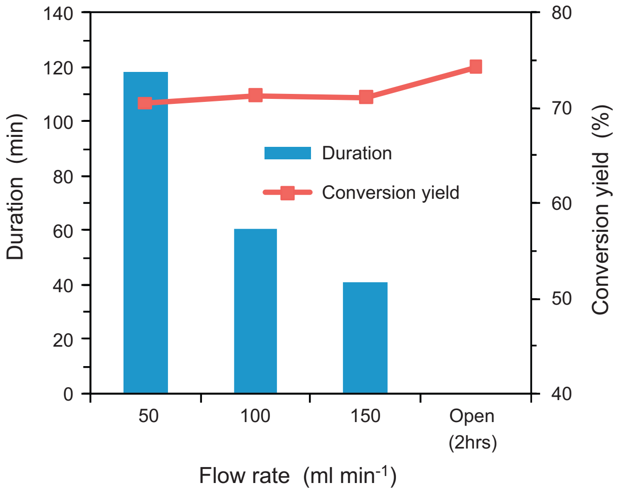

Fig. 4. Duration period and conversion yield obtained at MHR under constant flow rates. Hydrolysis was carried out with 5 g MgH_2 tablet in 100 ml of 1.04 mol l^{-1} citric acid, under flow rate control.

Further studies on hydrolysis conditions with fewer additives, and the recycling or regeneration of byproducts [7], are in progress.

4. Conclusion

Tablet and powder Mg were hydrogenated in a 50-kg-batch furnace. The resultant MgH_2 had a hydrogenation yield of 93% or higher. Hydrogenation was influenced by the pressure applied for preparing the Mg tablet, which induced mechanical deformation in the Mg ribbon to create trap sites for hydrogen. A hydrolysis technique using citric acid was employed to generate hydrogen under

373 K. A high concentration of citric acid and elevated temperature accelerated the hydrolysis reactivity.

A hydrogen reactor based on the hydrolysis of MgH_2 tablet was developed. The reactor supplied a constant hydrogen flow autonomously for 90% of the total duration. The conversion yield was around 70%, regardless of the flow rate. Thus, application of this system as a portable hydrogen generator for PEFCs is anticipated.

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