Production of Hydrogen Storage Material MgH_2 and its Applications

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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 ($Mg \rightarrow Mg^{2+} + 2e$; Eo=-2.37V vs. SHE)
(f) High oxidation heat ($Mg + H_2O \rightarrow MgO + H_2$; ΔH = -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] proposes 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];

$$MgEt_2 \rightarrow MgH_2 + 2C_2H_4 \quad (1)$$

$$Mg + H_2 \rightarrow MgH_2 \quad (2)$$

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.

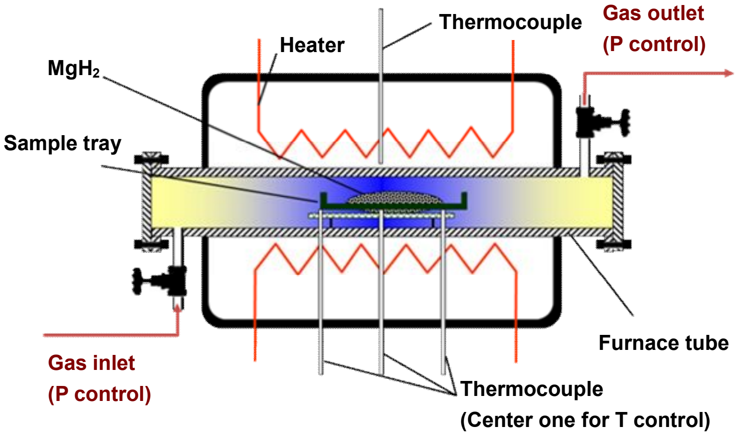


Figure 1: Schematic diagram of hydrogenation furnace for magnesium [12].

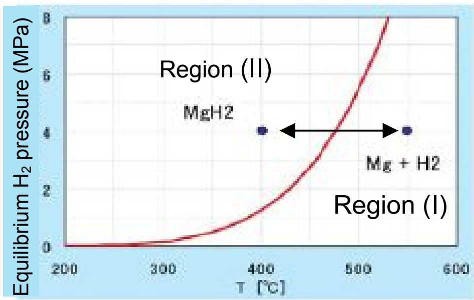


Figure 2: Equilibrium diagram of MgH_2 and ($Mg+H_2$).

The basic idea of our proposed process can be explained with Mg-MgH_2 equilibrium, shown in Figure 2. First, raw material mainly consisting Mg powder is kept at Region (I) in which Mg and H_2 are thermodynamically stable. Under such condition, surface film is effectively removed. Next, the chamber atmosphere is changed to Region (II) in which MgH_2 is preferentially formed. By going back and forth between Regions (I) and (II), MgH_2 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 MgH_2. The average production yield attains 95.8 % with a good reproducibility. Figure 3 shows XRD chart of obtained MgH_2. The result of a commercially available MgH_2 reagent is also shown for reference. Both samples show peaks at the same diffraction angles.

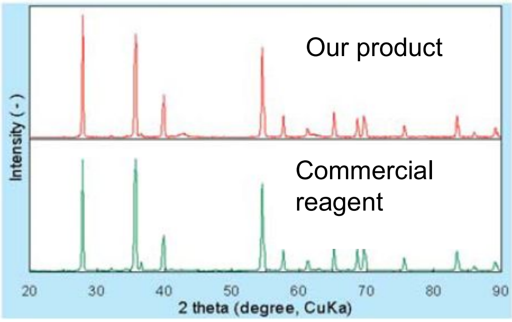


Figure 3: XRD chart of MgH_2

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%).

Chemical reaction	Include H_2O	Exclude H_2O	
$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$	3.3	8.2	(3)
$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$	6.4	15.2	(4)

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_2. Here, HPY is calculated as follows;

HPY(%) = [H_2 gas collected after 60 min. of operation] / [theoretical value calculated from Eq.(4)].

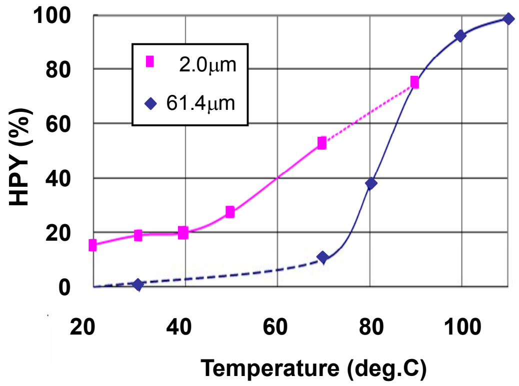


Figure 4: Effect of MgH_2 grain size and temperature on HPY.

Smaller grain size is effective if operation temperature is low. Table 2 shows the influence of temperature, additives and ultrasonic wave radiation on HPY. The positive effect of ultrasonic wave radiation is evident, which can be explained by enhanced mass-transfer and localized heating by cavitation phenomenon.

It is interesting to note that HPY shows maxima at frequency of 28 and 100kHz, suggesting the presence of optimum frequency for detaching H_2 bubbles or viscous $Mg(OH)_2$ at Mg-solution interface [26]. The addition of citric acid and $MgCl_2$ break the surface film that accelerates depassivation even at lower temperature.

5. Development of Mag-H2 Reactor and its Application

5.1 Development of Mag-H2 Reactor

Mag-H2 reactor is an apparatus for providing H_2 gas on-demand utilizing the hydrolysis of MgH_2. The process flow for generating electricity combined with FC is shown in Figure 5.

Table 3 shows the specification of Mag-H2 reactor. MHR3, which is suitable for educational purpose, equips three fuel tubes inside the cartridge, and each tube contains 6 MgH_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%.)

Additives	Temp. (deg.C)	Grain size (μm)	Ultrasonic wave frequency (kHz)			
			0	28	45	100
None	20	61.4	<1%	10%	15%	1%
		2.0	14	**85**	22	**82**
	70	61.4	11	-	55	-
	92	61.4	**81**	-	-	-
Citric acid (15%)	20	61.4	**94**	-	-	-
$MgCl_2$(10%)	70	61.4	**90**	-	-	-
$MgCl_2$ (1%)	70	61.4	57	-	-	-

H_2O is supplied from reservoir to the bottom of reactor through water tube.

↓

H_2 is generated by the hydrolysis of MgH_2 inside fuel tubes.

↓

After passing through a dryer, H_2 gas is introduced to FC.

↓

FC generates electricity.

↓

Hydrolysis of MgH_2 continues with keeping the water level of fuel tubes.

↓

If there is no need of electricity, H_2 partial pressure inside the reactor increases, which pushes out H_2O in water tube.

↓

FC stops generation of electricity.

Figure 5: Process flow of Mag-H2 reactor to generate electricity with FC.

Figure 6 shows the appearance of Mag-H2 reactor (MHR30). Depending on the application or operation mode, adequate amount of MgH_2 powder or pellet can be selected.

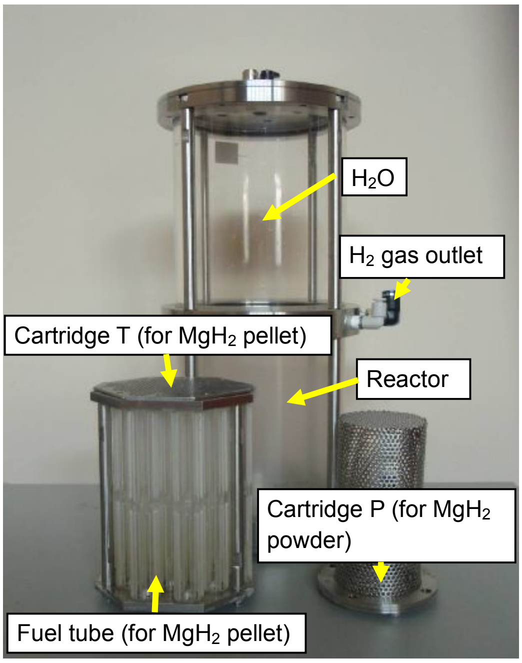


Figure 6: Mag-H2 reactor (MHR30).

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

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

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. MgH_2 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.

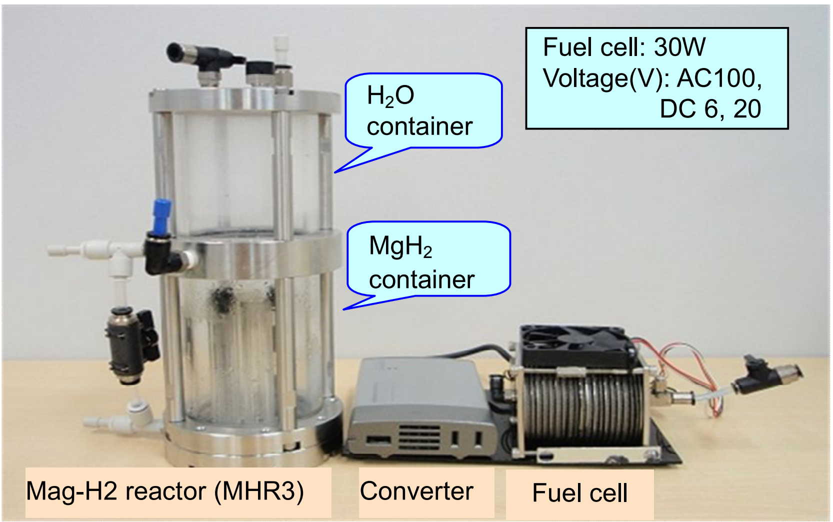
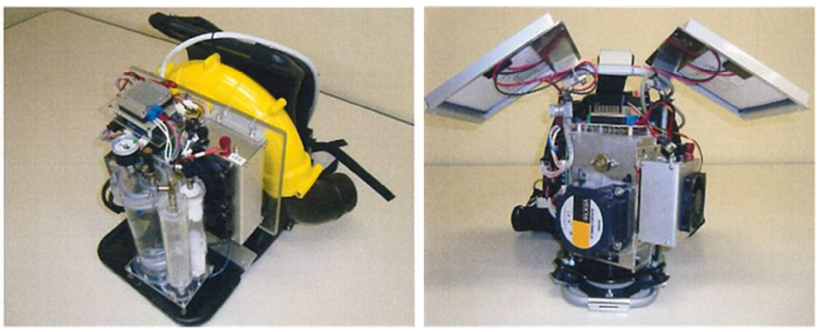


Figure 7: FC system for educational use.

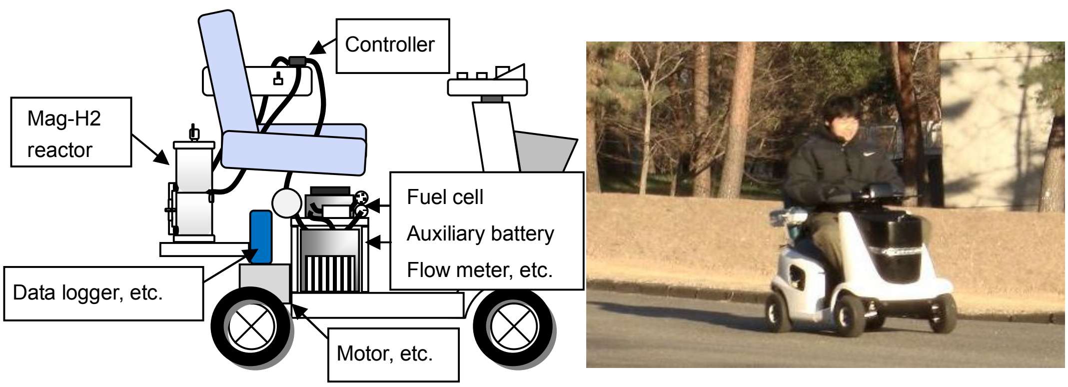
Figure 8: Portable power supply.



(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.

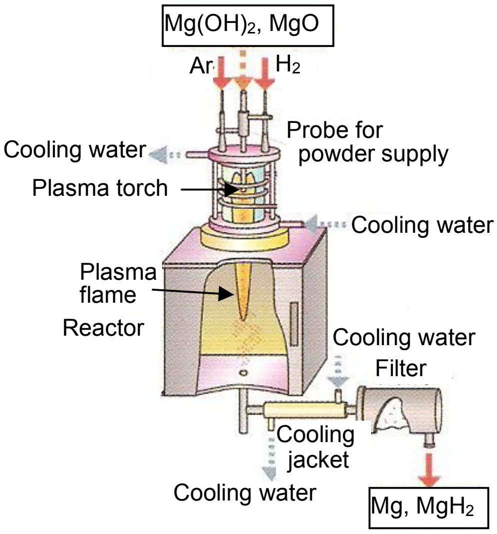


Figure 11: Schematic diagram of plasma-assisted regeneration system.

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.

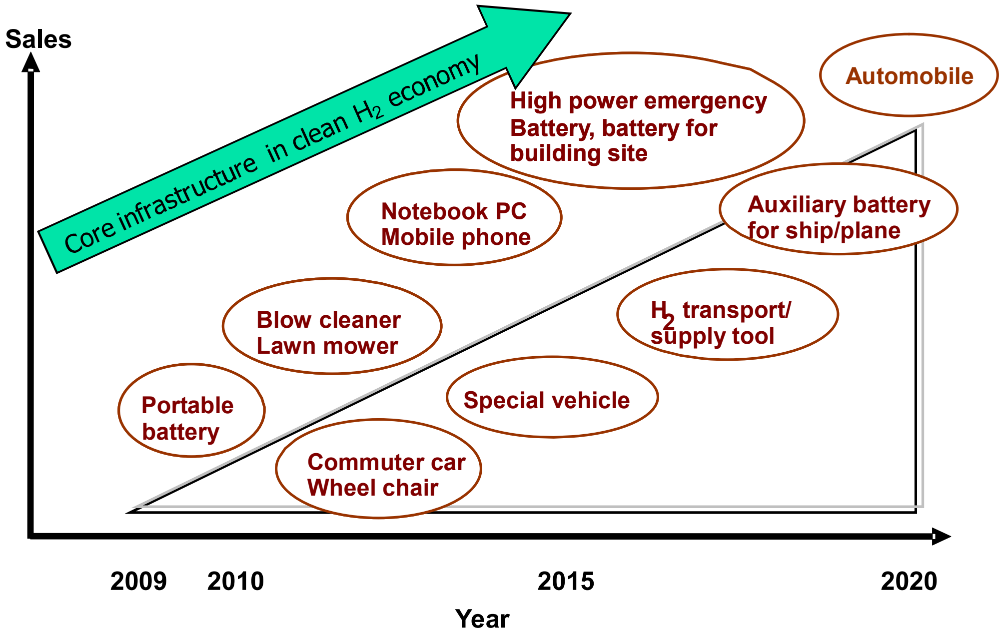


Figure 12: Perspective of Mag-H2 reactor +FC application.

Finally, a comprehensive recycling system of MgH_2 is proposed, which is shown in Figure 13. Among them, following three issues are considered as main tasks to be accomplished;

- Cost down of MgH_2. A production furnace with 50 kg MgH_2 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, MgH_2, 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 H_2 economy.

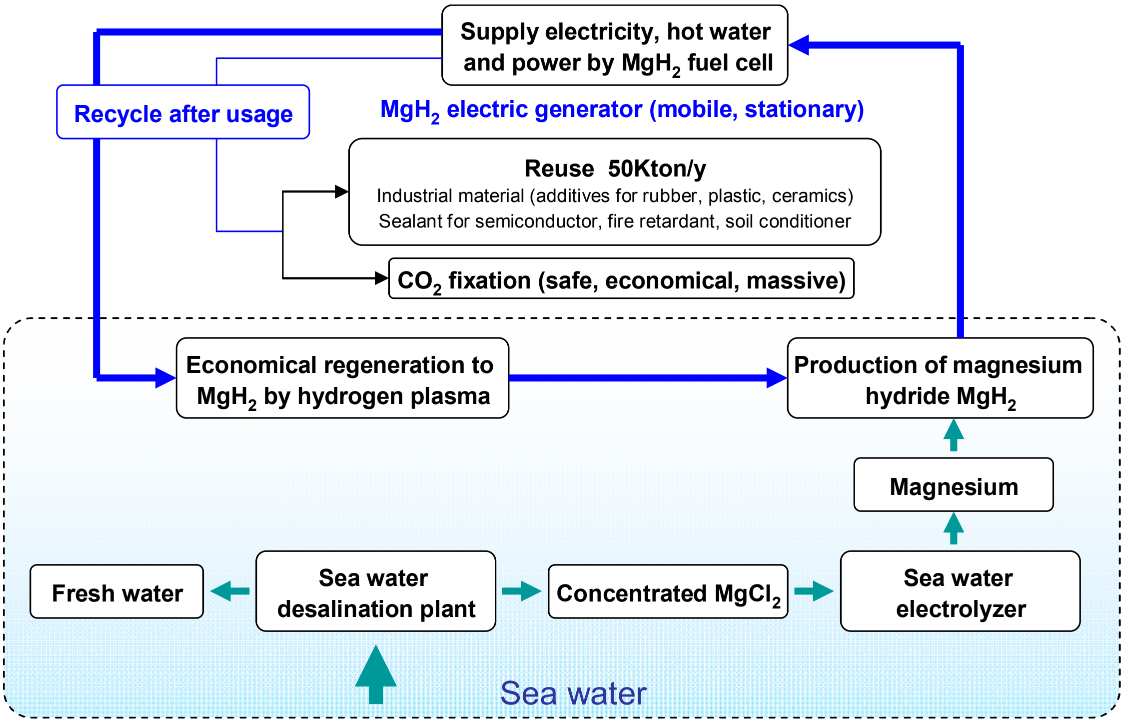


Figure 13: Comprehensive recycling process of MgH_2

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