

**Abstract**

The storage and generation of hydrogen is a basic problem for its use in fuel cells. Chemical hydrides such as  $\text{NaBH}_4$ ,  $\text{LiH}$  and  $\text{NaH}$  are known as high hydrogen containing materials.  $\text{NaBH}_4$ , in particular, is stable compared with other chemical hydrides, easy to handle and can be synthesized from common natural resources. However, with mixing of  $\text{NaBH}_4$  and  $\text{H}_2\text{O}$  at room temperature, only a small amount of the theoretical yield of hydrogen is liberated. In this work, we show that  $\text{Pt-LiCoO}_2$  is an excellent catalyst for releasing hydrogen by hydrolysis of

$\text{NaBH}_4$  solution. Using the catalyst with a stoichiometric amount of water ( $\text{H}_2\text{O}/\text{NaBH}_4$ : 2 mol/mol) at a high  $\text{H}_2$  pressure above 0.6 MPa produced nearly the theoretical  $\text{H}_2$  yield. The 10-kW-scale hydrogen generator comprised a storage vessel of  $\text{NaBH}_4$  solution, a solution pump, a byproduct storage tank for the  $\text{NaBO}_2$  solution, a separator and a hydride reactor. The reactor contained a honeycomb monolith coated with the  $\text{Pt-LiCoO}_2$  catalyst.  $\text{NaBH}_4$  was synthesized by annealing  $\text{NaBO}_2$  with  $\text{MgH}_2$  under high  $\text{H}_2$  pressure.

**Keywords**

Sodium borohydride, Catalyst, Chemical hydride, Magnesium hydride, Hydrogen generator

## 1. Introduction

A fuel cell is a device that continuously converts the chemical energy of hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) into electric energy. Since fuel cells have an efficiency much higher than that of conventional combustion engines, a fuel cell vehicle (FCV) is expected to have a high efficiency.<sup>1)</sup> A polymer electrolyte fuel cell (PEFC, PEM fuel cell) is the prime power source for FCVs. One of the most widely envisioned sources of fuel for FCVs is  $H_2$  itself. In such a system, it would be necessary to have a storage tank of  $H_2$  to start the system on demand. The first FCVs were produced on December 2, 2002. These FCVs feature a 35 MPa  $H_2$  storage tank and can travel 300-355 km on a full tank. The driving ranges of the vehicles are obviously small compared to those of gasoline vehicles and this represents the biggest hurdle to FCVs. The improvement of this range depends on a new  $H_2$  storage system.

$H_2$  can be stored in many different forms including as compressed or liquefied  $H_2$  in tanks,<sup>1)</sup> by adsorption on activated carbon<sup>1-3)</sup> and carbon nanotubes,<sup>1, 4)</sup> as a hydrogen-absorbing alloy,<sup>1, 5)</sup> as chemical hydrides including  $NaBH_4$ ,<sup>6-8)</sup>  $NaH$ ,<sup>9)</sup>  $LiH$ ,<sup>10)</sup>  $NaAlH_4$ ,<sup>11)</sup>  $MgH_2$ ,<sup>12)</sup>  $LiBH_4$ <sup>13, 14)</sup> and metal nitrides,<sup>15, 16)</sup> or as organic hydrides (methylcyclohexane, decalin).<sup>17)</sup> Among these methods, much attention has recently been given to the hydrolysis of a chemical hydride, in particular,  $NaBH_4$ <sup>6-8)</sup> because of its stability compared with other chemical hydrides and its easy conversion to  $H_2$  by a catalyst. The reaction of  $NaBH_4$  and  $H_2O$  is shown as follows.<sup>6)</sup>



Under appropriate conditions, 0.213 g of  $H_2$  is liberated per 1 g of  $NaBH_4$ , or alternatively, 0.109 g of hydrogen per 1 g of  $NaBH_4$  and  $2H_2O$ . Conventional catalysts are metal halides ( $NiCl_2$ ,  $CoCl_2$ ), colloidal platinum, activated carbon, Raney nickel,<sup>6)</sup> Ru supported on ion exchange resin beads<sup>7)</sup> and fluorinated particles of a Mg-based material.<sup>8)</sup>

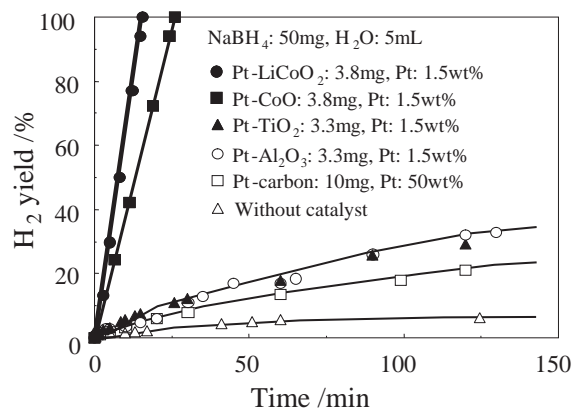
In this review, we first describe in **Section 2**, hydrogen generation using a catalyst that can achieve a sufficient rate and quantity of  $H_2$  generation in a fuel cell. It is shown that by using

$NaBH_4$ , a stoichiometric amount of water, Pt-LiCoO<sub>2</sub> and a high  $H_2$  pressure,  $H_2$  can be generated in large quantities. In **Section 3**, we describe the development of a 10-kW-scale hydrogen generator using  $NaBH_4$  as the hydrogen storage material and Pt-LiCoO<sub>2</sub> as the catalyst for releasing  $H_2$ . In **Section 4**, we demonstrate that  $NaBO_2$  can be recycled back to  $NaBH_4$  using coke.

## 2. Hydrogen generation using catalysts<sup>18)</sup>

The  $H_2$  production profiles of reaction of  $NaBH_4$  and water ( $H_2O/NaBH_4$ : 210 mol/mol) with or without a catalyst are shown in **Fig. 1**. Without using a catalyst, the amount of  $H_2$  increases with time and approaches a constant conversion value of 7 % because of the increased solution pH. The amount of  $H_2$  generated is increased by using a catalyst. The  $H_2$  generation rates using Pt-LiCoO<sub>2</sub> and Pt-CoO are constant and do not change over time. The stoichiometric amount of  $H_2$  is generated in 15 minutes using the Pt-LiCoO<sub>2</sub> catalyst. The catalysts are not consumed during the hydrolysis and are reusable. Sodium borohydride reacts more than 10 times faster using Pt-LiCoO<sub>2</sub> than the Ru catalyst.<sup>7)</sup>

**Figure 2** shows a transmission electron micrograph of Pt-LiCoO<sub>2</sub>. The dark areas are nano-Pt particles of about 2 nm diameter. The nano-Pt particles are dispersed on the LiCoO<sub>2</sub> substrate. The  $H_2$  generation rate is higher using Pt on LiCoO<sub>2</sub> than on other metal oxide substrates. It is supposed that the high surface area of the nano-Pt particles and the LiCoO<sub>2</sub> surface results in the highest  $H_2$  generation



**Fig. 1**  $H_2$  production profiles for reaction of  $NaBH_4$  with water.

rate. The reaction model shows an electron is released through catalyzed oxidation of the  $\text{BH}_4$  ion. This electron reduces the  $\text{H}^+$  in water and for two such reactions  $\text{H}_2$  gas is liberated.

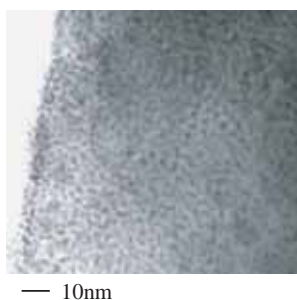
The  $\text{H}_2$  yield using the Pt-LiCoO<sub>2</sub> catalyst increases with an increase in water content and is 89 % at a  $\text{H}_2\text{O}/\text{NaBH}_4$  molar ratio of 4. An X-ray diffraction intensity curve of the byproduct indicates that the diffraction peaks of the byproduct are from  $\text{NaBO}_2 \cdot 2\text{H}_2\text{O}$ . As such, the reaction is approximated as follows.



The gravimetric and volumetric  $\text{H}_2$  densities of this reaction are 5.3 wt% and 5.4 kg/100 L, respectively, when the weight of water is taken into account.

In a closed pressure vessel, the reaction of  $\text{NaBH}_4$  with the Pt-LiCoO<sub>2</sub> catalyst and a stoichiometric amount of water drastically increases the pressure owing to generation of large quantities of  $\text{H}_2$  gas due to a synergism of the high  $\text{H}_2$  pressure above 0.6 MPa and the catalyst.<sup>19)</sup> The gravimetric  $\text{H}_2$  density has a maximum value of 9.0 wt% at a catalyst content of 0.2 g/g and a unit weight of  $\text{NaBH}_4$ . This indicates that the  $\text{H}_2$  generation is described by Eq. (1).

**Table 1** shows the gravimetric  $\text{H}_2$  density of various  $\text{H}_2$  storage materials.  $\text{MgH}_2$  contains 7.6 wt% of  $\text{H}_2$ ,<sup>1)</sup> but the dissociation pressure of 1 bar is not at room temperature but at 573 K. The decomposition temperature of  $\text{NaAlH}_4$  could be lowered by doping the hydride with a catalyst such as Ti clusters.<sup>20)</sup>  $\text{NaAlH}_4$  requires 373 K to absorb 3.4 wt%  $\text{H}_2$  within 7 min at 10 MPa. To date, the highest  $\text{H}_2$  absorption and desorption reported for any hydrogen-absorbing alloy is 2.5 wt%.<sup>5)</sup> The best value of  $\text{H}_2$  adsorption for carbon materials is 5.1



**Fig. 2** TEM of Pt-LiCoO<sub>2</sub> catalyst.

wt% at a temperature of 77 K.<sup>2)</sup> The hydrolysis of sodium hydride produces  $\text{H}_2$  at 4 wt%.<sup>9)</sup> LiH produces a  $\text{H}_2$  yield of 34 % upon addition of stoichiometric amounts of water,<sup>21)</sup> which corresponds to a gravimetric  $\text{H}_2$  density of 2.6 wt%. In comparison, the gravimetric  $\text{H}_2$  density of  $\text{NaBH}_4$  is 5.3 wt% by hydrolysis with water.<sup>18)</sup> Using the Pt-LiCoO<sub>2</sub> catalyst, hydrolysis of  $\text{NaBH}_4$  with a stoichiometric amount of water in a pressure vessel yields more than 2 times the  $\text{H}_2$  than the  $\text{H}_2$  storage materials mentioned above that are utilized at around room temperature. This table does not include carbon nanotubes because conflicting results have been published concerning the reversible storage of  $\text{H}_2$  in carbon nanotubes.<sup>4, 22)</sup> At an operating pressure of 70 MPa and 298 K, gaseous  $\text{H}_2$  can be stored at a volumetric density of 39 kg $\text{H}_2/\text{m}^3$ .<sup>23)</sup> The volumetric  $\text{H}_2$  density of the system including  $\text{NaBH}_4$ ,  $\text{H}_2\text{O}$  and the Pt-LiCoO<sub>2</sub> catalyst is 101 kg $\text{H}_2/\text{m}^3$ , providing 160 % more capacity than compressed  $\text{H}_2$  at 70 MPa.

### 3. Hydrogen generator<sup>24)</sup>

**Figure 3** shows a photograph of our generator system. The size of the body is 380 × 650 × 800 mm<sup>3</sup>. The hydrogen generator is made up of a fuel tank of  $\text{NaBH}_4$  solution, a solution pump, a byproduct storage tank for the  $\text{NaBO}_2$  solution, a separator (internal volume 4 L) and a hydride reactor (internal volume 2 L). The reactor contains a honeycomb monolith coated with Pt-LiCoO<sub>2</sub> catalyst, as shown in Fig. 3. For the hydrogen

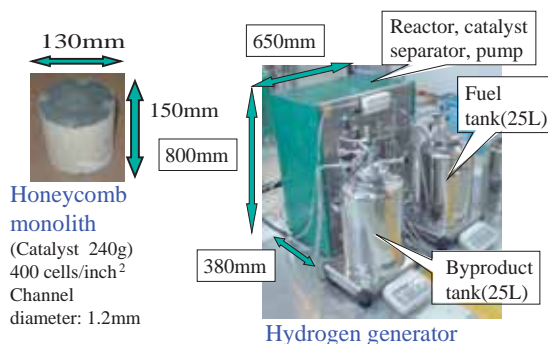
**Table 1** Gravimetric  $\text{H}_2$  densities of various  $\text{H}_2$  storage materials.

Materials	Temperature/K	Gravimetric $\text{H}_2$ density/wt% (references)
$\text{NaBH}_4 + 2\text{H}_2\text{O} + \text{Pt-LiCoO}_2$ catalyst+high pressure	296	9.0(19)
$\text{NaBH}_4 + 4\text{H}_2\text{O}$	296	5.3(18)
$\text{LiH} + \text{H}_2\text{O}$ ( $\text{H}_2$ yield: 34 %)	Ordinary temperature	2.6(21)
$\text{NaH} + 1.5\text{H}_2\text{O}$	Ordinary temperature	4.0(9)
$\text{MgH}_2$	573	7.6(1)
$\text{NaAlH}_4$	373	3.4(20)
Ti-xV-Cr-Mn (x=45 and 55; Ti/Cr/Mn=24:31:10, $\text{H}_2$ pressure: 7-0.01MPa)	313	2.5 (5)
Super activated carbon (AX-21, 5 MPa)	298	0.9(2)
(AX-21, 3 MPa)	77	5.1(2)

generator,  $\text{NaBH}_4$  solution enters the bottom of the reactor via a pump at 296 K and flows upward through the channel. The solution flow rate is controlled from 25 to 300 mL/min using the pump. Upon contact with the honeycomb monolith, the fuel solution generated  $\text{H}_2$  gas and  $\text{NaBO}_2$  (in solution) corresponding with a temperature rise. The  $\text{H}_2$  gas and the  $\text{NaBO}_2$  solution are separated by the separator, which also acts as a small storage buffer for  $\text{H}_2$  gas.

When we start pumping the  $\text{NaBH}_4$  solution into the Pt-LiCoO<sub>2</sub>-coated honeycomb monolith (Pt-LiCoO<sub>2</sub>: 240 g) in the generator,  $\text{H}_2$  gas is generated. After 200 seconds, the  $\text{H}_2$  generation rate reaches a constant value. By switching off the pump, the  $\text{H}_2$  generation ceases, also in 200 seconds. The response is stable and independent of the concentration and the feed rate. The steady-state  $\text{H}_2$  generation rates are shown as a function of the  $\text{NaBH}_4$  concentration in **Fig. 4**. As the  $\text{NaBH}_4$  concentration is increased, the  $\text{H}_2$  generation rate linearly increases and reaches a value of 120 NL/min (12 kW) at 25 wt%. Without catalyst in the generator, the  $\text{H}_2$  generation rate is 0-1 NL/min. The  $\text{NaBH}_4$  solution is quite stable when maintained at a high pH.<sup>7, 24)</sup> As the  $\text{NaBH}_4$  flow rate increases, the  $\text{H}_2$  generation rate increases and reaches 120 NL/min at the feed rate of 200 ml/min. The temperature of the byproduct solution increases rapidly inside the reactor due to the highly exothermic reaction.

The gravimetric and volumetric  $\text{H}_2$  densities of the generator containing the fuel tank and the byproduct tank are 1.3 wt% and 0.5 kg/100 L, respectively.



**Fig. 3** Overview photographs of honeycomb monolith and hydrogen generator.

Assuming that the ratio of weight/volume of the tanks is constant (12 kg/25 L), these densities increase with the size of the fuel tank and the byproduct tank (gravimetric  $\text{H}_2$  density: 2 wt%, volumetric  $\text{H}_2$  density: 1.5 kg $\text{H}_2$ /100 L, fuel tank: 60 kg, 125 L, byproduct tank: 60 kg, 125 L). The volumetric  $\text{H}_2$  density is similar to that of a compressed  $\text{H}_2$  system at 30 MPa, because storing 1.5 kg of  $\text{H}_2$  requires a volume of 100 L at 30 MPa.<sup>23)</sup> The volumetric  $\text{H}_2$  density was calculated by assuming that the ratio of outer/inner volume is 1.3.

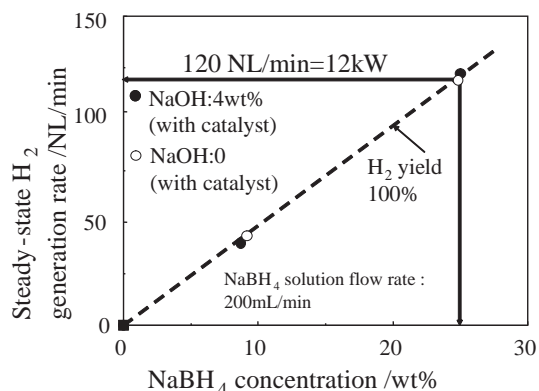
#### 4. Recycling process<sup>25)</sup>

$\text{NaBH}_4$  can be formed by a reaction of  $\text{NaBO}_2$  with  $\text{CaH}_2$ <sup>26)</sup> or with  $\text{MgH}_2$ .<sup>25, 27)</sup> As  $\text{CaH}_2$  vigorously reacts with water and is difficult to handle, attention has focused on  $\text{MgH}_2$ . The reaction of  $\text{NaBO}_2$  and  $\text{MgH}_2$  is represented as follows.



As the standard-free-energy change  $\Delta G^\circ$  for the reaction is -270 kJ,<sup>28)</sup> the reaction can proceed spontaneously.  $\text{NaBH}_4$  is synthesized by annealing a mixture of the byproduct  $\text{NaBO}_2$  and  $\text{MgH}_2$  under high  $\text{H}_2$  pressure. Temperature desorption scans, infrared absorption<sup>29)</sup> and X-ray diffraction measurements indicate that annealing of the substrate mixture under a high  $\text{H}_2$  pressure produces  $\text{NaBH}_4$  and  $\text{MgO}$ .

**Figure 5** shows the  $\text{NaBH}_4$  yield as a function of temperature. As the temperature increases, the yield increases and has a maximum value of 97 % at 823 K (pressure; 7 MPa). Figure 5 also shows the



**Fig. 4** Influence of  $\text{NaBH}_4$  solution concentration on steady-state  $\text{H}_2$  generation rate.

hydrogen desorption curve of  $\text{MgH}_2$ . There is prominent desorption centered at 733 K. The observed decrease of the yield above 823 K is attributed to the melting of  $\text{NaBH}_4$  (778 K).<sup>29)</sup> The yield increases with pressure and approaches a constant value of 97 % at 7 MPa and 823 K. When  $\text{NaBO}_2$  is mixed with magnesium, the yield is only 10 % and is much lower than that using  $\text{MgH}_2$  as shown in Fig. 5. The low reactivity is probably due to agglomeration of Mg particles at 823 K.

The recycling of  $\text{NaBH}_4$  is shown in Fig. 6. This process uses coke and  $\text{NaBO}_2$  and can be described by a combination of Eq. (3) and the following general reactions.<sup>30, 31)</sup>

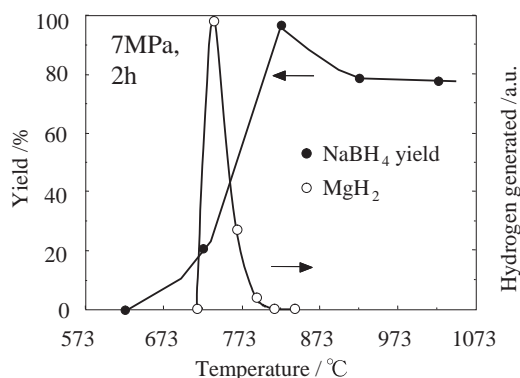
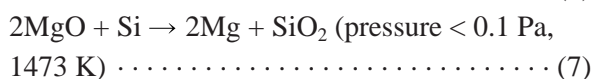
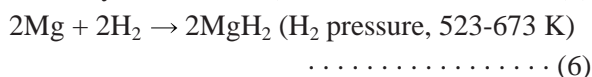
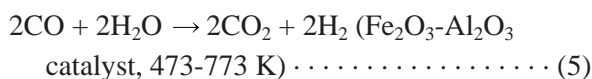
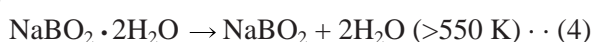


Fig. 5 Influence of temperature on  $\text{NaBH}_4$  yield (7MPa, 2h) and temperature desorption scan of  $\text{MgH}_2$ .

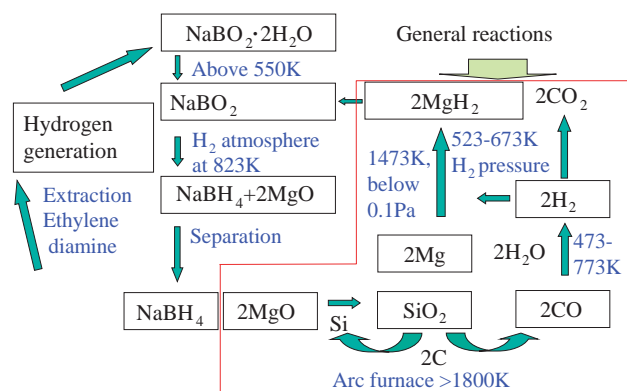
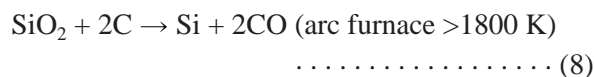


Fig. 6 Recycling process of  $\text{NaBH}_4$ .



Reactions (3)-(8) combine to produce



If this is combined with the onboard hydrogen generation reaction (Eq. (2)), the overall reaction is



Thus,  $\text{NaBO}_2$  can be recycled back to  $\text{NaBH}_4$  using coke at a high temperature above 1800 K. This corresponds to a low energy efficiency.

## 5. Conclusions

We have developed  $\text{H}_2$  storage and generation using a chemical hydride. Pt-LiCoO<sub>2</sub> synthesized using the conventional impregnation method was an excellent catalyst for releasing  $\text{H}_2$  from the stabilized  $\text{NaBH}_4$  solution, and a 10-kW-scale hydrogen generator that generates high purity  $\text{H}_2$  gas from aqueous solutions of  $\text{NaBH}_4$  was developed.  $\text{NaBH}_4$  was synthesized by annealing a mixture of  $\text{NaBO}_2$  with  $\text{MgH}_2$  under high  $\text{H}_2$  pressure.  $\text{NaBO}_2$  could be recycled back to  $\text{NaBH}_4$  using coke at high temperature. As the energy efficiency of the recycling process is low, the very high gravimetric and volumetric  $\text{H}_2$  densities in the chemical hydride system may be highly effective as a  $\text{H}_2$  storage system for a fuel cell uninterrupted power supply (FCUPS) or for any emergency power source.

## Acknowledgements

We are greatly indebted to N. Suzuki, Dr. G. J. Shafer and Dr. T. Hioki of the Toyota Central R&D Labs., Inc. for their help and valuable discussions.

## References

- Schlapbach, L. and Züttel, A., *Nature*, **414**(2001), 353
- Chahine, R. and Bose, T. K. : *Int. J. Hydrogen Energy*, **19**(1994), 161
- Kojima, Y. and Suzuki, N. : *Appl. Phys. Lett.*, **84**(2004), 4113
- Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S. and Heben, M. J. : *Nature*, **386**(1997), 377
- Tamura, T., Tominaga, Y., Matumoto, K., Fuda, T., Kuriwa, T., Kamegawa, A., Takamura, H., and Okada, M. : *J. Alloys Compd.*, **330/332**(2002), 522
- Schlesinger, H. I., Brown, H. C., Finholt, A. E., Gilbreath, J. R., Hoekstra, H. R. and Hyde, E. K. : *J. Am. Chem. Soc.*, **75**(1953), 215
- Amendola, S. C., Sharp-Goldman, S. L., Janjua, M. S., Kelly, M. T., Petillo, P. J. and Binder, M. : *J. Power Sources*, **85**(2000), 186

- 8) Suda, S., Sun, Y. M., Uchida, M., Liu, B. H., Zhou, Y., Morimitsu, S., Arai, K., Zhou, Y., Tsukamaoto, N., Candra, Y. and Li, Z. P. : *Metals and Materials-Korea*, **7**(2001), 73
- 9) DiPietro, J. P. and Skolnik, E. G. : *Proc. of the 2000 DOE Hydrogen Program Rev. NREL/CP- 570-28890*, (2000)
- 10) McClaine, A. W., Breault, R. W., Larsen, C., Konduri, R., Rolfe, J., Becker, F. and Miskolczy, G. : *Proc. of the 2000 U.S. DOE Hydrogen Program Rev. NREL/CP-570-28890*, (2000)
- 11) Bogdanovic, B. and Schwickardi, M. : *J. Alloys Compd.*, **253/254**(1997), 1
- 12) Kojima, Y., Suzuki, K., and Kawai, Y. : *J. Mater. Sci. Lett.*, **39**(2004), 2227
- 13) Kojima, Y., Kawai, Y., Kimbara, M., Nakanishi, H. and Matsumoto, S. : *Int. J. Hydrogen Energy*, **29**(2004), 1213
- 14) Kong, V. C. Y., Foulkes, F. R., Kirk, D. W. and Hinatsu, J. T. : *Int. J. Hydrogen Energy*, **2**(1999), 665
- 15) Chen, P., Xiong, Z., Luo, J., Lin, J. and Tan, K. L. : *Nature*, **420**(2002), 302
- 16) Kojima, Y. and Kawai, K. : *Chem. Commun.*, **19**(2004), 2210
- 17) Newson, E., Haueter, Th., Hottinger, P., Von Roth, F., Scherer, G. W. H. and Schucan, Th. H. : *Int. J. Hydrogen Energy*, **23**(1998), 905
- 18) Kojima, Y., Suzuki, K., Fukumoto, K., Sasaki, M., Yamamoto, T., Kawai, Y. and Hayashi, H. : *Int. J. Hydrogen Energy*, **27**(2002), 1029
- 19) Kojima, Y., Kawai, Y., Nakanishi, H. and Matsumoto, S. : *J. Power Sources*, **135**(2004), 36
- 20) Fichtner, M., Engel, J., Fuhr, O., Kircher, O. and Rubner, O. : *Mater. Sci. Eng.*, **B108**(2004), 42
- 21) Dunn, P. M., Egan, C. J., Harbison, W. L. and Pitcher, G. K. : *Proc. of the 26th Intersociety Energy Convers. Eng. Conf.*, **3**(1991), 527
- 22) Ye, Y., Ahn, C. C., Witham, C., Fultz, B., Liu, J., Rinzler, A. G., Colbert, D., Smith, K. A. and Smalley, R. E. : *Appl. Phys. Lett.*, **74**(1999), 2307
- 23) Comings, E. W. : *High Pressure Technology*, (1956), 486, McGraw-Hill, New York.
- 24) Kojima, Y., Suzuki, K., Fukumoto, K., Kawai, Y., Kimbara, M., Nakanishi, H. and Matsumoto, S. : *J. Power Sources*, **125**(2004), 22
- 25) Kojima, Y. and Haga, T. : *Int. J. Hydrogen Energy*, **28**(2003), 989
- 26) Goerrig, D., Schabacher, W. and Schubert, F. : *Ger. Patent No. 103622*, (1956)
- 27) Li, Z. P., Liu, B. H., Arai, K., Morigazaki, N. and Suda, S. : *J. Alloys Compd.*, **356/357**(2003), 469
- 28) *CRC Handbook of Chemistry and Physics*, 79th : Ed by Lide, D. R., (1998), section 5, CRC Press, Boca Raton, FL, USA.
- 29) James, B. D. and Wallbridge, M. G. H. : *Prog. Inorg. Chem.*, **11**(1970), 99
- 30) *Inorg. Chem., An Industrial and Environment Perspective* : Ed by Swaddle, T. W., (1997), Academic Press
- 31) Wilson, C. B., Claus, K. G., Earlam, M. R. and Hillis, J. E. : *Magnesium and Magnesium Alloys*, Kroshwitz, J. I., executive editor, Howe-Grant, M., editor : *Encyclopedia of Chemical Technology*, 4th ed., (1995), 622-674, Wiley, New York, USA.

(Report received on Feb. 7, 2005)



#### Yoshitsugu Kojima

Research fields : Hydrogen storage materials

Academic degree : Dr. Eng.

Academic society : Jpn. Inst. Met., Soc. Polym. Sci., Jpn., Soc. Fiber Sci. Technol., Jpn.

Who'Who in Sci. and Eng. 8th Ed. (Marquis, New Providence, NJ, USA), 2005-2006

Awards : The Awards for Best Posters, Jpn. Soc. High Press. Sci. Technol., 1995