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AMMONIA-BASED HYDROGEN SOURCE FOR FUEL CELL APPLICATIONS

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Ammonia-based hydrogen source for fuel cell applications

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Abstract

Generation of hydrogen from the reaction of ammonia (NH₃) with magnesium hydride (MgH₂) was studied. Experiments were conducted at near ambient temperatures (75–150 °C), which are lower than that required by ammonia cracking and/or metal hydride thermal decomposition reactions. Effects of selected catalysts/promoters for the production of hydrogen by the NH₃–MgH₂ reaction were evaluated. Addition of ammonium chloride (NH₄Cl) accelerated the NH₃–MgH₂ reaction. MgH₂ doped with either PdCl₂ or PtCl₄ also showed increased reactivity towards NH₃ for H₂ production in the presence of NH₄Cl. Results from this study demonstrated the feasibility of hydrogen production from ammonia-based reactions in support of potable hydrogen fuel cells. These preliminary results warrant further systematic studies to elucidate the activation mechanism of PdCl₂ or PtCl₄ as catalysts, as well as the role of NH₄Cl as an additive, a reactant and/or a catalyst in the reaction system of interest.

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1. Introduction

A compact and lightweight hydrogen source based on rapid and efficient energy conversion of convenient, inexpensive, and safe hydrogen-laden chemicals is needed for widespread use of small hydrogen-air fuel cells (H/AFCs). Most typically used performance criteria for hydrogen storage are gravimetric and volumetric densities [1]. Table 1 shows relative values of various hydrogen storage options.

In consideration of storage, handling, and deployment, ammonia has been identified as one of the attractive and feasible hydrogen-laden chemicals to provide hydrogen for small H/AFCs. Ammonia (NH₃) is a stable and widely available energy source with a relatively high hydrogen density (17.6%). Since the vapor pressure of ammonia at 104 °F (40 °C) is 225 psi (15.5 bar), it can be stored under modest pressure as a liquid. The challenge remains in the rapid and efficient conversion of ammonia into hydrogen. Cracking ammonia to hydrogen and nitrogen is an endothermic reaction, which begins at temperatures of 450–500 °C [2,3]. However, the rate and extent of ammonia cracking in the existing processes are not satisfactory

for deployable fuel cell applications. At temperatures as high as 1000 °C, a trace amount of ammonia remains [4]. Because of the heat requirements for cracking ammonia and vaporizing liquid ammonia, part of the ammonia load would have to be used as fuel for the conversion process. A high-temperature converter system is likely to be bulky and may require catalysts and other necessary features such as heat exchange devices and insulation. Since ammonia degrades the performance of H/AFCs, the ammonia conversion must be complete and/or special processing units must be equipped to remove residual ammonia from the hydrogen product stream.

A new approach of reacting ammonia with metal hydrides to produce hydrogen has recently been evaluated. Several research groups have explored the ammonia–lithium aluminum hydride (LiAlH₄) reaction [5], ammonia–magnesium hydride (MgH₂) reaction [6], and ammonia–aluminum hydride (AlH₃) reaction [7].

Metal hydrides are metals either ionically or covalently bonded with hydrogen, which is negatively polarized. Early work on metal hydrides, dates back more than 140 years, and was well documented by German chemists in 1930s (Gmelins Handbuchs). Extensive studies on metal hydrides were conducted in the 1960s through 1980s [8,9] due to the

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Table 1 Gravimetric and volumetric densities of selected H_2 storage options

Material	H2 (wt%)	H-atoms/cm ³ (×10 ²²)
H ₂ (gas) 25 °C, 200 bar	100	0.99
H ₂ (liquid) $-253 ^{\circ}$ C, 1 bar	100	4.2
CH ₄ (liquid) -162 °C, 1 bar	25	6.4
NH ₃ (liquid) $-33 ^{\circ}$ C, 1 bar	17.6	7.2
MgH ₂ (solid)	7.6	6.5
Mg_2NiH_4 (solid)	3.6	5.9
FeTiH ₂ (solid)	1.89	6.0
LaNi5H6 (solid)	1.37	5.5

potential technological importance of this class of materials in hydrogen-based energy conversion schemes. One of the early interests that stimulated extensive studies in metal hydrides was their potential application as moderator, reflector, or shield components for high-temperature mobile nuclear reactors [8]. Catalytic reactions of metal hydrides have also drawn considerable interest [10]. Currently, there is a renewed interest in various applications involving metal hydrides. These applications include using metal hydrides as hydrogen storage, heat storage, storage batteries, and a means to separate hydrogen from gas mixtures [11]. One example is MgH₂-Mg-systems that have been studied for hydrogen storage, purification, and separation, and heat storage [12]. Attractive features of this system include relatively low material and construction costs, satisfactory kinetics with low loading pressure, and high hydrogen (6.5–7.0 wt%) and heat (18 kcal/mol) capacity. However, a heat source of 300-350 °C is needed to release the bonded hydrogen. Another example is metal hydride storage batteries developed in 1970s [13]. Many of these batteries, such as nickel-metal hydride (Ni-MH) batteries, are widely used today. Typical Ni-MH batteries have a capacity of about 55-65 W h/kg [11].

The key issues involving the use of metal hydrides include the control of the rate of as well as chemical activation of hydride reactions at ambient temperatures. Saline hydrides are powerful reducing agents, and can ignite spontaneously upon contacting with air to form metal oxide and water. Saline hydrides react instantly with water to evolve hydrogen. Desorption of hydrogen from metal hydrides typically occurs at temperatures greater than 250 °C, except for AlH₃ (150 °C) and LiAlH₄ (180 °C) [14]. In addition, metal hydrides with higher H₂ content display higher desorption temperature, such as MgH₂ (7.6 wt%)

at 360 °C, and LiH (12.6 wt%) at 720 °C. Saline hydrides also react with ammonia rapidly at ambient temperatures, but the reaction typically forms hydrogen and metal amide [15]. Chemical activation of MgH₂ is accomplished by blending a small amount of LiBH₄ [16] and carbon/noncarbon additives [17]. The catalyst approach has also been reported for other metal hydrides, such as LiAlH₄ [18] and NaAlH₄ [19]. The enhancement of hydrogen uptake/release characteristics by using selected catalysts has been well documented in these studies.

This experimental study investigated the reaction between ammonia and magnesium hydride (MgH_2) as a potential hydrogen source for field-deployable fuel cell applications.

$$2\mathrm{NH}_{3~(g)} + 3\mathrm{MgH}_{2~(cr)} \rightleftharpoons \mathrm{Mg}_{3}\mathrm{N}_{2~(cr)} + 6\mathrm{H}_{2~(g)}$$
$$\Delta\mathrm{H}^{0} = -33.52~\mathrm{kcal}.$$

The heat of reaction calculated from Chase [20] indicates this reaction is exothermic. The reverse reaction is known to proceed by heating magnesium nitride (Mg_3N_2) with hydrogen [21]. Magnesium reacts with ammonia to form magnesium nitride and hydrogen [22], but the load utilization efficiency is about 50% of that achievable by the proposed ammonia–magnesium hydride.

Two key evaluation criteria for energy storage/conversion systems are (1) specific energy (kW h/kg) and (2) energy density (kW h/L), where the weight and volume are those of the systems, i.e., chemicals plus equipment. Table 2 provides a comparison of these two criteria for the proposed NH_3 – MgH_2 reaction system, existing electrical energy storage/conversion systems, and target fuel cell systems.

2. Experimental

Magnesium hydride was obtained from Aldrich Chemical Co. in powder form (90% purity, balance magnesium). MgH₂ has a bulk density of 1.45 g/cm^3 and decomposes at $280 \,^{\circ}\text{C}$ under high vacuum. The MgH₂ feedstock contained about 10% magnesium as the result of its manufacturing process. The following compounds were used as promoters (i.e., additive, reactant, or catalyst) to enhance the baseline reaction: ammonium chloride (NH₄Cl, Sigma, 99.9+%), silver chloride (AgCl, Baker, 99.9%), cuprous chloride (CuCl, Baker, 94.8%), zinc, Baker, 99.8%), zinc oxide (ZnO, Fisher Sci., 99.9%),

Table 2

Specific energy and energy density of selected energy systems

Electrical energy storage/conversion system	Specific energy (kW h/kg)	Energy density (kWh/L)
Lead-acid battery	0.04	0.07
Zinc-MnO ₂ -NH ₄ Cl (Leclanché) battery	0.09	0.2
Zinc-air battery	0.2	0.08
Lithium batteries	0.2	0.3
NH ₃ (Cracking at 650 °C)-H/AFCs	0.4	0.3
NH ₃ -MgH ₂ -H/AFCs (50% efficiency)	~ 1 (Estimated)	~ 1 (Estimated)
Current fuel cell system target	1	1
Future fuel cell system target	2	2

iron (Fe, Fisher Chemicals, 99%), palladium chloride (PdCl₂, Aldrich, 99%), and platinum chloride (PtCl₄, Aldrich, 98%).

All batch tests were conducted using 15-mL glass vials sealed with Teflon septums. Tests at each experiment condition were carried out in triplicates. The following describes two procedures (purge and vacuum) used for sample loading/preparation and catalyst doping procedure.

The purge procedure: Prescribed amounts of the chemicals were weighed and loaded into a 15-mL glass vial. The vial was sealed with a rubber septum. Two hypodermic needles were poked through the septum (one was connected with nitrogen supply and the other one was a vent), and the loaded vial was purged with nitrogen for about 30 s. Then, ammonia gas was charged into the vial from the ammonia cylinder with the regulator set at a pressure of 20 or 10 psi. The loaded vials were placed into an oven preset at a desired test temperature and the reaction time was set at zero. After a preset reaction time, the vials were cooled to ambient temperature, and the gas in the headspace was sampled and analyzed using a gas chromatograph.

The vacuum procedure: The first two steps were the same as those in the purge procedure. Only one hypodermic needle was poked through the septum. The vial was vacuumed to 29.8 inHg and charged with nitrogen to 10 psi, and this procedure was repeated for three times. Then, ammonia gas was charged into the vial at a pressure of 10 psi. The rest steps were the same as those in the purge procedure.

The catalyst doping procedure: First, 1, 5, 25, and 50 mg of $PdCl_2$ or $PtCl_4$ were dissolved in separate vials each containing 5 mL of methanol, respectively. Then, 500 mg of MgH_2 were added to each of the solutions. The methanol was vacuum evaporated methanol. The dried $PdCl_2$ or $PtCl_4$ doped MgH_2 was kept as the feedstock.

3. Results and discussion

Results from the magnesium hydride-ammonia reaction (MgH₂-NH₃) at 150 °C in terms of hydrogen formation rates are shown in Fig. 1, in which three reactions possibly involved in this system are also listed. In addition to the reaction of interest, thermal decomposition of magnesium hydride was possible. Therefore, tests were conducted using magnesium hydride in the presence of only nitrogen to evaluate thermal effect of hydrogen production. The reaction of magnesium with ammonia could also contribute to the hydrogen formation since the magnesium hydride feedstock contained about 10% magnesium as the result of its manufacturing process. Tests using this combination of reactants were also conducted. At reaction times of 20-30 h, the hydrogen concentration in the vial reached about 30%. Of this total, about 15% was due to the thermal decomposition reaction of MgH₂ while about 2% was derived from the Mg-NH₃ reaction. By subtraction, the MgH₂-NH₃ reaction contributed about 13% of the hydrogen in the gas mixture, or 43% of the hydrogen production. It was also believed that the hydrogen concentration data represented a minimum level of hydrogen produced at each test condition since the loss of hydrogen was likely to have occurred due to



Fig. 1. Hydrogen evolution from the $\rm MgH_2-\rm NH_3$ reaction using batch reactors.

gas permeation through the rubber septum over the extended test period at 150 °C.

All of the early batch tests were conducted using the purge procedure. Low levels of oxygen and nitrogen were detected by the gas chromatography analysis in some of the off-gas samples from the sealed glass vials. The presence of oxygen may be resulted from incomplete purge of the headspace in the vial, and could affect the route and extent of the hydride reactions. Therefore, additional tests were conducted using the vacuum procedure. Results from the tests using both purge and vacuum procedures, as shown in Fig. 1, appeared to be consistent.

This study also explored the effect of selected catalysts and/or promoters on the rate of hydrogen generation involving the MgH₂–NH₃ reaction. These compounds include: NH₄Cl, AgCl, CuCl, Zn, ZnO, Fe, PdCl₂, PtCl₄. The first six compounds were added in the test vials to form admixtures with magnesium hydride prior to the temperature exposure. The last two compounds were doped onto the magnesium hydride according to the doping procedure described in the Experimental section.

All of these compounds showed a certain degree of enhancement of hydrogen formation rate at the test temperature of 75 °C. The results derived from the first six compounds are shown in Fig. 2. A baseline was established for MgH₂–NH₃ without adding any catalyst/promoter at 75 °C, 10 psi and at 150 °C, 20 psi, respectively, and shown by the two lines in Fig. 2. Of the three chloride compounds, AgCl and CuCl enhanced the rates of hydrogen formation comparable to those obtained without adding these compounds at 150 °C. Furthermore, the presence of NH₄Cl resulted in significant increase in the hydrogen concentration, which could be attributed to two factors. First, ammonium chloride is in equilibrium with ammonia and hydrochloric acid (HCl). Although the equilibrium constant is very small ($K_{25 \circ C} = 10^{-16}$), HCl is extremely reactive with MgH₂. Second, NH₄Cl may interact with MgH₂ according to the following pathway: $4MgH_2 + 2NH_4Cl = Mg_3N_2 + MgCl_2 +$ 8H₂. Additional tests showed that the MgH₂–NH₄Cl mixture did not react unless either water or ammonia was present.



Fig. 2. Hydrogen evolution from the $MgH_2\mbox{-}NH_3$ reaction—effects of additives.



Fig. 3. $\rm H_2$ evolution from the $\rm MgH_2-\rm NH_3$ reaction—effects of additives/catalysts.

The former, when condenses on the surface of the reactants, ionizes NH₄Cl and creates a suitable medium for the reaction of MgH₂ and HCl. The latter may play a similar but less effective role, since its ionization constant ($K_{-50 \circ C} = 10^{-30}$) is much less than that of water ($K_{w 25 \circ C} = 10^{-14}$).

The MgH₂–NH₃ conversion reaction was also conducted with NH₄Cl additive and PdCl₂ and PtCl₄ catalyst, respectively. Fig. 3 shows a significant increase in hydrogen production as compared to the baseline systems (i.e., MgH₂–NH₃ and MgH₂–NH₃–NH₄Cl). For tests conducted at 75 °C with a reaction time of 1 h, the combination of NH₄Cl and PdCl₂ resulted in the highest hydrogen concentration. Again, the results from the tests using the different loading procedures (purge and vacuum) appeared to be comparable.

Based on these results, experiments were further conducted using the $PdCl_2$ to evaluate the effect of catalyst dosage on the rate of hydrogen formation. Fig. 4 shows the results from the



Fig. 4. H₂ evolution from the MgH₂-NH₃ reaction-effect of catalyst dosage.

PdCl₂ tests. The first set of data (gas sampling 1 h after test) show the rate of hydrogen production doubled as compared to the baseline (i.e., MgH₂-NH₃-NH₄Cl without PdCl₂). It should be noted that when gas samples were taken again 16 h later from the test vials, which were kept at ambient temperature, the hydrogen concentration increased to about 43% for three samples, and nearly 60% for the sample with the highest PdCl₂ dosage. Theoretical limits of two possible reactions were shown in Fig. 4. The first line at the hydrogen concentration of 15.6% indicates the level that could be reached if hydrogen were produced only by the MgH2-HCl reaction based on the available HCl (limiting species) from the ammonium chloride loading. Similarly, the second line at the hydrogen concentration of 42.5% reflects the amount of hydrogen that could be produced if the reaction were to proceed according to $4MgH_2 + 2NH_4Cl = Mg_3N_2 + MgCl_2 + 8H_2$. In addition, the data point corresponding to the 50 mg PdCl₂ dosage shows that the concentration of hydrogen is about 60%, nearly 20% higher than the stoichiometry of the above reaction. These levels suggest that the observed hydrogen concentrations are within the ranges from several plausible reactions, but further tests are needed to confirm the reaction mechanism for these systems.

4. Conclusion

Hydrogen was produced from the reaction between ammonia (NH₃) and magnesium hydride (MgH₂) in the temperature range of 75–150 °C. Among various additives tested, NH₄Cl displayed the most pronounced effect of enhancing the reactivity of MgH₂ at near-ambient temperatures. MgH₂ doped with either PdCl₂ or PtCl₄ in combination with ammonia and NH₄Cl further increased the rate of hydrogen formation. Results from this study demonstrated the feasibility of hydrogen production from ammonia-based reactions in support of potable hydrogen fuel cells. These preliminary results warrant further systematic studies to elucidate the activation mechanism of PdCl₂ or PtCl₄ as catalysts, as well as the role of NH₄Cl as an additive, a reactant and/or a catalyst in the ammonia-based reaction systems of interest.

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References

- Hynek S, Fuller W, Bentley J. Hydrogen storage by carbon sorption. Int J Hydrogen Energy 1997;22(6):601–10.
- [2] Buchner W, Schliebs RG, Winter KH, Buchel KH. Industrial inorganic chemistry. New York, NY: VCH Publishers; 1989.
- [3] Collins JP, Way JD. Catalytic decomposition of ammonia in a membrane reactor. J Membrane Sci 1994;96:259–74.
- [4] LeBlanc Jr JR, Madhavan S, Porter RE, Kellogg P. Ammonia. Kirk-Othmer encyclopedia of chemical technology, vol. 2. New York, NY: Wiley; 1982. p. 470–516.
- [5] Wilkes JS. Hydrogen storage materials for personal electric power. Private communications based on a joint project between General Electric Global Research Center and US Air Force Academy, Colorado Springs, CO; 2004.
- [6] Hurley JA, Li L. Ammonia-based hydrogen source for deployable fuel cell applications. AFRL/MLQL final report unpublished, Air Force Research Laboratory; 2003.
- [7] Serenbrennikov V, Damle A, Storojenko P. Ammonia-based hydrogen sources for small fuel cells. SBIR phase I final report (DAAD-19-00-C-0020), November 15, 2000.
- [8] Mueller WM, Blackledge JP, Libowitz GG. Metal hydrides. New York, NY: Academic Press; 1968.
- [9] Dedieu A. Transition metal hydrides. New York, NY: VCH Publishing, Inc.; 1992.
- [10] Slocum DW, Moser WR. Catalytic transition metal hydrides. Ann New York Acad Sci 1983;415.

- [11] Sastri MVC, Viswanathan B, Murthy SS. Metal hydrides—fundamentals and applications. New York, NY: Narosa Publishing House; 1998.
- [12] Bogdanovic B, Spliethoff B. Active MgH₂–M-systems for hydrogen storage. In: Hydrogen energy progress VI—proceedings of the sixth world hydrogen energy conference, Vienna, Austria, July 20–24, 1986, New York, NY: Pergamon Press; 1986.
- [13] Beck F, Ruetschi P. Rechargeable batteries with aqueous electrolytes. Electochim Acta 2000;45:2467–82.
- [14] Grochala W, Edwards P. Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen. Chem Rev 2004;104(3):1283–315.
- [15] Wiberg E, Amberger E. Hydrides of the elements of main groups I–IV. New York, NY: Elsevier Publishing Co.; 1971.
- [16] Johnson SR, Anderson PA, Edwards PP, Gameson I, Prendergast JW, Al-Mamouri M, et al. Chemical activation of MgH₂; a new route to superior hydrogen storage materials. Chem Commun, 2005; 2823–5.
- [17] Wu CZ, Wang P, Yao X, Liu C, Chen DM, Lu GQ, Cheng HM, Effect of carbon/noncarbon addition on hydrogen storage behaviors of magnesium hydride. J Alloys Comp 2006;414 (1–2):259–64.
- [18] Resan M, Hampton MD, Lomness JK, Slattery DK. Effects of various catalysts on hydrogen release and uptake characteristics of LiAlH₄. Int J Hydrogen Energy 2005;30:1413–6.
- [19] Kircher O, Fichtner M, Kinetic studies of the decomposition of NaAlH₄ doped with a Ti-based catalyst. J Alloys Comp 2005;(404–406):339–42.
- [20] Chase Jr MW. NIST-JANAF thermodynamical tables, 4th ed. J Phys Chem Ref Data Monograph 1998; 9.
- [21] Gmelins Handbuch Der Anorganischen Chemie, vol. N: Mvol. 2, 331. Berlin, Germany: Verlag Chemie, G.M.B.H.; 1935.
- [22] Gmelins Handbuch Der Anorganischen Chemie, vol. Mg: Mvol.B1, 68–70. Berlin, Germany: Verlag Chemie, G.M.B.H.; 1937.