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Integrated Advanced Energy Systems Research at IIT

By

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Summary

This report consists of Two research projects; Sustainable Buildings and Hydrogen Storage. Sustainable Building Part includes: Wind and the self powered built environment by professor P. Land and his research group and experimental and computational works by professor D. Rempfer and his research group. Hydrogen Storage part includes: Hydrogen Storage Using Mg-Mixed Metal Hydrides by professor H. Arastoopour and his research team and Carbon Nanostructure as Hydrogen Storage Material by professor J. Prakash and his research team.

Sustainable Buildings

WIND AND THE SELF POWERED BUILT ENVIROMENT

Vision

The concept of a building or a structure generating energy, mechanical or electrical, for its users or its functioning is not new. It was common in many applications and forms in ancient and recent times and is now being reinvented in response to rising energy costs, pollution and transmission challenges. Several new pioneering projects have been built, concepts and technologies are being developed, and research is underway in different countries. The Illinois Institute of Technology work in this area is unique, it reveals the enormous potential of the concept and the need for accelerated research including optimization of building forms and performance, and in the design and efficiency of wind turbines specifically for the tall building and wide span structures.

Objectives

Wind turbine farms may be located at considerable distances from centers of energy consumption, such as industry and urban concentrations. Approximately 10% of transmission power may be lost depending upon terrain, climate and other factors. Serious opposition may also be encountered on aesthetic grounds and avian migrations.

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The principle underlying this work is to generate energy at its point of consumption in the structures of the built environment, as far as is practical. Generated energy is for users of the built environment and for activating climate control devices built into the fabric of the built environment. The built environment consists of wide span and tall structures. The design and research group at the Illinois Institute of Technology lead by Professor Peter Land has developed a range of proposals for these two categories of built-form over several years. The group includes advanced level undergraduate and graduate students. The design work in the first semester of each academic year focuses on the wide span concept and the second semester on high-rise.

The objective of the design work is to develop proposals for structures and buildings which:

- 1) Are shaped to accelerate wind flows and focus the flow onto turbine rotors and,
- 2) Are shaped so that solar radiation impacts the envelope of the building at the most favorable angle for solar electric or solar energy collection, where solar energy is part of the design strategy.

The proposals are designed for environments where the wind is predominately from:

- 1) One direction (mono-directional).
- 2) Two directions (bi-directional).
- 3) Or, is without a predominant direction (multi-directional).

All conditions are encountered in reality. However, special emphasis has been placed on the multi-directional concept as this represents the most common and challenging design concept. During the period of the DOE grant June 2009 until May 2010, over 10 research based tall building design proposals were made for the range of wind conditions. Proposals were made for both steel and concrete structures. Designs were worked out in detail with several drawings for each proposal. Drawings of selected and illustrated concepts are shown in Figure 1.

Figure 1 Projects Prepared in Studio under Direction of Peter Land

The concepts of these design proposals have been formulated after intensive studies of related work and components including structures and turbines, and the criteria of the above noted different wind environments.

After design completion, several concepts were selected for preliminary wind flow and wind focus evaluation using the Illinois Institute of Technology wind tunnel facilities and in collaboration with the Aerospace Engineering Department. This first phase of the optimization process was planned to determine what building forms perform best against the criteria of acceleration and focus for the adjustment to building form, turbine locations and turbine types.

Accurate physical models were made, positioned in the tunnel with flow and focus visualizations recorded for different wind velocities and angles. Sample images are shown Figure 2. The data shows the flow and velocity characteristics and therefore the energy production potential of the several design proposals. Based upon this data, the best performing design proposals will be adjusted and the designs fine-tuned. It is intended to also evaluate the selected designs using computational fluid dynamics CFD to complement the wind tunnel work as part of the optimization strategy of the design proposals and to confirm the wind tunnel data.

Working method

The first semester focuses on wide span building/structures and the second semester on tall building/structures. In the first part of each semester, each student researches into and documents the characteristics of about 50

Figure 2: Wind Tunnel Flow Visualization Concepts
Projects and Models Prepared in Studio under Direction of Prof. Peter Land

pioneering and new cutting-edge projects recommended by Prof. Land. The initial research period is intensive, lasts about three weeks, and is designed to equip students with important knowledge before any design work begins. The research continues in a lower key, parallel with the design work, and terminates at the end of the semester with a compendium of researched projects.

Figure 3 Models built for Wind Tunnel Tests

After three weeks, design work begins. Prof. Land issues to the group a set of diagrams of different design concepts which have potential. Each student selects one design and development begins based on the initial diagram in collaboration with Prof. Land. During the course of the design development with inputs from the student and Prof. Land, the initial concept embodied in the diagram will evolve and might change completely and a better concept may emerge. When the design concept is established, the process of concept development in all its aspects begins. Emphasis is placed on rigor and thoroughness during design development and key details, which in some cases are of fundamental importance to the design concept. High quality final drawings are prepared of the completed project, covering design, structure, details and special features.

In a subsequent and separate stage, a number of designs are selected for wind-flow acceleration and focus efficiency using the Illinois Institute of Technology wind tunnel facilities and expertise. To optimize and improve the efficiency of the designs by changes to the building form, turbine type and placement, etc, this test data will be used. The wind tunnel and digital test models will be adjusted and re-tested to arrive at an optimized, efficient design.

In addition to the test models of actual buildings, models of new form concepts representing sections of hypothetical buildings, need to be fabricated and tested for wind energy potential.

Specialized expertise has been obtained from time to time in related engineering areas at the Illinois Institute of Technology, especially the aerospace program. Also, interdisciplinary committee, IIT Team for Energy and a Sustainable Built Environment (ESBE), was formed and chaired by Prof. Land to disseminate and exchange information and ideas about the on-going research and design development.

Efficiency

A building generating electrical energy for its users from wind and other non-polluting renewable sources is obviously a good idea. However, in the small number of projects built, electrical production as a percentage of user need using only wind is low, in comparison with the theoretical potential. This reflects the relative infancy of the current technology and design concepts and the need to intensify research into building form, turbine efficiency, and design. There is a need to combine the technology for extracting energy from wind with solar and other renewable sources, which has also been initiated at the Illinois Institute of Technology.

Experimental Work

We have performed a series of wind tunnel experiments, including both streak line (stream line) visualizations and point measurements of velocities for steady flows around seven candidate designs as shown in Figure 1. We note that models M1, M4, M5, M7, and M8 are *omni-directional*, meaning they are designed to deliver wind power independent of the direction of the wind. In contrast, models M2 and M9 are *bi-directional*, and are thus meant for locations that have one predominant wind direction, which is typical for coastal areas. Models M5 and M9 will have small-diameter vertical wind turbines installed on the outside of the buildings, the other models are designed for horizontal-axis machines suspended between the main "pillars" of the buildings.

Figure 2: Building models for wind tunnel testing

For each of the models in Figure 1, flow visualizations were performed in up to two horizontal planes, and for a set of wind directions ranging from 0 to 60 degrees in 15-degree increments. Because of the symmetry of the building models involved in this study, the angles chosen cover the whole range of possible flow scenarios for each of the buildings. Figure 2 shows one representative flow visualization for each of the building models.

Visualization Model M1, 0 degrees

Visualization Model M2, 0 degrees

Visualization Model M4, 0 degrees

Visualization Model M5, 0 degrees

Visualization Model M7, 0 degrees

Figure 3: Flow visualizations. All of the figures show photographs taken from two different angles, with the main flow direction indicated by the yellow arrow. Local flow velocities shown in red.

Pertinent findings from these studies are as follows:

- All of the building shapes generate accelerated flows in locations that are of interest for installation of wind turbines. Typically, the flow velocity is increased by about 80%. We note that this corresponds to an increase of the power that can be generated from a typical wind turbine by a factor of about six, meaning an increase in available power by about 500%.
- Our *omni-directional designs* (Models M1, M4, M5, M7, and M8) indeed show only a weak dependence of the maximum flow velocity on the direction of the wind.

Computational Work

We have also started to perform computer simulations of flow around the above models. Figure 3 shows results for studies of Models M1 and M7.

Figure 4: CFD results for models M1 and M7

The simulations were done using the commercial software package Fluent, assuming a free-stream velocity of $U=10$ m/s, and using the standard $k-\varepsilon$ turbulence model in Fluent.

Both streamlines and absolute values of velocities show good agreement with our measurements. In ongoing work, we are currently simulating additional wind directions to match our experimental data.

Hydrogen Storage

Hydrogen Storage Using Mg-Mixed Metal Hydrides

To minimize the adverse effect of ever increasing global energy consumption per capita, there is a need for significant energy production from renewable resources and non carbon molecules such as hydrogen to become energy carrier. The lack of satisfactory hydrogen storage systems which are safe, cheap and simple is one of the main problems for the transition to a hydrogen-based energy carrier system. Mg-based alloys show potential as hydrogen storage material because of the high gravimetric density of MgH_2 (7.6 wt. %), as well as its abundant supply and low cost as a raw material. However, they exhibit high enthalpies of formation, poor

hydrogenation/dehydrogenation kinetics, poor charge/discharge cycling stability and high temperature requirements. Literature studies showed that the addition of LaNi_5 to MgH_2 reduces hydrogen absorption temperature and accelerates the kinetics at room temperature and yields higher hydrogen storage capacity at elevated temperatures. Furthermore, literature showed that Nb_2O_5 is the most effective catalyst for the hydrogen sorption reaction of Mg. In this work, Mg- LaNi_5 - Nb_2O_5 composite systems were prepared and studied to obtain a better understanding of hydrogen storage capacity, adsorption/desorption rates. Hydrogen storage capacities of our sorbent were measured by performing adsorption/desorption experiments at different temperatures. The results of the experiments were analyzed and compared with available data from the literature. The results of our experiments showed that our sorbent (MgH_2 - 20 wt. % LaNi_5 - 7.3 wt. % Nb_2O_5) has higher capacity for absorption and higher rate of absorption and desorption at different temperatures than the available sorbents in the literature today.

Introduction

Persistent urban air pollution, climate change, limited nature of traditional fuels and the need to reduce the foreign oil imports make renewable energies more desirable. Because of the unpredicted nature of renewable energies, a simple storage infrastructure for renewable energies is needed. Hydrogen with no carbon is possibly the best way to store renewable energies with no harm to the environment. To overcome the difficulties to use hydrogen as an energy carrier; a safe, cheap, simple and efficient hydrogen storage technology is required.

Because of the low volumetric energy density of hydrogen, storage is the key part of the hydrogen economy. The cost, weight, volume, heat requirements and charge/discharge rates are the major technical issues to be addressed while designing a storage system for hydrogen. The U.S Department of Energy hydrogen storage goals addresses most of the technical issues. So far, the 2010 goals have not been reached.

With their higher volumetric storage capacity, lower pressure requirements, high selectivity, low cost of storing options and safety, metal hydrides are the potential for onboard reversible hydrogen storage. Compared to other metal hydrides, magnesium hydrides have significant advantages like cheap and abundant supply of magnesium, high theoretical hydrogen storage capacity (7.6 wt. %), lightweight and one step desorption. However, their high temperature requirements and slow rates during desorption are some of the major disadvantages of magnesium hydrides. To overcome these disadvantages, literature proposes to mix magnesium with another chemical component, add a small amount of a catalytically active metal and use smaller particle sizes. In the literature, it is shown that using smaller particle sizes results a higher diffusion rate of hydrogen atoms through the hydride which might be a possible solution for the slow hydrogenation/dehydrogenation problem of magnesium hydrides (Zaluska, A., L. Zaluski, and J. O. Ström - Olsen. "Nanocrystalline Magnesium for Hydrogen Storage"

Journal of Alloys and Compounds 288.1-2 (1999): 217-223.). However, the stability of magnesium hydrides cannot be easily reduced by using smaller particles alone. In the literature, LaNi_5 is known with its fast hydriding/dehydriding kinetics at ambient temperatures. Adding LaNi_5 can alternate the thermodynamic behavior of magnesium based composite materials by reducing the temperature of hydrogen adsorption and desorption, accelerating kinetics at room temperature, and yielding high hydrogen storage capacity at elevated temperatures (Au, M., "Hydrogen Storage Properties of Magnesium Based Nanostructured Composite Materials." *Materials Science and Engineering B* 117.1 (2005): 37-44.). And also the literature shows that Nb_2O_5 is the most effective catalyst for hydrogen sorption reaction of Mg known so far (Barkhordarian, G., T. Klassen, and R. Bormann. "Fast Hydrogen Sorption Kinetics of Nanocrystalline Mg Using Nb_2O_5 as Catalyst" *Scripta Materialia* 3rd ser. 49 (2003): 213-217.).

In this study, it is aimed to combine all three of the methods mentioned above to prepare and test a new Mg-based metal hydride by using LaNi_5 and Nb_2O_5 which has high hydrogen sorption and desorption rates at low temperatures and high hydrogen storage capacity.

Experimental Section

Commercial Mg, LaNi_5 and Nb_2O_5 powders with an average particle size of less than 50 μm and an average purity of 99.5 % from Sigma-Aldrich, Inc were used to prepare Mg- LaNi_5 - Nb_2O_5 by high energy ball milling. 7.27 g MgH_2 , 0.73 g Nb_2O_5 and 2 g LaNi_5 were weighed and put into a 45 mL zirconia ceramic vial. The diameter and length of the vial were 6.35 cm and 6.8 cm. Two 12.7 mm diameter zirconia ceramic balls from SPEX SamplePrep 8005 Vial Set were put into the vial. And the vial was loaded in a SPEX-8000TM high energy ball mill. Every 90 minutes, the vial was taken out for scraping the material adhering on the wall. In this work, the ball-milling process took about 6 hours. To avoid any possible oxidation, the powder was handled and processed in an argon-filled glove box near atmospheric pressure.

Figure 1 Schematic representation of ball milling

After the ball-milling procedure, SRA150 by Microtrac, USA was used to measure the sample size of the new composite material. The particle size determination procedure started with dispersing and circulating the particles in water through the laser beam with a pump. The scattered laser was then collected by detectors and the software interpreted the average particle size of the new composite material around 5 - 7 μm . The composition of the sorbent was Mg – 20 wt. % LaNi_5 – 7.3 wt. % Nb_2O_5 with a bulk density of 1.37 g/cm^3 .

The main idea of our experimental setup was to test the capacity of the hydrogen storage material during both charging and discharging. Usually the capacity is measured in terms of hydrogen to storing material weight percent (H/M wt. %). The absorption/desorption capacity of the sample and the rate of adsorption/desorption were measured using a manual controlled Sievert apparatus equipped with computer data acquisition.

Figure 2 Experimental Setup

High pressure zone is where high pressure hydrogen gas was initially trapped before each adsorption set (or vacuumed before each desorption set) and the sample chamber zone is where the sorbent was placed. The calculations were based on the pressure difference between the two zones. Before each adsorption experiment, the sample chamber zone was at atmospheric pressure and high pressure zone was set to the desired pressure. When the valve between the two zones was opened, an equilibrium pressure was reached and the difference between the initial pressure in two zones and the equilibrium pressure gave the amount of hydrogen adsorbed by the sorbent. This amount was recorded in the unit of wt. % with first equilibrium pressure and the valve between the two zones was closed. Again, the high pressure zone was filled with hydrogen at the desired pressure and the valve between the two zones was opened. The same procedure was repeated till the difference between the desired and the

equilibrium pressures was insignificant. The desorption procedure started right after the end of the adsorption procedure. In the beginning of the desorption procedure, the sample chamber zone was at the last equilibrium pressure from the adsorption procedure, and the high pressure zone was vacuumed. Again, the valve between the two zones were opened and the equilibrium pressure was recorded with the amount of hydrogen (in wt. %) desorbed (based on the difference between the two pressures). At the end of the first cycle, the valve between the two zones was closed and the high pressure zone was vacuumed. The same procedure was repeated till the difference between the initial high pressure zone and the equilibrium pressures was insignificant. The recorded equilibrium pressure and adsorbed/desorbed amount of hydrogen (in wt. %) data were used to conduct the Pressure Composition Isotherms (PCI curves) at different temperatures for adsorption and desorption.

During the course of the experiments, several assumptions were made in order to simplify the calculations. While calculating the volume occupied by the sample material, the bulk density was used and the porosity of the sorbent particles was ignored. This amount was taken into account while calculating the amount of hydrogen adsorbed/desorbed in the sample. The amount of hydrogen adsorbed/desorbed depends on the difference between the high and equilibrium pressures. Since the compressibility factor of hydrogen is about 1 within the operating temperature and pressure range used during the experiments; ideal gas assumption was used to calculate the number of moles of hydrogen adsorbed/desorbed. Also, during experiments which took place at temperatures higher than room temperature (100, 200 and 300°C), sample chamber was the only part heated up to those temperatures. Because of the lack of a better heating system that would heat up the entire system to the desired temperature including the hydrogen source or a better temperature sensor which would monitor the temperature at different parts of the setup; sample chamber zone was assumed to be at experimental temperature and high pressure zone was assumed to be at room temperature during the absorption and desorption experiments.

Results and Discussion

Figure 3 shows the effect of temperature on the hydrogen storage capacity and the rate of the sorbent. Both figures indicate that the hydrogen storage capacity and rate increase with increasing temperature. Also, it was not possible to release all of the adsorbed hydrogen during desorption. On average, 85 % of the adsorbed hydrogen could be released successfully during desorption experiments. However, the percentage of the hydrogen released during desorption decreases with increasing temperature. For instance, 91 % of the hydrogen could be released successfully at 20°C while 86 % did at 100°C, 84 % did at 200°C and 80% at 300°C. And the absorption rate is higher than the desorption rate at all temperature ranges. However, the

difference between the adsorption and desorption rates can be seen more prominently at higher temperatures.

Figure 3 The Effect of Temperature on Hydrogen Storage Capacity and Rate of the Sorbent

Although our sorbent's adsorption/desorption rates exceeded the ones from the literature, Figure 3 indicates that our sorbent's hydrogen storage rates were lower than 0.005 wt. %/s except at 300°C. The dramatic difference between adsorption/desorption rates at 200°C and 300°C can be explained by magnesium hydrides' superior hydrogen storage rates at high temperatures.

To form MgH_2 , first H_2 needs to overcome an activation barrier for dissociation. The heat of formation of H_2 is - 286 kJ/mol. Therefore, 286 kJ/mol of energy is needed to break the bond between the hydrogen atoms of the hydrogen molecule. On the other hand, the heat of formation of MgH_2 is - 78 kJ/mol. As a result, the process of breaking the bond between the hydrogen atoms and forming a magnesium hydride is highly endothermic because of the high energy needs of dissociation of hydrogen (around 208 kJ/mol of energy needed in total). Also, the heat of formation of LaNi_5H_6 is -285.6 kJ/mol. Since 3 moles of H_2 need to be dissociated in order to form one mole of LaNi_5H_6 , the dissociation reaction of hydrogen molecule and formation reaction of LaNi_5H_6 combined with heat of formation of LaNi_5 is highly endothermic. When the heat of formation of H_2 (-286 kJ/mol), MgH_2 (-78 kJ/mol), LaNi_5 (-159.1 kJ/mol) and LaNi_5H_6 (-159.1 kJ/mol) taken into account; it could be seen that the dissociation reaction of H_2 and formation reactions of MgH_2 and LaNi_5H_6 together is highly endothermic which means the hydrogen absorption reactions of both hydrides are favored at higher temperatures. Similarly, the desorption reactions are highly endothermic and favored at higher temperatures. Based on the heat of reaction data provided so far and Figure 3, it can be concluded that both absorption and desorption reactions would be more favorable at 400°C compared to 300°C.

Figure 4 Adsorption and Desorption PCI Curves at 300°C

Figure 4 shows both the adsorption and desorption pressure composition isotherms of $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material at 300°C. Table 1 shows that at around 500 psi and 300°C, $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material adsorbed about 5.94 wt.% hydrogen with a rate of 0.211 wt. %/s and desorbed about 4.74 wt.% hydrogen with a rate of 0.0532 wt. %/s. The adsorption/desorption capacity of $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material is higher than the adsorption and desorption capacity of $\text{MgH}_2\text{-LaNi}_5$. According to Au's work in 2005, $\text{MgH}_2\text{-LaNi}_5$ composite material gave a hydrogen storage capacity of 5.5 wt. % with a rate of 0.0183 wt. %/s and the desorption capacity of the material was 4.2 wt. % with a rate of 0.00175 wt. %/s at 300°C and around 435 psi (Au, M., "Hydrogen Storage Properties of Magnesium Based Nanostructured Composite Materials." *Materials Science and Engineering B* 117.1 (2005): 37-44.). Both $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ and $\text{MgH}_2\text{-LaNi}_5$ had 20 wt. % LaNi_5 . Therefore, removing 7.3 wt. % of the MgH_2 and replacing it by Nb_2O_5 not only improved the adsorption and desorption capacity, but also increased the rate of adsorption/desorption rates of the composite material. The difference in adsorption and desorption rates is even more clear, 30 times faster desorption and 10 times faster adsorption were observed when 7.3 wt. % of the MgH_2 was replaced by Nb_2O_5 . Using LaNi_5 in addition to $\text{MgH}_2\text{-Nb}_2\text{O}_5$ had a positive effect on hydrogen storage capacity while using Nb_2O_5 in addition to $\text{MgH}_2\text{-LaNi}_5$ significantly increased the adsorption rate.

Table 1 Summary of the Experimental Results Compared to the Literature at 300°C

HYDROGEN STORAGE CAPACITY - <i>in wt. %</i>					
		Our Data Mg-LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg-20 wt. % LaNi ₅ (approx. 435 psi)	Barkhordarian (2003) Mg-7.3 wt. % Nb ₂ O ₅ (approx. 421 psi)	Wu (2006) Mg (approx. 428 psi)
Average	absorption	5.94	5.5	4.9	5.5
	desorption	4.74	4.2	4.7	4 (* 350°C)
RATE - <i>in wt. %/s</i>					
		Our Data Mg-LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg-20 wt. % LaNi ₅ (approx. 435 psi)	Barkhordarian (2003) Mg-7.3 wt. % Nb ₂ O ₅ (approx. 421 psi)	Wu (2006) Mg (approx. 428 psi)
Average	absorption	0.211	0.0183	0.185	0.00233
	desorption	0.0532	0.00175	0.0492	0.0011 (350°C)

Figure 5 Adsorption and Desorption PCI Curves at 200°C

The absorption and desorption pressure composition isotherms of MgH₂-LaNi₅-Nb₂O₅ composite material at 200°C are shown in Figure 5. Table 2 indicates that MgH₂-LaNi₅-Nb₂O₅ composite material adsorbed about 3.30 wt.% hydrogen with a rate of 0.00827 wt. %/s and desorbed about 2.81 wt.% hydrogen with a rate of 0.00635 wt.%/s at around 500 psi and 200°C.

Table 2 Summary of the Experimental Results Compared to the Literature at 200°C

HYDROGEN STORAGE CAPACITY - in wt. %				
		Our Data Mg-LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg-20 wt. % LaNi ₅ (approx. 435 psi)	Wu (2006) Mg (approx. 428 psi)
Average	absorption	3.3	2.9	2.5
	desorption	2.81	2.3	1.7
RATE - in wt. %/s				
		Our Data Mg-LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg-20 wt. % LaNi ₅ (approx. 435 psi)	Wu (2006) Mg (approx. 428 psi)
Average	absorption	0.00827	0.00242	0.000347
	desorption	0.00635	0.000958	0.000236

Compared to MgH₂-LaNi₅, MgH₂-LaNi₅-Nb₂O₅ composite material has higher adsorption/desorption capacity and rate. In 2005, Au showed that MgH₂-LaNi₅ composite material has hydrogen storage capacity of 2.9 wt. % with a rate of 0.00242 wt. %/s and desorption capacity of the material was 2.3 wt. % with a rate of 0.000958 wt. %/s at 200°C and around 435 psi (Au, M., "Hydrogen Storage Properties of Magnesium Based Nanostructured Composite Materials." *Materials Science and Engineering B* 117.1 (2005): 37-44.). As mentioned before, both MgH₂-LaNi₅-Nb₂O₅ and MgH₂-LaNi₅ had 20 wt. % LaNi₅. Again, removing 7.3 wt. % of the MgH₂ and replacing it by Nb₂O₅ not only improved the adsorption and desorption capacity, but also increased the rate of adsorption/desorption rates of the composite material. The difference in adsorption and desorption rates is even more clear, 4 times faster desorption and 7 times faster adsorption were observed when 7.3 wt. % of the MgH₂ was replaced by Nb₂O₅. When the adsorption/desorption capacity and rate of MgH₂-LaNi₅-Nb₂O₅ are compared to the data of MgH₂ in the literature, it can be seen that the new composite material has a higher adsorption/desorption capacity and rate than MgH₂ alone (Wu, C. Z., P. Wang, X. Yao, C. Liu, D. M. Chen, G. Q. Lu, and H. M. Cheng. "Effect of Carbon/Noncarbon Addition on Hydrogen Storage Behaviors of Magnesium Hydride" *Journal of Alloys and Compounds* 414.1-2 (2006): 259-264.). The adsorption/desorption rate of the new composite material is about 25 times higher than MgH₂.

Figure 6 Adsorption and Desorption PCI Curves at 100°C

Figure 6 shows both the adsorption and desorption pressure composition isotherms of $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material at 100°C. And from Table 3, it can be seen that $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material adsorbed about 2.82 wt.% hydrogen with a rate of 0.00718 wt. %/s and desorbed about 2.37 wt.% hydrogen with a rate of 0.0054 wt. %/s at around 500 psi and 100°C. Compared to $\text{MgH}_2\text{-LaNi}_5$, $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material has higher adsorption/desorption capacity and rate. In 2005, Au showed that $\text{MgH}_2\text{-LaNi}_5$ composite material has hydrogen storage capacity of 2.4 wt.% with a rate of 0.000333 wt. %/s and desorption capacity of the material was 1.9 wt.% with a rate of 0.000264 wt. %/s at 100°C and around 435 psi []. As mentioned before, both $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ and $\text{MgH}_2\text{-LaNi}_5$ had 20 wt.% LaNi_5 . Again, removing 7.3 wt.% of the MgH_2 and replacing it by Nb_2O_5 not only improved the adsorption and desorption capacity, but also increased the rate of adsorption/desorption rates of the composite material. The difference in adsorption and desorption rates is even more clear, almost 25 times faster adsorption and desorption were observed when 7.3 wt.% of the MgH_2 was replaced by Nb_2O_5 . When the adsorption/desorption capacity and rate of $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ are compared to the data of MgH_2 in the literature, it can be seen that the new composite material has a higher adsorption/desorption capacity and rate than MgH_2 alone []. In 2006, Liu et al showed that MgH_2 has hydrogen storage capacity of 1.5 wt.% with a rate of 0.0002 wt. %/s and desorption capacity of the material was 0.9 wt.% with a rate of 0.000125 wt. %/s at 100°C and around 1000 psi. Although the pressure used was two times higher than this work, adding LaNi_5 and Nb_2O_5 to MgH_2 significantly increased the hydrogen adsorption/desorption capacity and rate. The new composite material worked a lot better than MgH_2 with 2 - 3 times higher adsorption and desorption capacity and 40 times higher absorption/desorption rate at lower pressures.

Table 3 Summary of the Experimental Results Compared to the Literature at 100°C

HYDROGEN STORAGE CAPACITY - <i>in wt. %</i>				
		Our Data Mg-LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg- 20 wt. % LaNi ₅ (approx. 435 psi)	Liu (2006) Mg (approx. 1000 psi)
Average	absorption	2.82	2.4	1.5
	desorption	2.37	1.9	0.9
RATE - <i>in wt. %/s</i>				
		Our Data Mg-LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg- 20 wt. % LaNi ₅ (approx. 435 psi)	Liu (2006) Mg (approx. 1000 psi)
Average	absorption	0.00718	0.000333	0.0002
	desorption	0.0054	0.000264	0.000125

Figure 7 Adsorption and Desorption PCI Curves at 20°C

The adsorption and desorption pressure composition isotherms of $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material at 20°C are shown in Figure 7. Table 4 shows that $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material adsorbed about 2.22 wt.% hydrogen with a rate of 0.00152 wt. %/s and desorbed about 2.02 wt.% hydrogen with a rate of 0.00127 wt.%/s at around 500 psi and 20°C. Compared to $\text{MgH}_2\text{-LaNi}_5$, $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite material has higher adsorption/desorption capacity and rate. In 2005, Au showed that $\text{MgH}_2\text{-LaNi}_5$ composite material has hydrogen storage capacity of 1.9 wt.% with a rate of 0.000264 wt.%/s and desorption capacity of the material was 1.7 wt.% with a rate of 0.000236 wt.%/s at 25°C and around 435 psi []. As mentioned before, both $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ and $\text{MgH}_2\text{-LaNi}_5$ had 20 wt.% LaNi_5 . Again, removing 7.3 wt.% of the MgH_2 and replacing it by Nb_2O_5 not only improved the adsorption and desorption capacity, but also increased the rate of adsorption/desorption rates of the composite material. The difference in adsorption and desorption rates is even more clear, almost 5 times faster adsorption and desorption were observed when 7.3 wt.% of the MgH_2 was replaced by Nb_2O_5 . Also, the adsorption/desorption capacity and rate of the $\text{MgH}_2\text{-LaNi}_5$, $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ composite materials were compared to the LaNi_5 data from the literature. In 1999, Srivastava et al showed that using only LaNi_5 as hydrogen storage material gave a hydrogen storage capacity of 1.6 wt.% with a rate of 0.000148 wt.%/s and desorption capacity of the material was 1.5 wt.% with a rate of 0.000481 wt.%/s at 33°C and around 730 psi []. The results showed that adding MgH_2 and Nb_2O_5 to LaNi_5 gave about 2 times higher hydrogen adsorption/desorption capacity and 25 times higher adsorption/desorption rate. When the adsorption/desorption capacity and rate of $\text{MgH}_2\text{-LaNi}_5\text{-Nb}_2\text{O}_5$ are compared to the data of MgH_2 in the literature, it can be seen that the new composite material has a higher adsorption/desorption capacity and rate than MgH_2 alone []. In 2006, Liu et al showed that MgH_2 has hydrogen storage capacity of 0.5 wt.% with a rate of 0.0000694 wt.%/s and desorption capacity of the material was 0.2 wt.% with a rate of 0.0000278 wt.%/s at 25°C and around 1000 psi. Although the pressure used was two times higher than this work, adding LaNi_5 and Nb_2O_5 to MgH_2 significantly increased the hydrogen adsorption/desorption capacity and rate. The new composite material worked a lot better than MgH_2 with 5 - 10 times higher adsorption and desorption capacity and 40 times higher adsorption/desorption rate at lower pressures.

Table 4 Summary of the Experimental Results Compared to the Literature at 100°C

HYDROGEN STORAGE CAPACITY - <i>in wt. %</i>					
		Our Data Mg- LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg-20 wt. % LaNi ₅ at 25 C and approx. 435 psi	Srivastava (1999) LaNi ₅ at 33 C and approx. 730 psi	Liu (2006) Mg at 25 C and approx. 1000 psi
Average	absorption	2.22	1.9	1.6	0.5
	desorption	2.02	1.7	1.5	0.2
RATE - <i>in wt. %/s</i>					
		Our Data Mg- LaNi ₅ -Nb ₂ O ₅ (approx. 500 psi)	Au (2005) Mg-20 wt. % LaNi ₅ at 25 C and approx. 435 psi	Srivastava (1999) LaNi ₅ at 33 C and approx. 730 psi	Liu (2006) Mg at 25 C and approx. 1000 psi
Average	absorption	0.00152	0.000264	0.00148	0.0000694
	desorption	0.00127	0.000236	0.000481	0.0000278

In summary, the results of our experiments showed that our sorbent (MgH₂-20 wt.% LaNi₅-7.3 wt.% Nb₂O₅) has higher capacity for adsorption and shows higher rate of adsorption and desorption at different temperatures than the available sorbents in the literature today.

Conclusions

This research study provided a better understanding of the effects of alloying LaNi₅ and Nb₂O₅ and with MgH₂. The rate and capacity of MgH₂-LaNi₅-Nb₂O₅ were measured by performing adsorption and desorption experiments at different temperatures and the results were compared to the data in the literature.

- The results of our experiments showed that our sorbent (MgH₂-20 wt.% LaNi₅-7.3 wt.% Nb₂O₅) has higher capacity for adsorption and has also higher rate of adsorption and desorption at all temperature ranges in comparison with MgH₂ alone, MgH₂-LaNi₅ and MgH₂-Nb₂O₅ composite sorbents available in the literature today.
- The positive effect of adding LaNi₅ and Nb₂O₅ to MgH₂ on adsorption/desorption capacity and rate was observed more prominently at lower temperatures.

- At 300°C, hydrogen storage capacity of our sorbent was reached to the Department of Energy 2010 goal. As temperature decreases the hydrogen storage capacity of our sorbent decreases and becomes almost half of the 2010 DOE goal at 20°C. Hydrogen storage rate of our sorbent is 25% of the 2010 DOE goal at 300°C and the rate decreases as temperature is lowered. At 20°C, the hydrogen storage rate of our sorbent is less than 1% of the 2010 DOE goal.

Carbon Nanostructure as Hydrogen Storage Material

Sepiolite derived carbon nanofibers (SDCN) were investigated as hydrogen storage material. The hydrogen storage capacity of SDCN at room temperature showed linear dependency on hydrogen pressure up to 70bar but low values at around 0.1wt%. At cryogenic temperature of 77K and 50bar, higher uptake capacities were observed at about 2wt%. Thermodynamic investigation indicated that the change of chemical potential of the hydrogen molecules in the gas phase with temperature and pressure lead to the improved hydrogen storage capacity. The hydrogen uptake measurements of various carbon structures showed that the hydrogen storage capacity has a large dependency on the carbon micropore volume (< 3nm) at room temperature, while at 77K the BET surface area plays a more important role. Pretreatment of SDCN at 1000°C in N₂ did not improve the hydrogen storage capacity.

Synthesis and Characterization

Ethylene or propylene were loaded and pyrolyzed in the gas phase in one step using a three-zone furnace. Quartz boats containing sepiolite were placed within a quartz tube. The temperature of the oven was gradually increased from room temperature to 700 °C. The oven was then held at the target temperature for 4 hours. The clay from the loaded/pyrolyzed sepiolite sample was removed using HF, rinsed to neutral pH, and refluxed with concentrated HCl for 2 hours. The sample was washed with distilled water until the pH was > 5 to ensure that there was no acid left. The resultant carbon was oven dried overnight at 150 °C. The other carbon samples used in the present work were obtained from several suppliers. Graphitic carbon fiber and mesocarbon microbead (MCMB) were obtained from Argonne National Lab (IL, USA). Carbon black produced by subjecting heavy residual oil feedstock to high temperature was obtained from CABOT, USA. Single wall carbon nanotube (SWNT) was obtained from Hanyang University, South Korea.

Results and discussion

TEM image analysis on the sepiolite derived carbon nanofiber (SDCN) is shown in Figure 1. Fibrous structures are formed along the channels of sepiolite and in the size ranges of ~100Å in thickness and ~2µm in length.

Figure 2 shows the hydrogen pressure changes with time at 298K after opening the valve from the high pressure reservoir to the sample reactor containing SDCN. The pressure drops are mostly caused by the volume expansion and hydrogen sorption in the carbon. Temperature change by gas expansion is also considered to lead to the pressure change. Hydrogen sorption is observed to reach equilibrium quickly, as pressure change becomes negligible in several minutes. The fast equilibrium for hydrogen sorption is the characteristic of physisorption.

The hydrogen storage capacity was found to be about 0.1wt% and repeatable with the cycle number as characteristic of physisorption. After the first cycle, the subsequent cycles show

a little higher hydrogen storage capacity, which is due to the removals of inert materials from the carbon surface during the first cycle of hydrogen sorption/desorption. The same phenomenon of the increment of hydrogen storage capacity after first cycle was also observed on the other carbon samples. In the test pressure range, the hydrogen storage capacities of SDCN at room temperature are far below the DOE goal of 6.5wt% for hydrogen powered vehicle. It is known that hydrogen adsorption potential on carbon changes with carbon pore size, as smaller carbon pores generate higher interaction forces on hydrogen molecule by providing more carbon in the neighbor to the gas. The estimated adsorption potential of the outer surface of an individual SWNT is around -0.09eV and this value is in the same order of magnitude as the energy of thermal motion of gas molecules on the carbon surface at room temperature. Thus, most of the hydrogen release from the carbon surface occurs by thermal motion. From this consideration, small area of SDCN is necessary effective for hydrogen sorption at room temperature.

Figure 3, shows the hydrogen storage capacities of various carbon structures studied at 298K and 77K. The pressures are 90bar and 50bar, respectively. SWNT is seen to have the highest hydrogen storage capacities among the carbon samples. We also investigated the hydrogen storage capacities of the carbon structures at 298K and 90bar and correlated this with the carbon BET specific surface areas and the carbon micro-structure (pore volumes of less than 3nm as pore diameter). It was observed that the hydrogen storage capacity is in better correlation with the carbon micropore volume than with the carbon BET specific surface area. Based on the fact that the adsorption potential changes with the carbon pore size, the result is reasonable considering that carbon micropores (< 3nm) have high adsorption potentials and that is necessary to attain hydrogen sorption at room temperature.

Conclusions

Sepiolite derived carbon nanofiber (SDCN) was investigated as hydrogen storage material. SDCN showed good reversible hydrogen sorption behavior but low hydrogen storage capacity of about 0.1wt% at 298K. At 77K, the storage capacity increased to about 2wt% at 50bar. Thermodynamic investigation was performed to understand the hydrogen sorption behaviors observed at different temperatures and pressures for the carbon structure. The study on the hydrogen storage capacities of the various carbon structures revealed that the carbon micropore volume (< 3nm) is an important factor affecting hydrogen storage capacity at room temperature, while the carbon BET specific surface area at 77K. Pretreatment effect on hydrogen adsorption was observed with a small improvement in hydrogen storage capacity by the external heating at 1000°C in N₂, but no improvement by the external heating at 800°C.

Figure 1. Transmission electron micrograph showing the appearance of carbon nanofibers derived from the pyrolytic decomposition of propane in sepiolite.

Figure 2. Hydrogen pressure change with time at 298K after opening the valve from the reservoir to the sample reactor containing SDCN

(a)

(b)

Figure 3. Hydrogen sorption isotherms of the various carbon structures: (a) T = 298K and P = 90bar; (b) T = 77K and P = 50bar